Elementary Methods of Molecular Quantum Mechanics

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Coulson-Fischer AO for $H_2(^1\Sigma_g^+)$

Preface

This is a teaching book for graduate University students of Chemistry and Physics, where emphasis is placed on the Methods of Quantum Mechanics from an elementary point of view as applied to the theoretical study of the electronic structure of atoms and molecules. It can be considered mostly as a book of applied mathematics. The book is intended not as a treatise covering all aspects of applications to Chemistry and to many problems in Molecular Physics, rather to present in the simplest possible self-contained way the mathematical machinery needed for a critical understanding of what is implied in the black boxes of the software which is today currently in use by chemists in this area. In a sense, the book aims to bridge the gap between the classic Coulson's *Valence*, where applications of wave mechanical principles to valence theory is presented in a fully non-mathematical way, and McWeeny's *Methods of Molecular Quantum Mechanics*, where recent advances in the application of quantum mechanical methods to molecular problems are presented at research level in a full mathematical way. Many examples and mathematical points are given as Problems at the end of each Chapter, with a hint for their solution. Solutions are worked out in detail in the last Section of each Chapter. The required background for students of Chemistry and Physics is that of a few courses in mathematics and physics.

The central idea is that the majority of the applications in the field of electronic molecular structure rests on the fundamental expansion theorem of Quantum Mechanics, where a well-behaved mathematical function is expanded into an appropriate basis of regular functions. The expansion coefficients arising from the quantum mechanical operators representing physical observables are then obtained in terms of matrix elements, so giving to matrix algebra a fundamental role in applications. Truncation of the expansion gives rise to finite matrices with matrix algebra replacing solution of differential equations. The Ritz version of Rayleigh's variation theorem, where integrals replace derivatives, is then the building stone of any practical orbital application, and molecular orbitals and valence bond methods stem directly from it. The content is divided into 13 Chapters.

After an axiomatic introduction of the basic principles of Quantum Mechanics (Chapter 1), where atomic units are introduced from the beginning to get maximum simplification in the mathematical expressions, a Chapter is devoted to elementary matrix methods (Chapter 2) with emphasis on the solution of eigenvalue and pseudoeigenvalue problems. Chapters 3 and 4 contain, respectively, the application of the basic principles to the particle in the box and the atomic 1-electron (or hydrogen-like) system. It is believed that these two examples are exhaustive enough to explain in detail the general techniques of solution of the exactly solvable Schroedinger eigenvalue equations. The methods described in Chapter 4 can be used either for the free atom or the atom in a field (see Chapter 11), and allow us to introduce from first principles the quantum numbers characterizing those particular atomic orbitals (AOs) known as hydrogen-like orbitals. The Chapter ends with a generalization to Slater (STO) and Gaussian (GTO) AOs which are mostly used today in quantum chemical calculations.

The variation method is next introduced in Chapter 5 as the most powerful way of proceeding to working approximations, and simple atomic and molecular examples are discussed there in some detail, with a short outline of the method due to Wentzel–Kramers–Brillouin (WKB). Simple Pauli spin methods for treating electrons and nuclei of spin $1/2$ are given in Chapter 6 as a prerequisite to the following Chapter 7. Besides the simple matrix approach, both Kotani and Löwdin methods are introduced to some extent.

In Chapter 7 the many-electron wavefunctions needed to deal properly with complex quantum mechanical systems are discussed together with their reduction in terms of density functions and density matrices. All techniques described there are based on the Slater method of writing antisymmetric wavefunctions in the form of determinants, the independent particle model (IPM) being assumed to be central to the discussion of many-electron systems. The Hartree–Fock (HF) method is then introduced as the middle step of a ladder having Hall–Roothaan LCAO-MO-SCF methods below it up to semiempirical and Hückel methods, and post-HF methods above it, from CI and MC-SCF to various many–body perturbation and variational techniques such as MP2 and M2-R12, up to recent CCSD-R12. Some space is also devoted to non-orbital approaches, to a short outline of second quantization as alternative to the Slater method, and to the principles of functional density (FDT) techniques.

Chapter 8 describes how symmetry can be used for simplifying molecular calculations mostly using matrix methods inside elementary group theory. An outline of continuous and symmetric groups completes the Chapter.

Chapter 9 contains a short introduction on the vector model and on how many-electron wavefunctions of the correct angular symmetry can be derived for atoms, ending with an explanation of the various coupling coefficients and symbols needed in more advanced work on angular momentum.

The investigation of the chemical bond inside the orbital model, mostly through valence bond (VB) methods, is presented in Chapter 10 with applications to a few simple organic and inorganic molecules. Because of his historical and didactical importance, an unusual space is devoted to the classical work by Pauling on conjugated and aromatic molecules, including the meaning of the important word “resonance”, still today largely in use among organic chemists. It is also shown there that useful information on electron and spin density distributions in hydrocarbons can be obtained in some cases without doing effective energy calculations. Hybridization and its consequences on the study of directed valency in polyatomic molecules is examined next, with a short outline of recent advances in the theory allowing for ab-initio VB calculations.

Stationary Rayleigh–Schroedinger (RS) perturbation methods, the other fundamental technique of approximation in Molecular Quantum Mechanics, are postponed until Chapter 11, where emphasis is given to the Ritz variational approximations for second-order energies in terms of linear pseudostates. Detailed applications are given in this Chapter on the electric properties of atoms and molecules in view of their further use in the problem of molecular interactions.

Chapter 12 is concerned with the application of RS and MS-MA (Murrell–Shaw–Musher–Amos) perturbation methods to the direct study of atomic and molecular interactions over the entire range of intermolecular separations, from the region of the chemical bond to that of the Van der Waals (VdW) bond. The study is first focused on the simplest model systems H–H$^+$ and H–H, with the Heitler–London theory of H_2 considered as a first-order perturbation theory including exchange, then extending the understanding of the physical nature of the interaction between many-electron molecules using charge density operators and density matrix techniques. The Chapter ends with a short discussion of the VdW bond which occurs at long range between closed-shell atoms and molecules.

Lastly, as a preliminary to all energy computations in terms of orbitals having the correct radial behaviour, methods for the evaluation of molecular integrals over STOs are considered in Chapter 13, where all 1- and 2-electron integrals over $1s$ STOs for the H–H interaction are evaluated in an elementary way, including the difficult 2-centre 2-electron exchange integral. An outline of the possible ways of calculation of the general 2-centre integrals and some consideration of the 3-centre nuclear attraction and the 4-centre 2-electron integral over $1s$ STOs conclude this Chapter.

An extensive set of alphabetically ordered references is presented at the end, with particular attention to the fundamental contributions from all pioneers of the subject, mostly on the side of Physics. Author index and Subject index complete the book.

Finally, I wish to thank the many persons who aided me to complete the book, in the first place Dr. Camilla Costa for her suggestions and her essential help in preparing the electronic files, next my young granddaughter Laura who patiently prepared the drawings at the computer and my son Mario who revised them, up to Professors Michele Battezzati, Giuseppe Figari and Gian Franco Musso for their useful discussions on many aspects of the subject, and to all my former students over the many years of teaching in the Department of Chemistry of the University of Genoa. Special thanks are due to my old friend and Colleague Dr. Deryk Wynn Davies, who helped me by reading the manuscript and revising my English. Of course, the responsibility of all contents and possible mistakes is mine, and I will appreciate much all who contribute to detecting them.

Valerio Magnasco

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Basic Principles of Quantum Mechanics

1.1 THE ORBITAL MODEL

The forces keeping together electrons and nuclei in atoms and molecules are essentially electrostatic in nature, and, at the microscopic level, satisfy the principles of quantum mechanics. Experimental evidence (Karplus and Porter, 1970) brings us to formulate a planetary model of the atom (Rutherford[1]) made by a point-like nucleus (with a diameter of 0.01–0.001 pm) carrying the whole mass and the whole positive charge $+Ze$, surrounded by electrons, each having a negative elementary charge $-e$ and a mass about 2000 times smaller than that of proton, carrying the whole negative charge $-Ne$ of the atom ($N = Z$ for neutral atoms) distributed as a charge-cloud in an atomic volume with a diameter of about 100 pm. The distribution of the electrons is apparent from the density contours

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[1] Rutherford Ernest (Lord) 1871–1937, English physicist, Professor at the Universities of Montreal, Manchester, Cambridge and London. 1908 Nobel Prize for Chemistry.

obtained from X-ray diffraction spectra of polycyclic hydrocarbons (Bacon, 1969). The electron density in atoms can be described in terms of atomic orbitals (AOs), which are one-electron functions $\psi(\mathbf{r})$ depending on a single centre (the nucleus of the atom), while electron density in molecules can be described in terms of molecular orbitals (MOs), many-centre one-electron functions depending on the different nuclei of the molecule. This is the basis for the so called orbital model, with which the majority of applications is concerned.

The physical meaning of $\psi(\mathbf{r})$ is such that:

$$|\psi(\mathbf{r})|^2 d\mathbf{r} = \begin{array}{l}\text{probability of finding in } d\mathbf{r}\\ \text{the electron in state } \psi(\mathbf{r})\end{array} \tag{1}$$

provided we satisfy the normalization condition:

$$\int d\mathbf{r} |\psi(\mathbf{r})|^2 = 1, \tag{2}$$

where integration is extended over all space, and ψ^* is the complex conjugate to ψ: $|\psi|^2 = \psi^*\psi$. This implies some physical restrictions on the form of the mathematical functions $\psi(\mathbf{r})$ (single valued, continuity of the function with its first derivatives, quadratic integrability) that are obtained as permissible solutions of a variety of eigenvalue equations which can be traced back to some space form of Schroedinger[2] type differential equations. For a single electron the equation can be written:

$$\hat{H}\psi = E\psi, \tag{3}$$

where $\hat{H}$ is the total energy operator (Hamilton[3] or Hamiltonian operator), sum of the kinetic energy and potential energy operators of the electron in the atom, and E is the value assumed by the electron energy in state ψ.

For a deeper understanding of the physical foundations of the orbital model, we introduce in the simplest way the basic principles of quantum mechanics (Margenau, 1961), which is needed for a correct physical description of the subatomic world.

1.2 THE FUNDAMENTAL POSTULATES OF QUANTUM MECHANICS

The simplest formulation of quantum mechanical principles is in the form of three postulates.

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[2] Schroedinger Erwin 1887–1961, Austrian physicist, Professor at the Universities of Breslav, Zürich, Berlin, Oxford and Dublin. 1933 Nobel Prize for Physics.

[3] Hamilton William Rowan (Sir) 1806–1865, Irish mathematical physicist, Professor of astronomy at the University of Dublin.

1.2.1 Correspondence Between Observables and Operators

There is a correspondence between dynamical variables in classical physics (observables) and linear Hermitian[4] operators in quantum mechanics.

In coordinate space, the basic correspondence is:

$$x \Rightarrow \hat{x} = x\cdot \qquad p_x \Rightarrow \hat{p}_x = \frac{h}{2\pi i}\frac{\partial}{\partial x} = -i\hbar\frac{\partial}{\partial x}, \tag{4}$$

where x is the position coordinate, p_x the x-component of the linear momentum, $\hat{p}_x$ the corresponding quantum mechanical operator, $\hbar = h/2\pi$ the reduced Planck[5] constant, and $i = \sqrt{-1}$ the imaginary unit ($i^2 = -1$). The like holds for the remaining y and z components. The caret $\hat{}$ symbol will be henceforth used to denote operators.

Def. An operator is a rule (denoted by $\hat{A}$) that transforms a function into another function (e.g. $\hat{A} = \partial/\partial x$, the first partial derivative; $\hat{A} = \partial^2/\partial x^2$, the second partial derivative, etc.). $\hat{A}\psi$ must hence be intended as a new function, as a whole, so that $\hat{A}\psi/\psi$ will never be simplified by eliminating ψ! We shall see later the properties of linear and Hermitian operators.

In 3-dimensions:

$$\mathbf{p} = \mathbf{i}p_x + \mathbf{j}p_y + \mathbf{k}p_z \qquad \text{a vector} \tag{5}$$

$$\hat{\mathbf{p}} = -i\hbar\nabla \qquad \text{a vector operator} \tag{6}$$

(a vector whose components are operators)

$$\nabla = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z} \qquad \text{the gradient operator in Cartesian coordinates.} \tag{7}$$

Examples of further observables.

x-component of the kinetic energy of a particle of mass m $\qquad T = \frac{p_x^2}{2m} \Rightarrow \hat{T} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}.$

In 3-dimensions:

$$T = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \Rightarrow \hat{T} = -\frac{\hbar^2}{2m}\nabla^2, \tag{8}$$

where:

$$\nabla^2 = \nabla \cdot \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{9}$$

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[4] Hermite Charles 1822–1901, French mathematician, Professor at the Sorbonne, Member of the Académie des Sciences.

[5] Planck Max 1858–1947, German physicist, Professor at the Universities of Kiel and Berlin. 1918 Nobel Prize for Physics.

is the Laplacian[6] operator, and the dot stands for the scalar product.

$$\text{Total energy} \Rightarrow \text{Total energy operator } \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V, \tag{10}$$

(Hamiltonian operator)

where V is the potential energy characterizing a given physical system. V is usually a multiplicative operator function of the coordinates. We take a few examples.

(i) One-dimensional free particle.

$$V = 0 \qquad \hat{H} = \hat{T} = \frac{\hat{p}_x^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{11}$$

kinetic energy only.

(ii) One-dimensional harmonic oscillator.

$$V = \frac{kx^2}{2} \qquad \hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{kx^2}{2}, \tag{12}$$

where k is the force constant.

(iii) Angular momentum of a particle of linear momentum $\mathbf{p}$ and vector position $\mathbf{r}$.

$$\begin{aligned} \boldsymbol{L} = \mathbf{r} \times \mathbf{p} &= \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \\ &= \underbrace{\mathbf{i}(yp_z - zp_y)}_{L_x} + \underbrace{\mathbf{j}(zp_x - xp_z)}_{L_y} + \underbrace{\mathbf{k}(xp_y - yp_x)}_{L_z} \end{aligned} \tag{13}$$

$$\hat{\boldsymbol{L}} = \mathbf{r} \times (-i\hbar\nabla) = -i\hbar \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ \dfrac{\partial}{\partial x} & \dfrac{\partial}{\partial y} & \dfrac{\partial}{\partial z} \end{vmatrix} = \mathbf{i}\hat{L}_x + \mathbf{j}\hat{L}_y + \mathbf{k}\hat{L}_z \tag{14}$$

$$\begin{aligned} &\hat{L}_x = -i\hbar\left(y\tfrac{\partial}{\partial z} - z\tfrac{\partial}{\partial y}\right) \qquad \hat{L}_y = -i\hbar\left(z\tfrac{\partial}{\partial x} - x\tfrac{\partial}{\partial z}\right) \\ &\hat{L}_z = -i\hbar\left(x\tfrac{\partial}{\partial y} - y\tfrac{\partial}{\partial x}\right), \end{aligned} \tag{15}$$

where the cross stands for the vector product of two vectors, and the cyclic permutation $(x \to y \to z)$ of indices should be noted. We then have for the square of the angular momentum operator in Cartesian coordinates:

$$\hat{L}^2 = \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{L}} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2. \tag{16}$$

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[6] De Laplace Pierre Simon 1749–1827, French mathematician and astronomer, Member of the Académie des Sciences.

In spherical coordinates (r, θ, ϕ) $\hat{L}^2$ can be related to the Laplacian operator:

$$\hat{L}^2 = -r^2\nabla^2 + r^2\nabla_r^2 = -\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}, \tag{17}$$

where

$$\nabla_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} \tag{18}$$

is the radial Laplacian. The operator in braces depends only on angles and is said the Legendre[7] operator (or Legendrian).

(iv) Particle of mass m and charge $-e$ in an electromagnetic field of scalar potential $\Phi(x, y, z)$ and vector potential $\mathbf{A}(x, y, z)$. The classical Hamiltonian is:

$$\begin{aligned} H &= \frac{1}{2m}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2 - e\Phi = \frac{1}{2m}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)\cdot\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right) - e\Phi \\ &= \frac{1}{2m}\left(\mathbf{p}^2 + \frac{e}{c}\mathbf{p}\cdot\mathbf{A} + \frac{e}{c}\mathbf{A}\cdot\mathbf{p} + \frac{e^2}{c^2}\mathbf{A}^2\right) - e\Phi, \end{aligned} \tag{19}$$

where c is the velocity of light. The corresponding quantum mechanical operator can be derived from this classical expression taking into consideration that the resulting operator must be Hermitian:

$$\begin{aligned} \hat{H} &= \frac{1}{2m}\left(-\hbar^2\nabla^2 - i\frac{\hbar e}{c}\nabla\cdot\mathbf{A} - i\frac{\hbar e}{c}\mathbf{A}\cdot\nabla + \frac{e^2}{c^2}\mathbf{A}^2\right) - e\Phi \\ &= -\frac{\hbar^2}{2m}\nabla^2 - i\frac{\hbar e}{2mc}(\nabla\cdot\mathbf{A}) - i\frac{\hbar e}{mc}\mathbf{A}\cdot\nabla + \frac{e^2}{2mc^2}\mathbf{A}^2 - e\Phi, \end{aligned} \tag{20}$$

where $(\nabla\cdot\mathbf{A})$ (the divergence of $\mathbf{A}$) does no longer operate on the function Ψ, since:

$$(\nabla\cdot\mathbf{A})\Psi = \Psi(\nabla\cdot\mathbf{A}) + \mathbf{A}\cdot\nabla\Psi. \tag{21}$$

(v) The 1-electron atomic system (the hydrogen-like system).

It consists of a single electron moving in the field of $+Ze$ nuclear charges ($Z = 1$ is the hydrogen atom). In the SI system:

$$V = V(r) = \frac{Ze^2}{4\pi\varepsilon_0 r} \tag{22}$$

the Coulomb[8] law of attraction of the electron by the nucleus.

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[7] Legendre Adrien Marie 1752–1833, French mathematician, Professor at the École Militaire and the École Polytechnique of Paris.

[8] Coulomb Charles Augustin 1736–1806, French physicist, Member of the Académie des Sciences.

The Hamiltonian will be:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}. \tag{23}$$

Because of the spherical symmetry of the atom, it is convenient to use spherical coordinates (r, θ, φ), where ∇^2 becomes:

$$\begin{aligned}\nabla^2 &= \nabla_r^2 - \frac{\hat{L}^2}{r^2} \\ &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}.\end{aligned} \tag{24}$$

The advantage of using spherical coordinates lies in the fact that it allows to separate radial from angular coordinates.

We notice that all of the previous formulae involve universal physical constants (e, $\hbar$, m, $4\pi\varepsilon_0$), whose value is well known. To simplify notation we introduce a system of atomic units, defined by posing:

$$e = \hbar = m = 4\pi\varepsilon_0 = 1 \qquad \text{atomic units.} \tag{25}$$

The relation between atomic units and physical constants will be examined later in Section 1.5 of this Chapter.

The hydrogenic Hamiltonian in atomic units will simplify to:

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}. \tag{26}$$

Comparison with the previous formula makes immediately clear the great advantage of using atomic units, as also the next two examples show.

(vi) The 2-electron atomic system.

In atomic units, the Hamiltonian will be:

$$\hat{H} = \frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} = \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}}, \tag{27}$$

where $\hat{h} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$ is the hydrogen-like Hamiltonian (a 1-electron operator), and $\frac{1}{r_{12}}$ the 2-electron operator describing electron repulsion. For $Z = 2$ we have the He atom.

(vii) The hydrogen molecule H_2.

R is the internuclear distance, r_{12} the interelectronic distance, the remaining ones the electron-nucleus distances. The full Born-Oppenheimer Hamiltonian (Chapter 10) looks rather complicated:

$$\begin{aligned}\hat{H} = &-\frac{\hbar^2}{2M_A}\nabla_A^2 - \frac{\hbar^2}{2M_B}\nabla_B^2 \\ &-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0 r_1} - \frac{e^2}{4\pi\varepsilon_0 r_2} \\ &-\frac{e^2}{4\pi\varepsilon_0 r_{B1}} - \frac{e^2}{4\pi\varepsilon_0 r_{A2}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} + \frac{e^2}{4\pi\varepsilon_0 R}\end{aligned} \tag{28}$$

but in atomic units the expression simplifies to:

$$\begin{aligned}\hat{H} &= -\frac{1}{2M}\nabla_A^2 - \frac{1}{2M}\nabla_B^2 - \frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 \\ &\quad -\frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_{B1}} - \frac{1}{r_{A2}} + \frac{1}{r_{12}} + \frac{1}{R} \\ &= -\frac{1}{2M}\nabla_A^2 - \frac{1}{2M}\nabla_B^2 + \hat{h}_{A1} + \hat{h}_{B2} + V,\end{aligned} \tag{29}$$

where:

$M = \dfrac{M_x}{m}$ is the proton mass in units of the electron mass

$\hat{h}_x = -\dfrac{1}{2}\nabla^2 - \dfrac{1}{r}$ the Hamiltonian of each separate atom

$V = -\dfrac{1}{r_{B1}} - \dfrac{1}{r_{A2}} + \dfrac{1}{r_{12}} + \dfrac{1}{R}$ the interatomic potential.

We now turn to the second postulate of quantum mechanics.

1.2.2 State Function and Average Values of Observables

There is a state function (or wavefunction) Ψ which describes in a probabilistic way the dynamical state of a microscopic system. In coordinate space, Ψ (generally, a complex function) is a function of coordinate x and time t such that:

$$\Psi(x,t)\Psi^*(x,t)dx = \text{probability at time } t \text{ of finding in } dx \text{ the system in state } \Psi \tag{30}$$

provided Ψ is normalized:

$$\int dx\,\Psi^*(x,t)\Psi(x,t) = 1 \tag{31}$$

the integration being extended over all space.

As already said for the orbitals, Ψ must be restricted by:

- Single-valuedness.
- Continuity conditions with its first derivatives.
- Square integrability, i.e. $\Psi(x,t)$ should vanish at infinity.

These are the conditions that must always be satisfied because a mathematical function Ψ must describe a physical probability. We shall call such a function a Q-class function (function belonging to the L_2 Hilbert[9] space, normalizable or regular function).

As a consequence of the probabilistic meaning of Ψ, the average (expectation) value of the physical quantity A (with quantum mechanical operator $\hat{A}$), characterizing the system in state Ψ, is given by:

$$\langle A\rangle = \frac{\int dx\,\Psi^*(x,t)\hat{A}\Psi(x,t)}{\int dx\,\Psi^*(x,t)\Psi(x,t)} = \int dx\,\hat{A}\,\underbrace{\frac{\Psi(x,t)\Psi^*(x,t)}{\int dx\,\Psi^*(x,t)\Psi(x,t)}}_{\text{probability density function}}, \tag{32}$$

where the integration is extended over all space. Notice that $\hat{A}$ acts always upon Ψ and not on Ψ^*, and that it must be Hermitian. The state function is hence needed to evaluate average values of physical observables, which are the only quantities that can be measured by experiment.

1.2.3 Time Evolution of State Function

Ψ is obtained by solving the time-dependent Schroedinger equation:

$$\hat{H}\Psi = i\hbar\dot{\Psi}, \tag{33}$$

where $\dot{\Psi} = \partial\Psi/\partial t$. This is a partial differential equation in the position coordinate x and the time t, which are treated on a different footing.

If $\hat{H}$ does not depend in an explicit way on t (stationary state), the variables can be separated by posing:

$$\Psi(x,t) = \psi(x)g(t) \tag{34}$$

and we obtain:

$$\frac{\hat{H}\psi}{\psi} = -\frac{\hbar}{i}\frac{d\ln g}{dt} = E. \tag{35}$$

Since the left side of this equation depends only on x and the right on t, each side must be equal to a constant E, known as separation constant. In this way, we obtain two separate differential equations, one in x, the other in t:

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[9] Hilbert David 1862–1943, German mathematician, Professor at the University of Göttingen.

$$\hat{H}\psi(x) = E\psi(x) \tag{36}$$

$$d\ln g(t) = -i\frac{E}{\hbar}dt. \tag{37}$$

The latter equation can be immediately integrated to:

$$g(t) = g_0 \exp\left(-i\,\frac{E}{\hbar}t\right) = g_0 \exp(-i\omega t) \qquad \frac{E}{\hbar} = \omega \tag{38}$$

giving the time evolution of the stationary state (always the same).

From a mathematical standpoint, the Schroedinger equation (36) determining $\psi(x)$ has the form of an *eigenvalue equation*, namely that particular differential equation where the operator acting upon the function gives the function itself (the eigenfunction of the operator) multiplied by a constant (the eigenvalue of the operator). When several eigenfunctions belong to the same eigenvalue, we speak of degeneracy of the eigenvalue (for instance, the first excited level of the H atom is 4 times degenerate, i.e. there are 4 different states belonging to this eigenvalue, i.e. 2s, 2p$_x$, 2p$_y$, 2p$_z$). We notice that, entering in both Schroedinger equations, the energy observable (hence, the Hamiltonian operator) plays a peculiar role among all physical observables of quantum mechanics.

We now look to the physical plausibility of our postulates by investigating the nature of measurements at the subatomic level.

1.3 THE PHYSICAL PRINCIPLES OF QUANTUM MECHANICS

1.3.1 Wave–Particle Dualism

Experimental observation shows that electromagnetic waves present both a wave-like and a particle-like character. For light and X-rays this is shown by interference and diffraction phenomena on the one hand, and by the photo-electric and Compton[10] effects on the other. A typical matter particle such as the electron can give diffraction figures characteristic of a wave-like nature.

We shall consider in some detail the Compton effect (1923), where a monochromatic X-ray beam impinging on a substance is scattered in all directions with a wavelength that increases with increasing the scattering angle. The photon of frequency ν impinging on the particle along the the x-direction is scattered in the direction specified by the angle θ with a frequency ν'. The conservation of linear momentum gives:

$$\frac{h\nu}{c} = \frac{h\nu'}{c}\cos\theta + p_x \qquad 0 = \frac{h\nu'}{c}\sin\theta - p_y \tag{39}$$

from which, squaring and adding the two components, assuming $\nu' \simeq \nu$:

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[10] Compton Arthur Holly 1892–1962, U.S. physicist, 1927 Nobel Prize for Physics.

$$\begin{aligned} p^2 &= \frac{h^2\nu^2}{c^2}(1 - 2\cos\theta + \cos^2\theta + \sin^2\theta) \\ &\approx 2\frac{h^2\nu^2}{c^2}(1 - \cos\theta) = 2\frac{h^2}{\lambda^2}(1 - \cos\theta), \end{aligned} \tag{40}$$

where $p^2 = p_x^2 + p_y^2$ is the squared momentum of the particle and we have used $\nu = c/\lambda$.

On the other hand, conservation of the total energy gives:

$$h\nu = h\nu' + \frac{p^2}{2m} \quad h\nu' < h\nu, \tag{41}$$

where the particle, even at rest, acquires a kinetic energy given by the second term in the equation. Hence we get for p^2:

$$\begin{aligned} p^2 &= 2hm(\nu - \nu') = 2hmc\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right) = 2hmc\frac{\lambda' - \lambda}{\lambda\lambda'} \\ &\approx 2hmc\frac{\lambda' - \lambda}{\lambda^2}. \end{aligned} \tag{42}$$

Equating to the previous expression for the momentum, we get immediately that the wavelength shift is a function of the scattering angle θ given by:

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{mc}(1 - \cos\theta). \tag{43}$$

The Compton effect shows hence that, as a result of photon-particle interaction, the wavelength of the scattered photon increases with θ.

For the electron, the constant will be:

$$\begin{aligned} \frac{h}{mc} &= \frac{6.626 \times 10^{-34}\ \mathrm{J\,s}}{9.109 \times 10^{-31}\ \mathrm{kg} \times 2.998 \times 10^{8}\ \mathrm{m\,s^{-1}}} \\ &= 2.426 \times 10^{-12}\ \mathrm{m} = 0.0243\ \text{Å}. \end{aligned}$$

The Compton effect shows that the photon is a particle of light, with a mass given by the Einstein [11] relation:

$$m = \frac{E}{c^2} = \frac{h\nu}{c^2} = \frac{h}{\lambda c} = \frac{h}{c}k, \tag{44}$$

where k is the wavenumber, λ^{-1}. So the photon mass depends on the spectral region as shown in Table 1.1.

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[11] Einstein Albert 1879–1955, German mathematical physicist, Professor at the Universities of Zürich, Berlin and Princeton. 1921 Nobel Prize for Physics.

Table 1.1.

Photon mass in different spectral regions

Region	k (m^{-1})	m (kg)
MW	10^2	2.2×10^{-40}
IR	10^5	2.2×10^{-37}
VIS	10^6	2.2×10^{-36}
UV	10^7	2.2×10^{-35}
X	10^{10}	2.2×10^{-32}
γ	10^{11}	2.2×10^{-31}

Table 1.2.

Properties of γ-rays from atomic sources

Isotope	λ (m)	k (m^{-1})	E (MeV)	m (10^{-31} kg)
^{298}U	2.50×10^{-11}	4.00×10^{10}	5.08×10^{-2}	0.88
^{7}Be	2.60×10^{-12}	3.85×10^{11}	4.77×10^{-1}	8.51
^{60}Co	1.03×10^{-12}	9.71×10^{11}	1.20×10^{0}	21.4
^{22}Na	9.70×10^{-13}	1.03×10^{12}	1.28×10^{0}	22.7
^{14}N	1.90×10^{-13}	5.26×10^{12}	6.52×10^{0}	116

Recalling that:

$$m = \frac{h}{c} k = 2.210 \times 10^{-42}\, k \tag{45}$$

for 1 eV we have:

$$\begin{aligned} k = \frac{E}{hc} &= \frac{1.602 \times 10^{-19}\ \mathrm{J}}{6.626 \times 10^{-34}\ \mathrm{J\,s} \times 2.998 \times 10^{8}\ \mathrm{m\,s^{-1}}} \\ &= 8.065 \times 10^{5}\ \mathrm{m}^{-1} \end{aligned} \tag{46}$$

and, for a MeV:

$$1\ \mathrm{MeV} = 10^{6}\ \mathrm{eV} = 8.065 \times 10^{11}\ \mathrm{m}^{-1}. \tag{47}$$

In Table 1.2 we give some properties of γ-rays obtained from different atomic sources.

We see from the Table that the isotope ^{7}Be emits γ-rays having a mass comparable with that of the electron, $m = 9.109 \times 10^{-31}$ kg.

Just after the discovery of the Compton effect, in his famous thesis (1924, 1925) de Broglie[12] suggested the wave-like character of material particles, assuming that the relation:

$$p = \frac{h\nu}{c} = \frac{h}{\lambda} = hk, \tag{48}$$

true for photons (particles of light), should equally be valid for particles (e.g. electrons, particles of matter). In this way, a property of particles, the linear momentum, is proportional through Planck's constant to a property of waves, the wave number k. Any moving microscopic body has associated a "wave", whose wavelength is related to the momentum by the relation above. This hypothesis was later verified by experiment studying the diffraction pattern of electrons reflected from a nickel surface (Davisson and Germer, 1927) and by the formation of diffraction rings from cathode rays diffused through thin films of aluminium, gold and celluloid (Thomson, 1928).

1.3.2 Atomicity of Matter

A characteristic of atomic and molecular physics is the *atomicity* of matter (electron, $-e$; proton, $+e$), energy ($h\nu$, Planck), linear momentum (h/λ), angular momentum ($\hbar$, Bohr[13]). This implies the peculiar character that any experimental measurement has in atomic physics (i.e. on a microscopic scale), particularly its limits that become apparent in the Heisenberg[14] principle (1927) as a direct consequence of the interaction between the experimental apparatus and the object of measurement, which has a direct ineliminable effect on the physical property that must be measured at the microscopic level.

- Heisenberg uncertainty principle.

Quantities that are canonically conjugate (in the sense of analytical mechanics) are related by the uncertainty relations:

$$\Delta x \Delta p_x \sim h \qquad \Delta E \Delta t \sim h, \tag{49}$$

where h is the Planck constant, Δx the uncertainty in the x-coordinate of the position of the particle, and Δp_x the simultaneous uncertainty in the x-component of the linear momentum of the particle. In other words, the product of the uncertainties of two conjugate dynamical variables (e.g. x and p_x) is of the order of Planck's constant, namely, the attempt to attain the exact measure of the coordinate position along x ($\Delta x = 0$) implies the infinite uncertainty in the measure of the corresponding conjugate component of the linear momentum ($\Delta p_x = \infty$). In quantum mechanical terms we may say that:

$$x\hat{p}_x - \hat{p}_x x = [x, \hat{p}_x] \neq 0, \tag{50}$$

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[12] de Broglie Louis Victor 1892–1987, French physicist, Professor at the University of Paris, Member of the Académie des Sciences. 1929 Nobel Prize for Physics.

[13] Bohr Niels Heinrik David 1885–1962, Danish physicist, Professor at the University of Copenhagen. 1922 Nobel Prize for Physics.

[14] Heisenberg Werner 1901–1976, German physicist, Professor at the Universities of Leipzig and Göttingen. 1932 Nobel Prize for Physics.

i.e. the commutator of the corresponding operators is different from zero (we say the two operators do not commute). The Heisenberg principle does not hold for non-conjugate components:

$$[x, \hat{p_y}] = 0, \tag{51}$$

i.e. quantities whose commutator vanishes can be measured at the same time with arbitrary accuracy. For a more general definition see Margenau (1961, pp. 46–47). The uncertainty principle must be considered as a law of nature, and stems directly from the interaction between experiment and object at the microscopic level, as the following examples will show.

(i) Macroscopic body (the cannon ball).
Let us try to make an extremely accurate measurement of the position of this macroscopic body, say 1 micron, $\Delta x = 10^{-6}$ m. This corresponds to an unmeasurably small uncertainty in the corresponding value of the conjugate momentum:

$$\Delta p_x = \frac{6.626 \times 10^{-34}\ \mathrm{J\,s}}{10^{-6}\ \mathrm{m}} = 6.626 \times 10^{-28}\ \mathrm{kg\,m\,s^{-1}}. \tag{52}$$

(ii) Microscopic body (the electron in a field).
Consider an electron accelerated through a potential difference of 50 volts. Since 1 eV is the energy acquired by an electron in a potential difference of 1 volt (Coulson, 1958):

$$1\ \mathrm{eV} = 1.602\,177 \times 10^{-19}\ \mathrm{J} \tag{53}$$

the kinetic energy acquired by the electron in the field will be:

$$T = \frac{p^2}{2m} = 50\ \mathrm{eV} = 8.011 \times 10^{-18}\ \mathrm{J} \tag{54}$$

with the momentum:

$$\begin{aligned} p &= \sqrt{2mT} \\ &= \{2 \times 9.109 \times 10^{-31}\ \mathrm{kg} \times 8.011 \times 10^{-18}\ \mathrm{kg\,m^2\,s^{-2}}\}^{1/2} \\ &= 3.821 \times 10^{-24}\ \mathrm{kg\,m\,s^{-1}}. \end{aligned} \tag{55}$$

For a specification of the electron within an atomic dimension (1 Å $= 10^{-10}$ m), not a very accurate requirement:

$$\begin{aligned} \Delta x &= 10^{-10}\ \mathrm{m} \\ \Delta p_x &= \frac{6.626 \times 10^{-34}\ \mathrm{J\,s}}{10^{-10}\ \mathrm{m}} = 6.626 \times 10^{-24}\ \mathrm{kg\,m\,s^{-1}} \end{aligned} \tag{56}$$

so that the uncertainty in the momentum exceeds its calculated magnitude!

(iii) The Heisenberg γ-ray microscope.
It is a typical "gedanken experiment", an experiment ideally devised by Heisenberg (1930) to show the uncertainty principle for a couple of conjugated dynamical variables (e.g. x and p_x).

Suppose we want to determine the position and the linear momentum of an electron impinged by a photon traveling along the x-direction. The optical axis of our microscope tube will be along the perpendicular y-coordinate. The way of proceeding is much along the same lines as for the Compton effect. The resolving power of our microscope is:

$$\Delta x = \frac{\lambda}{2\sin\varepsilon}, \tag{57}$$

where 2ε is the angular aperture of the lens of our objective. To improve precision in the determination of the electron position we must reduce Δx, namely we must reduce the wavelength λ or increase the frequency, i.e. the wave number k, of our inciding photon. We saw in Table 1.2 that the weak γ-rays from the ^{7}Be source have a photon mass comparable to that of the electron. Hence, illuminating our microscope with a photon of this energy we shall have the collision of particles of like mass, which will be scattered in different directions. If θ is the scattering angle, the conservation of linear momentum along x gives:

$$\frac{h\nu}{c} = \frac{h\nu'}{c}\cos\theta + p_x \tag{58}$$

$$\begin{aligned} p_x &= \frac{h}{c}(\nu - \nu'\cos\theta) \approx \frac{h\nu}{c}(1-\cos\theta) \\ &= \frac{h}{\lambda}(1-\cos\theta). \end{aligned} \tag{59}$$

Because the scattered photon becomes observable, it must be scattered inside the microscope tube, so that θ will be restricted to:

$$\left(\frac{\pi}{2} - \varepsilon\right) \le \theta \le \left(\frac{\pi}{2} + \varepsilon\right) \qquad \cos\left(\frac{\pi}{2} - \varepsilon\right) \le \cos\theta \le \cos\left(\frac{\pi}{2} + \varepsilon\right) \tag{60}$$

$$\sin\varepsilon \le \cos\theta \le -\sin\varepsilon \qquad \frac{h}{\lambda}(1 - \sin\varepsilon) \le p_x \le \frac{h}{\lambda}(1 + \sin\varepsilon). \tag{61}$$

The momentum of the electron, p_x, can hence be determined to within an uncertainty of:

$$\Delta p_x = \frac{h}{\lambda} 2\sin\varepsilon \tag{62}$$

from which follows Heisenberg's uncertainty principle for the x-component.

On the other hand, the conservation of the linear momentum in the perpendicular y-direction gives:

$$0 = \frac{h\nu'}{c}\sin\theta - p_y \tag{63}$$

$$p_y = \frac{h\nu'}{c}\sin\theta \approx \frac{h\nu}{c}\sin\theta \tag{64}$$

with:

$$\cos\varepsilon \leq \sin\theta \leq \cos\varepsilon. \tag{65}$$

The only possible value for $\sin\theta$ is now $\cos\varepsilon$, and therefore the transverse component of the momentum is exactly measurable:

$$p_y = \frac{h}{\lambda}\cos\varepsilon \qquad \Delta p_y = 0. \tag{66}$$

As already said, this is in agreement with the fact that Heisenberg uncertainty relation does not hold for dynamical quantities that are not conjugate, and which are described by commuting operators:

$$[x, \hat{p_x}] = i\hbar \qquad [x, \hat{p_y}] = 0. \tag{67}$$

From this follows Dirac's observation that the greatest possible specification of a given physical system is to find the maximum set of commuting operators. In this case, it is possible to find a set of observables, such that simultaneous exact knowledge of all members of the set is possible (Troup, 1968).

As a consequence of the uncertainty principle, the only possible description of the dynamical state of a microscopic system is a *probabilistic* one, as contrasted with the *deterministic* description of classical mechanics. The problem is now to find the function which describes such a probability.

1.3.3 Schroedinger Wave Equation

Schroedinger (1926) writes for a progressive wave the complex form:

$$\Psi = A\exp(i\alpha) = A\exp[2\pi i(kx - \nu t)], \tag{68}$$

where A is the amplitude and α the phase of a monochromatic plane wave of wave number k and frequency ν which propagates along x.

Taking into account the relations of de Broglie and Planck:

$$k = \frac{p}{h}, \qquad \nu = \frac{E}{h} \tag{69}$$

the phase of a matter wave can be written:

$$\alpha = \frac{1}{\hbar}(px - Et), \tag{70}$$

so that the wave equation for a matter particle will be:

$$\Psi = A \exp\left[\frac{i}{\hbar}(px - Et)\right] = \Psi(x, t) \tag{71}$$

which defines Ψ as a function of x and t, with constant values of p and E. Taking the derivatives of Ψ with respect to x and t, we have the correspondences:

$$\frac{\partial \Psi}{\partial x} = \frac{i}{\hbar} p \Psi \quad \text{hence} \quad \underset{\substack{\text{classical}\\ \text{variable}}}{p} \Rightarrow \underset{\substack{\text{quantum mechanical}\\ \text{operator}}}{-i\hbar \frac{\partial}{\partial x} = \hat{p}} \tag{72}$$

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} E \Psi \quad \text{hence} \quad \underset{\substack{\text{total}\\ \text{energy}}}{E} \Rightarrow \underset{\substack{\text{quantum mechanical}\\ \text{operator (Hamiltonian)}}}{i\hbar \frac{\partial}{\partial t} = \hat{H}.} \tag{73}$$

These two relations give the basic correspondences we have seen before between physical variables (observables) in classical mechanics and linear Hermitian operators in quantum mechanics. The last equation is nothing but the time-dependent Schroedinger equation giving the time evolution of Ψ, and can be written in the usual form:

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}. \tag{74}$$

1.3.4 Born Interpretation

Born[15] (Born, 1926) suggested that the intensity of de Broglie's wave $\propto |\Psi|^2$ should be regarded as a *probability density* (probability per unit volume). In other words, Born's interpretation of de Broglie and Schroedinger waves is such that:

$$\Psi(\mathbf{x}, t)\Psi^*(\mathbf{x}, t)d\mathbf{x} = |\Psi(\mathbf{x}, t)|^2 d\mathbf{x} = \begin{array}{l}\text{probability of finding the particle}\\ \text{in the infinitesimal volume}\\ \text{element } d\mathbf{x} \text{ at the point } \mathbf{x} \text{ at time t.}\end{array} \tag{75}$$

For this interpretation being correct, it must be:

$$\int d\mathbf{x} \Psi^*(\mathbf{x}, t)\Psi(\mathbf{x}, t) = 1, \tag{76}$$

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[15] Born Max 1882–1970, German physicist, Professor at the Universities of Berlin, Frankfurt, Göttingen and Edinburgh. 1954 Nobel Prize for Physics.

where integration is over all space. For a correct definition of probability, Ψ must be normalized to 1. For a stationary state the probability does not depend on time. In fact:

$$|\Psi(\mathbf{x},t)|^2 d\mathbf{x} \propto |\psi(\mathbf{x})|^2 |g_0|^2 d\mathbf{x} \tag{77}$$

is constant on time.

We can conclude by saying that the wave-like character of particles is due to the fact that the probability function ψ does satisfy a wave equation. This is the explanation of the wave-particle duality which was at first so difficult to understand.

1.3.5 Measure of Observables

We must first introduce here few mathematical definitions on Q-class functions, which will be specified later in detail in Section 1.4.

(i) The Dirac[16] notation for the scalar product of two functions φ, ψ:

$$\int dx \varphi^*(x)\psi(x) = \langle\varphi|\psi\rangle. \tag{78}$$

(ii) The concept of orthonormal set $\{\varphi_k(x)\}$, implying $\langle\varphi_k|\varphi_{k'}\rangle = \delta_{kk'}$, where $\delta_{kk'}$ is the Kronecker delta ($= 1$ for $k' = k$, $= 0$ for $k' \neq k$).

(iii) The expansion theorem for any function $F(x)$:

$$F(x) = \sum_k \varphi_k(x) C_k = \sum_k |\varphi_k\rangle\langle\varphi_k|F\rangle, \tag{79}$$

where $\{\varphi_k(x)\}$ is any suitable set of orthonormal basis functions.

Now, let $\{A_k\}$ and $\{\varphi_k(x)\}$, with $\langle\varphi_k|\varphi_{k'}\rangle = \delta_{kk'}$, be the set of eigenvalues and eigenfunctions of the Hermitian operator $\hat{A}$ corresponding to the physical observable A. The average value of A in state Ψ is given by:

$$\langle A\rangle = \int dx \Psi^*(x,t)\hat{A}\Psi(x,t) = \langle\Psi|\hat{A}\Psi\rangle \tag{80}$$

provided the state function Ψ is normalized:

$$\langle\Psi|\Psi\rangle = 1. \tag{81}$$

- If Ψ is an eigenstate of $\hat{A}$ with eigenvalue A_k, then:

  $$\langle A\rangle = A_k \tag{82}$$

  so that, doing a measure of A at the time t, we shall certainly obtain for the observable A the value A_k.

---

[16] Dirac Paul Adrien Maurice 1902–1984, English physicist, Professor of mathematics at the University of Cambridge. 1933 Nobel Prize for Physics.

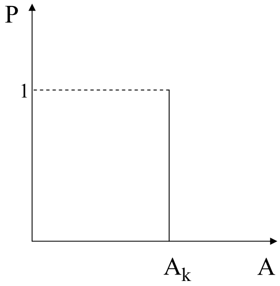

Figure 1.1 Definite value for the k-th eigenvalue.

- If Ψ is not an eigenstate of $\hat{A}$, we can expand Ψ into the complete set of the eigenstates of $\hat{A}$, obtaining:

$$\langle A \rangle = \sum_k \sum_{k'} C_k^*(t) C_{k'}(t) \langle \varphi_k | \hat{A} \varphi_{k'} \rangle = \sum_k |C_k(t)|^2 A_k \tag{83}$$

so that, doing a measure of A at the time t, we shall have the probability $P_k(t) = |C_k(t)|^2$ of observing for A the value A_k.

Probability distribution:

$$P_k(t) = |C_k(t)|^2 = C_k(t) C_k^*(t) \tag{84}$$

$$C_k(t) = \langle \varphi_k | \Psi \rangle, \qquad C_k^*(t) = \langle \Psi | \varphi_k \rangle. \tag{85}$$

(a) If at time t Ψ is an eigenstate of $\hat{A}$:

$$\Psi \equiv \varphi_k \qquad C_k(t) = 1 \qquad C_{k'}(t) = 0 \quad \text{for any } k' \neq k \tag{86}$$

we have a 100% probability of observing for A the value A_k:

(b) Otherwise, we can expand Ψ into stationary states:

$$\begin{aligned} \Psi &= \sum_{k''} a_{k''} \exp(-i\omega_{k''} t) \psi_{k''}(x) \\ \Psi^* &= \sum_{k'} a_{k'}^* \exp(+i\omega_{k'} t) \psi_{k'}^*(x) \\ \omega_k &= \frac{E_k}{\hbar} \end{aligned} \tag{87}$$

$$P_k(t) = \sum_{k'} \sum_{k''} a_{k'}^* a_{k''} \exp[-i(\omega_{k''} - \omega_{k'})t] \langle \psi_{k'} | \varphi_k \rangle \langle \varphi_k | \psi_{k''} \rangle, \tag{88}$$

where the last two integrals are space integrals. Then we have:

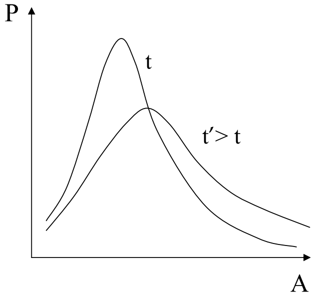

Figure 1.2 Fluctuation in time of eigenvalue distribution.

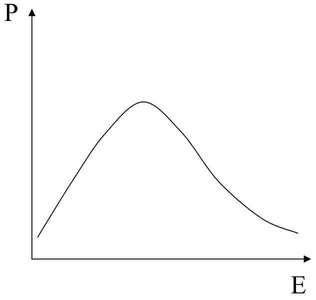

Figure 1.3 Energy eigenvalue distribution.

- If A is an observable different from E, the probability $P_k(t)$ fluctuates in time.
- If $A = E$ (the total energy):

$$\hat{A} = \hat{H}, \qquad \varphi_k(x) = \psi_k(x) \qquad \langle \psi_k | \psi_{k'} \rangle = \delta_{kk'} \tag{89}$$

$$P_k(t) = \sum_{k'} \sum_{k''} a^*_{k'} a_{k''} \exp[-i(\omega_{k''} - \omega_{k'})] \delta_{kk'} \delta_{kk''} = |a_k|^2 \tag{90}$$

since $k' = k'' = k$ is the only surviving term. In this case, we obtain for the energy a distribution constant in time:

$$\langle \hat{H} \rangle = E = \sum_k |a_k|^2 E_k, \tag{91}$$

where E_k is the k-th energy eigenvalue (the energy level).

1.4 THE MATHEMATICS OF QUANTUM MECHANICS

The essential point for any application is the *expansion theorem* (Section 1.4.4), that allows to reformulate the eigenvalue equations of the quantum mechanical Hermitian operators in terms of matrix representatives. Let us now introduce in some detail some mathematical definitions regarding functions of the L_2 Hilbert space (in short, normalizable or Q-class functions), while greater space on matrices will be devoted to Chapter 2.

1.4.1 Dirac Notation and Sets of Normalizable Functions

$$\text{(i) Function} \quad \varphi(x) = |\varphi\rangle \Longrightarrow \text{ket} \tag{92}$$

$$\text{Complex conjugate} \quad \varphi^*(x) = \langle\varphi| \Longrightarrow \text{bra} \tag{93}$$

Then the scalar product of φ^* by φ can be written in the bracket form (a notation due to Dirac):

$$\int dx\varphi^*(x)\varphi(x) = \langle\varphi|\varphi\rangle \geq 0. \tag{94}$$

The bracket of a function with itself is a non-negative number. Dirac notation is useful as a shorthand and is largely used in the Literature.

(ii) Normalization and orthogonality.
If:

$$\int d\mathbf{x}\psi^*(\mathbf{x})\psi(\mathbf{x}) = \int d\mathbf{x}|\psi(\mathbf{x})|^2 = \langle\psi|\psi\rangle = 1 \tag{95}$$

we say that ψ is normalized (to 1). If:

$$\langle\psi|\psi\rangle = A > 0, \tag{96}$$

where A is said the norm of ψ, ψ can be normalized by multiplying it by $N = A^{-1/2}$, where N is called the normalization factor.
If:

$$\int d\mathbf{x}\psi'^*(\mathbf{x})\varphi'(\mathbf{x}) = \langle\psi'|\varphi'\rangle = S(\neq 0) \tag{97}$$

with ψ', φ' both normalized to 1, φ' is not orthogonal to ψ', and their scalar product is said to be the non-orthogonality integral. If $\langle\psi'|\varphi'\rangle = 0$, the functions are orthogonal. φ' can be orthogonalized to ψ' through the linear combination:

$$\varphi = \varphi' - S\psi'$$

as can be verified immediately. φ can then be normalized:

$$\varphi = (1 - S^2)^{-1/2}(\varphi' - S\psi') \tag{98}$$

giving what is known as Schmidt (unsymmetrical) orthogonalization.

(iii) Schmidt orthogonalization.

$$\langle\psi'|\psi'\rangle = \langle\varphi'|\varphi'\rangle = 1 \qquad \langle\psi'|\varphi'\rangle = \langle\varphi'|\psi'\rangle = S \neq 0.$$

We take the new set:

$$\psi = \psi'$$

$$\varphi = A\varphi' + B\psi',$$

where we impose on φ the orthogonality and normalization conditions:

$$\langle\varphi|\psi\rangle = \langle A\varphi' + B\psi'|\psi'\rangle = AS + B = 0$$

$$\langle\varphi|\varphi\rangle = \langle A\varphi' + B\psi'|A\varphi' + B\psi'\rangle = A^2 + B^2 + 2ABS = 1.$$

We obtain the system:

$$\begin{cases} AS + B = 0 \qquad \dfrac{B}{A} = -S \quad A \neq 0 \\ A^2 + B^2 + 2ABS = 1 \end{cases}$$

$$A^2\left\{1 + \left(\frac{B}{A}\right)^2 + 2\left(\frac{B}{A}\right)S\right\} = A^2(1 - S^2) = 1$$

$$A = (1 - S^2)^{-1/2}, \qquad B = -S(1 - S^2)^{-1/2}$$

so that the Schmidt orthonormalized function will be:

$$\varphi = \frac{\varphi' - S\psi'}{\sqrt{1 - S^2}}.$$

Schmidt orthogonalization of 3 and n functions is examined in Problems 1.9 and 1.10.

(iv) Set of orthonormal functions.
Let:

$$\{\varphi_k(\mathbf{x})\} = (\varphi_1\varphi_2 \cdots \varphi_k \cdots \varphi_i \cdots) \tag{99}$$

be a set of functions. If:

$$\langle\varphi_k|\varphi_i\rangle = \delta_{ki} \quad k, i = 1, 2, \cdots \tag{100}$$

the set is said orthonormal, and δ_{ki} is the Kronecker delta.

(v) Linear independence and basis sets.
A set of functions is said to be linearly independent if:

$$\sum_k \varphi_k(\mathbf{x})C_k = 0 \quad \text{with } C_k = 0 \text{ for any } k. \tag{101}$$

A set of linearly independent functions gives a *basis* in the function space, where we can expand any other function of that space into a linear combination of the basis functions. We can easily show that the expansion is unique, simply trying to have two expansions in the *same* basis with *different* coefficients:

$$\sum_k \varphi_k(\mathbf{x})C_k = \sum_k \varphi_k(\mathbf{x})C'_k \implies \sum_k \varphi_k(\mathbf{x})(C'_k - C_k) = 0. \tag{102}$$

But for linearly independent functions $C'_k - C_k = 0 \implies C'_k = C_k$ and the expansion is unique. Condition for linear independence is that:

$$\det \mathbf{M}_{ki} \neq 0, \tag{103}$$

where $\mathbf{M}$ is the metric matrix with elements $M_{ki} = \langle \varphi_k | \varphi_i \rangle$. A set of orthonormal functions ($M_{ki} = \delta_{ki}$) is therefore a linearly independent set.

1.4.2 Linear Operators

(i) Let $\varphi = \varphi(\mathbf{x})$ be a regular function. A linear operator $\hat{A}$ transforms $\varphi(\mathbf{x})$ according to the following definitions:

$$\begin{cases} \hat{A}[\varphi_1(\mathbf{x}) + \varphi_2(\mathbf{x})] = \hat{A}\varphi_1(\mathbf{x}) + \hat{A}\varphi_2(\mathbf{x}) \\ \hat{A}[a\varphi(\mathbf{x})] = a[\hat{A}\varphi(\mathbf{x})] \quad a = \text{complex constant.} \end{cases} \tag{104}$$

Examples:

$$\hat{A} = \frac{\partial}{\partial x} \implies \hat{A}\varphi = \frac{\partial \varphi}{\partial x} \qquad \text{the first } x\text{-derivative}$$

$$\hat{A} = \frac{\partial^2}{\partial x^2} \implies \hat{A}\varphi = \frac{\partial^2 \varphi}{\partial x^2} \qquad \text{the second } x\text{-derivative.}$$

Either $\partial/\partial x$ or $\partial^2/\partial x^2$ are linear operators in as much as they satisfy the definitions above. As an example of a non-linear operator, we can take $\{\ \}^2$.

(ii) Sum and product of operators.
The algebraic sum of two operators is commutative:

$$\begin{aligned} (\hat{A} + \hat{B})\varphi(\mathbf{x}) &= \hat{A}\varphi(\mathbf{x}) + \hat{B}\varphi(\mathbf{x}) \\ &= \hat{B}\varphi(\mathbf{x}) + \hat{A}\varphi(\mathbf{x}) = (\hat{B} + \hat{A})\varphi(\mathbf{x}). \end{aligned} \tag{105}$$

In general, the product of two operators is not commutative:

$$\hat{A}(\hat{B}\varphi(\mathbf{x})) = \hat{A}f(\mathbf{x}) = g(\mathbf{x}) \tag{106}$$

$$\hat{B}(\hat{A}\varphi(\mathbf{x})) = \hat{B}F(\mathbf{x}) = G(\mathbf{x}). \tag{107}$$

If $\hat{A}\hat{B} = \hat{B}\hat{A}$ we say that the two operators commute. The quantities:

$$\hat{A}\hat{B} - \hat{B}\hat{A} = [\hat{A}, \hat{B}] \qquad \hat{A}\hat{B} + \hat{B}\hat{A} = [\hat{A}, \hat{B}]_+ \tag{108}$$

are called the commutator and anticommutator of the operators $\hat{A}$, $\hat{B}$, respectively.

1.4.3 Hermitian Operators

They are linear operators satisfying the "turn-over" rule:

$$\begin{gathered} \langle\psi|\hat{A}\varphi\rangle = \langle\hat{A}\psi|\varphi\rangle \\ \int dx\,\psi^*(x)\big(\hat{A}\varphi(x)\big) = \int dx\big(\hat{A}\psi(x)\big)^*\varphi(x) \end{gathered} \tag{109}$$

where the * means to take the complex conjugate. As an example:

$$\psi(x) = A(x) + iB(x) \qquad (\psi(x))^* = A(x) - iB(x), \tag{110}$$

where $A(x)$ and $B(x)$ are real functions.

- The Hermitian operators have the following properties:

(i) Real eigenvalues
(ii) Orthogonal (or orthogonalizable) eigenfunctions
(iii) Their eigenfunctions form a *complete* set.

The first two properties can be easily derived from the definition.

(i) $\langle\varphi|\hat{A}\varphi\rangle = \langle\hat{A}\varphi|\varphi\rangle$ Def.
with:

$$\hat{A}\varphi = A\varphi \qquad \big(\hat{A}\varphi\big)^* = A^*\varphi^* \quad A = \text{eigenvalue}$$

$$\langle\varphi|\hat{A}\varphi\rangle = A\langle\varphi|\varphi\rangle \qquad \langle\hat{A}\varphi|\varphi\rangle = A^*\langle\varphi|\varphi\rangle$$

and, by subtracting the first from the second equation:

$$0 = (A^* - A)\langle\varphi|\varphi\rangle \quad \langle\varphi|\varphi\rangle \neq 0 \Longrightarrow A^* = A.$$

(ii) $\hat{A}\varphi_\lambda = A_\lambda\varphi_\lambda \qquad \hat{A}\varphi_\mu = A_\mu\varphi_\mu \quad A_\lambda, A_\mu$ are two eigenvalues.

We have two cases:

- $A_\lambda \neq A_\mu$ not degenerate eigenvalues

$$\langle \varphi_\lambda | \hat{A}\varphi_\mu \rangle = A_\mu \langle \varphi_\lambda | \varphi_\mu \rangle$$

$$\langle \hat{A}\varphi_\lambda | \varphi_\mu \rangle = A_\lambda^* \langle \varphi_\lambda | \varphi_\mu \rangle = A_\lambda \langle \varphi_\lambda | \varphi_\mu \rangle$$

and, by subtracting:

$$0 = (A_\lambda - A_\mu)\langle \varphi_\lambda | \varphi_\mu \rangle \qquad A_\lambda - A_\mu \neq 0 \Longrightarrow \langle \varphi_\lambda | \varphi_\mu \rangle = 0$$

- $A_\lambda = A_\mu = A$ degenerate eigenvalue

$$\hat{A}\varphi_\lambda = A\varphi_\lambda \qquad \hat{A}\varphi_\mu = A\varphi_\mu .$$

We have now two linearly independent functions belonging to the *same* eigenvalue, so that the demonstration above is no longer valid. But we can always orthogonalize φ_μ to φ_λ (e.g. by the Schmidt method) without changing the eigenvalue.

$$\underset{\text{non-orthogonal set}}{(\varphi_\lambda \varphi_\mu)} \quad \Longrightarrow \quad \underset{\text{orthonormal set}}{(\varphi'_\lambda \varphi'_\mu)}$$

$$\begin{cases} \varphi'_\lambda = \varphi_\lambda \\ \varphi'_\mu = \dfrac{\varphi_\mu - S\varphi_\lambda}{\sqrt{1-S^2}} \end{cases} \qquad S = \langle \varphi_\lambda | \varphi_\mu \rangle = \langle \varphi_\mu | \varphi_\lambda \rangle \neq 0.$$

It can be verified immediately that:

$$\begin{aligned} \hat{A}\varphi'_\lambda &= A\varphi'_\lambda \\ \hat{A}\varphi'_\mu &= \hat{A}\frac{\varphi_\mu - S\varphi_\lambda}{\sqrt{1-S^2}} = \frac{\hat{A}\varphi_\mu - S(\hat{A}\varphi_\lambda)}{\sqrt{1-S^2}} \\ &= A\frac{\varphi_\mu - S\varphi_\lambda}{\sqrt{1-S^2}} = A\varphi'_\mu \end{aligned}$$

so that the orthogonal set belongs to the same degenerate eigenvalue.

It can be easily shown by partial integration (see Problems 1.11) that are Hermitian the operators:

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \qquad \hat{\mathbf{p}} = -i\hbar\nabla$$

$$\hat{p}_x^2 = -\hbar^2\frac{\partial^2}{\partial x^2} \qquad \hat{p}^2 = \hat{\mathbf{p}}\cdot\hat{\mathbf{p}} = -\hbar^2\nabla^2$$

$$\hat{T} = -\tfrac{\hbar^2}{2m}\nabla^2 \qquad \hat{H} = \hat{T} + \hat{V}$$

provided the potential energy V is Hermitian. In these expressions, $\nabla = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}$ is the gradient operator seen previously, and $\nabla^2 = \nabla\cdot\nabla$ the Laplacian operator. We can show, instead, that the operators $\frac{\partial}{\partial x}$ and ∇ are *not* Hermitian:

$$\left\langle\psi\left|\frac{\partial\varphi}{\partial x}\right.\right\rangle = -\left\langle\left.\frac{\partial\psi}{\partial x}\right|\varphi\right\rangle \qquad \langle\psi|\nabla\varphi\rangle = -\langle\nabla\psi|\varphi\rangle. \tag{111}$$

Such operators are said to be anti-Hermitian.

1.4.4 Expansion Theorem: From Operators to Matrices

(i) Any normalizable (Q-class) function can be expanded exactly into the *complete* set of the eigenfunctions of any Hermitian operator $\hat{A}$ (Courant and Hilbert, 1953):

$$F(x) = \sum_k \varphi_k(x)C_k \qquad \hat{A}\varphi_k = A_k\varphi_k \qquad \hat{A}^\dagger = \hat{A}, \tag{112}$$

where the expansion coefficients are given by:

$$C_k = \int dx'\varphi_k^*(x')F(x') = \langle\varphi_k|F\rangle. \tag{113}$$

Using Dirac notation, the complete expansion can be rewritten as:

$$|F\rangle = \sum_k |\varphi_k\rangle\langle\varphi_k|F\rangle, \tag{114}$$

where:

$$\sum_k |\varphi_k\rangle\langle\varphi_k| = \sum_k \varphi_k(x)\varphi_k^*(x') = \delta(x-x') \tag{115}$$

is the Dirac δ-function (a distribution, see Courant and Hilbert, 1962), having the property:

$$\int dx'\delta(x-x')F(x') = F(x). \tag{116}$$

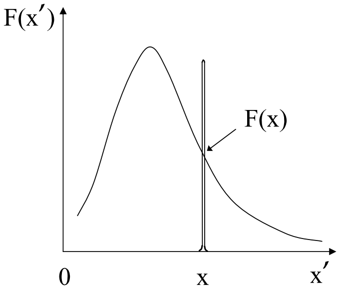

Figure 1.4 Dirac δ as a spike selecting a given function value.

$\delta(x-x')$, which can be recognized as the kernel of an integral operator, can be visualized as an infinitely sharp Gaussian function selecting a given value of the function itself (Figure 1.4).

If the set $\{\varphi_k(x)\}$ of basis functions is *not* complete (as usually happens in practice), equality (112) is no longer true, and truncation errors occur:

$$F(x) \cong \sum_k \varphi_k(x) C_k. \tag{117}$$

(ii) From operators to matrices.

Using the expansion theorem we can pass from operators (which act on functions) to matrices (which act on vectors). Let us limit ourselves to a finite dimension n of an orthonormal basis $\{\varphi_k(x)\}$ $k=1,2,\cdots n$. Then, if $\hat{A}$ is any Hermitian operator:

$$\hat{A}\varphi_i(x) = \sum_k \varphi_k(x) A_{ki} = \sum_k |\varphi_k\rangle\langle\varphi_k|\hat{A}\varphi_i\rangle \tag{118}$$

where the expansion coefficients A_{ki} are elements of the square matrix (order n):

$$A_{ki} = \langle\varphi_k|\hat{A}\varphi_i\rangle = \int dx' \varphi_k^*(x')\big(\hat{A}\varphi_i(x')\big) \tag{119}$$

$$\{A_{ki}\} \Longrightarrow \mathbf{A} = \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ & \cdot\ \cdot\ \cdot\ \cdot\ \cdot & & \\ A_{n1} & A_{n2} & \cdots & A_{nn} \end{pmatrix} \tag{120}$$

which is called the *matrix representative* of the operator $\hat{A}$ in the basis $\{\varphi_k\}$. In this way, the eigenvalue equations of quantum mechanics transform into eigenvalue equations for the corresponding representative matrices. A complete set implies matrices of infinite order.

Even if we postpone to Chapter 2 a deeper analysis on finite matrices, it is important to mention here that:

- a matrix representative depends on the given basis, and
- changing the basis from $\{\varphi\}$ to $\{\varphi'\}$ through transformation with a unitary matrix $\mathbf{U}$ changes the representative to:

$$\boldsymbol{\varphi}' = \boldsymbol{\varphi}\mathbf{U} \Longrightarrow \mathbf{A}' = \mathbf{U}^{\dagger}\mathbf{A}\mathbf{U}, \tag{121}$$

where:

$$\mathbf{A} = \boldsymbol{\varphi}^{\dagger}\hat{A}\boldsymbol{\varphi} \tag{122}$$

and the † means "starring and transposing". $\boldsymbol{\varphi}$ is the row vector of the original basis functions, $\boldsymbol{\varphi}^{\dagger}$ the column of the corresponding complex conjugate functions, and the notation $\boldsymbol{\varphi}^{\dagger}\boldsymbol{\varphi}$ implies taking the scalar product of the basis vectors. The matrix form for a Hermitian operator $\hat{A}$ in a given basis $\{\varphi\}$ is:

$$\mathbf{A}^{\dagger} = \mathbf{A}. \tag{123}$$

1.4.5 ∇ Vector Operator and Its Properties

In Cartesian coordinates, the vector operator ∇ (the gradient) is defined as (Rutherford, 1962):

$$\nabla = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}. \tag{124}$$

- Let $F(x, y, z)$ be a scalar function of the space point P. Then:

$$\nabla F = \mathbf{i}\frac{\partial F}{\partial x} + \mathbf{j}\frac{\partial F}{\partial y} + \mathbf{k}\frac{\partial F}{\partial z} = \operatorname{grad} F \tag{125}$$

a vector, the gradient of F.
- Now, let $\mathbf{F}$ be a vector with components F_x, F_y, F_z. Then:

$$\nabla \cdot \mathbf{F} = \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} = \operatorname{div} \mathbf{F} \tag{126}$$

is the scalar product of ∇ by $\mathbf{F}$, the divergence of $\mathbf{F}$ (a scalar). As a particular case:

$$\nabla \cdot \nabla = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{127}$$

the scalar product of ∇ by itself, the Laplacian operator (a scalar).

$$\nabla \times \mathbf{F} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ F_x & F_y & F_z \end{vmatrix} = \operatorname{curl} \mathbf{F} \tag{128}$$

is the vector product of ∇ by $\mathbf{F}$, the curl of $\mathbf{F}$, a vector with components:

$$\begin{aligned} \mathrm{curl}_x\,\mathbf{F} &= \frac{\partial F_z}{\partial y} - \frac{\partial F_y}{\partial z} \\ \mathrm{curl}_y\,\mathbf{F} &= \frac{\partial F_x}{\partial z} - \frac{\partial F_z}{\partial x} \\ \mathrm{curl}_z\,\mathbf{F} &= \frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} \end{aligned} \tag{129}$$

so that:

$$\nabla \times \mathbf{F} = \mathbf{i}\,\mathrm{curl}_x\,\mathbf{F} + \mathbf{j}\,\mathrm{curl}_y\,\mathbf{F} + \mathbf{k}\,\mathrm{curl}_z\,\mathbf{F}. \tag{130}$$

1.4.6 Systems of Orthogonal Coordinates

Any problem in mathematical physics is best solved in terms of a coordinate system reflecting the symmetry of the system. Orthogonal systems are those systems of coordinates where the surfaces, whose intersections determine the position of a given point in space, do intersect at right angles. Most useful (but not exhaustive) for our purposes are Cartesian, spherical and spheroidal coordinates. We give the definition, the interval of variation of each coordinate covering the whole space, and the elementary volume element $d\mathbf{r}$.

- Cartesian coordinates: x, y, z

$$x, y, z \in (-\infty, \infty) \tag{131}$$

$$d\mathbf{r} = dx\,dy\,dz. \tag{132}$$

- Spherical coordinates: r, θ, φ

$$r(0, \infty), \qquad \theta(0, \pi), \qquad \varphi(0, 2\pi) \tag{133}$$

$$d\mathbf{r} = r^2 dr \sin\theta\, d\theta\, d\varphi \tag{134}$$

with (see Figure 1.5):

$$x = r\sin\theta\sin\varphi, \qquad y = r\sin\theta\cos\varphi, \qquad z = r\cos\theta \tag{135}$$

$$x^2 + y^2 + z^2 = r^2 \quad r = (x^2 + y^2 + z^2)^{1/2} \geq 0. \tag{136}$$

- Spheroidal (prolate spheroidal or confocal elliptic) coordinates: μ, ν, φ

$$\mu(1, \infty), \qquad \nu(-1, 1), \qquad \varphi(0, 2\pi) \tag{137}$$

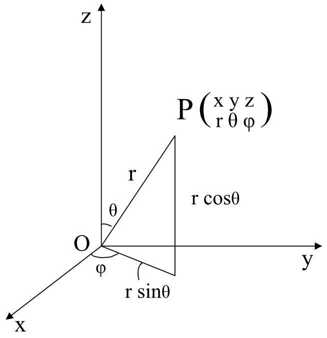

Figure 1.5 Cartesian and spherical coordinate systems.

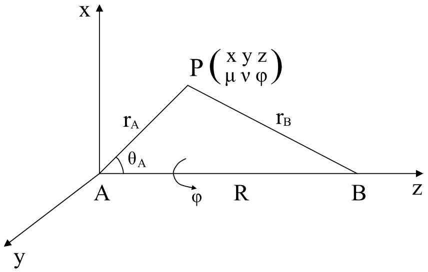

Figure 1.6 Cartesian and spheroidal coordinate systems.

$$d\mathbf{r} = \left(\frac{R}{2}\right)^3 (\mu^2 - \nu^2)\, d\mu d\nu d\varphi \tag{138}$$

with (see Figure 1.6):

$$\mu = \frac{r_A + r_B}{R}, \qquad \nu = \frac{r_A - r_B}{R}, \qquad \varphi, \tag{139}$$

where R is a *fixed* distance along the z-axis.

1.4.7 Generalized Coordinates

Let:

$$x = x(q_1, q_2, q_3) \qquad y = y(q_1, q_2, q_3) \qquad z = z(q_1, q_2, q_3) \tag{140}$$

be the functional relations connecting the Cartesian coordinates (x, y, z) to the generalized coordinates (q_1, q_2, q_3). Then (Eyring et al., 1944; Margenau and Murphy, 1956):

$$h_i^2 = \left(\frac{\partial x}{\partial q_i}\right)^2 + \left(\frac{\partial y}{\partial q_i}\right)^2 + \left(\frac{\partial z}{\partial q_i}\right)^2 \quad i = 1, 2, 3, \tag{141}$$

where:

$$h_1h_2h_3 = |J| = \begin{vmatrix} \frac{\partial x}{\partial q_1} & \frac{\partial y}{\partial q_1} & \frac{\partial z}{\partial q_1} \\ \frac{\partial x}{\partial q_2} & \frac{\partial y}{\partial q_2} & \frac{\partial z}{\partial q_2} \\ \frac{\partial x}{\partial q_3} & \frac{\partial y}{\partial q_3} & \frac{\partial z}{\partial q_3} \end{vmatrix} \tag{142}$$

is the Jacobian[17] determinant of the transformation. We notice that:

$$J^2 = \begin{vmatrix} \frac{\partial x}{\partial q_1} & \frac{\partial y}{\partial q_1} & \frac{\partial z}{\partial q_1} \\ \frac{\partial x}{\partial q_2} & \frac{\partial y}{\partial q_2} & \frac{\partial z}{\partial q_2} \\ \frac{\partial x}{\partial q_3} & \frac{\partial y}{\partial q_3} & \frac{\partial z}{\partial q_3} \end{vmatrix} \cdot \begin{vmatrix} \frac{\partial x}{\partial q_1} & \frac{\partial x}{\partial q_2} & \frac{\partial x}{\partial q_3} \\ \frac{\partial y}{\partial q_1} & \frac{\partial y}{\partial q_2} & \frac{\partial y}{\partial q_3} \\ \frac{\partial z}{\partial q_1} & \frac{\partial z}{\partial q_2} & \frac{\partial z}{\partial q_3} \end{vmatrix} = \begin{vmatrix} h_1^2 & 0 & 0 \\ 0 & h_2^2 & 0 \\ 0 & 0 & h_3^2 \end{vmatrix}, \tag{143}$$

where in the second determinant we have interchanged rows with columns, and the last result is a consequence of the fact that the coordinate systems considered here are orthogonal (so that all off-diagonal elements vanish). In generalized coordinates, the infinitesimal volume element $d\mathbf{r}$, the gradient ∇ and the Laplacian operator ∇^2 are given by the symmetrical expressions:

$$d\mathbf{r} = h_1h_2h_3\, dq_1dq_2dq_3 \tag{144}$$

$$\nabla = \mathbf{e}_1\frac{1}{h_1}\frac{\partial}{\partial q_1} + \mathbf{e}_2\frac{1}{h_2}\frac{\partial}{\partial q_2} + \mathbf{e}_3\frac{1}{h_3}\frac{\partial}{\partial q_3} \tag{145}$$

$$\nabla^2 = \frac{1}{h_1h_2h_3}\left\{\frac{\partial}{\partial q_1}\left(\frac{h_2h_3}{h_1}\frac{\partial}{\partial q_1}\right) + \frac{\partial}{\partial q_2}\left(\frac{h_3h_1}{h_2}\frac{\partial}{\partial q_2}\right) + \frac{\partial}{\partial q_3}\left(\frac{h_1h_2}{h_3}\frac{\partial}{\partial q_3}\right)\right\}. \tag{146}$$

- Cartesian coordinates (x, y, z)

$$q_1 = x \qquad q_2 = y \qquad q_3 = z \qquad h_x = h_y = h_z = 1 \tag{147}$$

---

[17] Jacobi Karl Gustav Jacob 1805–1851, German mathematician, Professor at the University of Königsberg.

$$
\begin{aligned}
d\mathbf{r} &= dx\,dy\,dz \\
\nabla &= \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z} \\
\nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.
\end{aligned}
\tag{148}
$$

- Spherical coordinates (r, θ, φ)

$$q_1 = r \qquad q_2 = \theta \qquad q_3 = \varphi \tag{149}$$

$$x = r\sin\theta\cos\varphi \qquad y = r\sin\theta\sin\varphi \qquad z = r\cos\theta \tag{150}$$

$$
\begin{aligned}
&\frac{\partial x}{\partial r} = \sin\theta\cos\varphi && \frac{\partial y}{\partial r} = \sin\theta\sin\varphi && \frac{\partial z}{\partial r} = \cos\theta \\
&\frac{\partial x}{\partial \theta} = r\cos\theta\cos\varphi && \frac{\partial y}{\partial \theta} = r\cos\theta\sin\varphi && \frac{\partial z}{\partial \theta} = -r\sin\theta \\
&\frac{\partial x}{\partial \varphi} = -r\sin\theta\sin\varphi && \frac{\partial y}{\partial \varphi} = r\sin\theta\cos\varphi && \frac{\partial z}{\partial \varphi} = 0.
\end{aligned}
\tag{151}
$$

Then:

$$
\begin{aligned}
h_r^2 &= \sin^2\theta(\cos^2\varphi + \sin^2\varphi) + \cos^2\theta = \sin^2\theta + \cos^2\theta = 1 \\
&\Longrightarrow h_r = 1
\end{aligned}
$$

$$
\begin{aligned}
h_\theta^2 &= r^2\cos^2\theta(\cos^2\varphi + \sin^2\varphi) + r^2\sin^2\theta = r^2 \\
&\Longrightarrow h_\theta = r
\end{aligned}
$$

$$
\begin{aligned}
h_\varphi^2 &= r^2\sin^2\theta(\sin^2\varphi + \cos^2\varphi) = r^2\sin^2\theta \\
&\Longrightarrow h_\varphi = r\sin\theta
\end{aligned}
$$

$$d\mathbf{r} = r^2 dr\sin\theta d\theta d\varphi = r^2 dr d\Omega, \tag{152}$$

where we use Ω to denote the couple of angles θ, φ.

$$\nabla = \mathbf{e}_r\frac{\partial}{\partial r} + \mathbf{e}_\theta\frac{1}{r}\frac{\partial}{\partial \theta} + \mathbf{e}_\varphi\frac{1}{r\sin\theta}\frac{\partial}{\partial \varphi} \tag{153}$$

$$
\begin{aligned}
\nabla^2 = \frac{1}{r^2\sin\theta}\Bigg\{ &\frac{\partial}{\partial r}\left(\frac{r^2\sin\theta}{1}\frac{\partial}{\partial r}\right) + \frac{\partial}{\partial \theta}\left(\frac{r\sin\theta}{r}\frac{\partial}{\partial \theta}\right) \\
&+ \frac{\partial}{\partial \varphi}\left(\frac{r}{r\sin\theta}\frac{\partial}{\partial \varphi}\right)\Bigg\}
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right. \\
&\qquad\qquad\qquad\qquad\qquad \left. + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\} \\
&= \nabla_r^2 - \frac{\hat{L}^2}{r^2},
\end{aligned}
\tag{154}
$$

where $\hat{L}^2$ is the square of the angular momentum operator (17). In spherical coordinates, the radial component of ∇^2:

$$
\nabla_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}
\tag{155}
$$

separates from its angular part ($\hat{L}^2$).

- Spheroidal coordinates (μ, ν, φ)

$$
q_1 = \mu \qquad q_2 = \nu \qquad q_3 = \varphi
\tag{156}
$$

$$
\mu = \frac{r_A + r_B}{R} \qquad \nu = \frac{r_A - r_B}{R} \qquad \varphi
\tag{157}
$$

$$
\begin{aligned}
x &= a\sqrt{(\mu^2-1)(1-\nu^2)}\cos\varphi \\
y &= a\sqrt{(\mu^2-1)(1-\nu^2)}\sin\varphi \\
z &= a(\mu\nu + 1)
\end{aligned}
\tag{158}
$$

$$
a = \frac{R}{2}
\tag{159}
$$

$$
\begin{aligned}
&\frac{\partial x}{\partial\mu} = a\mu\sqrt{\frac{1-\nu^2}{\mu^2-1}}\cos\varphi && \frac{\partial y}{\partial\mu} = a\mu\sqrt{\frac{1-\nu^2}{\mu^2-1}}\sin\varphi && \frac{\partial z}{\partial\mu} = a\nu \\
&\frac{\partial x}{\partial\nu} = -a\nu\sqrt{\frac{\mu^2-1}{1-\nu^2}}\cos\varphi && \frac{\partial y}{\partial\nu} = -a\nu\sqrt{\frac{\mu^2-1}{1-\nu^2}}\sin\varphi && \frac{\partial z}{\partial\nu} = a\mu \\
&\frac{\partial x}{\partial\varphi} = -a\sqrt{(\mu^2-1)(1-\nu^2)}\sin\varphi && \frac{\partial y}{\partial\varphi} = a\sqrt{(\mu^2-1)(1-\nu^2)}\cos\varphi && \frac{\partial z}{\partial\varphi} = 0.
\end{aligned}
\tag{160}
$$

Hence, we have

$$h_\mu^2 = a^2\left[\mu^2\left(\frac{1-\nu^2}{\mu^2-1}\right)(\cos^2\varphi+\sin^2\varphi)+\nu^2\right] = a^2\frac{\mu^2-\nu^2}{\mu^2-1}$$

$$\Longrightarrow h_\mu = a\sqrt{\frac{\mu^2-\nu^2}{\mu^2-1}}$$

$$h_\nu^2 = a^2\left[\nu^2\left(\frac{\mu^2-1}{1-\nu^2}\right)(\cos^2\varphi+\sin^2\varphi)+\mu^2\right] = a^2\frac{\mu^2-\nu^2}{1-\nu^2}$$

$$\Longrightarrow h_\nu = a\sqrt{\frac{\mu^2-\nu^2}{1-\nu^2}}$$

$$h_\varphi^2 = a^2[(\mu^2-1)(1-\nu^2)(\sin^2\varphi+\cos^2\varphi)] = a^2(\mu^2-1)(1-\nu^2)$$

$$\Longrightarrow h_\varphi = a\sqrt{(\mu^2-1)(1-\nu^2)}$$

$$d\mathbf{r} = a^3(\mu^2-\nu^2)\,d\mu d\nu d\varphi \tag{161}$$

$$\nabla = \frac{1}{a}\left\{\mathbf{e}_\mu\sqrt{\frac{\mu^2-1}{\mu^2-\nu^2}}\frac{\partial}{\partial\mu}+\mathbf{e}_\nu\sqrt{\frac{1-\nu^2}{\mu^2-\nu^2}}\frac{\partial}{\partial\nu}\right.$$
$$\left.+\,\mathbf{e}_\varphi\frac{1}{\sqrt{(\mu^2-1)(1-\nu^2)}}\frac{\partial}{\partial\varphi}\right\} \tag{162}$$

$$\begin{aligned}\nabla^2 &= \frac{1}{a^2(\mu^2-\nu^2)}\left\{\frac{\partial}{\partial\mu}\left[(\mu^2-1)\frac{\partial}{\partial\mu}\right]+\frac{\partial}{\partial\nu}\left[(1-\nu^2)\frac{\partial}{\partial\nu}\right]\right.\\ &\qquad\left.+\,\frac{\mu^2-\nu^2}{(\mu^2-1)(1-\nu^2)}\frac{\partial^2}{\partial\varphi^2}\right\}\\ &= \frac{1}{a^2(\mu^2-\nu^2)}\left\{\nabla_\mu^2+\nabla_\nu^2+\frac{\mu^2-\nu^2}{(\mu^2-1)(1-\nu^2)}\frac{\partial^2}{\partial\varphi^2}\right\},\end{aligned} \tag{163}$$

where:

$$\nabla_\mu^2 = \frac{\partial}{\partial\mu}\left[(\mu^2-1)\frac{\partial}{\partial\mu}\right] = (\mu^2-1)\frac{\partial^2}{\partial\mu^2}+2\mu\frac{\partial}{\partial\mu} \tag{164}$$

$$\nabla_\nu^2 = \frac{\partial}{\partial\nu}\left[(1-\nu^2)\frac{\partial}{\partial\nu}\right] = (1-\nu^2)\frac{\partial^2}{\partial\nu^2}-2\nu\frac{\partial}{\partial\nu}. \tag{165}$$

1.5 FUNDAMENTAL PHYSICAL CONSTANTS AND ATOMIC UNITS

The fundamental physical constants are continually revised. Recent SI values to ten figures are (Mohr and Taylor, 2003):

Elementary charge	$e = 1.602\,176\,462 \times 10^{-19}$ C
Proton mass	$m_p = 1.672\,621\,58(1) \times 10^{-27}$ kg
Electron mass	$m = 9.109\,381\,88(7) \times 10^{-31}$ kg
Reduced Planck's constant	$\hbar = 1.054\,571\,597 \times 10^{-34}$ J s
Vacuum permittivity	$4\pi\varepsilon_0 = 1.112\,650\,056 \times 10^{-10}\ \mathrm{J^{-1}\,C^2\,m^{-1}}$
Light velocity in vacuum	$c = 2.997\,924\,58 \times 10^{8}\ \mathrm{m\,s^{-1}}$
Avogadro number	$N_A = 6.022\,141\,99(5) \times 10^{23}\ \mathrm{mol^{-1}}$
Boltzmann constant	$k = 1.380\,650\,3(24) \times 10^{-23}\ \mathrm{J\,K^{-1}}$.

Atomic units (a.u.) are conveniently introduced when dealing with equations resulting for atomic and molecular problems. They are obtained by posing:

- $e = m = \hbar = 4\pi\varepsilon_0 = 1$ (166)

so that the fundamental physical constants may be dropped from all equations where they occur. At the end of a calculation in atomic units, the actual values can be obtained by taking into account the SI values of the physical constants. The definition and the SI equivalents of the most commonly used atomic units are:

Charge, e	$e = 1.602\,176\,462 \times 10^{-19}$ C
Length, Bohr	$a_0 = 4\pi\varepsilon_0 \dfrac{\hbar^2}{me^2} = 5.291\,772\,087 \times 10^{-11}$ m
Energy, Hartree	$E_h = \dfrac{1}{4\pi\varepsilon_0}\dfrac{e^2}{a_0} = 4.359\,743\,802 \times 10^{-18}$ J
Time	$\tau = \dfrac{\hbar}{E_h} = 2.418\,884\,331 \times 10^{-17}$ s.

The atomic unit of length, a_0, is the radius of the 1s orbit in the Bohr theory of the hydrogen atom. The atomic unit of time, τ, is the time taken for an electron in the 1s orbit of hydrogen to travel one Bohr radius.

As far as the atomic unit of energy is concerned, we have for 1 mol:

$$N_A E_h = 2625.499\,624 \text{ kJ mol}^{-1} = 27.211\,383\,41 \text{ eV mol}^{-1}$$
$$= 219.474\,631\,4 \times 10^3 \text{ cm}^{-1}\text{ mol}^{-1} = 315.774\,655\,5 \times 10^3 \text{ K mol}^{-1}$$

with the submultiples:

$10^{-3}\,\mathrm{E}_h = \mathrm{mE}_h$	$10^{-6}\,\mathrm{E}_h = \mu\mathrm{E}_h$	$10^{-9}\,\mathrm{E}_h = \mathrm{nE}_h$
milli	micro	nano
$10^{-12}\,\mathrm{E}_h = \mathrm{pE}_h$	$10^{-15}\,\mathrm{E}_h = \mathrm{fE}_h$	$10^{-18}\,\mathrm{E}_h = \mathrm{aE}_h.$
pico	femto	atto

As an example, let us calculate the SI equivalent of 1 hartree to 7 significant figures:

$$E_h = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{a_0} = \frac{me^4}{(4\pi\varepsilon_0)^2\hbar^2}$$
$$= \frac{9.109\,382 \times 10^{-31} \times (1.602\,176 \times 10^{-19})^4}{(1.112\,650 \times 10^{-10})^2 \times (1.054\,571 \times 10^{-34})^2}\,\frac{\mathrm{kg\,C^4}}{\mathrm{J^{-2}\,C^4\,m^{-2}\,J^2\,s^2}}$$
$$= 4.359\,744 \times 10^{-18} \text{ J}.$$

1.6 PROBLEMS 1

1.1. Taking into account the relations between Cartesian and spherical coordinates, and their inverse relations, calculate the derivatives of (r, θ, φ) with respect to (x, y, z).

Answer:

$$\frac{\partial r}{\partial x} = \frac{x}{r} = \sin\theta\cos\varphi \qquad \frac{\partial r}{\partial y} = \frac{y}{r} = \sin\theta\sin\varphi \qquad \frac{\partial r}{\partial z} = \frac{z}{r} = \cos\theta$$

$$\frac{\partial \theta}{\partial x} = \frac{\cos\theta\cos\varphi}{r} \qquad \frac{\partial \theta}{\partial y} = \frac{\cos\theta\sin\varphi}{r} \qquad \frac{\partial \theta}{\partial z} = -\frac{\sin\theta}{r}$$

$$\frac{\partial \varphi}{\partial x} = -\frac{\sin\varphi}{r\sin\theta} \qquad \frac{\partial \varphi}{\partial y} = \frac{\cos\varphi}{r\sin\theta} \qquad \frac{\partial \varphi}{\partial z} = 0.$$

Hint:
The relations between the two coordinate systems are:

$$x = r\sin\theta\cos\varphi \qquad y = r\sin\theta\sin\varphi \qquad z = r\cos\theta$$

$$r = (x^2 + y^2 + z^2)^{1/2} \qquad \theta = \cos^{-1}(z/r) \qquad \varphi = \tan^{-1}(y/x).$$

We must remember the rules of derivation of the inverse trigonometric functions for $u(x, y, z)$:

$$\frac{d\cos^{-1}u}{du} = -(1-u^2)^{-1/2} \qquad \frac{d\tan^{-1}u}{du} = (1+u^2)^{-1}$$

and that:

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial}{\partial \theta}\frac{\partial \theta}{\partial x} + \frac{\partial}{\partial \varphi}\frac{\partial \varphi}{\partial x} \quad \text{etc.}$$

1.2. Using the results of Problem 1.1, find the expression in spherical coordinates of the three components $\hat{L}_x, \hat{L}_y, \hat{L}_z$ of the angular momentum operator.

Answer:

$$\begin{aligned}
\hat{L}_x &= -i\left(-\sin\varphi\frac{\partial}{\partial\theta} - \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)\\
\hat{L}_y &= -i\left(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)\\
\hat{L}_z &= -i\frac{\partial}{\partial\varphi}.
\end{aligned} \tag{167}$$

Hint:
Start from the expression of the components $\hat{L}_x, \hat{L}_y, \hat{L}_z$ in Cartesian coordinates.

1.3. Using the results of Problem 1.2, find the expression of $\hat{L}^2$ (the square of the angular momentum operator) in spherical coordinates.

Answer:

$$\begin{aligned}
\hat{L}^2 &= -\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}\\
&= -\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right).
\end{aligned} \tag{168}$$

Hint:
Remember that:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

and that:

$$\hat{L}_x^2(fg) = \hat{L}_x[\hat{L}_x(fg)] = \hat{L}_x[g(\hat{L}_x f) + f(\hat{L}_x g)] \quad \text{etc.,}$$

where f, g are functions of angles θ, φ.

1.4. Find the expression in spherical coordinates of the ladder operators $\hat{L}_+ = \hat{L}_x + i\hat{L}_y$ and $\hat{L}_- = \hat{L}_x - i\hat{L}_y$.

Answer:

$$\begin{aligned}\hat{L}_+ &= \exp(i\varphi)\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)\\ \hat{L}_- &= \exp(-i\varphi)\left(-\tfrac{\partial}{\partial\theta} + i\cot\theta\tfrac{\partial}{\partial\varphi}\right).\end{aligned} \tag{169}$$

Hint:
Use the expression of $\hat{L}_x$ and $\hat{L}_y$ in spherical coordinates as found in Problem 1.2.

1.5. Using Cartesian coordinates, find the relation connecting the Laplacian ∇^2 to the square of the angular momentum operator $\hat{L}^2$.

Answer:

$$\nabla^2 = \nabla_r^2 - \frac{\hat{L}^2}{r^2}, \tag{170}$$

where ∇_r^2 is the radial Laplacian:

$$\nabla_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}. \tag{171}$$

Hint:
Start from the expression of $\hat{L}^2$ in Cartesian coordinates:

$$\begin{aligned}\hat{L}^2 &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2\\ &= -\left\{\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)^2 + \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)^2 + \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)^2\right\}\end{aligned}$$

and calculate the derivatives taking into account that:

$$\frac{\partial}{\partial z}(fg) = g\left(\frac{\partial f}{\partial z}\right) + f\left(\frac{\partial g}{\partial z}\right) \quad \text{etc.,}$$

where f, g are arbitrary functions of (x, y, z). Furthermore, notice that:

$$\begin{aligned}\mathbf{r}\cdot\nabla &= x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z} = r\frac{\partial}{\partial r}\\ (\mathbf{r}\cdot\nabla)^2 &= \left(r\frac{\partial}{\partial r}\right)\left(r\frac{\partial}{\partial r}\right) = r^2\frac{\partial^2}{\partial r^2} + r\frac{\partial}{\partial r}.\end{aligned}$$

1.6. Find the commutators of the components $\hat{L}_x, \hat{L}_y, \hat{L}_z$ of the angular momentum operator $\hat{\boldsymbol{L}}$ with themselves and with $\hat{L}^2$.

Answer:

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hat{L}_z \qquad \left[\hat{L}_y, \hat{L}_z\right] = i\hat{L}_x \qquad \left[\hat{L}_z, \hat{L}_x\right] = i\hat{L}_y \tag{172}$$

that can be summarized as: $\hat{\boldsymbol{L}} \times \hat{\boldsymbol{L}} = i\hat{\boldsymbol{L}}$

$$\left[\hat{L}^2, \hat{L}_x\right] = \left[\hat{L}^2, \hat{L}_y\right] = \left[\hat{L}^2, \hat{L}_z\right] = 0. \tag{173}$$

We conclude that the three components of the angular momentum operator cannot be specified simultaneously, but we can exactly specify each individual component and the square of the angular momentum.

Hint:
Use the expressions of $\hat{L}_x, \hat{L}_y, \hat{L}_z$ in Cartesian coordinates.

1.7. Find the commutators of $\hat{L}_z$ and $\hat{L}^2$ with the ladder operators $\hat{L}_+$ and $\hat{L}_-$.

Answer:

$$\left[\hat{L}_z, \hat{L}_+\right] = \hat{L}_+ \qquad \left[\hat{L}_z, \hat{L}_-\right] = -\hat{L}_- \tag{174}$$

$$\left[\hat{L}^2, \hat{L}_+\right] = \left[\hat{L}^2, \hat{L}_-\right] = 0. \tag{175}$$

Hint:
Use the commutators for the components of the angular momentum operator found in Problem 1.6.

1.8. Find the expression of $\hat{L}^2$ in spherical coordinates using the corresponding expressions of the ladder operators $\hat{L}_+$ and $\hat{L}_-$.

Answer:

$$\begin{aligned}\hat{L}^2 &= -\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\\ &= -\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}.\end{aligned} \tag{176}$$

Hint:
Find first the relations between $\hat{L}^2$ and $\hat{L}_+, \hat{L}_-$:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = \hat{L}_+\hat{L}_- - \hat{L}_z + \hat{L}_z^2 = \hat{L}_-\hat{L}_+ + \hat{L}_z + \hat{L}_z^2. \tag{177}$$

Next use the expressions in spherical coordinates found in Problems 1.2 and 1.4.

1.9. Schmidt orthogonalize the three normalized non-orthogonal functions $(\chi_1' \chi_2' \chi_3')$.

Hint:
Orthogonalize first function χ_2' to χ_1', next χ_3' to the resulting orthogonalized ones.

1.10. Schmidt orthogonalize the set of normalized non-orthogonal functions $\{\chi_\mu'\}$ $\mu = 1, 2, 3, \cdots n$.

Hint:
Use in a stepwise way the simple Schmidt procedure found for $n = 1, 2, 3$.

1.11. The Hermitian operators.

- 1-dimensional problems.

1.11.1. Show that:

$$\left\langle \varphi \left| \frac{d\psi}{dx} \right.\right\rangle = -\left\langle \frac{d\varphi}{dx} \left| \psi \right.\right\rangle$$

so that d/dx is anti-Hermitian.

1.11.2. Show that:

$$\left\langle \varphi \left| i\frac{d\psi}{dx} \right.\right\rangle = \left\langle i\frac{d\varphi}{dx} \left| \psi \right.\right\rangle$$

so that $i\, d/dx$ is Hermitian.

1.11.3. Show that:

$$\left\langle \varphi \left| \frac{d^2\psi}{dx^2} \right.\right\rangle = \left\langle \frac{d^2\varphi}{dx^2} \left| \psi \right.\right\rangle$$

so that d^2/dx^2 is Hermitian.

- 3-dimensional problems.

Let $\varphi(x, y, z)$ and $\psi(x, y, z)$ be well-behaved functions of the three variables (x, y, z).

1.11.4. Show that:

$$\left\langle \varphi \left| i\frac{\partial\psi}{\partial x} \right.\right\rangle = \left\langle i\frac{\partial\varphi}{\partial x} \left| \psi \right.\right\rangle$$

so that $i\, \partial/\partial x$ is Hermitian.

1.11.5. Show that:

$$\left\langle \varphi \middle| \frac{\partial^2 \psi}{\partial x^2} \right\rangle = \left\langle \frac{\partial^2 \varphi}{\partial x^2} \middle| \psi \right\rangle$$

so that $\partial^2/\partial x^2$ is Hermitian.

Proceeding in a like way for the y, z-components, we can show that $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is Hermitian. Hence, $\hat{T} = -\frac{\hbar^2}{2m}\nabla^2$, the kinetic energy operator, is Hermitian.

Hint:
Make use of the partial integration. In fact:

$$d(uv) = u\,dv + v\,du \tag{178}$$

and, by integration:

$$\int u dv = uv - \int v du, \tag{179}$$

where:

$u, v =$ finite factors $\qquad du, dv =$ differential factors.

1.12. Find the relation between (x, y, z) and (μ, ν, φ).

Answer:

$$\begin{aligned} x &= \frac{R}{2}\left[(\mu^2 - 1)(1 - \nu^2)\right]^{1/2} \cos\varphi \\ y &= \frac{R}{2}\left[(\mu^2 - 1)(1 - \nu^2)\right]^{1/2} \sin\varphi \\ z &= \frac{R}{2}(\mu\nu + 1). \end{aligned} \tag{158}$$

Hint:
Let $P(x, y, z)$ be the point in the Cartesian coordinate system which corresponds to $P(\mu, \nu, \varphi)$ in spheroidal coordinates. Use the definitions of spheroidal and spherical coordinates of point P, and the Carnot theorem for the angle $\theta_A = \widehat{r_A z}$.

1.13. Give a geometric derivation of the infinitesimal volume element $d\mathbf{r}$ in spherical coordinates.

Hint:
Consider the circular sectors having an infinitesimal basis.

1.7 SOLVED PROBLEMS

1.1. The inverse transformations are:

$$r=(x^2+y^2+z^2)^{1/2}\ \theta=\cos^{-1}\underbrace{\left[z(x^2+y^2+z^2)^{-1/2}\right]}_{u}\ \varphi=\tan^{-1}\underbrace{(yx^{-1})}_{u}$$

$$\frac{\partial r}{\partial x}=\frac{1}{2}(x^2+y^2+z^2)^{-1/2}2x=\frac{x}{r}\qquad\frac{\partial r}{\partial y}=\frac{y}{r}\qquad\frac{\partial r}{\partial z}=\frac{z}{r}$$

$$\begin{aligned}\frac{\partial\theta}{\partial x}&=-(1-u^2)^{-1/2}\frac{\partial u}{\partial x}\\&=-\left[1-z^2(x^2+y^2+z^2)^{-1}\right]^{-1/2}\left[-\frac{1}{2}z(x^2+y^2+z^2)^{-3/2}2x\right]\\&=\left(\frac{x^2+y^2+z^2-z^2}{x^2+y^2+z^2}\right)^{-1/2}zx(x^2+y^2+z^2)^{-3/2}\\&=\frac{zx}{(x^2+y^2)^{1/2}}(x^2+y^2+z^2)^{-1}\\&=\frac{r^2\cos\theta\sin\theta\cos\varphi}{r\sin\theta}r^{-2}=\frac{\cos\theta\cos\varphi}{r}\end{aligned}$$

$$\begin{aligned}\frac{\partial\theta}{\partial y}&=-(1-u^2)^{-1/2}\frac{\partial u}{\partial y}\\&=-\left[1-z^2(x^2+y^2+z^2)^{-1}\right]^{-1/2}\left[-\frac{1}{2}z(x^2+y^2+z^2)^{-3/2}2y\right]\\&=\left(\frac{x^2+y^2+z^2}{x^2+y^2}\right)^{1/2}yz(x^2+y^2+z^2)^{-3/2}\\&=\frac{\cos\theta\sin\varphi}{r}\end{aligned}$$

$$\begin{aligned}\frac{\partial\theta}{\partial z}&=-(1-u^2)^{-1/2}\frac{\partial u}{\partial z}\\&=-\left[1-z^2(x^2+y^2+z^2)^{-1}\right]^{-1/2}\Big[(x^2+y^2+z^2)^{-1/2}\\&\quad-\frac{1}{2}z(x^2+y^2+z^2)^{-3/2}2z\Big]\\&=-\left(\frac{x^2+y^2+z^2}{x^2+y^2}\right)^{1/2}(x^2+y^2+z^2)^{-1/2}\left(\frac{x^2+y^2+z^2-z^2}{x^2+y^2+z^2}\right)\end{aligned}$$

$$
\begin{aligned}
&= -\frac{(x^2+y^2)^{1/2}}{x^2+y^2+z^2} \\
&= -\frac{\sin\theta}{r}
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial\varphi}{\partial x} &= (1+u^2)^{-1}\frac{\partial u}{\partial x} \\
&= \left[1+(yx^{-1})^2\right]^{-1} y(-x^{-2}) \\
&= \left(\frac{x^2+y^2}{x^2}\right)^{-1}\left(-\frac{y}{x^2}\right) \\
&= -\frac{y}{x^2+y^2} \\
&= -\frac{r\sin\theta\sin\varphi}{r^2\sin^2\theta} = -\frac{\sin\varphi}{r\sin\theta}
\end{aligned}
$$

$$
\frac{\partial\varphi}{\partial y} = (1+u^2)^{-1}\frac{\partial u}{\partial y} = \left(\frac{x^2+y^2}{x^2}\right)^{-1}(x^{-1}) = \frac{x}{x^2+y^2} = \frac{\cos\varphi}{r\sin\theta}
$$

$$
\frac{\partial\varphi}{\partial z} = (1+u^2)^{-1}\frac{\partial u}{\partial z} = 0.
$$

1.2.

$$
\begin{aligned}
\hat{L}_x &= -i\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\
&= -i\left\{r\sin\theta\sin\varphi\left(\frac{\partial}{\partial r}\frac{\partial r}{\partial z} + \frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial z} + \frac{\partial}{\partial\varphi}\frac{\partial\varphi}{\partial z}\right)\right. \\
&\qquad \left. - r\cos\theta\left(\frac{\partial}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial}{\partial\theta}\frac{\partial\theta}{\partial y} + \frac{\partial}{\partial\varphi}\frac{\partial\varphi}{\partial y}\right)\right\} \\
&= -i\left\{r\sin\theta\sin\varphi\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right)\right. \\
&\qquad \left. - r\cos\theta\left(\sin\theta\sin\varphi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\right)\right\} \\
&= -i\left(-\sin^2\theta\sin\varphi\frac{\partial}{\partial\theta} - \cos^2\theta\sin\varphi\frac{\partial}{\partial\theta} - \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right) \\
&= -i\left(-\sin\varphi\frac{\partial}{\partial\theta} - \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right),
\end{aligned}
$$

where use was made of the results of Problem 1.1.

$$\begin{aligned}
\hat{L}_y &= -i\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\\
&= -i\left\{r\cos\theta\left(\frac{\partial}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial}{\partial \theta}\frac{\partial \theta}{\partial x} + \frac{\partial}{\partial \varphi}\frac{\partial \varphi}{\partial x}\right)\right.\\
&\quad \left. - r\sin\theta\cos\varphi\left(\frac{\partial}{\partial r}\frac{\partial r}{\partial z} + \frac{\partial}{\partial \theta}\frac{\partial \theta}{\partial z} + \frac{\partial}{\partial \varphi}\frac{\partial \varphi}{\partial z}\right)\right\}\\
&= -i\left\{r\cos\theta\left(\sin\theta\cos\varphi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial \theta} - \frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial \varphi}\right)\right.\\
&\quad \left. - r\sin\theta\cos\varphi\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial \theta}\right)\right\}\\
&= -i\left(\cos\varphi\frac{\partial}{\partial \theta} - \cot\theta\sin\varphi\frac{\partial}{\partial \varphi}\right)
\end{aligned}$$

$$\begin{aligned}
\hat{L}_z &= -i\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\\
&= -i\left\{r\sin\theta\cos\varphi\left(\frac{\partial}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial}{\partial \theta}\frac{\partial \theta}{\partial y} + \frac{\partial}{\partial \varphi}\frac{\partial \varphi}{\partial y}\right)\right.\\
&\quad \left. - r\sin\theta\sin\varphi\left(\frac{\partial}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial}{\partial \theta}\frac{\partial \theta}{\partial x} + \frac{\partial}{\partial \varphi}\frac{\partial \varphi}{\partial x}\right)\right\}\\
&= -ir\sin\theta\left\{\cos\varphi\left(\sin\theta\sin\varphi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial \theta} + \frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial \varphi}\right)\right.\\
&\quad \left. - \sin\varphi\left(\sin\theta\cos\varphi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial \theta} - \frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial \varphi}\right)\right\}\\
&= -i\left\{(\cos^2\varphi + \sin^2\varphi)\frac{\partial}{\partial \varphi}\right\} = -i\frac{\partial}{\partial \varphi}.
\end{aligned}$$

1.3.

$$\hat{L}_x^2 = -\left(\sin\varphi\frac{\partial}{\partial \theta} + \cot\theta\cos\varphi\frac{\partial}{\partial \varphi}\right)\left(\sin\varphi\frac{\partial}{\partial \theta} + \cot\theta\cos\varphi\frac{\partial}{\partial \varphi}\right).$$

But:

$$\frac{\partial}{\partial \theta}\cot\theta = -1 - \cot^2\theta$$

$$\hat{L}_x^2 = -\left\{\sin^2\varphi\frac{\partial^2}{\partial\theta^2} + \sin\varphi\cos\varphi\frac{\partial}{\partial\varphi}(-1-\cot^2\theta) + \cot\theta\frac{\partial}{\partial\theta}\cos^2\varphi\right.$$
$$\left. + \cot^2\theta\cos^2\varphi\frac{\partial^2}{\partial\varphi^2} - \cot^2\theta\cos\varphi\sin\varphi\frac{\partial}{\partial\varphi}\right\}$$

$$\begin{aligned}
\hat{L}_y^2 &= -\left(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)\left(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)\\
&= -\left\{\cos^2\varphi\frac{\partial^2}{\partial\theta^2} - \cos\varphi\sin\varphi\frac{\partial}{\partial\varphi}(-1-\cot^2\theta) + \cot\theta\frac{\partial}{\partial\theta}\sin^2\varphi\right.\\
&\qquad\left. + \cot^2\theta\sin^2\varphi\frac{\partial^2}{\partial\varphi^2} + \cot^2\theta\sin\varphi\cos\varphi\frac{\partial}{\partial\varphi}\right\}
\end{aligned}$$

$$\hat{L}_z^2 = \left(-i\frac{\partial}{\partial\varphi}\right)\left(-i\frac{\partial}{\partial\varphi}\right) = -\frac{\partial^2}{\partial\varphi^2}$$

$$\begin{aligned}
\hat{L}^2 &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2\\
&= -\left\{(\sin^2\varphi + \cos^2\varphi)\frac{\partial^2}{\partial\theta^2} + (\cos^2\varphi + \sin^2\varphi)\cot\theta\frac{\partial}{\partial\theta}\right.\\
&\qquad\left. + (\cos^2\varphi + \sin^2\varphi)\cot^2\theta\frac{\partial^2}{\partial\varphi^2} + \frac{\partial^2}{\partial\varphi^2}\right\}\\
&= -\left\{\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + (\cot^2\theta + 1)\frac{\partial^2}{\partial\varphi^2}\right\}\\
&= -\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\\
&= -\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}.
\end{aligned}$$

1.4.

$$\begin{aligned}
\hat{L}_+ &= \hat{L}_x + i\hat{L}_y\\
&= i\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right) + \left(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)\\
&= (\cos\varphi + i\sin\varphi)\frac{\partial}{\partial\theta} + i\cot\theta(\cos\varphi + i\sin\varphi)\frac{\partial}{\partial\varphi}\\
&= \exp(i\varphi)\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)
\end{aligned}$$

$$\begin{aligned}\hat{L}_- &= \hat{L}_x - i\hat{L}_y\\ &= i\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right) - \left(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)\\ &= -(\cos\varphi - i\sin\varphi)\frac{\partial}{\partial\theta} + i\cot\theta(\cos\varphi - i\sin\varphi)\frac{\partial}{\partial\varphi}\\ &= \exp(-i\varphi)\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right),\end{aligned}$$

where use has been made of Euler's formulae for imaginary exponentials:

$$\exp(\pm i\varphi) = \cos\varphi \pm i\sin\varphi. \tag{180}$$

As a further exercise, derive in an elementary way Euler's formulae (hint: use series expansions for exponentials and trigonometric functions, see Problem 4.3).

1.5.

$$\begin{aligned}\hat{L}^2 &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2\\ &= -\left\{\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right.\\ &\qquad + \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\\ &\qquad \left. + \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\left(x\frac{\partial}{\partial x} - y\frac{\partial}{\partial x}\right)\right\}\end{aligned}$$

$$\begin{aligned}&\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\\ &\quad = y^2\frac{\partial^2}{\partial z^2} - y\frac{\partial}{\partial y} - yz\frac{\partial^2}{\partial z\partial y} - zy\frac{\partial^2}{\partial y\partial z} - z\frac{\partial}{\partial z} + z^2\frac{\partial^2}{\partial y^2}.\end{aligned}$$

By cyclic permutation of (x, y, z), we immediately obtain:

$$\begin{aligned}&\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\\ &\quad = z^2\frac{\partial^2}{\partial x^2} - z\frac{\partial}{\partial z} - zx\frac{\partial^2}{\partial x\partial z} - xz\frac{\partial^2}{\partial z\partial x} - x\frac{\partial}{\partial x} + x^2\frac{\partial^2}{\partial z^2}\end{aligned}$$

$$\begin{aligned}
&\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)\\
&\quad=x^2\frac{\partial^2}{\partial y^2}-x\frac{\partial}{\partial x}-xy\frac{\partial^2}{\partial y\partial x}-yx\frac{\partial^2}{\partial x\partial y}-y\frac{\partial}{\partial y}+y^2\frac{\partial^2}{\partial x^2}.
\end{aligned}$$

By adding the three components altogether:

$$\begin{aligned}
-\hat{L}^2&=x^2\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+y^2\left(\frac{\partial^2}{\partial z^2}+\frac{\partial^2}{\partial x^2}\right)+z^2\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)+\cdots\\
&=x^2\nabla^2+y^2\nabla^2+z^2\nabla^2-x^2\frac{\partial^2}{\partial x^2}-y^2\frac{\partial^2}{\partial y^2}-z^2\frac{\partial^2}{\partial z^2}+\cdots\\
&=r^2\nabla^2-\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right)\\
&\quad-\left\{\left(x^2\frac{\partial^2}{\partial x^2}+x\frac{\partial}{\partial x}\right)+xy\frac{\partial^2}{\partial x\partial y}+xz\frac{\partial^2}{\partial x\partial z}\right.\\
&\qquad+yx\frac{\partial^2}{\partial y\partial x}+\left(y^2\frac{\partial^2}{\partial y^2}+y\frac{\partial}{\partial y}\right)+yz\frac{\partial^2}{\partial y\partial z}\\
&\qquad\left.+zx\frac{\partial^2}{\partial z\partial x}+zy\frac{\partial^2}{\partial z\partial y}+\left(z^2\frac{\partial^2}{\partial z^2}+z\frac{\partial}{\partial z}\right)\right\}\\
&=r^2\nabla^2-(\mathbf{r}\cdot\nabla)-(\mathbf{r}\cdot\nabla)(\mathbf{r}\cdot\nabla)\\
&=r^2\nabla^2-r\frac{\partial}{\partial r}-\left(r^2\frac{\partial^2}{\partial r^2}+r\frac{\partial}{\partial r}\right)\\
&=r^2\nabla^2-r^2\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)=r^2\nabla^2-r^2\nabla_r^2.
\end{aligned}$$

Hence:

$$\nabla^2=\nabla_r^2-\frac{\hat{L}^2}{r^2}.$$

1.6.

$$\begin{aligned}
[\hat{L}_x,\hat{L}_y]&=\hat{L}_x\hat{L}_y-\hat{L}_y\hat{L}_x\\
&=-\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)\\
&\quad+\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)
\end{aligned}$$

$$
\begin{aligned}
&= -\left(y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial z\partial x} - xy\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial y\partial x} + zx\frac{\partial^2}{\partial y\partial z}\right) \\
&\quad + \left(yz\frac{\partial^2}{\partial x\partial z} - z^2\frac{\partial^2}{\partial x\partial y} - xy\frac{\partial^2}{\partial z^2} + x\frac{\partial}{\partial y} + zx\frac{\partial^2}{\partial z\partial y}\right) \\
&= x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} = i\left[-i\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right] = i\hat{L}_z.
\end{aligned}
$$

By cyclic permutation of (x, y, z), it follows:

$$
[\hat{L}_y, \hat{L}_z] = i\hat{L}_x \qquad [\hat{L}_z, \hat{L}_x] = i\hat{L}_y.
$$

$$
\begin{aligned}
[\hat{L}^2, \hat{L}_x] &= \hat{L}^2\hat{L}_x - \hat{L}_x\hat{L}^2 \\
&= (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2)\hat{L}_x - \hat{L}_x(\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) \\
&= \hat{L}_y\hat{L}_y\hat{L}_x + \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_y\hat{L}_y - \hat{L}_x\hat{L}_z\hat{L}_z.
\end{aligned}
$$

By adding and subtracting appropriate terms:

$$
\begin{aligned}
[\hat{L}^2, \hat{L}_x] &= \hat{L}_y\hat{L}_y\hat{L}_x - \hat{L}_y\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x\hat{L}_y \\
&\quad + \hat{L}_z\hat{L}_z\hat{L}_x - \hat{L}_z\hat{L}_x\hat{L}_z + \hat{L}_z\hat{L}_x\hat{L}_z \\
&\quad - \hat{L}_x\hat{L}_y\hat{L}_y + \hat{L}_y\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x\hat{L}_y \\
&\quad - \hat{L}_x\hat{L}_z\hat{L}_z + \hat{L}_z\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x\hat{L}_z \\
&= -\hat{L}_y[\hat{L}_x, \hat{L}_y] + \hat{L}_z[\hat{L}_z, \hat{L}_x] \\
&\quad - [\hat{L}_x, \hat{L}_y]\hat{L}_y + [\hat{L}_z, \hat{L}_x]\hat{L}_z \\
&= -i\hat{L}_y\hat{L}_z + i\hat{L}_z\hat{L}_y - i\hat{L}_z\hat{L}_y + i\hat{L}_y\hat{L}_z = 0
\end{aligned}
$$

so that $\hat{L}^2$ commutes with the $\hat{L}_x$-component. By cyclic permutation it follows immediately:

$$
[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0.
$$

1.7.

$$
\begin{aligned}
[\hat{L}_z, \hat{L}_+] &= \hat{L}_z\hat{L}_+ - \hat{L}_+\hat{L}_z \\
&= \hat{L}_z\,(\hat{L}_x + i\hat{L}_y) - (\hat{L}_x + i\hat{L}_y)\hat{L}_z \\
&= [\hat{L}_z, \hat{L}_x] - i[\hat{L}_y, \hat{L}_z] = i\hat{L}_y - i(i\hat{L}_x) \\
&= \hat{L}_x + i\hat{L}_y = \hat{L}_+
\end{aligned}
$$

$$\begin{aligned}[\hat{L}_z, \hat{L}_-] &= \hat{L}_z\hat{L}_- - \hat{L}_-\hat{L}_z \\ &= \hat{L}_z(\hat{L}_x - i\hat{L}_y) - (\hat{L}_x - i\hat{L}_y)\hat{L}_z \\ &= [\hat{L}_z, \hat{L}_x] + i[\hat{L}_y, \hat{L}_z] = i\hat{L}_y + i(i\hat{L}_x) \\ &= -\hat{L}_x + i\hat{L}_y = -(\hat{L}_x - i\hat{L}_y) = -\hat{L}_-\end{aligned}$$

$$[\hat{L}^2, \hat{L}_\pm] = 0$$

since $\hat{L}_\pm$ is a linear combination of $\hat{L}_x$ and $\hat{L}_y$, and $\hat{L}^2$ commutes with all components of $\hat{\boldsymbol{L}}$.

1.8.

$$\begin{aligned}\hat{L}_+\hat{L}_- - \hat{L}_z + \hat{L}_z^2 &= (\hat{L}_x + i\hat{L}_y)(\hat{L}_x - i\hat{L}_y) - \hat{L}_z + \hat{L}_z^2 \\ &= (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) - i[\hat{L}_x, \hat{L}_y] - \hat{L}_z \\ &= (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) - i(i\hat{L}_z) - \hat{L}_z \\ &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2\end{aligned}$$

$$\begin{aligned}\hat{L}_-\hat{L}_+ + \hat{L}_z + \hat{L}_z^2 &= (\hat{L}_x - i\hat{L}_y)(\hat{L}_x + i\hat{L}_y) + \hat{L}_z + \hat{L}_z^2 \\ &= (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) + i[\hat{L}_x, \hat{L}_y] + \hat{L}_z \\ &= (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) + i(i\hat{L}_z) + \hat{L}_z \\ &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2.\end{aligned}$$

First of all remember that: $\frac{\partial \cot\theta}{\partial\theta} = -1 - \cot^2\theta$.

Then, using the results of Problems 1.2 and 1.4:

$$\begin{aligned}\hat{L}_+\hat{L}_- &= \exp(i\varphi)\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)\exp(-i\varphi)\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right) \\ &= \exp(i\varphi)\left\{\frac{\partial}{\partial\theta}\left(-\exp(-i\varphi)\frac{\partial}{\partial\theta}\right) + \frac{\partial}{\partial\theta}\left(i\cot\theta\exp(-i\varphi)\frac{\partial}{\partial\varphi}\right)\right. \\ &\quad \left. + i\cot\theta\frac{\partial}{\partial\varphi}\left(-\exp(-i\varphi)\frac{\partial}{\partial\theta}\right) + i\cot\theta\frac{\partial}{\partial\varphi}\left(i\cot\theta\exp(-i\varphi)\frac{\partial}{\partial\varphi}\right)\right\} \\ &= \exp(i\varphi)\left\{-\exp(-i\varphi)\frac{\partial^2}{\partial\theta^2} + i\exp(-i\varphi)\frac{\partial}{\partial\varphi}(-1 - \cot^2\theta)\right.\end{aligned}$$

$$-\exp(-i\varphi)\cot\theta\frac{\partial}{\partial\theta}-\cot^2\theta\left(\exp(-i\varphi)\frac{\partial^2}{\partial\varphi^2}-i\exp(-i\varphi)\frac{\partial}{\partial\varphi}\right)\Bigg\}$$

$$=-\frac{\partial^2}{\partial\theta^2}-i(1+\cot^2\theta)\frac{\partial}{\partial\varphi}-\cot\theta\frac{\partial}{\partial\theta}-\cot^2\theta\frac{\partial^2}{\partial\varphi^2}+i\cot^2\theta\frac{\partial}{\partial\varphi}$$

$$\begin{aligned}\hat{L}_+\hat{L}_- - \hat{L}_z + \hat{L}_z^2 &= -\frac{\partial^2}{\partial\theta^2}-\cot\theta\frac{\partial}{\partial\theta}-\cot^2\theta\frac{\partial^2}{\partial\varphi^2}-i\frac{\partial}{\partial\varphi}+i\frac{\partial}{\partial\varphi}-\frac{\partial^2}{\partial\varphi^2}\\
&=-\left\{\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}+(1+\cot^2\theta)\frac{\partial^2}{\partial\varphi^2}\right\}\\
&=-\left(\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\\
&=-\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}.\end{aligned}$$

1.9. Schmidt orthogonalization of three functions.

If $(\chi_1'\chi_2'\chi_3')$ is the set of three normalized but non-orthogonal functions having non-orthogonalities S_{12}, S_{13}, S_{23}, the normalized Schmidt-orthogonalized set $(\chi_1\chi_2\chi_3)$ is given by:

$$\begin{aligned}\chi_1 &= \chi_1'\\
\chi_2 &= N_2(\chi_2' - S_{12}\chi_1')\\
\chi_3 &= N_3(\chi_3' - A\chi_2 - B\chi_1),\end{aligned}$$

where:

$$\begin{aligned}N_2 &= (1-S_{12}^2)^{-1/2}\\
N_3 &= \left(\frac{1-S_{12}^2}{(1-S_{12}^2)(1-S_{13}^2)-(S_{23}-S_{12}S_{13})^2}\right)^{1/2}\\
A &= N_2(S_{23}-S_{12}S_{13}), \qquad B = S_{13}.\end{aligned}$$

The procedure is straightforward. We shall simply limit ourselves to check orthogonality and normalization of the transformed functions.

(i) Checking orthogonality

$$\langle\chi_1|\chi_2\rangle = N_2\langle\chi_1'|\chi_2' - S_{12}\chi_1'\rangle = N_2(S_{12}-S_{12}) = 0$$

$$\langle\chi_1|\chi_3\rangle = N_3\langle\chi_1|\chi_3' - A\chi_2 - B\chi_1\rangle = N_3\{\langle\chi_1'|\chi_3'\rangle - B\} = N_3(S_{13}-S_{13}) = 0$$

$$\begin{aligned}\langle\chi_2|\chi_3\rangle &= N_3\langle\chi_2|\chi_3' - A\chi_2 - B\chi_1\rangle = N_3\{\langle\chi_2|\chi_3'\rangle - A\}\\ &= N_3\{N_2\langle\chi_2' - S_{12}\chi_1'|\chi_3'\rangle - A\}\\ &= N_2N_3\{(S_{23} - S_{12}S_{13}) - (S_{23} - S_{12}S_{13})\} = 0.\end{aligned}$$

(ii) Checking normalization

$$\begin{aligned}\langle\chi_2|\chi_2\rangle &= N_2^2\langle\chi_2' - S_{12}\chi_1'|\chi_2' - S_{12}\chi_1'\rangle\\ &= N_2^2(1 + S_{12}^2 - 2S_{12}^2) = N_2^2(1 - S_{12}^2) = 1\end{aligned}$$

$$\begin{aligned}\langle\chi_3|\chi_3\rangle &= N_3^2\langle\chi_3' - A\chi_2 - B\chi_1|\chi_3' - A\chi_2 - B\chi_1\rangle\\ &= N_3^2\{1 + A^2 + B^2 - 2A\langle\chi_3'|\chi_2\rangle - 2B\langle\chi_3'|\chi_1\rangle\}\\ &= N_3^2\{1 + A^2 + B^2 - 2AN_2\langle\chi_3'|\chi_2' - S_{12}\chi_1'\rangle - 2BS_{13}\}\\ &= N_3^2\{1 + N_2^2(S_{23} - S_{12}S_{13})^2 - S_{13}^2 - 2N_2^2(S_{23} - S_{12}S_{13})^2\}\\ &= N_3^2\{(1 - S_{13}^2) - (1 - S_{12}^2)^{-1}(S_{23} - S_{12}S_{13})^2\}\\ &= N_3^2(1 - S_{12}^2)^{-1}\{(1 - S_{12}^2)(1 - S_{13}^2) - (S_{23} - S_{12}S_{13})^2\} = 1.\end{aligned}$$

1.10. The general Schmidt procedure is given by a *triangular* transformation which involves building the χ_μs in a stepwise fashion. The recurrence relation expressing χ_μ, the μ-th function of the orthonormalized set, in terms of χ_μ' and χ_ν $(\nu < \mu)$, is given by (Morse and Feshbach, 1953):

$$\chi_\mu = \frac{\chi_\mu' - \sum_{\nu=1}^{\mu-1}\chi_\nu S_{\nu\mu}'}{\sqrt{1 - \sum_{\nu=1}^{\mu-1} S_{\nu\mu}'^2}} \qquad \mu = 2, 3, \cdots n,$$

where:

$$S_{\nu\mu}' = \langle\chi_\nu|\chi_\mu'\rangle, \qquad S_{\nu\mu} = \langle\chi_\nu'|\chi_\mu'\rangle.$$

It can be shown that (i) orthogonalizing the power series x^n in the interval $(-1, 1)$ we obtain the Legendre polynomials $P_n(x)$ (Hobson, 1965), while (ii) orthogonalizing over the whole space the set of n Slater functions (Chapters 4 and 11):

$$\chi_\mu' = N_\mu' r^\mu R_{lm}(\mathbf{r})\psi_0,$$

we obtain (Magnasco et al., 1992) the set of associated Laguerre polynomials of order $(2l + 2)$ introduced by Löwdin and Shull (1956). In the expression above N_μ' is a normalization factor, $R_{lm}(\mathbf{r})$ a spherical tensor in real form, and ψ_0 the $1s$ STO with orbital exponent $c = 1$.

1.11.1.

$$\begin{aligned}
\left\langle \varphi \middle| \frac{d\psi}{dx} \right\rangle &= \int_{-\infty}^{\infty} dx \varphi^*(x) \frac{d\psi(x)}{dx} \\
&= \int_{-\infty}^{\infty} \underset{u}{\varphi^*(x)}\ \underset{dv}{d\psi(x)} \\
&= \underset{u}{\varphi^*(x)}\ \underset{v}{\psi(x)}\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \underset{v}{\psi(x)}\ \underset{du}{d\varphi^*(x)} \\
&= -\int_{-\infty}^{\infty} dx \frac{d\varphi^*(x)}{dx} \psi(x) \\
&= -\int_{-\infty}^{\infty} dx \left(\frac{d\varphi(x)}{dx}\right)^* \psi(x) \\
&= -\left\langle \frac{d\varphi}{dx} \middle| \psi \right\rangle.
\end{aligned}$$

Notice that, if $A(x)$ and $B(x)$ are real functions:

$$\varphi(x) = A(x) + iB(x) \qquad \varphi^*(x) = A(x) - iB(x)$$

$$\frac{d\varphi(x)}{dx} = \frac{dA}{dx} + i\frac{dB}{dx} \qquad \left(\frac{d\varphi(x)}{dx}\right)^* = \frac{dA}{dx} - i\frac{dB}{dx}$$

$$\frac{d\varphi^*(x)}{dx} = \frac{dA}{dx} - i\frac{dB}{dx}$$

so that:

$$\frac{d\varphi^*(x)}{dx} = \left(\frac{d\varphi(x)}{dx}\right)^*.$$

1.11.2.

$$\begin{aligned}
\left\langle \varphi \middle| i\frac{d\psi}{dx} \right\rangle &= \int_{-\infty}^{\infty} dx \varphi^*(x) \left(i\frac{d\psi(x)}{dx}\right) \\
&= \int_{-\infty}^{\infty} \underset{u}{\varphi^*(x)} \underset{dv}{d(i\psi(x))}
\end{aligned}$$

$$
\begin{aligned}
&= \underset{u}{\varphi^*(x)}\underset{v}{(i\psi(x))}\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \underset{v}{(i\psi(x))}\underset{du}{d\varphi^*(x)} \\
&= -\int_{-\infty}^{\infty} dx \frac{d\varphi^*(x)}{dx}(i\psi(x)) \\
&= \int_{-\infty}^{\infty} dx \left(i\frac{d\varphi(x)}{dx} \right)^* \psi(x) \\
&= \left\langle i\frac{d\varphi}{dx} \middle| \psi \right\rangle.
\end{aligned}
$$

1.11.3.

$$
\begin{aligned}
\left\langle \varphi \middle| \frac{d^2\psi}{dx^2} \right\rangle &= \int_{-\infty}^{\infty} dx \varphi^*(x) \frac{d^2\psi(x)}{dx^2} \\
&= \int_{-\infty}^{\infty} \underset{u}{\varphi^*(x)}\, \underset{dv}{d\left(\frac{d\psi(x)}{dx} \right)} \\
&= \underset{u}{\varphi^*(x)}\, \underset{v}{\frac{d\psi(x)}{dx}} \Bigg|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \underset{v}{\frac{d\psi(x)}{dx}}\, \underset{du}{d\varphi^*(x)} \\
&= -\int_{-\infty}^{\infty} dx \frac{d\varphi^*(x)}{dx} \frac{d\psi(x)}{dx} \\
&= -\int_{-\infty}^{\infty} dx \left(\frac{d\varphi(x)}{dx} \right)^* \frac{d\psi(x)}{dx}
\end{aligned}
$$

$$
\begin{aligned}
\left\langle \frac{d^2\varphi}{dx^2} \middle| \psi \right\rangle &= \int_{-\infty}^{\infty} dx \left(\frac{d^2\varphi(x)}{dx^2} \right)^* \psi(x) \\
&= \int_{-\infty}^{\infty} dx \frac{d^2\varphi^*(x)}{dx^2} \psi(x) \\
&= \int_{-\infty}^{\infty} \underset{u}{\psi(x)}\, \underset{dv}{d\left(\frac{d\varphi^*(x)}{dx} \right)} \\
&= \underset{u}{\psi(x)}\, \underset{v}{\frac{d\varphi^*(x)}{dx}} \Bigg|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \underset{v}{\frac{d\varphi^*(x)}{dx}}\, \underset{du}{d\psi(x)}
\end{aligned}
$$

$$= -\int_{-\infty}^{\infty} dx \left(\frac{d\varphi(x)}{dx}\right)^{*} \frac{d\psi(x)}{dx}$$

$$= \left\langle \varphi \middle| \frac{d^2\psi}{dx^2} \right\rangle.$$

Notice that in all such examples, the term $uv|_{-\infty}^{\infty}$ vanishes for the Q-class properties of functions $\varphi(x)$, $\psi(x)$ and their first derivatives.

1.11.4.

$$\left\langle \varphi \middle| i\frac{\partial\psi}{\partial x} \right\rangle = \iiint_{-\infty}^{\infty} dx\,dy\,dz\,\varphi^{*}(x,y,z)\left(i\frac{\partial\psi(x,y,z)}{\partial x}\right)_{y,z}$$

$$= \iiint_{-\infty}^{\infty} dy\,dz\;\underset{u}{\varphi^{*}}\;\underset{dv}{d_x(i\psi)_{y,z}}$$

$$= \underset{\text{surface integral}}{\iint_{-\infty}^{\infty} dy\,dz\;\underset{u}{\varphi^{*}(x,y,z)}\;\underset{v}{(i\psi(x,y,z))}\Big|_{x=-\infty}^{x=\infty}}$$

$$\underset{\text{volume integral}}{-\iiint_{-\infty}^{\infty} dy\,dz\underset{v}{(i\psi(x,y,z))}\underset{du}{\left(\frac{\partial\varphi^{*}(x,y,z)}{\partial x}\right)_{y,z} dx}}$$

$$= \iiint_{-\infty}^{\infty} dx\,dy\,dz\left(i\frac{\partial\varphi(x,y,z)}{\partial x}\right)^{*}_{y,z}\psi(x,y,z)$$

$$= \left\langle i\frac{\partial\varphi}{\partial x} \middle| \psi \right\rangle$$

since the surface integral vanishes at infinity.

1.11.5.

$$\left\langle \varphi \middle| \frac{\partial^2\psi}{\partial x^2} \right\rangle = \iiint_{-\infty}^{\infty} dx\,dy\,dz\,\varphi^{*}(x,y,z)\left(\frac{\partial^2\psi(x,y,z)}{\partial x^2}\right)_{y,z}$$

$$= \iiint_{-\infty}^{\infty} dy\,dz\;\underset{u}{\varphi^{*}}\;\underset{dv}{d_x\left(\frac{\partial\psi}{\partial x}\right)_{y,z}}$$

$$= \underbrace{\iint_{-\infty}^{\infty} dy\,dz\, \underbrace{\varphi^*(x,y,z)}_{u} \underbrace{\left(\frac{\partial \psi(x,y,z)}{\partial x}\right)_{y,z}}_{v} \Bigg|_{x=-\infty}^{x=\infty}}_{\text{surface integral}}$$

$$\underbrace{-\iiint_{-\infty}^{\infty} dy\,dz\, \underbrace{\left(\frac{\partial \psi(x,y,z)}{\partial x}\right)_{y,z}}_{v} \underbrace{\left(\frac{\partial \varphi^*(x,y,z)}{\partial x}\right)_{y,z} dx}_{du}}_{\text{volume integral}}$$

$$= -\iiint_{-\infty}^{\infty} dx\,dy\,dz \left(\frac{\partial \varphi(x,y,z)}{\partial x}\right)_{y,z}^{*} \left(\frac{\partial \psi(x,y,z)}{\partial x}\right)_{y,z}$$

$$\left\langle \frac{\partial^2 \varphi}{\partial x^2} \middle| \psi \right\rangle = \iiint_{-\infty}^{\infty} dx\,dy\,dz \left(\frac{\partial^2 \varphi(x,y,z)}{\partial x^2}\right)_{y,z}^{*} \psi(x,y,z)$$

$$= \iiint_{-\infty}^{\infty} dy\,dz\, \underbrace{\psi}_{u}\, \underbrace{d_x \left(\frac{\partial \varphi^*}{\partial x}\right)_{y,z}}_{dv}$$

$$= \underbrace{\iint_{-\infty}^{\infty} dy\,dz\, \underbrace{\psi(x,y,z)}_{u} \underbrace{\left(\frac{\partial \varphi^*(x,y,z)}{\partial x}\right)_{y,z}}_{v} \Bigg|_{x=-\infty}^{x=\infty}}_{\text{surface integral}}$$

$$\underbrace{-\iiint_{-\infty}^{\infty} dy\,dz\, \underbrace{\left(\frac{\partial \varphi^*(x,y,z)}{\partial x}\right)_{y,z}}_{v} \underbrace{\left(\frac{\partial \psi(x,y,z)}{\partial x}\right)_{y,z} dx}_{du}}_{\text{volume integral}}$$

$$= -\iiint_{-\infty}^{\infty} dx\,dy\,dz \left(\frac{\partial \varphi(x,y,z)}{\partial x}\right)_{y,z}^{*} \left(\frac{\partial \psi(x,y,z)}{\partial x}\right)_{y,z}$$

$$= \left\langle \varphi \middle| \frac{\partial^2 \psi}{\partial x^2} \right\rangle.$$

1.12. With reference to Figure 1.6, the spheroidal coordinates are:

$$\mu = \frac{r_A + r_B}{R}, \qquad \nu = \frac{r_A - r_B}{R}, \qquad \varphi$$

with the inverse transformations:

$$r_A = \frac{R}{2}(\mu + \nu), \qquad r_B = \frac{R}{2}(\mu - \nu)$$

$$z = r_A \cos\theta_A, \qquad x = r_A \sin\theta_A \cos\varphi, \qquad y = r_A \sin\theta_A \sin\varphi.$$

The Carnot theorem gives:

$$r_B^2 = r_A^2 + R^2 - 2Rr_A \cos\theta_A$$

so that:

$$\begin{aligned}
\cos\theta_A &= \frac{r_A^2 - r_B^2 + R^2}{2Rr_A} \\
&= \frac{\left(\frac{R}{2}\right)^2[(\mu+\nu)^2 - (\mu-\nu)^2 + 4]}{4\left(\frac{R}{2}\right)^2(\mu+\nu)} \\
&= \frac{\mu^2 + \nu^2 + 2\mu\nu - \mu^2 - \nu^2 + 2\mu\nu + 4}{4(\mu+\nu)} \\
&= \frac{\mu\nu + 1}{\mu + \nu}
\end{aligned}$$

$$\begin{aligned}
\sin\theta_A &= \left(1 - \cos^2\theta_A\right)^{1/2} \\
&= \left(1 - \frac{(\mu\nu+1)^2}{(\mu+\nu)^2}\right)^{1/2} \\
&= \left(\frac{\mu^2 + \nu^2 + 2\mu\nu - \mu^2\nu^2 - 1 - 2\mu\nu}{(\mu+\nu)^2}\right)^{1/2} \\
&= \frac{[(\mu^2-1)(1-\nu^2)]^{1/2}}{\mu+\nu}.
\end{aligned}$$

Therefore we obtain:

$$z = r_A \cos\theta_A = \frac{R}{2}(\mu+\nu)\frac{\mu\nu+1}{\mu+\nu} = \frac{R}{2}(\mu\nu+1)$$

$$x = r_A \sin\theta_A \cos\varphi = \frac{R}{2}(\mu+\nu)\frac{[(\mu^2-1)(1-\nu^2)]^{1/2}}{\mu+\nu}\cos\varphi$$

$$= \frac{R}{2}\left[(\mu^2-1)(1-\nu^2)\right]^{1/2}\cos\varphi$$

$$y = r_A \sin\theta_A \sin\varphi = \frac{R}{2}[(\mu^2 - 1)(1 - \nu^2)]^{1/2} \sin\varphi.$$

1.13. This result corresponds to the infinitesimal volume of a solid with a curved basis $(r^2 dr \sin\theta d\theta d\varphi)$ having infinitesimal sides $(dr)(rd\theta)(r\sin\theta d\varphi)$, as Figure 1.7 shows.

In fact, we have for the circular sectors with infinitesimal basis the results of Figure 1.8. Since $d\theta$ is infinitesimal, the series expansion for $\sin x$ (x small) gives $\sin x \approx x$.

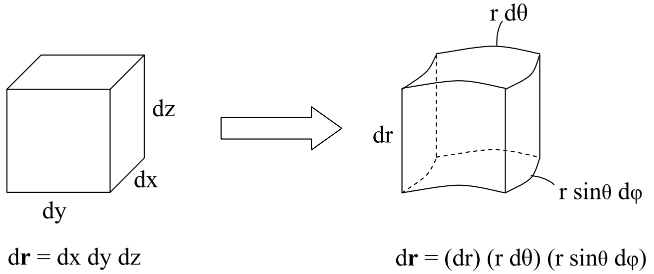

Figure 1.7 From Cartesian to spherical elementary volume.

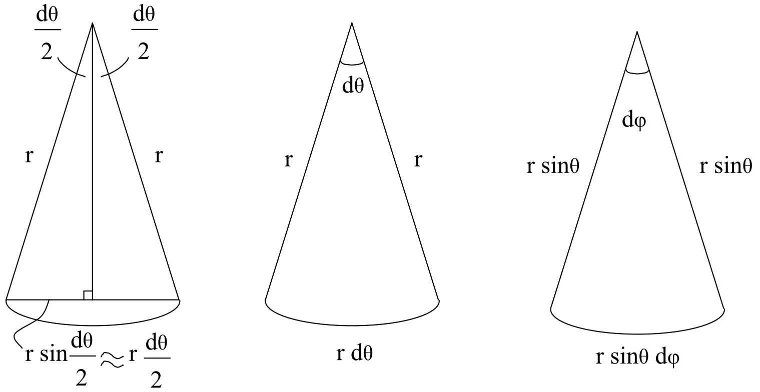

Figure 1.8 Circular sectors with infinitesimal bases.

– 2 –

Elementary Matrix Methods

2.1 INTRODUCTION

Matrices are particularly important for students of applied mathematics, hence for physics, chemistry and engineering students who use mathematics for practical applications (Margenau, 1961; Frazer et al., 1963; Hohn, 1964).

We want to stress here the following points.

1. Matrices offer a powerful compact algorithm which can be easily implemented on electronic calculators. With just a boldface symbol **A** we can represent a square matrix either of order 2 (4 elements) or order 1000 (10^6 elements) or more. Matrix multiplication, too, is well suited for computers.
2. Matrices are related to the necessity of solving systems of linear algebraic equations and of dealing in a compact notation with linear transformations from one set of variables to another set. Their algebra is henceforth linear, and so particularly simple.
3. As already said in Chapter 1, matrices in quantum mechanics arise as representatives of the (linear Hermitian) operators which describe the quantities that can be observed by experiment. Given a set of basis functions, we can pass from the differential equations of quantum mechanics to matrix equations which are governed by the algebra of matrices.

2.2 ELEMENTS OF MATRIX ALGEBRA

2.2.1 Definitions

An array of numbers or functions ordered according to m-rows and n-columns is called a matrix of order $m \times n$ and is denoted by $\mathbf{A}$:

$$\underset{m\times n}{\mathbf{A}} = \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ A_{m1} & A_{m2} & \cdots & A_{mn} \end{pmatrix}. \tag{1}$$

Short notation:

$$\mathbf{A} = \{A_{ij}\}, \tag{2}$$

where A_{ij} is a matrix element, with $i = 1, 2, \ldots m$ row index, $j = 1, 2, \ldots n$ column index. A matrix is rectangular if $m \neq n$, square if $m = n$. Elements with $j = i$ are called diagonal elements. A matrix containing only one row or one column is said to be a *vector*, a row vector or a column vector, respectively. To any square matrix one can associate a *determinant*, denoted by $|A_{ij}|$ or $|\mathbf{A}| = \det \mathbf{A}$, whose elementary properties will be briefly recalled later. The *trace* of a square matrix is the sum of the diagonal elements, $\operatorname{tr} \mathbf{A} = \sum_i A_{ii}$.

2.2.2 Properties of Matrices

1. Two matrices $\mathbf{A}$ and $\mathbf{B}$ are equal if they have the same order and $A_{ij} = B_{ij}$ for any i, j.
2. Addition and subtraction of matrices (same order):

$$\mathbf{A} \pm \mathbf{B} = \mathbf{C} \quad C_{ij} = A_{ij} \pm B_{ij}. \tag{3}$$

Addition and subtraction of matrices are commutative and associative:

$$\mathbf{A} \pm \mathbf{B} = \pm\mathbf{B} + \mathbf{A} \tag{4}$$

$$\mathbf{A} + \mathbf{B} + \mathbf{C} = (\mathbf{A} + \mathbf{B}) + \mathbf{C} = \mathbf{A} + (\mathbf{B} + \mathbf{C}). \tag{5}$$

3. Product of a matrix by a (complex) number c:

$$c\mathbf{A} = \mathbf{C} \quad C_{ij} = cA_{ij}. \tag{6}$$

Each element of the matrix is multiplied by c.

4. Product of matrices rows by columns:

$$\underset{m\times n}{\mathbf{A}}\,\underset{n\times p}{\mathbf{B}} = \underset{m\times p}{\mathbf{C}} \qquad C_{ij} = \sum_{\alpha=1}^{n} A_{i\alpha} B_{\alpha j}. \tag{7}$$

The number of columns of **A** must be equal to the number of rows of **B** (the matrices are then said conformable). In general, matrix multiplication is *not* commutative:

$$\mathbf{AB} \neq \mathbf{BA}. \tag{8}$$

If:

$$\mathbf{AB} = \mathbf{BA} \tag{9}$$

A and **B** are said to commute. The difference:

$$\mathbf{AB} - \mathbf{BA} = [\mathbf{A}, \mathbf{B}] \tag{10}$$

is said to be the commutator of **A** and **B**.

The product of more than two matrices is associative:

$$\mathbf{ABC} = (\mathbf{AB})\mathbf{C} = \mathbf{A}(\mathbf{BC}). \tag{11}$$

Proof:

$$(\mathbf{ABC})_{ij} = \sum_{\alpha}\sum_{\beta} A_{i\alpha} B_{\alpha\beta} C_{\beta j} = \sum_{\beta} (\mathbf{AB})_{i\beta} C_{\beta j} = \sum_{\alpha} A_{i\alpha} (\mathbf{BC})_{\alpha j}.$$

It may sometimes be convenient to consider a matrix as made of elements that are themselves matrices. In other words, matrices can be partitioned into *submatrices* for which the rules of matrix algebra hold.

We end by recalling that a matrix is said to be of *rank* r if and only if it has at least one non-singular square submatrix whose largest order is r.

2.2.3 Properties of Determinants

Let $|\mathbf{A}|$ be a determinant of order n (it contains n rows and n columns). We recall that if A_{ij} are numbers, the main difference between $|\mathbf{A}|$ and **A** is that $|\mathbf{A}|$ is a number (a scalar quantity) whereas **A** is an operator (which transforms vectors). We now state without proof some properties of determinants (Aitken, 1958).

1. Expansion of $|\mathbf{A}|$ according to the elements of a row or a column:

$$|\mathbf{A}| = \begin{vmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ A_{n1} & A_{n2} & \cdots & A_{nn} \end{vmatrix} = \sum_{j=1}^{n} A_{ij} a_{ij} = \sum_{i=1}^{n} A_{ij} a_{ij} \tag{12}$$

is the elementary expansion of $|\mathbf{A}|$ according to elements of the i-th row (i = fixed) or the j-th column (j = fixed). If we denote by $|A_{ij}|$ the *minor* of $|\mathbf{A}|$, a determinant of order $(n-1)$ obtained from $|\mathbf{A}|$ by deleting row i and column j, we call $a_{ij} = (-1)^{i+j}|A_{ij}|$ the corresponding signed minor (or *cofactor*) of $|\mathbf{A}|$. We notice that the expansion of a determinant of order n gives $n!$ terms.

2. Expansion of $|\mathbf{A}|$ according to Cauchy:

$$|\mathbf{A}| = A_{hk}a_{hk} - \sum_i \sum_j A_{ik}A_{hj}a_{hk,ij} \quad i \neq h,\ j \neq k, \tag{13}$$

   where a_{hk} (a determinant of order $n-1$) is the cofactor of A_{hk} and $a_{hk,ij}$ (a determinant of order $n-2$) the cofactor of A_{ij} in a_{hk}.
3. Expansion of $|\mathbf{A}|$ according to Laplace: it is an expansion of $|\mathbf{A}|$ according to minors from a certain m rows and their cofactors from the remaining $n-m$ rows, which was first given by Laplace in 1772.

   As a simple example, the Laplace expansion according to the first two and the last two rows of a determinant of order 4 will be:

$$\begin{aligned} |A_1B_2C_3D_4| &= |A_1B_2|\cdot|C_3D_4| - |A_1C_2|\cdot|B_3D_4| \\ &\quad + |A_1D_2|\cdot|B_3C_4| + |B_1C_2|\cdot|A_3D_4| \\ &\quad - |B_1D_2|\cdot|A_3C_4| + |C_1D_2|\cdot|A_3B_4|, \end{aligned} \tag{14}$$

   where the determinants have been denoted through the elements of their main diagonal.
4. Product of determinants: for two square matrices $\mathbf{A}$ and $\mathbf{B}$ (order n):

$$|\mathbf{AB}| = |\mathbf{A}|\cdot|\mathbf{B}| \tag{15}$$

   as can be shown using matrix partitioning to define suitable matrices of order $2n$:

$$\begin{pmatrix} \mathbf{1} & \mathbf{A} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}\begin{pmatrix} \mathbf{A} & \mathbf{0} \\ \mathbf{-1} & \mathbf{B} \end{pmatrix} = \begin{pmatrix} \mathbf{0} & \mathbf{AB} \\ \mathbf{-1} & \mathbf{B} \end{pmatrix}$$

   and the Laplace expansion of the resulting determinants according to the first n rows:

$$\begin{vmatrix} \mathbf{1} & \mathbf{A} \\ \mathbf{0} & \mathbf{1} \end{vmatrix}\cdot\begin{vmatrix} \mathbf{A} & \mathbf{0} \\ \mathbf{-1} & \mathbf{B} \end{vmatrix} = \begin{vmatrix} \mathbf{0} & \mathbf{AB} \\ \mathbf{-1} & \mathbf{B} \end{vmatrix}$$

$$1\cdot\{|\mathbf{A}|\cdot|\mathbf{B}|\} = |\mathbf{AB}|.$$

   Similarly:

$$|\mathbf{ABC}| = |\mathbf{A}|\cdot|\mathbf{BC}| = |\mathbf{A}|\cdot|\mathbf{B}|\cdot|\mathbf{C}| \tag{16}$$

   and so on.
5. Product of $|\mathbf{A}|$ by a (complex) number c:

$$c|\mathbf{A}| \tag{17}$$

   only *one* row (or column) of $|\mathbf{A}|$ will be multiplied by the number c.

6. Interchange of rows or columns: a determinant $|\mathbf{A}|$ changes sign upon interchanging any two rows or columns. The determinant is unchanged upon interchanging all rows and columns.
7. If all the elements of a row or column are zero, the determinant vanishes.
8. If two rows or two columns are identical, the determinant vanishes.

2.2.4 Special Matrices 1

1. The null matrix (square or rectangular) is a matrix whose elements are all zero:

$$\underset{m\times n}{\mathbf{0}} = \begin{pmatrix} 0 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & 0 \end{pmatrix}. \tag{18}$$

For matrices of the same order:

$$\mathbf{0} + \mathbf{A} = \mathbf{A} + \mathbf{0} = \mathbf{A}, \qquad \mathbf{0A} = \mathbf{A0} = \mathbf{0}. \tag{19}$$

2. The diagonal matrix is a square matrix which has non-zero elements only along the diagonal[1]:

$$\underset{n\times n}{\mathbf{\Lambda}} = \begin{pmatrix} \lambda_1 & 0 & \cdots & 0 \\ 0 & \lambda_2 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \lambda_n \end{pmatrix} \quad \lambda_{ij} = \lambda_i \delta_{ij}, \tag{20}$$

where δ_{ij} is the Kronecker delta.

3. A scalar matrix is a diagonal matrix whose diagonal elements are all equal to a number λ:

$$\mathbf{\Lambda} = \begin{pmatrix} \lambda & 0 & \cdots & 0 \\ 0 & \lambda & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \lambda \end{pmatrix} = \lambda\mathbf{1}. \tag{21}$$

4. The identity matrix is a scalar matrix whose diagonal elements are all 1:

$$\underset{n\times n}{\mathbf{1}} = \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & 1 \end{pmatrix} \quad 1_{ij} = \delta_{ij}. \tag{22}$$

For matrices of the same order:

$$\mathbf{A1} = \mathbf{1A} = \mathbf{A}. \tag{23}$$

---

[1] Take care that in Problems 2.15, 2.16, 2.17 we use λ as the ratio of coefficients.

5. Consider now a square matrix $\mathbf{A}$ of order n:

$$\underset{n\times n}{\mathbf{A}} = \{A_{ij}\}. \tag{24}$$

We can then construct from $\mathbf{A}$ the following matrices:

- $$\mathbf{B} = \mathbf{A}^* \quad B_{ij} = A_{ij}^* \quad \text{complex conjugate.} \tag{25}$$
  The complex conjugate is the matrix obtained by taking the complex conjugate (in short, starring) of all elements of $\mathbf{A}$.
- $$\mathbf{B} = \tilde{\mathbf{A}} \quad B_{ij} = A_{ji} \quad \text{transpose.} \tag{26}$$
  The transpose is the matrix obtained by interchanging rows by columns.
- $$\mathbf{B} = \mathbf{A}^\dagger = (\widetilde{\mathbf{A}^*}) \quad B_{ij} = A_{ji}^* \quad \text{adjoint.} \tag{27}$$
  The adjoint is the matrix obtained by starring and transposing all elements of $\mathbf{A}$.
- $$\mathbf{B} = \mathbf{A}^{-1} \quad \text{inverse.} \tag{28}$$
  The inverse matrix is such that:

  $$\mathbf{A}^{-1}\mathbf{A} = \mathbf{A}\mathbf{A}^{-1} = \mathbf{1}.$$

  $\mathbf{A}^{-1}$ exists provided $\mathbf{A}$ is non-singular, i.e.

  $$\det\mathbf{A} = |\mathbf{A}| \neq 0. \tag{29}$$

Between $\mathbf{A}$ and the transpose of the matrix of its cofactors (signed minors) $\tilde{\mathbf{a}}$ there exists the relation:

$$\mathbf{A}\tilde{\mathbf{a}} = \tilde{\mathbf{a}}\mathbf{A} = \mathbf{1}\cdot\det\mathbf{A} \tag{30}$$

from which follows the elementary definition of the inverse matrix:

$$\mathbf{A}^{-1} = (\det\mathbf{A})^{-1}\tilde{\mathbf{a}} \quad B_{ij} = (\det\mathbf{A})^{-1}\tilde{a}_{ij}. \tag{31}$$

Let $\mathbf{A} = (m \times n)$ and $\mathbf{B} = (n \times m)$ be rectangular matrices, then if:

$$\underset{m\times n}{\mathbf{A}}\ \underset{n\times m}{\mathbf{B}} = \mathbf{1}_m \tag{32}$$

$\mathbf{B}$ is said the *right* inverse,

$$\underset{n\times m}{\mathbf{B}}\ \underset{m\times n}{\mathbf{A}} = \mathbf{1}_n \tag{33}$$

$\mathbf{B}$ is said the *left* inverse of matrix $\mathbf{A}$. For a square matrix $(m = n)$, the right and left inverse coincide and we are left with just a unique inverse $\mathbf{A}^{-1}$.

Notice that the operations symbolized by *, $\tilde{}$, †, $^{-1}$ are such that each of them when performed twice restores the original matrix.

6. Properties of products:

$$\widetilde{\mathbf{AB}} = \tilde{\mathbf{B}}\tilde{\mathbf{A}} \qquad (\mathbf{AB})^\dagger = \mathbf{B}^\dagger\mathbf{A}^\dagger \qquad (\mathbf{AB})^{-1} = \mathbf{B}^{-1}\mathbf{A}^{-1}, \tag{34}$$

namely, the transpose of a matrix product is the product of the individual transposed matrices with the reverse order of factors, and so on.

Proof:

$$\mathbf{AB} = \mathbf{C} \quad C_{ij} = \sum_\alpha A_{i\alpha} B_{\alpha j}$$

$$(\tilde{\mathbf{C}})_{ij} = C_{ji} = \sum_\alpha A_{j\alpha} B_{\alpha i}$$

$$(\tilde{\mathbf{B}}\tilde{\mathbf{A}})_{ij} = \sum_\alpha (\tilde{\mathbf{B}})_{i\alpha} (\tilde{\mathbf{A}})_{\alpha j} = \sum_\alpha B_{\alpha i} A_{j\alpha}$$

so that:

$$(\tilde{\mathbf{C}})_{ij} = (\tilde{\mathbf{B}}\tilde{\mathbf{A}})_{ij} \Longrightarrow \tilde{\mathbf{C}} = \tilde{\mathbf{B}}\tilde{\mathbf{A}}.$$

2.2.5 Special Matrices 2

1. Consider a square matrix $\mathbf{A}$ of order n. Then, if:

$$\mathbf{A} = \mathbf{A}^* \quad \tilde{\mathbf{A}} \quad \mathbf{A}^\dagger \tag{35}$$

$\mathbf{A}$ is said to be real, symmetric, Hermitian (or self-adjoint), respectively.

2. If:

$$\mathbf{A}^{-1} = \quad \tilde{\mathbf{A}} \quad \mathbf{A}^\dagger \tag{36}$$

$\mathbf{A}$ is said to be orthogonal or unitary, respectively.

A typical orthogonal matrix is the matrix describing rotation of an angle α around an axis perpendicular to the plane where rotation occurs:

$$\mathbf{A}(\alpha) = \begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix} \qquad \widetilde{\mathbf{A}(\alpha)} = \begin{pmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{pmatrix} = \mathbf{A}^{-1}. \tag{37}$$

In this case, matrix $\mathbf{A}(\alpha)$ describes an anticlockwise (positive) rotation of α around the z-axis, and it is immediately evident that $\det\mathbf{A} = |\mathbf{A}| = 1$.

3. For Jacobian $\{\partial u_i/\partial x_j\}$, Hessian $\{\partial^2 u/\partial x_i \partial x_j\}$, Wronskian $\{d^{i-1}u_j/dx^{i-1}\}$ matrices and their determinants the reader is referred to Aitken (1958, pp. 128–132).

4. Further properties of trace.

   As already said at the beginning of this Chapter, the trace of a square matrix **A** is the sum of the elements of the main diagonal:

$$\operatorname{tr}\mathbf{A} = \sum_{i=1}^{n} A_{ii}. \tag{38}$$

   It has the remarkable property that the trace of a product of matrices is invariant (i.e. does not change) under a cyclic permutation of its factors:

$$\begin{aligned} &\operatorname{tr}\mathbf{AB} = \operatorname{tr}\mathbf{BA} \\ &\operatorname{tr}\mathbf{ABC} = \operatorname{tr}\mathbf{CAB} = \operatorname{tr}\mathbf{BCA} \end{aligned} \tag{39}$$

   but:

$$\operatorname{tr}\mathbf{ABC} \neq \operatorname{tr}\mathbf{BAC}.$$

2.3 MATRIX EIGENVALUE PROBLEM

2.3.1 Systems of Linear Equations

A system of linear inhomogeneous algebraic equations in the n unknowns $c_1, c_2, \ldots, c_n$:

$$\begin{cases} A_{11}c_1 + A_{12}c_2 + \cdots + A_{1n}c_n = b_1 \\ A_{21}c_1 + A_{22}c_2 + \cdots + A_{2n}c_n = b_2 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ A_{n1}c_1 + A_{n2}c_2 + \cdots + A_{nn}c_n = b_n \end{cases} \tag{40}$$

can be easily written in matrix form as:

$$\underset{n\times n}{\mathbf{A}}\ \underset{n\times 1}{\mathbf{c}} = \underset{n\times 1}{\mathbf{b}} \tag{41}$$

if we introduce the matrices:

$$\mathbf{A} = \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ A_{n1} & A_{n2} & \cdots & A_{nn} \end{pmatrix} \quad \text{square matrix of coefficients} \tag{42}$$

$$\mathbf{c} = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} \ \text{column vector of unknowns} \qquad \mathbf{b} = \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{pmatrix} \ \text{column vector of inhomogeneous terms} \tag{43}$$

and adopt matrix multiplication rules.

Matrix equation (41) can be interpreted as a linear transformation on the vectors **c**, which are transformed into vectors **b** under the action of matrix **A**. If $\mathbf{A}^{-1}$ exists ($\det\mathbf{A} \neq 0$), the solution of the system of linear equations is:

$$\mathbf{c} = \mathbf{A}^{-1}\mathbf{b} \tag{44}$$

which is nothing but the well-known Cramer's rule. In fact, let us look for the sake of simplicity to the case $n = 2$:

$$\left.\begin{aligned} c_1 &= (\det\mathbf{A})^{-1}\begin{vmatrix} b_1 & A_{12} \\ b_2 & A_{22} \end{vmatrix} = \frac{b_1A_{22} - b_2A_{12}}{\det\mathbf{A}} \\[2ex] c_2 &= (\det\mathbf{A})^{-1}\begin{vmatrix} A_{11} & b_1 \\ A_{21} & b_2 \end{vmatrix} = \frac{b_2A_{11} - b_1A_{21}}{\det\mathbf{A}} \end{aligned}\right\}\quad \text{Cramer} \tag{45}$$

$$\det\mathbf{A} = |\mathbf{A}| = A_{11}A_{22} - A_{12}A_{21} \neq 0.$$

From the definition (31) for the inverse $\mathbf{A}^{-1}$ it follows:

$$\mathbf{A}^{-1} = (\det\mathbf{A})^{-1}\widetilde{\begin{pmatrix} A_{22} & -A_{21} \\ -A_{12} & A_{11} \end{pmatrix}} = (\det\mathbf{A})^{-1}\begin{pmatrix} A_{22} & -A_{12} \\ -A_{21} & A_{11} \end{pmatrix} \tag{46}$$

and therefore (44) gives:

$$\begin{aligned} \mathbf{c} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} &= (\det\mathbf{A})^{-1}\begin{pmatrix} A_{22} & -A_{12} \\ -A_{21} & A_{11} \end{pmatrix}\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} \\ &= (\det\mathbf{A})^{-1}\begin{pmatrix} A_{22}b_1 - A_{12}b_2 \\ -A_{21}b_1 + A_{11}b_2 \end{pmatrix} \end{aligned} \tag{47}$$

and the results of Cramer's rule are recovered.

2.3.2 Eigenvalue Equation

Particular importance has the case where **b** is proportional to **c** through a number λ:

$$\mathbf{A}\mathbf{c} = \lambda\mathbf{c} \tag{48}$$

which is known as the eigenvalue equation for the square matrix **A**. If we write:

$$(\mathbf{A} - \lambda\mathbf{1})\mathbf{c} = \mathbf{0}, \tag{49}$$

where $(\mathbf{A} - \lambda\mathbf{1})$ is called the characteristic matrix of **A**, we obtain a system of linear homogeneous algebraic equations in the unknowns **c**, which is known to have non-trivial solutions (i.e. solutions different from $c_1 = c_2 = \cdots = c_n = 0$) if and only if the determinant of the coefficients vanishes:

$$\det(\mathbf{A} - \lambda \mathbf{1}) = \begin{vmatrix} A_{11} - \lambda & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} - \lambda & \cdots & A_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ A_{n1} & A_{n2} & \cdots & A_{nn} - \lambda \end{vmatrix} = 0. \tag{50}$$

Equation (50) is known as the characteristic equation (or, from astronomy, *secular equation*) of matrix $\mathbf{A}$. Expanding the determinant we find a polynomial of degree n in λ called the characteristic polynomial of $\mathbf{A}$:

$$P_n(\lambda) = \det(\mathbf{A} - \lambda \mathbf{1}) = a_0 + a_1\lambda + \cdots + a_{n-1}\lambda^{n-1} + a_n\lambda^n, \tag{51}$$

the equation

$$P_n(\lambda) = 0 \tag{52}$$

being an algebraic equation of degree n having n roots. If $\mathbf{\Lambda}$ is the diagonal matrix of the eigenvalues, (52) can be written in the alternative way:

$$P_n(\lambda) = (\lambda_1 - \lambda)(\lambda_2 - \lambda)\cdots(\lambda_n - \lambda) = 0 \tag{53}$$

and, on comparing coefficients of the different powers of λ, we find:

$$a_0 = \lambda_1\lambda_2\cdots\lambda_n = \det\mathbf{\Lambda}, \cdots, a_{n-1} = (-1)^{n-1}\sum_i \lambda_i, a_n = (-1)^n \tag{54}$$

and, in general:

$$a_k = (-1)^k \sum_{i=1}^{n} M_{ii}^{(n-k)} \qquad k \leq n, \tag{55}$$

where $M_{ii}^{(n-k)}$ is the principal minor (i.e. along the diagonal) of order $n-k$ of matrix $\mathbf{\Lambda}$.

As already said, the secular equation $P_n(\lambda) = 0$ is an algebraic equation of degree n in λ, which upon solution gives:

$$\begin{cases} \lambda_1, \lambda_2, \cdots \lambda_n & n \text{ roots (the eigenvalues of } \mathbf{A}) \\ \mathbf{c}_1, \mathbf{c}_2, \cdots \mathbf{c}_n & n \text{ column coefficients (the eigenvectors of } \mathbf{A}). \end{cases} \tag{56}$$

For a square matrix of order n, we obtain n eigenvalues λ_i and n eigenvectors $\mathbf{c}_i$ ($i = 1, 2, \cdots, n$). The full eigenvalue problem can be treated in a compact way by introducing two square matrices of order n:

$$\underset{n\times n}{\mathbf{\Lambda}} = \begin{pmatrix} \lambda_1 & 0 & \cdots & 0 \\ 0 & \lambda_2 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \lambda_n \end{pmatrix} \tag{57}$$

$$\mathbf{C} = (\mathbf{c}_1|\mathbf{c}_2|\cdots|\mathbf{c}_n) = \begin{array}{c} \left(\begin{array}{c|c|c|c} c_{11} & c_{12} & \cdots & c_{1n} \\ c_{21} & c_{22} & \dots & c_{2n} \\ \vdots & \vdots & \dots & \vdots \\ c_{n1} & c_{n2} & \cdots & c_{nn} \end{array}\right) \\ \begin{array}{cccc} \lambda_1 & \lambda_2 & \cdots & \lambda_n \end{array} \end{array}, \tag{58}$$

where $\mathbf{\Lambda}$ is the diagonal matrix collecting all the eigenvalues along the diagonal, and $\mathbf{C}$ the row matrix of the eigenvectors (a square matrix on the whole), where each column corresponds to a given eigenvalue (the column index). The *full* eigenvalue problem for the square matrix $\mathbf{A}$ is hence given by the single matrix equation:

$$\mathbf{AC} = \mathbf{C\Lambda}, \tag{59}$$

where each matrix is a square matrix of order n. Equation (59) replaces the n eigenvalue equations (one for each eigenvalue):

$$\mathbf{Ac}_1 = \lambda_1\mathbf{c}_1, \qquad \mathbf{Ac}_2 = \lambda_2\mathbf{c}_2, \cdots, \qquad \mathbf{Ac}_n = \lambda_n\mathbf{c}_n. \tag{60}$$

If $\det\mathbf{C} \neq 0$, $\mathbf{C}^{-1}$ exists, and the square matrix $\mathbf{A}$ is brought to *diagonal form* through the similarity transformation with the complete matrix of its eigenvectors:

$$\mathbf{C}^{-1}\mathbf{AC} = \mathbf{\Lambda}. \tag{61}$$

If $\mathbf{A}$ is Hermitian:

$$\mathbf{A} = \mathbf{A}^\dagger \tag{62}$$

it is possible to show that the eigenvalues are real numbers and the eigenvectors are orthonormal, namely:

$$\mathbf{c}_\mu^\dagger\mathbf{c}_\nu = \delta_{\mu\nu} \tag{63}$$

so that:

$$\mathbf{C}^\dagger\mathbf{C} = \mathbf{CC}^\dagger = \mathbf{1} \Longrightarrow \mathbf{C}^{-1} = \mathbf{C}^\dagger. \tag{64}$$

The complete matrix of the eigenvectors is now a unitary matrix, and therefore:

$$\mathbf{C}^\dagger\mathbf{AC} = \mathbf{\Lambda} \tag{65}$$

so that any Hermitian matrix $\mathbf{A}$ can be brought to diagonal form by a unitary transformation with the complete matrix of its eigenvectors. The name Hermitian arises from the French mathematician Charles Hermite (1822–1901), who is also known for his Hermite Polynomials which occur in the solution of the Schroedinger equation for the harmonic oscillator (Eyring et al., 1944).

2.3.3 Pseudoeigenvalue Equation

The eigenvalue equation (48) can be generalized to the case of a non-orthogonal metric $\mathbf{M} = \mathbf{1} + \mathbf{S}$ ($\mathbf{S} \neq \mathbf{0}$ describes non-orthogonality):

$$\mathbf{Ac} = \lambda\mathbf{Mc} \tag{66}$$

which is known as the *pseudoeigenvalue* equation for the Hermitian matrix **A**, giving the pseudosecular equation:

$$|\mathbf{A} - \lambda\mathbf{M}| = 0. \tag{67}$$

The full pseudoeigenvalue equation is then:

$$\mathbf{AC} = \mathbf{MC}\boldsymbol{\Lambda}, \tag{68}$$

and the problem is to find a matrix of eigenvectors **C** such that matrices **A** and **M** are simultaneously diagonalized, with **M** brought to identity:

$$\mathbf{C}^\dagger\mathbf{AC} = \boldsymbol{\Lambda} \qquad \mathbf{C}^\dagger\mathbf{MC} = \mathbf{1}. \tag{69}$$

It is worth noting that matrix **C** is no longer unitary. It is obvious from (69) that $\mathbf{C}' = \mathbf{M}^{1/2}\mathbf{C}$ is unitary, so that the full pseudoeigenvalue equation is equivalent to the ordinary eigenvalue equation:

$$\mathbf{A}'\mathbf{C}' = \mathbf{C}'\boldsymbol{\Lambda}' \tag{70}$$

for the symmetrically transformed matrix:

$$\mathbf{A}' = \mathbf{M}^{-1/2}\mathbf{A}\mathbf{M}^{-1/2} \tag{71}$$

having:

$$\underset{\textit{same}\text{ eigenvalues}}{\boldsymbol{\Lambda}' = \boldsymbol{\Lambda}} \qquad \underset{\textit{transformed}\text{ eigenvectors}}{\mathbf{C}' = \mathbf{M}^{1/2}\mathbf{C}.} \tag{72}$$

This can be immediately proved upon multiplication by $\mathbf{M}^{-1/2}$ of both members of (68) and noting that $\mathbf{M}^{-1/2}\mathbf{M}^{1/2} = \mathbf{1}$.

If $\mathbf{A} = \boldsymbol{\chi}^\dagger\hat{A}\boldsymbol{\chi}$ is the matrix representative of the Hermitian operator $\hat{A}$ in the non-orthogonal basis $\boldsymbol{\chi}$ (with metric $\mathbf{M} = \boldsymbol{\chi}^\dagger\boldsymbol{\chi}$), equation (70) can be interpreted as the full eigenvalue equation for the operator $\hat{A}$ in the Löwdin symmetrically orthogonalized set (see Problem 2.9):

$$\boldsymbol{\chi}' = \boldsymbol{\chi}\mathbf{M}^{-1/2}. \tag{73}$$

In fact, we have:

$$\mathbf{A}' = \chi'^{\dagger}\hat{A}\chi' = \mathbf{M}^{-1/2}\chi^{\dagger}\hat{A}\chi\mathbf{M}^{-1/2} = \mathbf{M}^{-1/2}\mathbf{A}\mathbf{M}^{-1/2} \tag{74}$$

$$\mathbf{M}' = \chi'^{\dagger}\chi' = \mathbf{M}^{-1/2}\chi^{\dagger}\chi\mathbf{M}^{-1/2} = \mathbf{M}^{-1/2}\mathbf{M}\mathbf{M}^{-1/2} = \mathbf{1}. \tag{75}$$

It will be shown later in Chapter 5 that, for $\hat{A} = \hat{H}$, $\Lambda = \mathcal{E}$, the pseudoeigenvalue equation (66) arises as necessary condition in the minimization of the total energy with respect to variations in the linear coefficients in the Ritz method for a non-orthogonal basis set.

2.4 FUNCTIONS OF HERMITIAN MATRICES

2.4.1 Analytic Functions

For $\mathbf{A} = \mathbf{A}^{\dagger}$, from:

$$\mathbf{C}^{\dagger}\mathbf{A}\mathbf{C} = \mathbf{\Lambda} \tag{76}$$

we obtain the reverse transformation:

$$\mathbf{A} = \mathbf{C}\mathbf{\Lambda}\mathbf{C}^{\dagger}. \tag{77}$$

Similarly:

$$\mathbf{A}^2 = \mathbf{A}\mathbf{A} = (\mathbf{C}\mathbf{\Lambda}\mathbf{C}^{\dagger})(\mathbf{C}\mathbf{\Lambda}\mathbf{C}^{\dagger}) = \mathbf{C}\mathbf{\Lambda}^2\mathbf{C}^{\dagger} \tag{78}$$

$$\mathbf{A}^n = \mathbf{A}\mathbf{A}\cdots\mathbf{A} = \mathbf{C}\mathbf{\Lambda}^n\mathbf{C}^{\dagger}. \tag{79}$$

In this way, we can define any analytic function (i.e. a function expressible as a power series) of the Hermitian matrix **A** in the form:

$$F(\mathbf{A}) = \mathbf{C}F(\mathbf{\Lambda})\mathbf{C}^{\dagger}, \tag{80}$$

where F specifies the kind of function (inverse, square root, exponential, etc.).

Examples are:

$$\mathbf{A}^{-1} = \mathbf{C}\mathbf{\Lambda}^{-1}\mathbf{C}^{\dagger}$$

$$\mathbf{A}^{1/2} = \mathbf{C}\mathbf{\Lambda}^{1/2}\mathbf{C}^{\dagger}$$

provided **A** is positive definite (positive eigenvalues). In fact, it is easily proved that:

$$\mathbf{A}\mathbf{A}^{-1} = \mathbf{A}\mathbf{C}\mathbf{\Lambda}^{-1}\mathbf{C}^{\dagger} = \mathbf{C}\mathbf{\Lambda}\mathbf{\Lambda}^{-1}\mathbf{C}^{\dagger} = \mathbf{C}\mathbf{C}^{\dagger} = \mathbf{1}$$

$$\mathbf{A}^{-1}\mathbf{A} = \mathbf{C}\mathbf{\Lambda}^{-1}\mathbf{C}^{\dagger}\mathbf{A} = \mathbf{C}\mathbf{\Lambda}^{-1}\mathbf{\Lambda}\mathbf{C}^{\dagger} = \mathbf{C}\mathbf{C}^{\dagger} = \mathbf{1}$$

(from: $\mathbf{A}^\dagger = \mathbf{A}$, $\boldsymbol{\Lambda}^\dagger = \boldsymbol{\Lambda}$, $\mathbf{AC} = \mathbf{C}\boldsymbol{\Lambda}$, $\mathbf{C}^\dagger\mathbf{A} = \boldsymbol{\Lambda}\mathbf{C}^\dagger$)

$$\mathbf{A}^{1/2}\mathbf{A}^{1/2} = \mathbf{C}\boldsymbol{\Lambda}^{1/2}\mathbf{C}^\dagger\mathbf{C}\boldsymbol{\Lambda}^{1/2}\mathbf{C}^\dagger = \mathbf{C}\boldsymbol{\Lambda}\mathbf{C}^\dagger = \mathbf{A}.$$

2.4.2 Canonical Form

Let us introduce the square matrix of order n:

$$\underset{n\times n}{\mathbf{A}_\mu} = \underset{n\times 1}{\mathbf{c}_\mu}\ \underset{1\times n}{\mathbf{c}_\mu^\dagger} \tag{81}$$

as the *projector* corresponding to the eigenvalue λ_μ. The projectors have the properties:

$$\mathbf{A}_\mu\mathbf{A}_\nu = \mathbf{A}_\mu\delta_{\mu\nu} \qquad (\nu = \mu \text{ idempotency, } \nu \neq \mu \text{ mutual exclusivity}) \tag{82}$$

$$\sum_{\mu=1}^{n}\mathbf{A}_\mu = \mathbf{1} \qquad \text{(completeness or resolution of the identity).} \tag{83}$$

Then:

$$\mathbf{A} = \sum_{\mu=1}^{n}\lambda_\mu\mathbf{A}_\mu \tag{84}$$

is called the canonical form of the Hermitian matrix $\mathbf{A}$. In fact, from the ν-th eigenvalue equation for $\mathbf{A}$, we obtain:

$$\mathbf{A}\mathbf{c}_\nu = \lambda_\nu\mathbf{c}_\nu \tag{85}$$

$$\left(\sum_\mu\lambda_\mu\mathbf{A}_\mu\right)\mathbf{c}_\nu = \sum_\mu\lambda_\mu\mathbf{c}_\mu\underbrace{\mathbf{c}_\mu^\dagger\mathbf{c}_\nu} = \sum_\mu\lambda_\mu\mathbf{c}_\mu\delta_{\mu\nu} = \lambda_\nu\mathbf{c}_\nu. \tag{86}$$

For a function F of the Hermitian matrix $\mathbf{A}$:

$$F(\mathbf{A}) = \sum_{\mu=1}^{n}F(\lambda_\mu)\mathbf{A}_\mu \tag{87}$$

is the canonical form for the analytic function $F(\mathbf{A})$.

2.4.3 Lagrange Interpolation Formula

The interpolation formula due to Lagrange:

$$F(\mathbf{A}) = \sum_{\mu=1}^{n}F(\lambda_\mu)\frac{\prod_{\nu\neq\mu}(\mathbf{A} - \lambda_\nu\mathbf{1})}{\prod_{\nu\neq\mu}(\lambda_\mu - \lambda_\nu)} \tag{88}$$

makes it possible to calculate any analytic function of a square matrix $\mathbf{A}$. It is not limited to symmetric matrices and, at variance with the canonical form, makes use only of eigenvalues and positive powers (up to order $n-1$) of $\mathbf{A}$.

By comparing the canonical form of $\mathbf{A}$ with that of Lagrange interpolation, it is seen that:

$$\mathbf{A}_{\mu} = \mathbf{c}_{\mu}\mathbf{c}_{\mu}^{\dagger} = \frac{\prod_{\nu \neq \mu}(\mathbf{A} - \lambda_{\nu}\mathbf{1})}{\prod_{\nu \neq \mu}(\lambda_{\mu} - \lambda_{\nu})} \tag{89}$$

so that the matrix corresponding to the μ-th projector can be expressed in terms of a polynomial matrix of order $n-1$ in $\mathbf{A}$ with numerical coefficients which depend only on the eigenvalues of $\mathbf{A}$. Now let $\mathbf{A}$ be a 2×2 symmetrical matrix $\mathbf{A}$ with eigenvalues λ_1 and λ_2 (see Problem 2.3):

$$\mathbf{A} = \begin{pmatrix} \alpha_1 & \beta \\ \beta & \alpha_2 \end{pmatrix}.$$

Then:

$$\begin{aligned} F(\mathbf{A}) &= F(\lambda_1)\frac{\mathbf{A} - \lambda_2\mathbf{1}}{\lambda_1 - \lambda_2} + F(\lambda_2)\frac{\mathbf{A} - \lambda_1\mathbf{1}}{\lambda_2 - \lambda_1} \\ &= \frac{F(\lambda_1)(\mathbf{A} - \lambda_2\mathbf{1}) - F(\lambda_2)(\mathbf{A} - \lambda_1\mathbf{1})}{\lambda_1 - \lambda_2} = p\mathbf{1} + q\mathbf{A} \end{aligned} \tag{90}$$

with:

$$p = \frac{\lambda_1 F(\lambda_2) - \lambda_2 F(\lambda_1)}{\lambda_1 - \lambda_2} \qquad q = \frac{F(\lambda_1) - F(\lambda_2)}{\lambda_1 - \lambda_2}. \tag{91}$$

2.4.4 Cayley–Hamilton Theorem

This theorem states that any square matrix $\mathbf{A}$ does satisfy its own characteristic equation:

$$P_n(\mathbf{A}) = a_0\mathbf{1} + a_1\mathbf{A} + a_2\mathbf{A}^2 + \cdots + a_n\mathbf{A}^n = \mathbf{0}. \tag{92}$$

An important application of this theorem concerns the possibility of calculating positive or negative n-th powers of $\mathbf{A}$ in terms of linear combinations of $\mathbf{1}$, $\mathbf{A}$, $\mathbf{A}^2$, $\cdots$, $\mathbf{A}^{n-1}$.

Proof. We first observe that a matrix whose elements are polynomials of degree n in a variable λ can always be written as a polynomial in λ with matrix coefficients. As an example:

$$\begin{pmatrix} \lambda^2 - 1 & 2\lambda - 2 & 0 \\ 2\lambda - 2 & \lambda^2 - 2\lambda + 1 & 0 \\ 0 & 0 & \lambda^2 - 5 \end{pmatrix}$$

$$= \begin{pmatrix} -1 & -2 & 0 \\ -2 & 1 & 0 \\ 0 & 0 & -5 \end{pmatrix} + \begin{pmatrix} 0 & 2 & 0 \\ 2 & -2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \lambda + \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \lambda^2 .$$

Consider now the expression for the inverse of the characteristic matrix of $\mathbf{A}$:

$$(\mathbf{A} - \lambda\mathbf{1})(\widetilde{\mathbf{a} - \lambda\mathbf{1}}) = |\mathbf{A} - \lambda\mathbf{1}|\mathbf{1}.$$

The transpose of the matrix of cofactors, $(\widetilde{\mathbf{a} - \lambda\mathbf{1}})$, is a matrix whose elements are polynomials of order $(n-1)$ in λ, namely:

$$(\widetilde{\mathbf{a} - \lambda\mathbf{1}}) = \mathbf{B} = \mathbf{B}_0 + \mathbf{B}_1\lambda + \mathbf{B}_2\lambda^2 + \cdots + \mathbf{B}_{n-1}\lambda^{n-1}$$

so that

$$\begin{aligned} &(\mathbf{A} - \lambda\mathbf{1})(\mathbf{B}_0 + \mathbf{B}_1\lambda + \mathbf{B}_2\lambda^2 + \cdots + \mathbf{B}_{n-1}\lambda^{n-1}) \\ &\quad = (a_0 + a_1\lambda + a_2\lambda^2 + \cdots + a_{n-1}\lambda^{n-1} + a_n\lambda^n)\mathbf{1} \end{aligned}$$

is an identity in λ. By identifying coefficients of different powers in λ:

$$\begin{array}{lrcll} \lambda^0 & \mathbf{A}\mathbf{B}_0 & = & a_0\mathbf{1} & \mathbf{1} \\ \lambda & \mathbf{A}\mathbf{B}_1 - \mathbf{B}_0 & = & a_1\mathbf{1} & \mathbf{A} \\ \lambda^2 & \mathbf{A}\mathbf{B}_2 - \mathbf{B}_1 & = & a_2\mathbf{1} & \mathbf{A}^2 \\ & & \cdots & & \\ \lambda^{n-1} & \mathbf{A}\mathbf{B}_{n-1} - \mathbf{B}_{n-2} & = & a_{n-1}\mathbf{1} & \mathbf{A}^{n-1} \\ \lambda^n & -\mathbf{B}_{n-1} & = & a_n\mathbf{1} & \mathbf{A}^n . \end{array}$$

By multiplying each term on the left by $\mathbf{1}$, $\mathbf{A}$, $\mathbf{A}^2$, $\cdots$, $\mathbf{A}^{n-1}$, $\mathbf{A}^n$, respectively, and adding, we find the Cayley–Hamilton theorem (92).

2.5 PROBLEMS 2

2.1. Show that a Hermitian matrix $\mathbf{A}$ has real eigenvalues.

Answer:
If $\mathbf{A}^\dagger = \mathbf{A}$ then $\mathbf{\Lambda}^\dagger = \mathbf{\Lambda}$.

Hint:
Use the μ-th eigenvalue equation for the Hermitian matrix $\mathbf{A}$ and its adjoint.

2.2. Show that a Hermitian matrix $\mathbf{A}$ has orthonormal eigenvectors, i.e. that $\mathbf{C}$ is unitary.

Answer:
If $\mathbf{A}^\dagger = \mathbf{A} \quad \mathbf{C}^\dagger\mathbf{A}\mathbf{C} = \mathbf{\Lambda} \quad \mathbf{C}^\dagger\mathbf{C} = \mathbf{C}\mathbf{C}^\dagger = \mathbf{1}$.

Hint:
Use the full eigenvalue equation for matrix **A** and its adjoint considering that $\mathbf{A}^\dagger = \mathbf{A}$ and $\boldsymbol{\Lambda}^\dagger = \boldsymbol{\Lambda}$.

2.3. Solve the complete 2 × 2 eigenvalue problem for the Hermitian matrix:

$$\mathbf{A} = \begin{pmatrix} \alpha_1 & \beta \\ \beta & \alpha_2 \end{pmatrix},$$

where, for the time being, we shall assume that $\alpha_1, \alpha_2, \beta$ are all real *negative* quantities (as in the Hamiltonian matrix)[2]. Show that the complete matrix **C** of the eigenvectors is a unitary matrix.

Answer:
Let

$$a = \left(\frac{\Delta + (\alpha_2 - \alpha_1)}{2\Delta}\right)^{1/2}, \qquad b = \left(\frac{\Delta - (\alpha_2 - \alpha_1)}{2\Delta}\right)^{1/2}$$

$$\Delta = \{(\alpha_2 - \alpha_1)^2 + 4\beta^2\}^{1/2} > 0.$$

Then:

$$2\lambda_1 = (\alpha_1 + \alpha_2) - \Delta \qquad \mathbf{c}_1 = \begin{pmatrix} a \\ b \end{pmatrix}$$

$$2\lambda_2 = (\alpha_1 + \alpha_2) + \Delta \qquad \mathbf{c}_2 = \begin{pmatrix} -b \\ a \end{pmatrix}$$

so that:

$$\mathbf{C} = (\mathbf{c}_1 \mathbf{c}_2) = \begin{pmatrix} a & -b \\ b & a \end{pmatrix} \qquad \mathbf{C}^\dagger \mathbf{C} = \mathbf{C}^\dagger \mathbf{C} = \mathbf{1}.$$

Hint:
Solve first the quadratic secular equation for **A**, next the system of homogeneous linear equations for each eigenvalue in turn, taking into account the normalization condition for the coefficients.

2.4. Show by actual calculation that the Hermitian matrix **A** is diagonalized by the unitary transformation with the complete matrix of its eigenvectors.

---

[2] If all matrix elements are *positive* (as in the metric matrix), we must change b into $-b$ in the expressions of $\mathbf{c}_1$ and $\mathbf{c}_2$, which implies the interchanging of signs in the off-diagonal elements of the projectors $\mathbf{A}_1$ and $\mathbf{A}_2$.

Answer:
$\mathbf{C}^{\dagger}\mathbf{A}\mathbf{C} = \mathbf{\Lambda}$.

Hint:
Use properties of a, b found in Problem 2.3.

2.5. Find the projectors for the Hermitian matrix $\mathbf{A}$ ($\alpha_1, \alpha_2, \beta < 0$) and verify its canonical form.

Answer:

$$\mathbf{A}_1 = \begin{pmatrix} a^2 & ab \\ ab & b^2 \end{pmatrix} \qquad \mathbf{A}_2 = \begin{pmatrix} b^2 & -ab \\ -ab & a^2 \end{pmatrix}$$

$$\lambda_1 \mathbf{A}_1 + \lambda_2 \mathbf{A}_2 = \mathbf{A}.$$

Hint:
Follow the definitions and make use of the properties of a, b found in Problem 2.3.

2.6. Find the inverse of the Hermitian matrix $\mathbf{A}$ through its canonical form.

Answer:

$$\mathbf{A}^{-1} = (\det \mathbf{A})^{-1} \begin{pmatrix} \alpha_2 & -\beta \\ -\beta & \alpha_1 \end{pmatrix}.$$

Hint:
Use:

$$\mathbf{A}^{-1} = \lambda_1^{-1} \mathbf{A}_1 + \lambda_2^{-1} \mathbf{A}_2$$

and some results of Problems 2.3 and 2.5.

2.7. Find the square root of the Hermitian matrix $\mathbf{A}$, provided it is positive definite (positive eigenvalues):

$$\mathbf{A} = \begin{pmatrix} \alpha_1 & \beta \\ \beta & \alpha_2 \end{pmatrix} \quad \alpha_1, \alpha_2, \beta > 0 \quad \lambda_1, \lambda_2 > 0.$$

Answer:

$$\mathbf{A}^{1/2} = \begin{pmatrix} Aa^2 + Bb^2 & -(A-B)ab \\ -(A-B)ab & Ab^2 + Ba^2 \end{pmatrix}$$

where (see Problem 2.3):

$$A=\lambda_1^{1/2},\qquad B=\lambda_2^{1/2},\qquad a=\left(\frac{\Delta+(\alpha_2-\alpha_1)}{2\Delta}\right)^{1/2},$$

$$b=\left(\frac{\Delta-(\alpha_2-\alpha_1)}{2\Delta}\right)^{1/2}.$$

Hint:
Use the canonical form of matrix **A** taking into account previous footnote 2:

$$\mathbf{A}^{1/2}=\lambda_1^{1/2}\mathbf{A}_1+\lambda_2^{1/2}\mathbf{A}_2.$$

2.8. Find the inverse of the square root of the positive definite Hermitian matrix **A**:

$$\mathbf{A}=\begin{pmatrix}\alpha_1 & \beta\\ \beta & \alpha_2\end{pmatrix}\quad \alpha_1,\alpha_2,\beta>0\quad \lambda_1,\lambda_2>0.$$

Answer:

$$\mathbf{A}^{-1/2}=\frac{1}{AB}\begin{pmatrix}Ab^2+Ba^2 & (A-B)ab\\ (A-B)ab & Aa^2+Bb^2\end{pmatrix}\quad A,B \text{ defined in Problem 2.7.}$$

Hint:
Use the canonical form of matrix **A** taking into account footnote 2:

$$\mathbf{A}^{-1/2}=\lambda_1^{-1/2}\mathbf{A}_1+\lambda_2^{-1/2}\mathbf{A}_2.$$

2.9. Show that if two Q-class functions χ_1 and χ_2 are normalized but not orthogonal, with $\langle\chi_1|\chi_2\rangle=\langle\chi_2|\chi_1\rangle=S$, the functions can be orthogonalized by a Löwdin symmetrical transformation.

Answer:
Let $\boldsymbol{\chi}=(\chi_1\chi_2)$ be the row vector of the basis functions. Then the metric (the matrix of the scalar products) is:

$$\mathbf{M}=\boldsymbol{\chi}^\dagger\boldsymbol{\chi}=\begin{pmatrix}1 & S\\ S & 1\end{pmatrix}$$

a positive definite matrix with $\lambda_1,\lambda_2>0$. Then, the Löwdin symmetrically orthogonalized set is given by:

$$\boldsymbol{\chi}'=\boldsymbol{\chi}\mathbf{M}^{-1/2}.$$

Hint:
Construct the inverse of the square root of the positive definite metric matrix **M** as done in Problem 2.8, taking $\alpha_1=\alpha_2=1$, $\beta=S$.

2.10. Find $\exp(\mathbf{A})$ and $\exp(-\mathbf{A})$.

Answer:

$$\exp(\mathbf{A}) = \begin{pmatrix} a^2\exp(\lambda_1) + b^2\exp(\lambda_2) & ab[\exp(\lambda_1) - \exp(\lambda_2)] \\ ab[\exp(\lambda_1) - \exp(\lambda_2)] & b^2\exp(\lambda_1) + a^2\exp(\lambda_2) \end{pmatrix}$$

$$\exp(-\mathbf{A}) = \begin{pmatrix} a^2\exp(-\lambda_1) + b^2\exp(-\lambda_2) & ab[\exp(-\lambda_1) - \exp(-\lambda_2)] \\ ab[\exp(-\lambda_1) - \exp(-\lambda_2)] & b^2\exp(-\lambda_1) + a^2\exp(-\lambda_2) \end{pmatrix},$$

where λ_1, λ_2 are the eigenvalues of $\mathbf{A}$, and a, b are defined in Problem 2.7.

2.11. Find the inverse of matrix $\mathbf{A}$ according to the Lagrange formula.

Answer:

$$\mathbf{A}^{-1} = (\det\mathbf{A})^{-1}\begin{pmatrix} \alpha_2 & -\beta \\ -\beta & \alpha_1 \end{pmatrix}.$$

Hint:
Calculate coefficients p, q for $F =$ inverse.

2.12. Find the square root of the positive definite Hermitian matrix $\mathbf{A}$ according to the Lagrange formula.

Answer:

$$\mathbf{A}^{1/2} = \begin{pmatrix} Aa^2 + Bb^2 & -(A-B)ab \\ -(A-B)ab & Ab^2 + Ba^2 \end{pmatrix},$$

where A, B, a, b were defined in Problem 2.7.

Hint:
Calculate coefficients p, q for $F = (\cdots)^{1/2}$.

2.13. Find the square root for the unsymmetrical matrix:

$$\mathbf{A} = \begin{pmatrix} 3 & -4 \\ 1 & -1 \end{pmatrix}.$$

Answer:

$$\mathbf{A}^{1/2} = \begin{pmatrix} 2 & -2 \\ \frac{1}{2} & 0 \end{pmatrix} \quad \text{or } \mathbf{A}^{1/2} = \begin{pmatrix} -2 & 2 \\ -\frac{1}{2} & 0 \end{pmatrix}.$$

Hint:
Since matrix $\mathbf{A}$ cannot be diagonalized by the usual techniques ($\mathbf{\Lambda}$ is the identity matrix), we must turn to solving the system of non-linear equations resulting from the definition:

$$\mathbf{A}^{1/2}\mathbf{A}^{1/2} = \mathbf{A}.$$

2.14. Find $\mathbf{A}^{-1}$ using the Cayley–Hamilton theorem.

2.15. Solve the complete 2×2 pseudoeigenvalue problem for the Hermitian matrices:

$$\mathbf{H} = \begin{pmatrix} \alpha_1 & \beta \\ \beta & \alpha_2 \end{pmatrix} \qquad \mathbf{M} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix},$$

where we assume that $\alpha_1, \alpha_2, \beta < 0$ and $S > 0$.

Answer:
Let:

$$A = -(1-S^2)^{-1/2}(\lambda + S), \;\; B = (1-S^2)^{-1/2}(1+\lambda S)$$

$$\lambda = \left(\frac{\Delta - (\alpha_2 - \alpha_1)}{\Delta + (\alpha_2 - \alpha_1)}\right)^{1/2} \left(\frac{|\beta - \alpha_1 S|}{|\beta - \alpha_2 S|}\right)^{1/2}$$

$$\Delta = \left\{(\alpha_2 - \alpha_1)^2 + 4(\beta - \alpha_1 S)(\beta - \alpha_2 S)\right\}^{1/2} > 0.$$

Then:

$$2(1-S^2)\varepsilon_1 = (\alpha_1 + \alpha_2 - 2\beta S) - \Delta, \qquad \mathbf{c}_1 = (1+\lambda^2+2\lambda S)^{-1/2}\begin{pmatrix} 1 \\ \lambda \end{pmatrix}$$

$$2(1-S^2)\varepsilon_2 = (\alpha_1 + \alpha_2 - 2\beta S) + \Delta, \qquad \mathbf{c}_2 = (1+\lambda^2+2\lambda S)^{-1/2}\begin{pmatrix} A \\ B \end{pmatrix}$$

so that:

$$\mathbf{C} = (\mathbf{c}_1\mathbf{c}_2) = (1+\lambda^2+2\lambda S)^{-1}\begin{pmatrix} 1 & A \\ \lambda & B \end{pmatrix}.$$

Hint:
Same as for Problem 2.3, taking into account non-orthogonality.

2.16. Show by direct matrix multiplication that, for the 2×2 pseudoeigenvalue problem:

$$\mathbf{C}^{\dagger}\mathbf{M}\mathbf{C} = \mathbf{1}$$

so that $\mathbf{C}' = \mathbf{M}^{1/2}\mathbf{C}$ is unitary.

Hint:
Use results and properties found in Problem 2.15.

2.17. Show by direct matrix multiplication that, for the 2 × 2 pseudoeigenvalue problem, matrix $\mathbf{H}$ is brought to diagonal form through a transformation with the non-unitary matrix $\mathbf{C}$:

$$\mathbf{C}^{\dagger}\mathbf{H}\mathbf{C} = \boldsymbol{\mathcal{E}}.$$

Hint:
Use results and properties found in Problem 2.15, and the fact that best λ diagonalizes the matrix representative of the Hermitian operator $\hat{H}$ over the MO basis resulting from the Ritz method.

2.6 SOLVED PROBLEMS

2.1. Real eigenvalues.

Consider the μ-th eigenvalue equation for the Hermitian matrix $\mathbf{A}$:

$$\mathbf{A}\mathbf{c}_{\mu} = \lambda_{\mu}\mathbf{c}_{\mu}.$$

Multiply both members on the left by the adjoint eigenvector $\mathbf{c}_{\mu}^{\dagger}$:

$$\mathbf{c}_{\mu}^{\dagger}\mathbf{A}\mathbf{c}_{\mu} = \lambda_{\mu}\mathbf{c}_{\mu}^{\dagger}\mathbf{c}_{\mu}.$$

Taking the adjoint of both members:

$$\mathbf{c}_{\mu}^{\dagger}\mathbf{A}^{\dagger}\mathbf{c}_{\mu} = \lambda_{\mu}^{*}\mathbf{c}_{\mu}^{\dagger}\mathbf{c}_{\mu}$$

namely, since $\mathbf{A}^{\dagger} = \mathbf{A}$:

$$\mathbf{c}_{\mu}^{\dagger}\mathbf{A}\mathbf{c}_{\mu} = \lambda_{\mu}^{*}\mathbf{c}_{\mu}^{\dagger}\mathbf{c}_{\mu}.$$

Subtracting the corresponding equations, we obtain:

$$0 = (\lambda_{\mu}^{*} - \lambda_{\mu})\mathbf{c}_{\mu}^{\dagger}\mathbf{c}_{\mu}$$

so that, since $\mathbf{c}_{\mu}^{\dagger}\mathbf{c}_{\mu} \neq 0$,

$$\lambda_{\mu}^{*} - \lambda_{\mu} = 0 \Longrightarrow \lambda_{\mu}^{*} = \lambda_{\mu}$$

and the eigenvalues are real.

Since this is true for all eigenvalues of $\mathbf{A}$, we thereby obtain:

$$\mathbf{\Lambda}^\dagger = \mathbf{\Lambda}.$$

If $\mathbf{c}_\mu^\dagger \mathbf{c}_\mu = 1$, the eigenvectors are normalized to 1.

2.2. Orthogonal eigenvectors.

Consider the complete eigenvalue equation for the Hermitian matrix $\mathbf{A}$:

$$\mathbf{AC} = \mathbf{C\Lambda}.$$

Multiplying both members on the left by $\mathbf{C}^{-1}$, we obtain:

$$\mathbf{C}^{-1}\mathbf{AC} = \mathbf{\Lambda}.$$

Taking the adjoint of the last equation:

$$\mathbf{C}^\dagger \mathbf{A}^\dagger (\mathbf{C}^{-1})^\dagger = \mathbf{\Lambda}^\dagger$$

where, since $\mathbf{A}^\dagger = \mathbf{A}$ and $\mathbf{\Lambda}^\dagger = \mathbf{\Lambda}$:

$$\mathbf{C}^\dagger \mathbf{A} (\mathbf{C}^{-1})^\dagger = \mathbf{\Lambda}.$$

Comparing with the previous equation for $\mathbf{\Lambda}$, we see that:

$$\mathbf{C}^{-1} = \mathbf{C}^\dagger, \quad \mathbf{C}^\dagger\mathbf{C} = \mathbf{C}\mathbf{C}^\dagger = \mathbf{1}$$

and $\mathbf{C}$ is a unitary matrix of orthonormal eigenvectors.

2.3. The complete 2×2 eigenvalue problem.

Let the Hermitian (symmetric) matrix $\mathbf{A}$ be:

$$\mathbf{A} = \begin{pmatrix} \alpha_1 & \beta \\ \beta & \alpha_2 \end{pmatrix},$$

where we assume that $\alpha_1, \alpha_2, \beta < 0$, as useful in applications (e.g. Hückel theory). We construct the secular equation:

$$P_2(\lambda) = \begin{vmatrix} \alpha_1 - \lambda & \beta \\ \beta & \alpha_2 - \lambda \end{vmatrix} = (\alpha_1 - \lambda)(\alpha_2 - \lambda) - \beta^2 = 0.$$

Solution of the resulting quadratic equation

$$\lambda^2 - (\alpha_1 + \alpha_2)\lambda + (\alpha_1\alpha_2 - \beta^2) = 0$$

gives two *real* roots:

$$2\lambda_1 = (\alpha_1 + \alpha_2) - \Delta \qquad 2\lambda_2 = (\alpha_1 + \alpha_2) + \Delta$$

$$\Delta = \left\{(\alpha_2 - \alpha_1)^2 + 4\beta^2\right\}^{1/2} > 0$$

having the properties:

$$\lambda_1 + \lambda_2 = \alpha_1 + \alpha_2 \qquad \lambda_2 - \lambda_1 = \Delta \qquad \lambda_1\lambda_2 = \alpha_1\alpha_2 - \beta^2 = \det \mathbf{A}.$$

We now solve for the eigenvectors, by introducing each eigenvalue in turn in the original system of linear homogeneous equations. We see that the solution of the system only gives the ratio of the coefficients, so that we introduce the auxiliary condition of normalization which will give normalized eigenvectors.

(i) First eigenvalue λ_1.

$$\begin{cases} (\alpha_1 - \lambda_1)c_1 + \beta c_2 = 0 \\ c_1^2 + c_2^2 = 1 \end{cases}$$

$$\begin{aligned} \left(\frac{c_2}{c_1}\right)_1 &= \frac{\lambda_1 - \alpha_1}{\beta} = -\frac{\Delta - (\alpha_2 - \alpha_1)}{2\beta} = \frac{\Delta - (\alpha_2 - \alpha_1)}{2|\beta|} \\ &= \left(\frac{\Delta - (\alpha_2 - \alpha_1)}{\Delta + (\alpha_2 - \alpha_1)}\right)^{1/2} > 0 \end{aligned}$$

since:

$$\begin{aligned} &\Delta^2 = (\alpha_2 - \alpha_1)^2 + 4\beta^2 \\ &4\beta^2 = [\Delta - (\alpha_2 - \alpha_1)][\Delta + (\alpha_2 - \alpha_1)] \\ &2|\beta| = \{[\Delta - (\alpha_2 - \alpha_1)][\Delta + (\alpha_2 - \alpha_1)]\}^{1/2}. \end{aligned}$$

From the normalization condition for the coefficients it follows:

$$c_1^2\left\{1 + \left(\frac{c_2}{c_1}\right)_1^2\right\} = c_1^2 \frac{2\Delta}{\Delta + (\alpha_2 - \alpha_1)} = 1.$$

Hence we have for the first eigenvector:

$$\underset{\substack{\uparrow \\ \text{refers to the} \\ \text{first eigenvalue}}}{c_{11}} = \left(\frac{\Delta + (\alpha_2 - \alpha_1)}{2\Delta}\right)^{1/2}, \qquad \underset{\uparrow}{c_{21}} = \left(\frac{\Delta - (\alpha_2 - \alpha_1)}{2\Delta}\right)^{1/2}.$$

(ii) Second eigenvalue λ_2.

To get the eigenvector corresponding to the second eigenvalue, we simply interchange $1 \to 2$ into the homogeneous system:

$$\begin{cases} (\alpha_2 - \lambda_2)c_2 + \beta c_1 = 0 \\ c_1^2 + c_2^2 = 1 \end{cases}$$

$$\begin{aligned} \left(\frac{c_1}{c_2}\right)_2 &= \frac{\lambda_2 - \alpha_2}{\beta} = \frac{\Delta + (\alpha_1 - \alpha_2)}{2\beta} = -\frac{\Delta + (\alpha_1 - \alpha_2)}{2|\beta|} \\ &= -\frac{\Delta - (\alpha_2 - \alpha_1)}{2|\beta|} = -\left(\frac{\Delta - (\alpha_2 - \alpha_1)}{\Delta + (\alpha_2 - \alpha_1)}\right)^{1/2} < 0 \end{aligned}$$

so that we have the important relation:

$$\left(\frac{c_1}{c_2}\right)_2 = -\left(\frac{c_2}{c_1}\right)_1 .$$

From the normalization condition, we get:

$$c_2^2\left\{1 + \left(\frac{c_1}{c_2}\right)_2^2\right\} = c_2^2\frac{2\Delta}{\Delta + (\alpha_2 - \alpha_1)} = 1$$

giving for the second eigenvector:

$$\underset{\substack{\uparrow \\ \text{refers to the} \\ \text{second eigen-} \\ \text{value}}}{c_{22}} = \left(\frac{\Delta + (\alpha_2 - \alpha_1)}{2\Delta}\right)^{1/2}, \qquad \underset{\uparrow}{c_{12}} = -\left(\frac{\Delta - (\alpha_2 - \alpha_1)}{2\Delta}\right)^{1/2}.$$

Hence, the unitary matrix diagonalizing **A** will be:

$$\mathbf{C} = (\mathbf{c}_1|\mathbf{c}_2) = (2\Delta)^{-1/2}\left(\begin{array}{c|c} [\Delta + (\alpha_2 - \alpha_1)]^{1/2} & -[\Delta - (\alpha_2 - \alpha_1)]^{1/2} \\ [\Delta - (\alpha_2 - \alpha_1)]^{1/2} & [\Delta + (\alpha_2 - \alpha_1)]^{1/2} \end{array}\right).$$

In short:

$$\mathbf{C} = \begin{pmatrix} a & -b \\ b & a \end{pmatrix} \qquad a = \left(\frac{\Delta + (\alpha_2 - \alpha_1)}{2\Delta}\right)^{1/2}, \quad b = \left(\frac{\Delta - (\alpha_2 - \alpha_1)}{2\Delta}\right)^{1/2}.$$

We now verify that matrix **C** is unitary:

$$\mathbf{C}^\dagger\mathbf{C} = \begin{pmatrix} a & b \\ -b & a \end{pmatrix}\begin{pmatrix} a & -b \\ b & a \end{pmatrix} = \begin{pmatrix} a^2 + b^2 & 0 \\ 0 & b^2 + a^2 \end{pmatrix} = \mathbf{1}$$

since:

$$a^2+b^2=\frac{\Delta+(\alpha_2-\alpha_1)}{2\Delta}+\frac{\Delta-(\alpha_2-\alpha_1)}{2\Delta}=1$$

$$\mathbf{C}\mathbf{C}^\dagger=\begin{pmatrix} a^2+b^2 & 0 \\ 0 & b^2+a^2 \end{pmatrix}=\mathbf{1}$$

so that $\mathbf{C}$ is a unitary matrix.

For $\alpha_2-\alpha_1=0$, $\Delta=2|\beta|$, so that:

$$a=b=\frac{1}{\sqrt{2}} \qquad \mathbf{C}=\begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}, \qquad \mathbf{C}^\dagger=\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}.$$

2.4. We must show by direct calculation that the Hermitian matrix $\mathbf{A}$ is diagonalized by the unitary transformation with the complete matrix of its eigenvectors:

$$\mathbf{A}=\begin{pmatrix} \alpha_1 & \beta \\ \beta & \alpha_2 \end{pmatrix} \qquad \mathbf{C}=\begin{pmatrix} a & -b \\ b & a \end{pmatrix} \qquad \mathbf{C}^\dagger=\begin{pmatrix} a & b \\ -b & a \end{pmatrix}.$$

Multiplication rows by columns gives:

$$\mathbf{C}^\dagger\mathbf{A}\mathbf{C}=\begin{pmatrix} a^2\alpha_1+b^2\alpha_2+2ab\beta & ab(\alpha_2-\alpha_1)+(a^2-b^2)\beta \\ ab(\alpha_2-\alpha_1)+(a^2-b^2)\beta & b^2\alpha_1+a^2\alpha_2-2ab\beta \end{pmatrix}.$$

We first notice that:

$$a^2=\frac{\Delta+(\alpha_2-\alpha_1)}{2\Delta} \qquad b^2=\frac{\Delta-(\alpha_2-\alpha_1)}{2\Delta}$$

$$a^2+b^2=1 \qquad a^2-b^2=\frac{\alpha_2-\alpha_1}{\Delta}$$

$$ab=\left(\frac{\Delta^2-(\alpha_2-\alpha_1)^2}{4\Delta^2}\right)^{1/2}=\frac{|\beta|}{\Delta}=-\frac{\beta}{\Delta}.$$

Then we have for the matrix elements:
11-element:

$$\begin{aligned} a^2\alpha_1+b^2\alpha_2+2ab\beta &= \frac{\Delta+(\alpha_2-\alpha_1)}{2\Delta}\alpha_1+\frac{\Delta-(\alpha_2-\alpha_1)}{2\Delta}\alpha_2-\frac{2\beta^2}{\Delta} \\ &= \frac{\Delta(\alpha_1+\alpha_2)+(\alpha_2-\alpha_1)(\alpha_1-\alpha_2)-4\beta^2}{2\Delta} \\ &= \frac{\alpha_1+\alpha_2}{2}-\frac{\Delta}{2}=\lambda_1. \end{aligned}$$

22-element:

$$\begin{aligned} b^2\alpha_1 + a^2\alpha_2 - 2ab\beta &= \frac{\Delta - (\alpha_2-\alpha_1)}{2\Delta}\alpha_1 + \frac{\Delta + (\alpha_2-\alpha_1)}{2\Delta}\alpha_2 + \frac{2\beta^2}{\Delta} \\ &= \frac{\Delta(\alpha_1+\alpha_2) - (\alpha_2-\alpha_1)(\alpha_1-\alpha_2) + 4\beta^2}{2\Delta} \\ &= \frac{\alpha_1+\alpha_2}{2} + \frac{\Delta}{2} = \lambda_2. \end{aligned}$$

12-element = 21-element:

$$ab(\alpha_2-\alpha_1) + (a^2-b^2)\beta = -\frac{\beta}{\Delta}(\alpha_2-\alpha_1) + \frac{\alpha_2-\alpha_1}{\Delta}\beta = 0$$

so that

$$\mathbf{C}^\dagger\mathbf{A}\mathbf{C} = \mathbf{\Lambda} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$$

as it must be.

2.5. Projectors of **A** $(\alpha_1, \alpha_2, \beta < 0)$[3] and its canonical form.
Using the results of Problem 2.3, the projectors are:

$$\mathbf{A}_1 = \mathbf{c}_1\mathbf{c}_1^\dagger = \begin{pmatrix} a \\ b \end{pmatrix}(a\ b) = \begin{pmatrix} a^2 & ab \\ ab & b^2 \end{pmatrix}$$

$$\mathbf{A}_2 = \mathbf{c}_2\mathbf{c}_2^\dagger = \begin{pmatrix} -b \\ a \end{pmatrix}(-b\ a) = \begin{pmatrix} b^2 & -ab \\ -ab & a^2 \end{pmatrix}.$$

We now verify the projector properties of $\mathbf{A}_1$ and $\mathbf{A}_2$:

$$\mathbf{A}_1\mathbf{A}_1 = \begin{pmatrix} a^2 & ab \\ ab & b^2 \end{pmatrix}\begin{pmatrix} a^2 & ab \\ ab & b^2 \end{pmatrix} = \begin{pmatrix} a^2(a^2+b^2) & ab(a^2+b^2) \\ ab(a^2+b^2) & b^2(a^2+b^2) \end{pmatrix} = \mathbf{A}_1$$

$$\begin{aligned} \mathbf{A}_2\mathbf{A}_2 &= \begin{pmatrix} b^2 & -ab \\ -ab & a^2 \end{pmatrix}\begin{pmatrix} b^2 & -ab \\ -ab & a^2 \end{pmatrix} \\ &= \begin{pmatrix} b^2(b^2+a^2) & -ab(b^2+a^2) \\ -ab(b^2+a^2) & a^2(b^2+a^2) \end{pmatrix} = \mathbf{A}_2 \end{aligned}$$

$$\mathbf{A}_1\mathbf{A}_2 = \begin{pmatrix} a^2 & ab \\ ab & b^2 \end{pmatrix}\begin{pmatrix} b^2 & -ab \\ -ab & a^2 \end{pmatrix} = \begin{pmatrix} a^2(b^2-b^2) & -ab(a^2-a^2) \\ ab(b^2-b^2) & b^2(a^2-a^2) \end{pmatrix} = \mathbf{0}$$

---

[3] We recall once more that, for $\alpha_1, \alpha_2, \beta > 0$, the signs of the off-diagonal elements of $\mathbf{A}_1$ and $\mathbf{A}_2$ must be interchanged.

$$\mathbf{A}_2\mathbf{A}_1 = \begin{pmatrix} b^2 & -ab \\ -ab & a^2 \end{pmatrix} \begin{pmatrix} a^2 & ab \\ ab & b^2 \end{pmatrix} = \begin{pmatrix} b^2(a^2-a^2) & ab(b^2-b^2) \\ a^2(ab-ab) & a^2(b^2-b^2) \end{pmatrix} = \mathbf{0}$$

$$\mathbf{A}_1 + \mathbf{A}_2 = \begin{pmatrix} a^2 & ab \\ ab & b^2 \end{pmatrix} + \begin{pmatrix} b^2 & -ab \\ -ab & a^2 \end{pmatrix} = \begin{pmatrix} a^2+b^2 & 0 \\ 0 & a^2+b^2 \end{pmatrix} = \mathbf{1},$$

as it must be since, from Problem 2.3, $a^2+b^2=1$.

We notice that $\det \mathbf{A}_1 = \det \mathbf{A}_2 = 0$, so that matrices $\mathbf{A}_1$ and $\mathbf{A}_2$ cannot be inverted. This is a characteristic property of all projectors. Now:

$$\begin{aligned} \lambda_1\mathbf{A}_1 + \lambda_2\mathbf{A}_2 &= \begin{pmatrix} \lambda_1 a^2 & \lambda_1 ab \\ \lambda_1 ab & \lambda_1 b^2 \end{pmatrix} + \begin{pmatrix} \lambda_2 b^2 & -\lambda_2 ab \\ -\lambda_2 ab & \lambda_2 a^2 \end{pmatrix} \\ &= \begin{pmatrix} \lambda_1 a^2 + \lambda_2 b^2 & -ab(\lambda_2-\lambda_1) \\ -ab(\lambda_2-\lambda_1) & \lambda_1 b^2 + \lambda_2 a^2 \end{pmatrix} \end{aligned}$$

11-element:

$$\begin{aligned} \lambda_1 a^2 + \lambda_2 b^2 &= \frac{(\alpha_1+\alpha_2)-\Delta}{2}\frac{\Delta+(\alpha_2-\alpha_1)}{2\Delta} \\ &\quad + \frac{(\alpha_1+\alpha_2)+\Delta}{2}\frac{\Delta-(\alpha_2-\alpha_1)}{2\Delta} \\ &= \frac{1}{4\Delta}\{\Delta(\alpha_1+\alpha_2)-\Delta^2+(\alpha_2^2-\alpha_1^2)-\Delta(\alpha_2-\alpha_1) \\ &\quad + \Delta(\alpha_1+\alpha_2)+\Delta^2-(\alpha_2^2-\alpha_1^2)-\Delta(\alpha_2-\alpha_1)\} \\ &= \frac{1}{4}\{2(\alpha_1+\alpha_2)-2(\alpha_2-\alpha_1)\} = \alpha_1 \end{aligned}$$

22-element:

$$\begin{aligned} \lambda_1 b^2 + \lambda_2 a^2 &= \frac{(\alpha_1+\alpha_2)-\Delta}{2}\frac{\Delta-(\alpha_2-\alpha_1)}{2\Delta} \\ &\quad + \frac{(\alpha_1+\alpha_2)+\Delta}{2}\frac{\Delta+(\alpha_2-\alpha_1)}{2\Delta} \\ &= \frac{1}{4\Delta}\{\Delta(\alpha_1+\alpha_2)-\Delta^2-(\alpha_2^2-\alpha_1^2)+\Delta(\alpha_2-\alpha_1) \\ &\quad + \Delta(\alpha_1+\alpha_2)+\Delta^2+(\alpha_2^2-\alpha_1^2)+\Delta(\alpha_2-\alpha_1)\} \\ &= \frac{1}{4}\{2(\alpha_1+\alpha_2)+2(\alpha_2-\alpha_1)\} = \alpha_2 \end{aligned}$$

12-element = 21-element:

$$-ab(\lambda_2-\lambda_1) = \frac{\beta}{\Delta}\Delta = \beta.$$

Hence:

$$\lambda_1\mathbf{A}_1 + \lambda_2\mathbf{A}_2 = \mathbf{A}.$$

2.6. Inverse of **A** through its canonical form.

$$\mathbf{A}^{-1} = \lambda_1^{-1}\mathbf{A}_1 + \lambda_2^{-1}\mathbf{A}_2 = \frac{1}{\lambda_1\lambda_2}\begin{pmatrix} a^2\lambda_2 + b^2\lambda_1 & ab(\lambda_2-\lambda_1) \\ ab(\lambda_2-\lambda_1) & a^2\lambda_1 + b^2\lambda_2 \end{pmatrix}.$$

We use some results of Problems 2.3 and 2.5.
11-element:

$$\frac{a^2\lambda_2 + b^2\lambda_1}{\lambda_1\lambda_2} = \frac{\alpha_2}{\det\mathbf{A}}$$

22-element:

$$\frac{a^2\lambda_1 + b^2\lambda_2}{\lambda_1\lambda_2} = \frac{\alpha_1}{\det\mathbf{A}}$$

12-element = 21-element:

$$ab\frac{\lambda_2-\lambda_1}{\lambda_1\lambda_2} = -\frac{\beta}{\Delta}\frac{\Delta}{\det\mathbf{A}} = -\frac{\beta}{\det\mathbf{A}}$$

so that:

$$\mathbf{A}^{-1} = (\det\mathbf{A})^{-1}\begin{pmatrix} \alpha_2 & -\beta \\ -\beta & \alpha_1 \end{pmatrix}$$

as obtained by the direct calculation of the inverse matrix. We can verify that:

$$\begin{aligned}\mathbf{A}\mathbf{A}^{-1} &= (\det\mathbf{A})^{-1}\begin{pmatrix} \alpha_1 & \beta \\ \beta & \alpha_2 \end{pmatrix}\begin{pmatrix} \alpha_2 & -\beta \\ -\beta & \alpha_1 \end{pmatrix} \\ &= (\det\mathbf{A})^{-1}\begin{pmatrix} \alpha_1\alpha_2-\beta^2 & 0 \\ 0 & \alpha_1\alpha_2-\beta^2 \end{pmatrix} = \mathbf{1}.\end{aligned}$$

2.7. Find $\mathbf{A}^{1/2}$ if **A** is positive definite ($\lambda_1, \lambda_2 > 0$).

Since now $\alpha_1, \alpha_2, \beta > 0$, we must interchange the signs in the off-diagonal elements of the projectors $\mathbf{A}_1$ and $\mathbf{A}_2$ of Problem 2.5. Hence, we get immediately for real positive eigenvalues:

$$\mathbf{A}^{1/2} = \lambda_1^{1/2}\mathbf{A}_1 + \lambda_2^{1/2}\mathbf{A}_2.$$

Put:

$$A = \lambda_1^{1/2} \qquad B = \lambda_2^{1/2}$$

$$A^2 + B^2 = \lambda_1 + \lambda_2 = \alpha_1 + \alpha_2 \qquad B^2 - A^2 = \lambda_2 - \lambda_1 = \Delta$$

$$A^2B^2 = \lambda_1\lambda_2 = \alpha_1\alpha_2 - \beta^2 = \det \mathbf{A}.$$

Then:

$$\mathbf{A}^{1/2} = \begin{pmatrix} Aa^2 + Bb^2 & -(A-B)ab \\ -(A-B)ab & Ab^2 + Ba^2 \end{pmatrix}$$

which can be checked by taking:

$$\mathbf{A}^{1/2}\mathbf{A}^{1/2} = \mathbf{A}.$$

In fact, we have:
11-element:

$$\begin{aligned}
&(Aa^2 + Bb^2)^2 + (A-B)^2a^2b^2 \\
&\quad = A^2a^4 + B^2b^4 + 2ABa^2b^2 + (A^2 + B^2 - 2AB)a^2b^2 \\
&\quad = \lambda_1\left(\frac{\Delta + (\alpha_2 - \alpha_1)}{2\Delta}\right)^2 + \lambda_2\left(\frac{\Delta - (\alpha_2 - \alpha_1)}{2\Delta}\right)^2 + (\lambda_1 + \lambda_2)\frac{\beta^2}{\Delta^2} \\
&\quad = \frac{1}{4\Delta^2}\{\lambda_1[\Delta^2 + (\alpha_2 - \alpha_1)^2 + 2\Delta(\alpha_2 - \alpha_1)] \\
&\qquad + \lambda_2[\Delta^2 + (\alpha_2 - \alpha_1)^2 - 2\Delta(\alpha_2 - \alpha_1)] + (\lambda_1 + \lambda_2)4\beta^2\} \\
&\quad = \frac{1}{4\Delta^2}\{2\Delta^2(\lambda_1 + \lambda_2) - 2\Delta(\alpha_2 - \alpha_1)(\lambda_2 - \lambda_1)\} \\
&\quad = \frac{1}{2}\left\{(\lambda_1 + \lambda_2) - \frac{(\lambda_2 - \lambda_1)}{\Delta}(\alpha_2 - \alpha_1)\right\} \\
&\quad = \frac{1}{2}\{(\alpha_1 + \alpha_2) - (\alpha_2 - \alpha_1)\} = \alpha_1
\end{aligned}$$

22-element:

$$\begin{aligned}
&(Ab^2 + Ba^2)^2 + (A-B)^2a^2b^2 \\
&\quad = A^2b^4 + B^2a^4 + 2ABa^2b^2 + (A^2 + B^2 - 2AB)a^2b^2 \\
&\quad = \lambda_1\left(\frac{\Delta - (\alpha_2 - \alpha_1)}{2\Delta}\right)^2 + \lambda_2\left(\frac{\Delta + (\alpha_2 - \alpha_1)}{2\Delta}\right)^2 + (\lambda_1 + \lambda_2)\frac{\beta^2}{\Delta^2} \\
&\quad = \frac{1}{4\Delta^2}\{\lambda_1[\Delta^2 + (\alpha_2 - \alpha_1)^2 - 2\Delta(\alpha_2 - \alpha_1)] \\
&\qquad + \lambda_2[\Delta^2 + (\alpha_2 - \alpha_1)^2 + 2\Delta(\alpha_2 - \alpha_1)] + (\lambda_1 + \lambda_2)4\beta^2\}
\end{aligned}$$

$$
\begin{aligned}
&= \frac{1}{4\Delta^2}\{2\Delta^2(\lambda_1+\lambda_2)+2\Delta(\alpha_2-\alpha_1)(\lambda_2-\lambda_1)\}\\
&= \frac{1}{2}\left\{(\lambda_1+\lambda_2)+\frac{(\lambda_2-\lambda_1)}{\Delta}(\alpha_2-\alpha_1)\right\}\\
&= \frac{1}{2}\{(\alpha_1+\alpha_2)+(\alpha_2-\alpha_1)\}=\alpha_2
\end{aligned}
$$

12-element = 21-element:

$$
\begin{aligned}
&-(A-B)ab[(Aa^2+Bb^2)+(Ab^2+Ba^2)]\\
&\quad=-(A-B)ab[(A+B)(a^2+b^2)]\\
&\quad=ab(a^2+b^2)(B^2-A^2)\\
&\quad=\frac{\beta}{\Delta}\cdot 1\cdot(\lambda_2-\lambda_1)=\frac{\beta}{\Delta}\cdot\Delta=\beta.
\end{aligned}
$$

Hence:

$$\mathbf{A}^{1/2}\mathbf{A}^{1/2}=\mathbf{A}$$

as it must be.

For $\alpha_1=\alpha_2=\alpha$, $a^2=b^2=ab=1/2$, and the square root matrix takes the simpler form:

$$\mathbf{A}^{1/2}=\begin{pmatrix}\dfrac{A+B}{2} & -\dfrac{A-B}{2}\\ -\dfrac{A-B}{2} & \dfrac{A+B}{2}\end{pmatrix}.$$

2.8. Find $\mathbf{A}^{-1/2}$ if $\mathbf{A}$ is a positive definite non-singular matrix.

$$
\begin{aligned}
\mathbf{A}^{-1/2}&=\lambda_1^{-1/2}\mathbf{A}_1+\lambda_2^{-1/2}\mathbf{A}_2\\
&=\frac{1}{AB}\begin{pmatrix}Ab^2+Ba^2 & ab(A-B)\\ ab(A-B) & Aa^2+Bb^2\end{pmatrix},
\end{aligned}
$$

where A, B are taken from Problem 2.7 and a, b from Problems 2.3, 2.4, 2.5. The result can be checked by taking:

$$\mathbf{A}^{-1/2}\mathbf{A}^{1/2}=\mathbf{1}.$$

In fact, we have:
11-element = 22-element:

$$(Ab^2+Ba^2)(Aa^2+Bb^2)-(A-B)^2a^2b^2$$

$$
\begin{aligned}
&= ABa^4 + A^2a^2b^2 + B^2a^2b^2 + ABb^4 - a^2b^2(A^2 + B^2 - 2AB) \\
&= AB(a^4 + b^4 + 2a^2b^2) = AB(a^2 + b^2)^2 = AB
\end{aligned}
$$

12-element = 21-element:

$$
-ab(A - B)[(Ab^2 + Ba^2) - (Ab^2 + Ba^2)] = 0.
$$

Hence:

$$
\mathbf{A}^{-1/2}\mathbf{A}^{1/2} = \frac{1}{AB}\begin{pmatrix} AB & 0 \\ 0 & AB \end{pmatrix} = \mathbf{1}
$$

as it must be.

For $\alpha_1 = \alpha_2 = \alpha$, $a^2 = b^2 = ab = 1/2$, and the inverse square root takes the simpler form:

$$
\mathbf{A}^{-1/2} = \frac{1}{AB}\begin{pmatrix} \dfrac{A+B}{2} & \dfrac{A-B}{2} \\ \dfrac{A-B}{2} & \dfrac{A+B}{2} \end{pmatrix} = \begin{pmatrix} \dfrac{B^{-1}+A^{-1}}{2} & \dfrac{B^{-1}-A^{-1}}{2} \\ \dfrac{B^{-1}-A^{-1}}{2} & \dfrac{B^{-1}+A^{-1}}{2} \end{pmatrix}.
$$

For $\alpha = 1, \beta = S > 0$:

$$
\mathbf{A} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} = \mathbf{M} \quad \lambda_1 = 1 - S \quad \lambda_2 = 1 + S
$$

$$
\mathbf{M}^{-1/2} = \begin{pmatrix} \dfrac{(1+S)^{-1/2} + (1-S)^{-1/2}}{2} & \dfrac{(1+S)^{-1/2} - (1-S)^{-1/2}}{2} \\ \dfrac{(1+S)^{-1/2} - (1-S)^{-1/2}}{2} & \dfrac{(1+S)^{-1/2} + (1-S)^{-1/2}}{2} \end{pmatrix}
$$

which is known as matrix of Löwdin symmetrical orthogonalization.

2.9. Löwdin symmetrical orthogonalization.

If $\boldsymbol{\chi} = (\chi_1 \chi_2)$, $\boldsymbol{\chi}^\dagger = \binom{\chi_1^*}{\chi_2^*}$ is a set of two normalized non-orthogonal basis functions:

$$
\langle \chi_1 | \chi_1 \rangle = \langle \chi_2 | \chi_2 \rangle = 1 \qquad \langle \chi_1 | \chi_2 \rangle = \langle \chi_2 | \chi_1 \rangle = S
$$

the metric of the basis will be the positive definite matrix:

$$
\mathbf{M} = \boldsymbol{\chi}^\dagger \boldsymbol{\chi} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}.
$$

Then the Löwdin symmetrically orthogonalized set is:

$$
\boldsymbol{\chi}' = \boldsymbol{\chi}\mathbf{M}^{-1/2}
$$

as can be immediately proved. In fact, the metric in the new basis is:

$$\mathbf{M}' = \boldsymbol{\chi}'^{\dagger}\boldsymbol{\chi}' = \mathbf{M}^{-1/2}\boldsymbol{\chi}^{\dagger}\boldsymbol{\chi}\mathbf{M}^{-1/2} = \mathbf{M}^{-1/2}\mathbf{M}\mathbf{M}^{-1/2} = \mathbf{1}$$

and the transformed functions are orthonormal. More in detail:

$$(\chi_1'\chi_2') = (\chi_1\chi_2)\begin{pmatrix} \dfrac{a+b}{2} & \dfrac{a-b}{2} \\ \dfrac{a-b}{2} & \dfrac{a+b}{2} \end{pmatrix}$$

where we pose for simplicity:

$$a = (1+S)^{-1/2}, \qquad b = (1-S)^{-1/2}$$

$$a^2 + b^2 = 2(1-S^2)^{-1}, \qquad a^2 - b^2 = -2S(1-S^2)^{-1}.$$

Then, the explicit form of the transformed functions will be:

$$\begin{cases} \chi_1' = \chi_1\dfrac{a+b}{2} + \chi_2\dfrac{a-b}{2} \\ \chi_2' = \chi_2\dfrac{a+b}{2} + \chi_1\dfrac{a-b}{2} \end{cases}$$

the reason for the name symmetrical orthogonalization becoming now apparent.

We can check in detail orthogonalization and normalization of the transformed functions.

$$\begin{aligned} \langle\chi_1'|\chi_2'\rangle &= \langle\chi_2'|\chi_1'\rangle \\ &= \frac{a^2-b^2}{4}(1+1) + \frac{(a+b)^2+(a-b)^2}{4}S \\ &= \frac{a^2-b^2}{2} + S\frac{a^2+b^2}{2} = -\frac{S}{1-S^2} + \frac{S}{1-S^2} = 0 \end{aligned}$$

$$\begin{aligned} \langle\chi_1'|\chi_1'\rangle &= \langle\chi_2'|\chi_2'\rangle \\ &= \frac{(a+b)^2+(a-b)^2}{4} + \frac{a^2-b^2}{2}S \\ &= \frac{a^2+b^2}{2} + S\frac{a^2-b^2}{2} = \frac{1}{1-S^2} - \frac{S^2}{1-S^2} = 1. \end{aligned}$$

2.10. Find $\exp(\mathbf{A})$ and $\exp(-\mathbf{A})$.

$$\begin{aligned} \exp(\mathbf{A}) &= \exp(\lambda_1)\mathbf{A}_1 + \exp(\lambda_2)\mathbf{A}_2 \\ &= \begin{pmatrix} a^2\exp(\lambda_1) + b^2\exp(\lambda_2) & ab[\exp(\lambda_1) - \exp(\lambda_2)] \\ ab[\exp(\lambda_1) - \exp(\lambda_2)] & b^2\exp(\lambda_1) + a^2\exp(\lambda_2) \end{pmatrix} \end{aligned}$$

$$
\begin{aligned}
\exp(-\mathbf{A}) &= \exp(-\lambda_1)\mathbf{A}_1 + \exp(-\lambda_2)\mathbf{A}_2 \\
&= \begin{pmatrix} a^2\exp(-\lambda_1) + b^2\exp(-\lambda_2) & ab[\exp(-\lambda_1) - \exp(-\lambda_2)] \\ ab[\exp(-\lambda_1) - \exp(-\lambda_2)] & b^2\exp(-\lambda_1) + a^2\exp(-\lambda_2) \end{pmatrix}.
\end{aligned}
$$

Using results for a, b from Problems 2.3, 2.4 we now verify that:

$$\exp(\mathbf{A}) \cdot \exp(-\mathbf{A}) = \mathbf{1}.$$

11-element:

$$
\begin{aligned}
&\big[a^2\exp(\lambda_1) + b^2\exp(\lambda_2)\big]\big[a^2\exp(-\lambda_1) + b^2\exp(-\lambda_2)\big] \\
&\qquad + a^2b^2[\exp(\lambda_1) - \exp(\lambda_2)][\exp(-\lambda_1) - \exp(-\lambda_2)] \\
&\quad = a^4 + a^2b^2\exp(\lambda_2 - \lambda_1) + a^2b^2\exp(\lambda_1 - \lambda_2) + b^4 \\
&\qquad + a^2b^2[1 - \exp(\lambda_1 - \lambda_2) - \exp(\lambda_2 - \lambda_1) + 1] \\
&\quad = a^4 + b^4 + 2a^2b^2 = \left(a^2 + b^2\right)^2 = 1
\end{aligned}
$$

22-element:

$$
\begin{aligned}
&a^2b^2[\exp(\lambda_1) - \exp(\lambda_2)][\exp(-\lambda_1) - \exp(-\lambda_2)] \\
&\qquad + \big[b^2\exp(\lambda_1) + a^2\exp(\lambda_2)\big]\big[b^2\exp(-\lambda_1) + a^2\exp(-\lambda_2)\big] \\
&\quad = a^2b^2[1 - \exp(\lambda_2 - \lambda_1) - \exp(\lambda_1 - \lambda_2) + 1] \\
&\qquad + b^4 + a^2b^2\exp(\lambda_2 - \lambda_1) + a^2b^2\exp(\lambda_1 - \lambda_2) + a^4 \\
&\quad = a^4 + b^4 + 2a^2b^2 = \left(a^2 + b^2\right)^2 = 1
\end{aligned}
$$

12-element = 21-element:

$$
\begin{aligned}
&\big[a^2\exp(\lambda_1) + b^2\exp(\lambda_2)\big]ab[\exp(-\lambda_1) - \exp(-\lambda_2)] \\
&\qquad + ab[\exp(\lambda_1) - \exp(\lambda_2)]\big[b^2\exp(-\lambda_1) + a^2\exp(-\lambda_2)\big] \\
&\quad = a^3b + ab^3\exp(\lambda_2 - \lambda_1) - a^3b\exp(\lambda_1 - \lambda_2) - ab^3 \\
&\qquad + ab^3 - ab^3\exp(\lambda_2 - \lambda_1) + a^3b\exp(\lambda_1 - \lambda_2) - a^3b = 0.
\end{aligned}
$$

If: $\alpha_1 = \alpha_2 = 0$, $\beta = 1$, $\Delta = 2$, $\lambda_1 = -1$, $\lambda_2 = 1$, $a^2 = b^2 = ab = 1/2$

$$
\begin{aligned}
\exp(\mathbf{A}) &= \begin{pmatrix} \dfrac{\exp(1) + \exp(-1)}{2} & -\dfrac{\exp(1) - \exp(-1)}{2} \\ -\dfrac{\exp(1) - \exp(-1)}{2} & \dfrac{\exp(1) + \exp(-1)}{2} \end{pmatrix} \\
&= \begin{pmatrix} \cosh 1 & -\sinh 1 \\ -\sinh 1 & \cosh 1 \end{pmatrix}
\end{aligned}
$$

$$
\begin{aligned}
\exp(-\mathbf{A}) &= \begin{pmatrix} \dfrac{\exp(1)+\exp(-1)}{2} & \dfrac{\exp(1)-\exp(-1)}{2} \\ \dfrac{\exp(1)-\exp(-1)}{2} & \dfrac{\exp(1)+\exp(-1)}{2} \end{pmatrix} \\
&= \begin{pmatrix} \cosh 1 & \sinh 1 \\ \sinh 1 & \cosh 1 \end{pmatrix}
\end{aligned}
$$

$$
\begin{aligned}
\exp(\mathbf{A}) \cdot \exp(-\mathbf{A}) &= \begin{pmatrix} \cosh^2 1 - \sinh^2 1 & 0 \\ 0 & \cosh^2 1 - \sinh^2 1 \end{pmatrix} \\
&= \mathbf{1}
\end{aligned}
$$

since (Abramowitz and Stegun, 1965):

$$
\cosh^2 1 - \sinh^2 1 = 1.
$$

2.11. Find the inverse of matrix $\mathbf{A}$ according to the Lagrange formula.
We recall that (equations (90), (91) and Problem 2.3):

$$
F(\mathbf{A}) = p\mathbf{1} + q\mathbf{A}
$$

$$
p = \frac{\lambda_1 F(\lambda_2) - \lambda_2 F(\lambda_1)}{\lambda_1 - \lambda_2}, \qquad q = \frac{F(\lambda_1) - F(\lambda_2)}{\lambda_1 - \lambda_2}.
$$

If $F(\mathbf{A}) = \mathbf{A}^{-1}$:

$$
p = \frac{\lambda_1 \lambda_2^{-1} - \lambda_2 \lambda_1^{-1}}{\lambda_1 - \lambda_2} = \frac{\lambda_1^2 - \lambda_2^2}{\lambda_1 \lambda_2 (\lambda_1 - \lambda_2)} = \frac{\lambda_1 + \lambda_2}{\lambda_1 \lambda_2} = \frac{\alpha_1 + \alpha_2}{\det \mathbf{A}}
$$

$$
q = \frac{\lambda_1^{-1} - \lambda_2^{-1}}{\lambda_1 - \lambda_2} = \frac{\lambda_2 - \lambda_1}{\lambda_1 \lambda_2 (\lambda_1 - \lambda_2)} = -\frac{1}{\lambda_1 \lambda_2} = -\frac{1}{\det \mathbf{A}}.
$$

Then:

$$
\begin{aligned}
\mathbf{A}^{-1} &= p\mathbf{1} + q\mathbf{A} = (\det \mathbf{A})^{-1} \begin{pmatrix} \alpha_1 + \alpha_2 - \alpha_1 & -\beta \\ -\beta & \alpha_1 + \alpha_2 - \alpha_2 \end{pmatrix} \\
&= (\det \mathbf{A})^{-1} \begin{pmatrix} \alpha_2 & -\beta \\ -\beta & \alpha_1 \end{pmatrix}
\end{aligned}
$$

which is the inverse required.

2.12. Find $\mathbf{A}^{1/2}$ according to the Lagrange formula.
We use results of Problems 2.3 and 2.7:

$$
p = \frac{\lambda_1 F(\lambda_2) - \lambda_2 F(\lambda_1)}{\lambda_1 - \lambda_2} = \frac{A\lambda_2 - B\lambda_1}{\Delta}
$$

$$q = \frac{F(\lambda_1) - F(\lambda_2)}{\lambda_1 - \lambda_2} = \frac{B - A}{\Delta}$$

$$\begin{aligned}
\mathbf{A}^{1/2} &= p\mathbf{1} + q\mathbf{A} \\
&= \Delta^{-1} \begin{pmatrix} (A\lambda_2 - B\lambda_1) + (B - A)\alpha_1 & (B - A)\beta \\ (B - A)\beta & (A\lambda_2 - B\lambda_1) + (B - A)\alpha_2 \end{pmatrix} \\
&= \Delta^{-1} \begin{pmatrix} B(\alpha_1 - \lambda_1) - A(\alpha_1 - \lambda_2) & (B - A)\beta \\ (B - A)\beta & B(\alpha_2 - \lambda_1) - A(\alpha_2 - \lambda_2) \end{pmatrix}
\end{aligned}$$

11-element:

$$\begin{aligned}
&B(\alpha_1 - \lambda_1) - A(\alpha_1 - \lambda_2) \\
&\quad = B\left(\alpha_1 - \frac{\alpha_1 + \alpha_2 - \Delta}{2}\right) - A\left(\alpha_1 - \frac{\alpha_1 + \alpha_2 + \Delta}{2}\right) \\
&\quad = \frac{1}{2}\{B[\Delta - (\alpha_2 - \alpha_1)] + A[\Delta + (\alpha_2 - \alpha_1)]\} \\
&\quad = \Delta\left\{A\left(\frac{\Delta + (\alpha_2 - \alpha_1)}{2\Delta}\right) + B\left(\frac{\Delta - (\alpha_2 - \alpha_1)}{2\Delta}\right)\right\} = \Delta(Aa^2 + Bb^2)
\end{aligned}$$

22-element:

$$\begin{aligned}
&B(\alpha_2 - \lambda_1) - A(\alpha_2 - \lambda_2) \\
&\quad = B\left(\alpha_2 - \frac{\alpha_1 + \alpha_2 - \Delta}{2}\right) - A\left(\alpha_2 - \frac{\alpha_1 + \alpha_2 + \Delta}{2}\right) \\
&\quad = \frac{1}{2}\{B[\Delta + (\alpha_2 - \alpha_1)] + A[\Delta - (\alpha_2 - \alpha_1)]\} \\
&\quad = \Delta\left\{A\left(\frac{\Delta - (\alpha_2 - \alpha_1)}{2\Delta}\right) + B\left(\frac{\Delta + (\alpha_2 - \alpha_1)}{2\Delta}\right)\right\} = \Delta(Ab^2 + Ba^2)
\end{aligned}$$

12-element = 21-element:

$$(B - A)\beta = (B - A)(ab\Delta) = \Delta\{-(A - B)ab\}$$

so that all elements of $\mathbf{A}^{1/2}$ are recovered upon multiplying by Δ^{-1}.

2.13. Find the square root of the unsymmetrical matrix:

$$\mathbf{A} = \begin{pmatrix} 3 & -4 \\ 1 & -1 \end{pmatrix}.$$

The characteristic equation gives:

$$P_2(\lambda) = \begin{vmatrix} 3-\lambda & -4 \\ 1 & -1-\lambda \end{vmatrix} = \lambda^2 - 2\lambda + 1 = (\lambda - 1)^2 = 0$$

so that $\lambda = 1$ is a twofold degenerate root, $\mathbf{\Lambda} = \mathbf{1}$, and we cannot obtain two linearly independent eigenvectors making an invertible matrix $\mathbf{C}$ which can diagonalize $\mathbf{A}$. The system of linear homogeneous equations determining the eigenvectors yields just a single eigenvector:

$$\begin{cases} (3-1)c_1 - 4c_2 = 0 & 2c_2 = c_1 \\ c_1 - 2c_2 = 0 & c_1^2 + c_2^2 = 1 \end{cases} \qquad \mathbf{c}_1 = \begin{pmatrix} \frac{2}{\sqrt{5}} \\ \frac{1}{\sqrt{5}} \end{pmatrix}$$

so that matrix $\mathbf{A}$ cannot be brought to diagonal form in the ordinary way. Even the Lagrange formula cannot be used because of the degeneracy of the eigenvalues. To find the square root of $\mathbf{A}$ we must therefore start from the definition:

$$\mathbf{A}^{1/2} = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \qquad \mathbf{A}^{1/2}\mathbf{A}^{1/2} = \begin{pmatrix} a^2 + bc & b(a+d) \\ c(a+d) & bc + d^2 \end{pmatrix} = \mathbf{A}$$

obtaining the system of non-linear equations:

$$\underset{1}{a^2 + bc = 3} \qquad \underset{2}{b(a+d) = -4} \qquad \underset{3}{c(a+d) = 1} \qquad \underset{4}{bc + d^2 = -1}$$

which can be solved by successive substitutions. Subtracting 1 and 4:

$$a^2 - d^2 = 4.$$

Dividing 2 by 3:

$$b = -4c,$$

and substituting in 4:

$$d^2 - 4c^2 = -1.$$

Then:

$$(a+d)(a-d) = 4 \quad a + d = \frac{1}{c} \quad (c \neq 0)$$

and we are left with the system:

$$\begin{cases} a + d = \dfrac{1}{c} \\ a - d = 4c. \end{cases}$$

Adding and subtracting, we obtain:

$$\begin{cases} 2a = \dfrac{1}{c} + 4c = \dfrac{1+4c^2}{c} \\ 2d = \dfrac{1}{c} - 4c = \dfrac{1-4c^2}{c} \end{cases}$$

giving:

$$a = \frac{1+4c^2}{2c}, \qquad d = \frac{1-4c^2}{2c}.$$

Upon substitution for d^2 in one of the previous equations we are left with the apparent quartic in c:

$$\left(\frac{1-4c^2}{2c}\right)^2 - 4c^2 = -1 \quad 4c^2 = 1$$

finally giving:

$$c = \pm\frac{1}{2}, \qquad b = \mp 2, \qquad a = \pm 2, \qquad d = 0$$

so that we obtain the two possible solutions for $\mathbf{A}^{1/2}$:

$$\mathbf{A}^{1/2} = \begin{pmatrix} 2 & -2 \\ \frac{1}{2} & 0 \end{pmatrix} \quad \text{or} \quad \begin{pmatrix} -2 & 2 \\ -\frac{1}{2} & 0 \end{pmatrix}$$

with $c \neq 0$. The result can be checked by direct calculation of $\mathbf{A}^{1/2}\mathbf{A}^{1/2} = \mathbf{A}$.

2.14. $\mathbf{A}^{-1}$ by the Cayley–Hamilton theorem.
Matrix $\mathbf{A}$ satisfies its characteristic equation of degree $n = 2$:

$$P_2(\mathbf{A}) = a_0\mathbf{1} + a_1\mathbf{A} + a_2\mathbf{A}^2 = \mathbf{0},$$

where:

$$a_0 = \det \mathbf{A} \neq 0 \qquad a_1 = -(\alpha_1 + \alpha_2) \qquad a_2 = 1$$

so that, multiplying through by $\mathbf{A}^{-1}$, we obtain:

$$a_0\mathbf{A}^{-1} + a_1\mathbf{1} + a_2\mathbf{A} = \mathbf{0}$$

$$
\begin{aligned}
\mathbf{A}^{-1} &= -\frac{1}{a_0}(a_1\mathbf{1}+a_2\mathbf{A}) \\
&= \frac{1}{a_0}\left[\begin{pmatrix}\alpha_1+\alpha_2 & 0 \\ 0 & \alpha_1+\alpha_2\end{pmatrix}+\begin{pmatrix}-\alpha_1 & -\beta \\ -\beta & -\alpha_2\end{pmatrix}\right] \\
&= (\det\mathbf{A})^{-1}\begin{pmatrix}\alpha_2 & -\beta \\ -\beta & \alpha_1\end{pmatrix}
\end{aligned}
$$

as it must be.

2.15. The complete 2×2 pseudoeigenvalue problem.
Given the Hermitian matrices:

$$
\mathbf{H}=\begin{pmatrix}\alpha_1 & \beta \\ \beta & \alpha_2\end{pmatrix} \qquad \mathbf{M}=\begin{pmatrix}1 & S \\ S & 1\end{pmatrix} \qquad \alpha_1,\ \alpha_2,\ \beta<0 \quad S>0
$$

the secular equation for the 2×2 pseudoeigenvalue problem:

$$
\begin{vmatrix}\alpha_1-\varepsilon & \beta-\varepsilon S \\ \beta-\varepsilon S & \alpha_2-\varepsilon\end{vmatrix}=0
$$

gives the quadratic equation in ε:

$$
(1-S^2)\varepsilon^2-(\alpha_1+\alpha_2-2\beta S)\varepsilon+(\alpha_1\alpha_2-\beta^2)=0
$$

with the two *real* roots:

$$
\begin{aligned}
&2(1-S^2)\varepsilon_1=(\alpha_1+\alpha_2-2\beta S)-\Delta \\
&2(1-S^2)\varepsilon_2=(\alpha_1+\alpha_2-2\beta S)+\Delta \\
&\Delta=\{(\alpha_2-\alpha_1)^2+4(\beta-\alpha_1 S)(\beta-\alpha_2 S)\}^{1/2}>0.
\end{aligned}
$$

The roots have the properties:

$$
\begin{aligned}
&(1-S^2)(\varepsilon_1+\varepsilon_2)=\alpha_1+\alpha_2-2\beta S \\
&(1-S^2)(\varepsilon_2-\varepsilon_1)=\Delta \\
&(1-S^2)\varepsilon_1\varepsilon_2=\alpha_1\alpha_2-\beta^2=\det\mathbf{A}
\end{aligned}
$$

which coincide with the results of Problem 2.3 when $S=0$.

(i) First eigenvalue ε_1

$$
\begin{cases}
(\alpha_1-\varepsilon_1)c_1+(\beta-\varepsilon_1 S)c_2=0 \\
c_1^2+c_2^2+2c_1c_2S=1 \Longrightarrow c_1^2\left\{1+\left(\dfrac{c_2}{c_1}\right)^2+2\left(\dfrac{c_2}{c_1}\right)S\right\}=1,
\end{cases}
$$

where we call λ the ratio of coefficients:

$$\left(\frac{c_2}{c_1}\right)_1 = \frac{\varepsilon_1 - \alpha_1}{\beta - \varepsilon_1 S} = \lambda_1 = \lambda.$$

Little calculation shows that:

$$\begin{aligned}
\varepsilon_1 - \alpha_1 &= -[2(1-S^2)]^{-1}\left\{[\Delta - (\alpha_2 - \alpha_1)] + 2S(\beta - \alpha_1 S)\right\} \\
\beta - \varepsilon_1 S &= [2(1-S^2)]^{-1}\left\{(\beta - \alpha_1 S) + (\beta - \alpha_2 S) + S\Delta\right\} \\
&= [2(1-S^2)]^{-1}\left\{[2(\beta - \alpha_2 S)] + S[\Delta + (\alpha_2 - \alpha_1)]\right\}
\end{aligned}$$

giving the ratio:

$$\frac{\varepsilon_1 - \alpha_1}{\beta - \varepsilon_1 S} = -\frac{[\Delta - (\alpha_2 - \alpha_1)] + S[2(\beta - \alpha_1 S)]}{[2(\beta - \alpha_2 S)] + S[\Delta + (\alpha_2 - \alpha_1)]} = -\frac{\Delta - (\alpha_2 - \alpha_1)}{2(\beta - \alpha_2 S)}$$

where the last identity can be verified by direct multiplication using the definition of Δ^2:

$$\begin{aligned}
&[\Delta - (\alpha_2 - \alpha_1)][2(\beta - \alpha_2 S)] + S[4(\beta - \alpha_1 S)(\beta - \alpha_2 S)] \\
&\quad = [\Delta - (\alpha_2 - \alpha_1)][2(\beta - \alpha_2 S)] + S[\Delta^2 - (\alpha_2 - \alpha_1)^2].
\end{aligned}$$

We shall call λ the polarity parameter, since it gives the polarity of the bonding MO ϕ_1, constructed by linear combination of the non-orthogonal basis functions χ_1 and χ_2:

$$\phi_1 = \frac{\chi_1 + \lambda\chi_2}{(1 + \lambda^2 + 2\lambda S)^{1/2}} \qquad S = \langle\chi_1|\chi_2\rangle = \langle\chi_2|\chi_1\rangle.$$

The considerations above show that:

$$\lambda = \frac{\Delta - (\alpha_2 - \alpha_1)}{2|\beta - \alpha_2 S|} = \left(\frac{\Delta - (\alpha_2 - \alpha_1)}{\Delta + (\alpha_2 - \alpha_1)}\right)^{1/2}\left(\frac{|\beta - \alpha_1 S|}{|\beta - \alpha_2 S|}\right)^{1/2}$$

which coincides with the result of Problem 2.3 when $S = 0$.

The last square root expression for λ is readily found since:

$$\begin{aligned}
\lambda &= \frac{\Delta - (\alpha_2 - \alpha_1)}{2|\beta - \alpha_2 S|} = \frac{\Delta - (\alpha_2 - \alpha_1)}{\{4(\beta - \alpha_1 S)(\beta - \alpha_2 S)\}^{1/2}}\left(\frac{|\beta - \alpha_1 S|}{|\beta - \alpha_2 S|}\right)^{1/2} \\
&= \frac{\Delta - (\alpha_2 - \alpha_1)}{\{\Delta^2 - (\alpha_2 - \alpha_1)^2\}^{1/2}}\left(\frac{|\beta - \alpha_1 S|}{|\beta - \alpha_2 S|}\right)^{1/2} \\
&= \left(\frac{\Delta - (\alpha_2 - \alpha_1)}{\Delta + (\alpha_2 - \alpha_1)}\right)^{1/2}\left(\frac{|\beta - \alpha_1 S|}{|\beta - \alpha_2 S|}\right)^{1/2}.
\end{aligned}$$

Hence we get for the eigenvector corresponding to the first eigenvalue:

$$\underset{\substack{\uparrow\\ \text{refers to the}\\ \text{first eigenvalue}}}{c_{11}} = (1+\lambda^2+2\lambda S)^{-1/2}, \qquad \underset{\uparrow}{c_{21}} = \lambda(1+\lambda^2+2\lambda S)^{-1/2}.$$

For $S = 0$:

$$\lambda = \left(\frac{\Delta - (\alpha_2 - \alpha_1)}{\Delta + (\alpha_2 - \alpha_1)}\right)^{1/2}$$

$$1 + \lambda^2 = \frac{\Delta + (\alpha_2 - \alpha_1) + \Delta - (\alpha_2 - \alpha_1)}{\Delta + (\alpha_2 - \alpha_1)} = \frac{2\Delta}{\Delta + (\alpha_2 - \alpha_1)}$$

$$c_{11} = \left(\frac{\Delta + (\alpha_2 - \alpha_1)}{2\Delta}\right)^{1/2}, \qquad c_{21} = \left(\frac{\Delta - (\alpha_2 - \alpha_1)}{2\Delta}\right)^{1/2}$$

as it must be.

(ii) Second eigenvalue ε_2
Interchanging $1 \to 2$ into the homogeneous system:

$$\begin{cases} (\alpha_2 - \varepsilon_2)c_2 + (\beta - \varepsilon_2 S)c_1 = 0 \\ c_1^2 + c_2^2 + 2c_1c_2S = 1 \Longrightarrow c_2^2\left\{1 + \left(\dfrac{c_1}{c_2}\right)^2 + 2\left(\dfrac{c_1}{c_2}\right)S\right\} = 1 \end{cases}$$

$$\begin{aligned} \varepsilon_2 - \alpha_2 &= [2(1-S^2)]^{-1}\{[\Delta - (\alpha_2 - \alpha_1)] - 2S(\beta - \alpha_2 S)\} \\ \beta - \varepsilon_2 S &= [2(1-S^2)]^{-1}\{(\beta - \alpha_1 S) + (\beta - \alpha_2 S) - S\Delta\} \\ &= [2(1-S^2)]^{-1}\{2(\beta - \alpha_1 S) - S[\Delta + (\alpha_2 - \alpha_1)]\} \end{aligned}$$

giving the ratio:

$$\frac{\varepsilon_2 - \alpha_2}{\beta - \varepsilon_2 S} = \frac{[\Delta - (\alpha_2 - \alpha_1)] - S[2(\beta - \alpha_2 S)]}{[2(\beta - \alpha_1 S)] - S[\Delta + (\alpha_2 - \alpha_1)]} = \frac{\Delta - (\alpha_2 - \alpha_1)}{2(\beta - \alpha_1 S)}$$

as can be shown by direct multiplication:

$$\begin{aligned} &[\Delta - (\alpha_2 - \alpha_1)][2(\beta - \alpha_1 S)] - S[4(\beta - \alpha_1 S)(\beta - \alpha_2 S)] \\ &\quad = [\Delta - (\alpha_2 - \alpha_1)][2(\beta - \alpha_1 S)] - S[\Delta^2 - (\alpha_2 - \alpha_1)^2]. \end{aligned}$$

Hence we get for λ_2:

$$\lambda_2 = \left(\frac{c_1}{c_2}\right)_2 = \frac{\varepsilon_2 - \alpha_2}{\beta - \varepsilon_2 S} = \frac{\Delta - (\alpha_2 - \alpha_1)}{2(\beta - \alpha_1 S)} = -\frac{\Delta - (\alpha_2 - \alpha_1)}{2|\beta - \alpha_1 S|}$$
$$= -\left(\frac{\Delta - (\alpha_2 - \alpha_1)}{\Delta + (\alpha_2 - \alpha_1)}\right)^{1/2}\left(\frac{|\beta - \alpha_2 S|}{|\beta - \alpha_1 S|}\right)^{1/2}$$

which coincides with the result of Problem 2.3 when $S = 0$.

In LCAO theory, λ_2 is the polarity parameter for the antibonding MO ϕ_2:

$$\phi_2 = \frac{\chi_2 + \lambda_2 \chi_1}{(1 + \lambda_2^2 + 2\lambda_2 S)^{1/2}}.$$

Using the previous result for $\lambda_1 = \lambda$, we see that:

$$\lambda_2 = -\lambda \frac{|\beta - \alpha_2 S|}{|\beta - \alpha_1 S|} = -\frac{\lambda + S}{1 + \lambda S} = -\lambda \frac{1 + \lambda^{-1} S}{1 + \lambda S},$$

where the last relation follows from the orthogonality relation between the MO's. So, there is only one *independent* variational parameter λ. Therefore, it follows:

$$\frac{1 + \lambda^{-1} S}{1 + \lambda S} = \frac{|\beta - \alpha_2 S|}{|\beta - \alpha_1 S|}$$

showing that λ does satisfy the quadratic equation (compare Coulson, 1937b):

$$(\beta - \alpha_2 S)\lambda^2 - (\alpha_2 - \alpha_1)\lambda - (\beta - \alpha_1 S) = 0$$

whose positive root:

$$\lambda = \frac{\Delta - (\alpha_2 - \alpha_1)}{2|\beta - \alpha_2 S|} = \left(\frac{\Delta - (\alpha_2 - \alpha_1)}{\Delta + (\alpha_2 - \alpha_1)}\right)^{1/2}\left(\frac{|\beta - \alpha_1 S|}{|\beta - \alpha_2 S|}\right)^{1/2} > 0$$

does minimize $\varepsilon_1(\lambda)$ with respect to λ (the other root giving a maximum). From:

$$\varepsilon_1 = \langle \phi_1 | \hat{H} | \phi_1 \rangle = (1 + \lambda^2 + 2\lambda S)^{-1}(\alpha_1 + \lambda^2 \alpha_2 + 2\lambda\beta)$$

it is easily shown that:

$$\frac{d\varepsilon_1}{d\lambda} = -2(1 + \lambda^2 + 2\lambda S)^{-2}\big\{(\beta - \alpha_2 S)\lambda^2 - (\alpha_2 - \alpha_1)\lambda - (\beta - \alpha_1 S)\big\}$$

so that for $\lambda > 0$ satisfying the quadratic equation:

$$\frac{d^2\varepsilon_1}{d\lambda^2} = 2(1 + \lambda^2 + 2\lambda S)^{-2}\big\{(\alpha_2 - \alpha_1) - 2\lambda(\beta - \alpha_2 S)\big\}$$

$$= 2\Delta(1+\lambda^2+2\lambda S)^{-2} > 0$$

and $\varepsilon_1(\lambda)$ reaches there its absolute minimum.

The other (negative) root:

$$\lambda = -\frac{\Delta + (\alpha_2 - \alpha_1)}{2|\beta - \alpha_2 S|}$$

when substituted in $\frac{d^2\varepsilon_1}{d\lambda^2}$ at the stationary point gives:

$$\frac{d^2\varepsilon_1}{d\lambda^2} = -2\Delta(1+\lambda^2+2\lambda S)^{-2} < 0$$

so that, for this value of λ, $\varepsilon_1(\lambda)$ reaches its absolute maximum.

In conclusion, for the second eigenvector we have the alternative expressions:

$$\underset{\substack{\uparrow\\ \text{refers to the}\\ \text{second eigen-}\\ \text{value}}}{c_{22}} = (1+\lambda_2^2+2\lambda_2 S)^{-1/2} = \left\{(1-S^2)(1+\lambda^2+2\lambda S)\right\}^{-1/2}(1+\lambda S)$$

$$\underset{\uparrow}{c_{12}} = \lambda_2(1+\lambda_2^2+2\lambda_2 S)^{-1/2} = -\left\{(1-S^2)(1+\lambda^2+2\lambda S)\right\}^{-1/2}(\lambda + S).$$

In terms of the *independent* parameter λ, the matrix collecting the eigenvectors of the complete 2 × 2 pseudoeigenvalue problem will be:

$$\mathbf{C} = (\mathbf{c}_1|\mathbf{c}_2) = (1+\lambda^2+2\lambda S)^{-1/2}\begin{pmatrix} 1 & A \\ \lambda & B \end{pmatrix}$$

$$A = -(1-S^2)^{-1/2}(\lambda+S), \qquad B = (1-S^2)^{-1/2}(1+\lambda S).$$

2.16. Show that, for the 2 × 2 pseudoeigenvalue problem:

$$\mathbf{C}^\dagger\mathbf{M}\mathbf{C} = \mathbf{1}.$$

Direct matrix multiplication gives:

$$(1+\lambda^2+2\lambda S)\,\mathbf{C}^\dagger\mathbf{M}\mathbf{C}$$
$$= \begin{pmatrix} 1+\lambda^2+2\lambda S & A(1+\lambda S)+B(\lambda+S) \\ A(1+\lambda S)+B(\lambda+S) & A^2+B^2+2ABS \end{pmatrix}.$$

Using results of Problem 2.15, we find:

$$A^2+B^2+2ABS$$

$$\begin{aligned}&= (1-S^2)^{-1}\left\{(\lambda+S)^2+(1+\lambda S)^2-2S(\lambda+S)(1+\lambda S)\right\}\\&= 1+\lambda^2+2\lambda S\end{aligned}$$

$$\begin{aligned}&A(1+\lambda S)+B(\lambda+S)\\&\quad= (1-S^2)^{-1/2}\left\{-(\lambda+S)(1+\lambda S)+(1+\lambda S)(\lambda+S)\right\}=0\end{aligned}$$

so that it is true that:

$$\mathbf{C}^\dagger\mathbf{M}\mathbf{C}=\mathbf{1}.$$

2.17. Show that, for the 2 × 2 pseudoeigenvalue problem:

$$\mathbf{C}^\dagger\mathbf{H}\mathbf{C}=\boldsymbol{\mathcal{E}},$$

where $\boldsymbol{\mathcal{E}}$ is the diagonal matrix of the eigenvalues.

Direct matrix multiplication gives:

$$\begin{aligned}&(1+\lambda^2+2\lambda S)\mathbf{C}^\dagger\mathbf{A}\mathbf{C}\\&\quad=\begin{pmatrix}\alpha_1+\lambda^2\alpha_2+2\lambda\beta & A(\alpha_1+\lambda\beta)+B(\beta+\lambda\alpha_2)\\ A(\alpha_1+\lambda\beta)+B(\beta+\lambda\alpha_2) & A^2\alpha_1+B^2\alpha_2+2AB\beta\end{pmatrix}.\end{aligned}$$

Using results of Problem 2.15, we have:

$$\begin{aligned}A^2&=(1-S^2)^{-1}(\lambda+S)^2\\B^2&=(1-S^2)^{-1}(1+\lambda S)^2\\AB&=-(1-S^2)^{-1}(\lambda+S)(1+\lambda S).\end{aligned}$$

To avoid lengthy calculations, it is useful to recall here that matrix **H** is the representative of the Hermitian operator $\hat{H}$ in the non-orthogonal basis $(\chi_1\chi_2)$. The two *orthogonal* MOs resulting in the LCAO approach are then given by:

$$\begin{aligned}\phi_1&=\frac{\chi_1+\lambda\chi_2}{(1+\lambda^2+2\lambda S)^{1/2}}\\\phi_2&=\frac{(1+\lambda S)\chi_2-(\lambda+S)\chi_1}{[(1-S^2)(1+\lambda^2+2\lambda S)]^{1/2}}\end{aligned}$$

so that, for best λ, **H** will be diagonal in the optimized MO basis:

$$\mathbf{H}_\phi=\boldsymbol{\phi}^\dagger\hat{H}\boldsymbol{\phi}=\begin{pmatrix}H_{11} & H_{12}\\ H_{21} & H_{22}\end{pmatrix}=\begin{pmatrix}\varepsilon_1 & 0\\ 0 & \varepsilon_2\end{pmatrix}$$

$$\begin{aligned}
H_{11} &= \langle \phi_1 | \hat{H} | \phi_1 \rangle \\
&= (1 + \lambda^2 + 2\lambda S)^{-1}(\alpha_1 + \lambda^2 \alpha_2 + 2\lambda\beta) = \varepsilon_1 \\
H_{22} &= \langle \phi_2 | \hat{H} | \phi_2 \rangle \\
&= \frac{(1 + \lambda S)^2 \alpha_2 + (\lambda + S)^2 \alpha_1 - 2(\lambda + S)(1 + \lambda S)\beta}{(1 - S^2)(1 + \lambda^2 + 2\lambda S)} \\
&= B^2 \alpha_2 + A^2 \alpha_1 + 2AB\beta = \varepsilon_2
\end{aligned}$$

$$\begin{aligned}
H_{12} = H_{21} &= \langle \phi_1 | \hat{H} | \phi_2 \rangle \\
&= \frac{-(\lambda + S)\alpha_1 + \lambda(1 + \lambda S)\alpha_2 + (1 - \lambda^2)\beta}{(1 - S^2)^{1/2}(1 + \lambda^2 + 2\lambda S)} \\
&= -\frac{(\beta - \alpha_2 S)\lambda^2 - (\alpha_2 - \alpha_1)\lambda - (\beta - \alpha_1 S)}{(1 - S^2)^{1/2}(1 + \lambda^2 + 2\lambda S)} = 0.
\end{aligned}$$

While the result for the off-diagonal terms is self-evident (the numerator vanishing since best λ is a solution of the previous quadratic equation), the results for the diagonal elements can be checked through a straightforward but rather lengthy calculation using the definitions of best λ and ε_1, ε_2.

– 3 –

The Particle in the Box

3.1 INTRODUCTION

There are only a few physical systems whose Schroedinger equation can be solved exactly: the free particle, the particle in the box or tunneling across a barrier, certain kinds of rotating bodies, the harmonic oscillator, the atomic 1-electron system, the molecular 1-electron 2-centre problem. The treatment of the first five systems can be found in many textbooks (among others, Pauling and Wilson, 1935; Eyring et al., 1944; Schiff, 1955; Kauzmann, 1957; Landau and Lifshitz, 1958; Levine, 2000), while the last one is a rather difficult task (Bates et al., 1953; Peek, 1965; Byers Brown and Steiner, 1966). To acquaint the reader with the application of the principles of Quantum Mechanics to exactly solvable problems, we shall limit ourselves to examine in some detail, first, the particle in the box and, next, the atomic 1-electron (or hydrogen-like) system. We believe that these two examples are exhaustive enough in explaining in detail the general techniques of solution of the Schroedinger eigenvalue equation. In this Chapter, after short consideration of the free particle in one and three dimensions, we shall focus attention mostly on the 1-dimensional problem of a particle confined in a box. Excellent and more complete treatments can be found in Schiff (1955) and Kauzmann (1957).

3.2 THE FREE PARTICLE IN ONE DIMENSION

Introducing the atomic units from the very beginning, the Schroedinger eigenvalue equation for a particle moving along a line x in a field-free space ($V = 0$) is:

$$-\frac{1}{2}\frac{d^2\psi}{dx^2} = E\psi \tag{1}$$

$$\frac{d^2\psi}{dx^2} + 2E\psi = 0 \tag{2}$$

having the general integral in complex form:

$$\psi(x) = A\exp(i\alpha x) + B\exp(-i\alpha x), \tag{3}$$

where A, B are two integration constants. Evaluating the second derivative and substituting in (2), we obtain the characteristic equation[1]

$$-\alpha^2 + 2E = 0 \Rightarrow \alpha = \sqrt{2E}. \tag{4}$$

Since there are no boundary conditions, except that the function ψ must be *finite* at $x = \pm\infty$, the quantity $\sqrt{2E}$ must be necessarily *real* so that E must be *positive*[2]. Since no further restrictions are imposed on E, we conclude that the energy has a *continuous* spectrum of eigenvalues, all positive values being allowed, and the energy is not quantized.

Each component of ψ (the fundamental integrals) is separately eigenfunction of the linear momentum operator $\hat{p}_x = -i\frac{d}{dx}$ with eigenvalue α or $-\alpha$, respectively, the first describing a particle moving along $+x$ with a definite value $\alpha = \sqrt{p_x^2} = \sqrt{2E}$ of the momentum, the second a particle moving along $-x$ with the same absolute value of the momentum. These quantities are the classical values of the momentum of a free particle having energy $E = p_x^2/2$.

Since the integral of $|\psi|^2$ over all values of x between $-\infty$ and ∞ is infinite, the function ψ cannot be normalized in the usual way. The problem of normalization of such a wavefunction is rather complicated and will not be further pursued here (Pauling and Wilson, 1935, and references therein; Kauzmann, 1957).

Since the probability density of each component will be a constant independent of x, we have equal probabilities of finding the particle at any value dx. This means that the uncertainty in the position of the particle is infinite. This is in accord with Heisenberg's principle since $\Delta p_x = 0$, as we have seen, so that:

$$\Delta x \Delta p_x \sim h \tag{5}$$

as it must be.

---

[1] Changing the sign of α simply means to interchange A with B. So, we can omit the ± signs in front to $\sqrt{2E}$ in equation (4).

[2] For $E < 0$, $\alpha = \sqrt{-2|E|} = i\sqrt{2|E|}$, so that $\psi(x) = A\exp(-\sqrt{2|E|}x) + B\exp(\sqrt{2|E|}x)$, the first term of which diverges at $x = -\infty$, the second at $x = \infty$. The wavefunction (3) is hence *oscillatory* and, in real form, is a combination of sine and cosine functions as in equation (40).

3.3 THE 3-DIMENSIONAL BOX OF SIDES a, b, c

A box is a system whose potential energy is zero when the particle is within a closed region and constant everywhere else. The potential energy is:

$$\begin{aligned} &V_x = 0 \quad 0 < x < a, && V_x \text{ elsewhere} \\ &V_y = 0 \quad 0 < y < b, && V_y \text{ elsewhere} \\ &V_z = 0 \quad 0 < z < c, && V_z \text{ elsewhere} \end{aligned} \tag{6}$$

where V_x, V_y, V_z are constant values, with:

$$V_x + V_y + V_z = V. \tag{7}$$

The Schroedinger eigenvalue equation is then:

$$\nabla^2\psi + 2(E - V) = 0 \tag{8}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{9}$$

If we choose:

$$\psi(x, y, z) = X(x)Y(y)Z(z) \tag{10}$$

the partial differential equation in three variables is separable in Cartesian coordinates into three equivalent 1-dimensional differential equations. In fact, we obtain upon substitution:

$$YZ\frac{\partial^2 X}{\partial x^2} + ZX\frac{\partial^2 Y}{\partial y^2} + XY\frac{\partial^2 Z}{\partial z^2} + 2(E - V_x - V_y - V_z)XYZ = 0 \tag{11}$$

and, dividing throughout by XYZ:

$$\underbrace{\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}}_{\text{depends only on } (x,\, y)} + 2(E - V_x - V_y) = \underbrace{-\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}}_{\text{depends only on } z} + 2V_z = 2E_z, \tag{12}$$

where $2E_z$ is a first separation constant, giving:

$$\frac{d^2 Z}{dz^2} + 2(E_z - V_z)Z = 0. \tag{13}$$

Proceeding in a similar way:

$$\underbrace{\frac{1}{X}\frac{\partial^2 X}{\partial x^2}}_{\text{depends only on } x} + 2(E - E_z - V_x) = \underbrace{-\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}}_{\text{depends only on } y} + 2V_y = 2E_y \tag{14}$$

$2E_y$ being a second separation constant. Hence, we finally obtain:

$$\frac{d^2Y}{dy^2} + 2(E_y - V_y)Y = 0 \tag{15}$$

$$\frac{d^2X}{dx^2} + 2(E_x - V_x)X = 0 \tag{16}$$

provided we put:

$$\begin{aligned} E - E_z - E_y &= E_x \\ E &= E_x + E_y + E_z. \end{aligned} \tag{17}$$

3.4 PARTICLE IN A 1-DIMENSIONAL BOX WITH IMPENETRABLE WALLS

With reference to Figure 3.1 we now consider the particle confined in the 1-dimensional box of side a with impenetrable walls, which means that outside the box the potential is infinite, while in the box we assume $V = V_x = 0$.

(i) *Outside* the box ($V = \infty$).
In regions I and III, where $V = \infty$, it must be:

$$\psi(x) = 0 \tag{18}$$

for all points, which means that the particle cannot be found outside the region $0 \leq x \leq a$.

(ii) *Inside* the box ($V = 0$).
The Schroedinger equation is:

$$\frac{d^2\psi}{dx^2} + 2E\psi = 0 \tag{19}$$

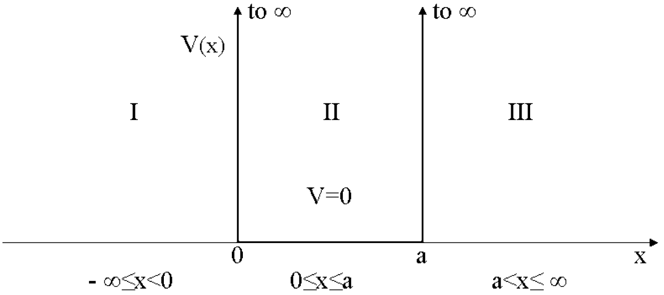

Figure 3.1 The three regions for the particle in the 1-dimensional box with impenetrable walls.

which has the solution:

$$\psi = A\exp(i\alpha x) + B\exp(-i\alpha x), \tag{20}$$

where A and B are integration constants. The value of the constant α is readily obtained since:

$$\psi' = i\alpha[A\exp(i\alpha x) - B\exp(-i\alpha x)], \qquad \psi'' = -\alpha^2\psi \tag{21}$$

from which follows the characteristic equation:

$$\alpha^2 = 2E \Rightarrow \alpha = \sqrt{2E}, \tag{22}$$

which is real since $E > 0$.

We must now impose upon ψ the boundary conditions arising from the fact that we must join in a continuous way the solutions at the edge of the box, hence $\psi(0) = \psi(a) = 0$.

First boundary condition:

$$\psi(0) = 0 \qquad A + B = 0 \Rightarrow B = -A \tag{23}$$

$$\psi(x) = A[\exp(i\alpha x) - \exp(-i\alpha x)] = 2iA\sin\alpha x = C\sin\alpha x, \tag{24}$$

where C is a normalization constant. Second boundary condition:

$$\psi(a) = 0 \qquad C\sin\alpha a = 0 \Rightarrow \alpha a = n\pi \quad n = 1, 2, 3, \cdots \tag{25}$$

so that the argument of the trigonometric function is *quantized*, giving:

$$\psi_n(x) = C\sin n\frac{\pi}{a}x \quad C = \left(\frac{2}{a}\right)^{1/2}. \tag{26}$$

The positive energy spectrum is now *quantized* according to:

$$E_n = \frac{\alpha^2}{2} = n^2\frac{\pi^2}{2a^2} \quad n = 1, 2, 3, \cdots \tag{27}$$

or, measuring the energy in units of $(\frac{\pi^2}{2a^2})$:

$$\frac{E_n}{\pi^2/2a^2} = n^2. \tag{28}$$

The energy levels and wavefunctions for the ground and the first two excited states of the particle in a box with impenetrable walls are given in Figure 3.2 for $C = 1$. It is seen that the functions have $(n - 1)$ nodes, while only the functions having $n =$

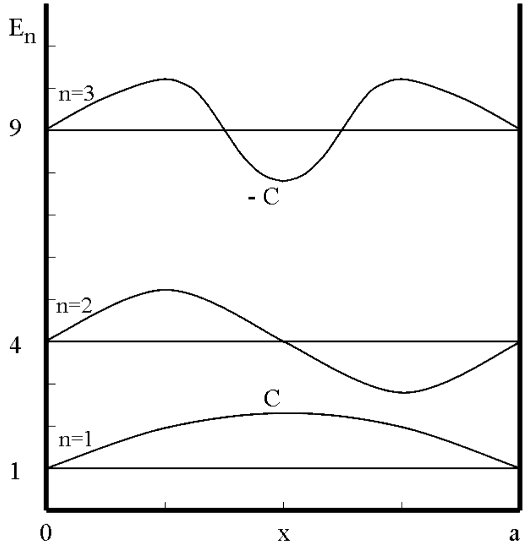

Figure 3.2 Energy levels (in units of $\pi^2/2a^2$) and wavefunctions for the first three lowest states of the particle in a box with impenetrable walls ($C = 1$).

even are zero at $x = a/2$. All functions are normalized to unity and orthogonal to each other.

In three dimensions, the corresponding results are:

$$\begin{aligned}\psi(x, y, z) &= X_{n_x}(x)Y_{n_y}(y)Z_{n_z}(z)\\ &= \left(\frac{8}{abc}\right)^{1/2} \sin n_x\frac{\pi}{a}x \cdot \sin n_y\frac{\pi}{b}y \cdot \sin n_z\frac{\pi}{c}z\end{aligned} \tag{29}$$

$$E = E_x + E_y + E_z = \frac{\pi^2}{2}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right). \tag{30}$$

These results are of great importance in the theory of the perfect gas.

3.5 PARTICLE IN A 1-DIMENSIONAL BOX OF FINITE HEIGHT

With reference to Figure 3.3, we now consider the case of a particle confined in a box of *finite* height V_0, the potential being zero inside the box.

The Schroedinger equation is:

$$\frac{d^2\psi}{dx^2} = 2(V_0 - E)\psi \tag{31}$$

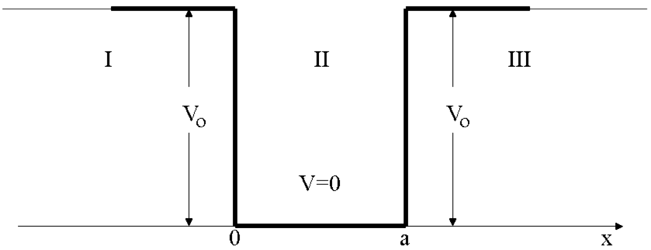

Figure 3.3 The three regions for the particle in the 1-dimensional box of finite height V_0.

with the solution:

$$\psi(x) = A\exp(i\alpha x) + B\exp(-i\alpha x) \tag{32}$$

with:

$$\alpha^2 = 2(E - V_0), \quad \alpha = \sqrt{2(E - V_0)}, \tag{33}$$

where $(E - V_0)$ is the kinetic energy of the particle. Then:

$$\psi(x) = A\exp\big(i\sqrt{2(E - V_0)}x\big) + B\exp\big(-i\sqrt{2(E - V_0)}x\big). \tag{34}$$

For $E > V_0$, we have the *free* particle case discussed in detail by Kauzmann (1957). For $E < V_0$, we have the *bound* particle case. In a classical description the particle does not have enough energy to escape from the box, but its quantum description is different. We have the following cases.

(i) Outside the box (regions I and III).
In this case $(E < V_0)$:

$$\alpha = i\sqrt{2(V_0 - E)} = i\beta, \quad \beta = \sqrt{2(V_0 - E)} > 0. \tag{35}$$

The boundary conditions give:

$$\begin{aligned} \psi_{\mathrm{I}} &= A_{\mathrm{I}}\exp(-\beta x) + B_{\mathrm{I}}\exp(\beta x) \quad -\infty \le x < 0 \\ \psi_{\mathrm{I}} &= B_{\mathrm{I}}\exp(\beta x) \quad \text{since } A_{\mathrm{I}} = 0 \end{aligned} \tag{36}$$

$$\begin{aligned} \psi_{\mathrm{III}} &= A_{\mathrm{III}}\exp(-\beta x) + B_{\mathrm{III}}\exp(\beta x) \\ \psi_{\mathrm{III}} &= A_{\mathrm{III}}\exp(-\beta x) \quad \text{since } B_{\mathrm{III}} = 0. \end{aligned} \tag{37}$$

There is a finite probability of finding the particle outside the box, in a region where the kinetic energy is negative (classically forbidden). As $V_0 \to \infty$, ψ_{I} and ψ_{III} tend to be zero everywhere.

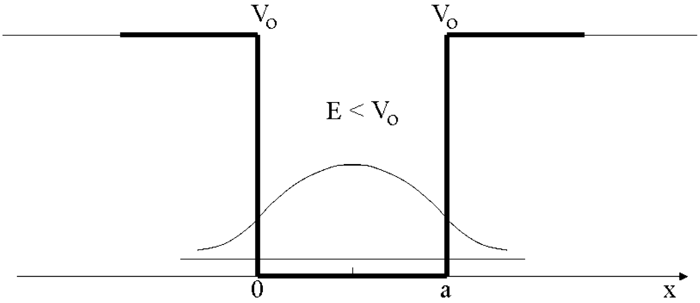

Figure 3.4 Wavefunction for the ground state in the bound region II. The particle has now a not negligible probability of being found outside the box.

(ii) Inside the box (region II, where $V = 0$).

The particle is bound, being confined into the box. Then:

$$\alpha = \sqrt{2E} \quad \text{real} \Rightarrow E = T > 0 \tag{38}$$

$$\psi_{\mathrm{II}}(x) = A\exp(i\alpha x) + B\exp(-i\alpha x) \tag{39}$$

in complex form, or, in real form:

$$\begin{aligned}\psi_{\mathrm{II}}(x) &= A(\cos\alpha x + i\sin\alpha x) + B(\cos\alpha x - i\sin\alpha x) \\ &= (A+B)\cos\alpha x + i(A-B)\sin\alpha x \\ &= C\sin\alpha x + D\cos\alpha x\end{aligned} \tag{40}$$

or, introducing the amplitude A_{II} and the phase ε:

$$\psi_{\mathrm{II}}(x) = A_{\mathrm{II}}\sin(\alpha x + \varepsilon) \tag{41}$$

since (see Chapter 4):

$$C = A_{\mathrm{II}}\cos\varepsilon, \qquad D = A_{\mathrm{II}}\sin\varepsilon. \tag{42}$$

Therefore (Figure 3.4):

$$\psi_{\mathrm{II}}(0) = A_{\mathrm{II}}\sin\varepsilon, \qquad \psi_{\mathrm{II}}(a) = A_{\mathrm{II}}\sin(\alpha a + \varepsilon) \tag{43}$$

ψ_{II} is *not* zero either at $x = 0$ or $x = a$, and the particle can be found in a region *outside* the box (quantum filtration).

To make further progress we must now introduce the continuity conditions for the function and its first derivative at the boundaries.

For $x = 0$:

$$\begin{aligned} &\psi_{\mathrm{I}}(0) = \psi_{\mathrm{II}}(0) \\ &\left(\frac{d\psi_{\mathrm{I}}}{dx}\right)_0 = \left(\frac{d\psi_{\mathrm{II}}}{dx}\right)_0. \end{aligned} \tag{44}$$

For $x = a$:

$$\begin{aligned} &\psi_{\mathrm{II}}(a) = \psi_{\mathrm{III}}(a) \\ &\left(\frac{d\psi_{\mathrm{II}}}{dx}\right)_a = \left(\frac{d\psi_{\mathrm{III}}}{dx}\right)_a. \end{aligned} \tag{45}$$

Let us calculate the first derivatives of the wavefunction:

$$\frac{d\psi_{\mathrm{I}}}{dx} = \beta\psi_{\mathrm{I}}, \qquad \frac{d\psi_{\mathrm{II}}}{dx} = \alpha A_{\mathrm{II}}\cos(\alpha x + \varepsilon), \qquad \frac{d\psi_{\mathrm{III}}}{dx} = -\beta\psi_{\mathrm{III}}. \tag{46}$$

From the continuity conditions it follows then:

$$\begin{cases} B_{\mathrm{I}} = A_{\mathrm{II}}\sin\varepsilon \qquad A_{\mathrm{II}}\sin(\alpha a + \varepsilon) = A_{\mathrm{III}}\exp(-\beta a) \\ \beta B_{\mathrm{I}} = \alpha A_{\mathrm{II}}\cos\varepsilon \qquad \alpha A_{\mathrm{II}}\cos(\alpha a + \varepsilon) = -\beta A_{\mathrm{III}}\exp(-\beta a) \end{cases} \tag{47}$$

$$\tan\varepsilon = \frac{\alpha}{\beta} = \sqrt{\frac{E}{V_0 - E}} \tag{48}$$

$$\frac{B_{\mathrm{I}}}{A_{\mathrm{II}}} = \sin\varepsilon = \frac{1}{\operatorname{cosec}\varepsilon} = \sqrt{\frac{1}{1 + \cot^2\varepsilon}} = \sqrt{\frac{1}{1 + \frac{\beta^2}{\alpha^2}}} = \frac{\alpha}{\sqrt{\alpha^2 + \beta^2}} = \sqrt{\frac{E}{V_0}} \tag{49}$$

$$\tan(\alpha a + \varepsilon) = -\frac{\alpha}{\beta}. \tag{50}$$

Now, since (Problem 3.1):

$$\tan(x + y) = \frac{\tan x + \tan y}{1 - \tan x \tan y} \tag{51}$$

$$\tan(\alpha a + \varepsilon) = \frac{\tan\alpha a + \tan\varepsilon}{1 - \tan\alpha a \cdot \tan\varepsilon} = \frac{\tan\alpha a + \frac{\alpha}{\beta}}{1 - \frac{\alpha}{\beta}\tan\alpha a} = -\frac{\alpha}{\beta}, \tag{52}$$

a formula which can be solved for $\tan\alpha a$ giving:

$$\tan\alpha a = -\frac{\alpha}{\beta} + \left(\frac{\alpha}{\beta}\right)^2 \tan\alpha a - \frac{\alpha}{\beta} \tag{53}$$

$$\tan \alpha a = \frac{-\frac{2\alpha}{\beta}}{1-\left(\frac{\alpha}{\beta}\right)^2} = \frac{2\alpha\beta}{\alpha^2-\beta^2} = \frac{2\sqrt{E(V_0-E)}}{2E-V_0}. \tag{54}$$

Therefore we obtain as quantization condition on the energy for the particle in a box of *finite* height:

$$\tan \sqrt{2a^2E} = \frac{2\sqrt{E(V_0-E)}}{2E-V_0}. \tag{55}$$

Measuring E and V_0 in units of $1/2a^2$, we get:

$$\tan \sqrt{E} = \frac{2\sqrt{\frac{E}{V_0}\left(1-\frac{E}{V_0}\right)}}{2\frac{E}{V_0}-1} \tag{56}$$

a trigonometric transcendental equation that can be solved numerically or graphically (Kauzmann, 1957) by seeking the intersection of the curves

$$\tan \sqrt{E} \text{ vs } E \text{ and } R(E) = \frac{2\sqrt{\frac{E}{V_0}\left(1-\frac{E}{V_0}\right)}}{2\frac{E}{V_0}-1} \text{ vs } E.$$

The intersection points (for different values of V_0) are the roots of the transcendental equation and, therefore, the permissible values for the eigenvalue E. We will content ourselves here in seeing that for V_0 very large ($V_0 \to \infty$):

$$\begin{aligned} &\tan \sqrt{E} = 0 \quad \sqrt{E} = n\pi \\ &E = n^2 \frac{\pi^2}{2a^2} \quad n = 1, 2, 3, \cdots \end{aligned} \tag{57}$$

the result found previously in Section 4. Schiff (1955) used translational symmetry arguments for working out an elegant graphical solution for the energy levels, while the wavefunctions are seen to fall into two classes, being even or odd with respect to the interchange of x into $-x$ (Problem 3.3).

3.6 PROBLEMS 3

3.1. Prove the trigonometric identity:

$$\tan(\alpha+\beta) = \frac{\tan\alpha + \tan\beta}{1-\tan\alpha\tan\beta}.$$

Hint:
Use the elementary definition of the tangent and the addition formulae for sine and cosine functions.

3.2. Calculate the mean values $\langle x\rangle$ and $\langle x^2\rangle$ for a particle in a box of side a with impenetrable walls.

Answer:

$$\langle x\rangle = \langle\psi|x|\psi\rangle = \frac{a}{2}$$
$$\langle x^2\rangle = \langle\psi|x^2|\psi\rangle = \frac{a^2}{3}\left(1-\frac{3}{2\pi^2 n^2}\right).$$

Hint:
Use the wavefunction $\psi_n = C\sin\alpha x$ with $\alpha a = n\pi$ ($n =$ non-zero integer) and the formulae for the corresponding definite integrals.

3.3. Prove by symmetry arguments (Schiff, 1955) that the wavefunctions of the particle in the box with impenetrable walls fall into two classes, being even or odd with respect to the interchange $x \to -x$.

Answer:

$$\psi_e(x) = B\cos n\frac{\pi}{a}x \quad n = 1,3,5,\cdots$$
$$\psi_o(x) = A\sin n\frac{\pi}{a}x \quad n = 2,4,6,\cdots$$

both belonging to the same non-degenerate energy eigenvalue:

$$E_n = n^2\frac{\pi^2}{2a^2}.$$

Hint:
Shift the origin of the coordinate system so as $V(-x) = V(x)$ and apply the boundary conditions.

3.7 SOLVED PROBLEMS

3.1. Using elementary trigonometric definitions and addition formulae we have:

$$\tan(\alpha+\beta) = \frac{\sin(\alpha+\beta)}{\cos(\alpha+\beta)} = \frac{\sin\alpha\cos\beta+\cos\alpha\sin\beta}{\cos\alpha\cos\beta-\sin\alpha\sin\beta}$$
$$= \frac{\frac{\sin\alpha\cos\beta+\cos\alpha\sin\beta}{\cos\alpha\cos\beta}}{\frac{\cos\alpha\cos\beta-\sin\alpha\sin\beta}{\cos\alpha\cos\beta}} = \frac{\tan\alpha+\tan\beta}{1-\tan\alpha\tan\beta}$$

that is the required trigonometric formula.

3.2. The general indefinite integrals needed in this Problem can be taken from Gradshteyn and Ryzhik's (Gradshteyn and Ryzhik, 1980) Tables:

$$\int dx\, x \sin^2 x = \frac{x^2}{4} - \frac{x}{4}\sin 2x - \frac{1}{8}\cos 2x$$

$$\int dx\, x^2 \sin^2 x = \frac{x^3}{6} - \frac{x}{4}\cos 2x - \frac{1}{4}\left(x^2 - \frac{1}{2}\right)\sin 2x$$

as can be easily verified by derivation of the integrand.

We now make the change of variable:

$$\alpha x = y, \quad x = \frac{y}{\alpha}, \quad dx = \frac{dy}{\alpha} \quad \begin{array}{c|c} x & y \\ \hline 0 & 0 \\ a & \alpha a \end{array}.$$

The definite integrals become:

$$\begin{aligned}\int_0^a dx\, x \sin^2 \alpha x &= \frac{1}{\alpha^2}\int_0^{\alpha a} dy\, y \sin^2 y \\ &= \frac{1}{\alpha^2}\left\{\frac{y^2}{4} - \frac{y}{4}\sin 2y - \frac{1}{8}\cos 2y\right|_0^{\alpha a} \\ &= \frac{1}{\alpha^2}\left\{\frac{(\alpha a)^2}{4} - \frac{(\alpha a)}{4}\sin 2\alpha a - \frac{1}{8}\cos 2\alpha a + \frac{1}{8}\right\}\end{aligned}$$

and, for $\alpha a = n\pi$:

$$\begin{aligned}\int_0^a dx\, x \sin^2 \alpha x &= \frac{1}{\alpha^2}\left\{\frac{(\alpha a)^2}{4} - \frac{(\alpha a)}{4}\sin 2\pi n - \frac{1}{8}\cos 2\pi n + \frac{1}{8}\right\} \\ &= \frac{1}{\alpha^2}\left\{\frac{(\alpha a)^2}{4} - \frac{1}{8} + \frac{1}{8}\right\} = \frac{a^2}{4}.\end{aligned}$$

Similarly:

$$\begin{aligned}\int_0^a dx\, x^2 \sin^2 \alpha x &= \frac{1}{\alpha^3}\int_0^{\alpha a} dy\, y^2 \sin^2 y \\ &= \frac{1}{\alpha^3}\left\{\frac{(\alpha a)^3}{6} - \frac{(\alpha a)}{4}\cos 2\alpha a - \frac{1}{4}\left((\alpha a)^2 - \frac{1}{2}\right)\sin 2\alpha a\right\}\end{aligned}$$

and, for $\alpha a = n\pi$:

$$\int_0^a dx\, x^2 \sin^2 \alpha x = \frac{1}{\alpha^3}\left\{\frac{(\alpha a)^3}{6} - \frac{\alpha a}{4}\right\} = \frac{a^3}{6}\left(1 - \frac{3}{2\pi^2 n^2}\right).$$

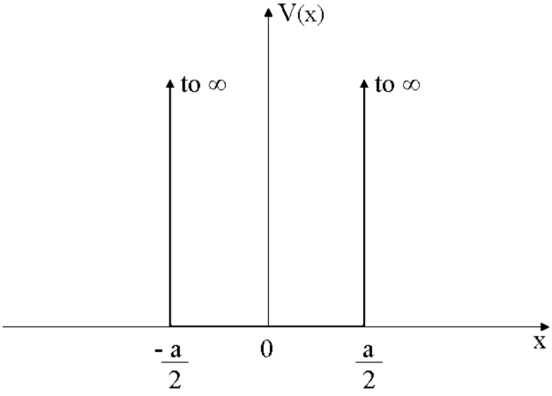

Figure 3.5 The new coordinate system for the particle in the box of side a with impenetrable walls.

Hence, we obtain:

$$\begin{aligned}\langle x\rangle = \langle\psi|x|\psi\rangle &= C^2\int_0^a dx\,x\sin^2\alpha x\\ &= C^2\cdot\frac{a^2}{4} = \frac{2}{a}\cdot\frac{a^2}{4} = \frac{a}{2}\end{aligned}$$

$$\begin{aligned}\langle x^2\rangle = \langle\psi|x^2|\psi\rangle &= C^2\int_0^a dx\,x^2\sin^2\alpha x\\ &= C^2\cdot\frac{a^3}{6}\left(1-\frac{3}{2\pi^2n^2}\right) = \frac{a^2}{3}\left(1-\frac{3}{2\pi^2n^2}\right).\end{aligned}$$

While the first result coincides with the classical average, the second differs from it by the second term in parenthesis, which becomes zero for high values of the quantum number n. The quantum corrections are 0.152, 0.038, 0.017, $\cdots$, 0.0015 for $n = 1, 2, 3, \cdots, 10$, respectively. This is an example of the *correspondence principle*, according to which classical mechanics and quantum mechanics give the same result for systems in highly excited quantum states.

3.3. With reference to Figure 3.5, we shift the origin of the coordinate system to $x = a/2$. We have the solution in real form:

$$\psi(x) = A\sin\alpha x + B\cos\alpha x \quad \alpha = \sqrt{2E} > 0.$$

We now apply the boundary conditions to the new situation. First boundary condition:

$$\psi\left(-\frac{a}{2}\right) = -A\sin\frac{\alpha a}{2} + B\cos\frac{\alpha a}{2} = 0.$$

Second boundary condition:

$$\psi\left(\frac{a}{2}\right) = A\sin\frac{\alpha a}{2} + B\cos\frac{\alpha a}{2} = 0.$$

Since we do not want both A and B to be zero simultaneously (which would imply $\psi = 0$ everywhere), we must have:

$$A\sin\frac{\alpha a}{2} = 0, \qquad B\cos\frac{\alpha a}{2} = 0.$$

Hence, there are two classes of solutions:

$$\begin{aligned} &A = 0,\ B \neq 0 \Rightarrow \cos\frac{\alpha a}{2} = 0 \\ &B = 0,\ A \neq 0 \Rightarrow \sin\frac{\alpha a}{2} = 0 \end{aligned}$$

both implying:

$$\begin{aligned} &\frac{\alpha a}{2} = n\frac{\pi}{2} \Rightarrow \alpha = n\frac{\pi}{a} \\ &E = \frac{\alpha^2}{2} = n^2\frac{\pi^2}{2a^2}, \end{aligned}$$

where n must be an odd integer for the first class and an even integer for the second class. Hence, the two classes of solutions are:

$$\begin{aligned} &\psi_e(x) = B\cos n\frac{\pi}{a}x \quad n = 1, 3, 5, \cdots \\ &\psi_o(x) = A\sin n\frac{\pi}{a}x \quad n = 2, 4, 6, \cdots \end{aligned}$$

where:

$$\begin{aligned} &\psi_e(-x) = \psi_e(x) && \textit{even}\ \text{function} \\ &\psi_o(-x) = -\psi_o(x) && \textit{odd}\ \text{function.} \end{aligned}$$

It can be easily verified that these ψ satisfy the boundary conditions at the edges of the box, and that at the middle of the box, where $x = 0$:

$$\begin{aligned} &\psi_e(0) = B \\ &\psi_o(0) = 0. \end{aligned}$$

All even functions are non-zero at the new origin, all odd functions are zero there. All these results are the consequence of the symmetry property of the potential in the new coordinate system, since:

$$V(-x) = V(x)$$

namely, of the fact that the potential is symmetric about $x = 0$.

– 4 –

The Hydrogen-Like System

4.1 INTRODUCTION

There are many reasons for choosing as our second example of exact solution of the Schroedinger eigenvalue equation the 1-electron atomic problem, the so called hydrogen-like system. Firstly, it is the only atomic case that can be solved exactly. The physically permissible solutions are the simplest example of atomic orbitals (AOs) and their properties. Secondly, the mathematical techniques of solution of the pertinent differential equations are typical of mathematical physics and completely general, and can also be applied to the hydrogen atom in electric or magnetic fields, so giving the possibility of exact evaluation of second-order properties such as electric polarizabilities or magnetic susceptibilities. Thirdly, the physical constraints imposed on the mathematical solutions do explain in a clear way the origin of quantum numbers, so justifying the rather mysterious assumptions of the Bohr theory. Finally, the possibility of disposing of relatively simple solutions in exact analytical form, is essential for checking unequivocally approximate solutions such as those obtained by use of the powerful variation theorem, as we shall see later in this book.

The hydrogen-like system consists of a single electron of mass m_2 and charge $-e$ attracted at distance r by a nucleus of mass m_1 and charge $+Ze$. It is a typical atomic

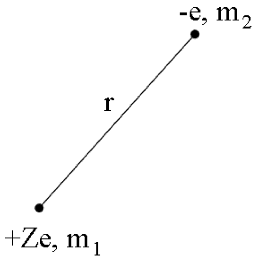

Figure 4.1 The hydrogen-like system.

(1-centre) 1-electron problem covering a whole series of isoelectronic physical systems depending on the value assumed by the nuclear charge Z: $Z = 1, 2, 3, 4, \ldots$ gives rise, respectively, to the H atom and the series of isoelectronic ions, He^+, Li^{+2}, Be^{+3}, … After separation of the motion of the centre-of-mass, we shall be mostly concerned with the solution of the Schroedinger equation describing the motion of the electron relative to the nucleus taken as origin of a system of internal coordinates. Upon introduction of the system of atomic units (a.u.) to get rid of all repetitive physical constants, we shall turn to express the resulting 3-dimensional partial differential equation in spherical coordinates (r, θ, φ), which are appropriate to the spherical symmetry of the potential. This allows us to separate radial from angular equations, which are typical of the square of the angular momentum of the electron. In the separation procedure, which is customary in all partial differential equations involving functions depending upon different variables, we are faced with separation constants which originate quantum numbers. The physical constraints imposed on the mathematical solutions, that are generally called the regularity conditions of the resulting functions, yield Laguerre polynomials for the radial part and Legendre polynomials for the angular part. The latter are well known in mathematical physics from the theory of potential. The complete solutions are the hydrogen-like AOs, and are obtained by multiplying the solutions of each separate differential equation, $\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi)$, where Y_{lm} are the spherical harmonics which are of general importance in atomic problems, whereas R_{nl} is the radial part, peculiar to the hydrogen-like orbitals only. Both radial and angular functions have a form which depends on the three quantum numbers n, l, m, so that hydrogen-like AOs can be simply denoted by specifying their values as the Dirac ket $\psi = |nlm\rangle$. The set of three quantum numbers also specifies the eigenvalues, which give the possible observable values assumed by energy, angular momentum and its z-component.

The Schroedinger equation for the hydrogen atom was also solved by Coulson and Robinson (1958) using spheroidal coordinates with the nucleus at one focus. The relations between spheroidal, spherical and parabolic wavefunctions for the hydrogen atom were also investigated by these authors, who shown that the two latter cases are respectively obtained as limits as $R \to 0$ and $R \to \infty$. Battezzati and Magnasco (2003) studied the behaviour of equations and solutions of the H_2^+ problem at the limit of the united atom He^+. It was shown there that, since when $R \to 0$, $\mu \to 2r/R$, $\nu \to \cos\theta$, the outer μ-equation goes into the correct radial equation for the hydrogen-like system He^+, with the separation constant $A \to -l(l+1)$ and the parameter for the bound state

$(E < 0)$ $\sigma + 1 = Zr/2p = \sqrt{2}/2Z(-E)^{-1/2} \to n$, where n and l are the principal and orbital quantum numbers of the hydrogen-like system with nuclear charge Z. However, while the outer μ-solution $X(\mu)$ goes into the correct radial function $R(r) \propto e^{-2r}$ as $R \to 0$, the inner ν-solution has an infinitesimal behaviour *different* from the hydrogen-like $\Theta(\cos\theta) \propto P_l^m(\cos\theta)$, because the term $-(Z_A - Z_B)R\nu$, characteristic of the H-like system in spheroidal coordinates, is missing in the H_2^+ case (where $Z_A = Z_B = 1$). In other words, even if the differential equations become identical for $R = 0$, the inner ν-solution for H_2^+ and the He^+ hydrogen-like $\Theta(\cos\theta)$ have a different behaviour for infinitesimal $R \neq 0$.

In Section 4.9, as alternative to the hydrogen-like AOs and mostly used today in atomic and molecular calculations, we introduce Slater (STOs) and Gaussian (GTOs) atomic orbitals and some simple atomic integrals over them.

The Chapter ends with a set of problems, where we have collected many mathematical details of the solution.

4.2 SEPARATION OF THE MOTION OF THE CENTRE-OF-MASS

To separate off the motion of the centre-of-mass (i.e., the translation of the system as a whole), we do a transformation from the Cartesian coordinates $(x_1, y_1, z_1; x_2, y_2, z_2)$ of the two particles (nucleus + electron) to a new coordinate system specifying the coordinates (X, Y, Z) of the centre-of-mass of the electron-nucleus system, and the internal coordinates (x, y, z) describing the motion of the electron with respect to the nucleus taken as origin of the new coordinate system.

If:

$$M = m_1 + m_2 \tag{1}$$

is the total mass (essentially, that of the atomic nucleus),

$$m = \frac{m_1 m_2}{m_1 + m_2} = m_2 \frac{1}{1 + \frac{m_2}{m_1}} \approx m_2 \tag{2}$$

the reduced mass (essentially, the mass of the electron), the Hamiltonian of the two particle system can be written in SI units (see Problem 4.1):

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_X^2 - \frac{\hbar^2}{2m}\nabla^2 + V, \qquad V = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}, \tag{3}$$

where V is the Coulomb attraction of the electron by the nucleus. The corresponding Schroedinger equation:

$$\hat{H}\Psi = W\Psi \tag{4}$$

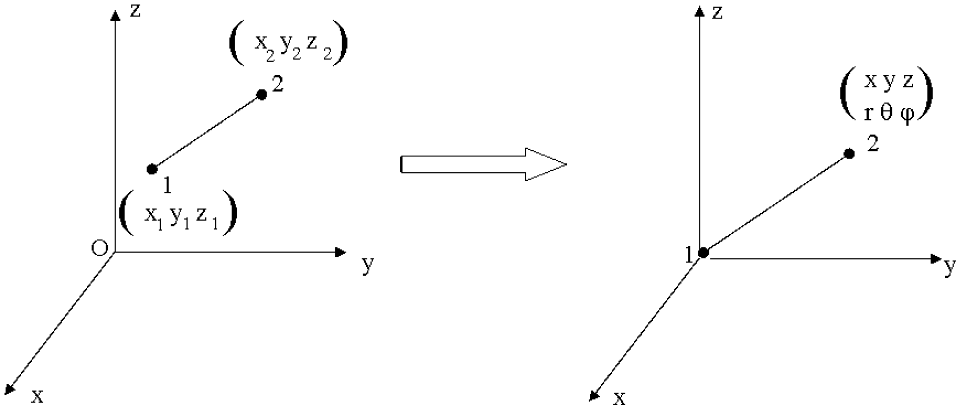

Figure 4.2 Transformation of the coordinate system.

can be separated by posing:

$$\Psi(X, x) = \Phi(X)\psi(x). \tag{5}$$

In fact, we can write:

$$\psi\left(-\frac{\hbar^2}{2M}\nabla_X^2\Phi\right) + \Phi\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = W\Phi\psi. \tag{6}$$

Dividing both members through by $\Phi\psi$:

$$\underset{\substack{\text{independent}\\ \text{variables}\\ (X,Y,Z)}}{\frac{-\frac{\hbar^2}{2M}\nabla_X^2\Phi}{\Phi}} = \underset{\text{independent variables } (x,y,z)}{W - \frac{\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi}{\psi}} = E_G. \tag{7}$$

Since the l.h.s. of (7) depends only on (X, Y, Z), the r.h.s. only on (x, y, z), and the equality must be true for all values of the independent variables, the expression itself must be equal to a separation constant, say E_G. Posing:

$$W = E_G + E \tag{8}$$

equation (4) separates into the two eigenvalue equations:

$$-\frac{\hbar^2}{2M}\nabla_X^2\Phi = E_G\Phi \tag{9}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi \tag{10}$$

the first being the Schroedinger equation for a free particle of mass M describing the translational motion of the centre-of-mass, the second the Schroedinger equation for the motion of the electron with respect to the nucleus.

We shall now consider in detail the solution of the latter equation, after introduction of the atomic units, in terms of which equation (10) can be written:

$$\left(-\frac{1}{2}\nabla^2 + V\right)\psi = E\psi. \tag{11}$$

4.3 SEPARATION OF THE RADIAL EQUATION IN SPHERICAL COORDINATES

Since:

$$r = (x^2 + y^2 + z^2)^{1/2} \geq 0 \tag{12}$$

it is readily seen that the potential energy term $V = -\frac{Z}{r}$ assumes its simplest form in the *spherical* coordinates:

$$x = r\sin\theta\cos\varphi, \qquad y = r\sin\theta\sin\varphi, \qquad z = r\cos\theta. \tag{13}$$

In these coordinates (see Chapter 1):

$$\nabla^2 = \nabla_r^2 - \frac{\hat{L}^2}{r^2} \tag{14}$$

$$\nabla_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} \tag{15}$$

$$\begin{aligned}\hat{L}^2 &= -\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\} \\ &= -\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right),\end{aligned} \tag{16}$$

where $\hat{L}^2$ is the square of the angular momentum operator and ∇_r^2 the radial Laplacian. The Schroedinger eigenvalue equation for the electron of the hydrogen-like system in spherical coordinates is hence given as the partial differential equation in three variables:

$$\left[-\frac{1}{2}\nabla_r^2 + \frac{\hat{L}^2}{2r^2} - \left(E + \frac{Z}{r}\right)\right]\psi(r,\theta,\varphi) = 0. \tag{17}$$

We now attempt to separate radial from angular part by posing:

$$\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi). \tag{18}$$

Upon substitution in equation (17) we obtain:

$$Y\left[-\frac{1}{2}\nabla_r^2 - \left(E + \frac{Z}{r}\right)\right]R = -\frac{R}{2r^2}\hat{L}^2\,Y \tag{19}$$

$$\frac{2r^2\left[-\frac{1}{2}\nabla_r^2 - \left(E + \frac{Z}{r}\right)\right]R}{R} = -\frac{\hat{L}^2\,Y}{Y} = -\lambda, \tag{20}$$

where λ is a separation constant. We obtain the two separate differential equations:

$$\left[-\frac{1}{2}\nabla_r^2 + \left(\frac{\lambda}{2r^2} - \frac{Z}{r}\right)\right]R(r) = E\,R(r) \tag{21}$$

$$\hat{L}^2\,Y(\theta,\varphi) = \lambda\,Y(\theta,\varphi) \quad \lambda \geq 0 \tag{22}$$

the latter being the eigenvalue equation for the square of the angular momentum operator, the first the one-dimensional Schroedinger equation for the electron in the spherical effective potential:

$$V_{\text{eff}}(r) = \frac{\lambda}{2r^2} - \frac{Z}{r}. \tag{23}$$

$V_{\text{eff}}(r)$ is the resultant of the repulsive centrifugal potential $\frac{\lambda}{2r^2}$ and the Coulomb potential $-\frac{Z}{r}$, describing the attraction of the negatively charged electron by the nucleus of charge $+Z$. The effective potential is purely *radial*, since it depends only on the distance of the electron from the nucleus.

We recall that the modulus of the classical radial centrifugal force is given by:

$$F(r) = \frac{mv^2}{r} = \frac{(mvr)^2}{mr^3} = \frac{L^2}{mr^3} = \frac{\lambda}{mr^3}, \tag{24}$$

where L^2 is the square of the angular momentum having the constant positive value λ. We shall see later in this Chapter that:

$$\lambda = l(l+1) \quad l = 0, 1, 2, 3, \cdots (n-1). \tag{25}$$

The force can be derived from the repulsive radial centrifugal potential:

$$F(r) = -\frac{dV(r)}{dr} \tag{26}$$

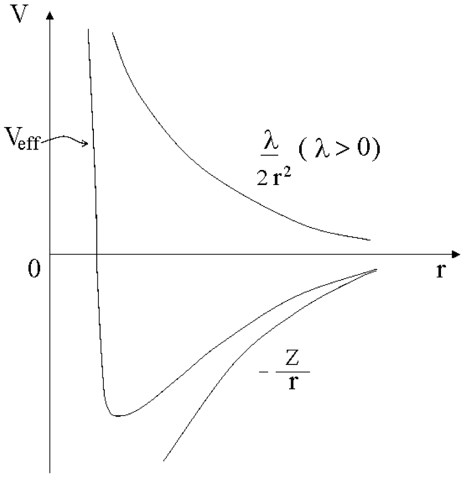

Figure 4.3 Radial effective potential for the hydrogen-like system.

$$V(r) = \frac{\lambda}{2mr^2} \quad \lambda \geq 0. \tag{27}$$

In fact:

$$F(r) = -\frac{\lambda}{2m}\frac{d}{dr}(r^{-2}) = \frac{\lambda}{mr^3}. \tag{28}$$

In atomic units, $m = 1$, and (27) recovers the expression obtained from the separation of the differential equation.

4.4 SOLUTION OF THE RADIAL EQUATION

Introducing (25), the radial equation can be written as:

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[2\left(E + \frac{Z}{r}\right) - \frac{l(l+1)}{r^2}\right]R = 0. \tag{29}$$

By posing:

$$R(r) = \frac{P(r)}{r} \tag{30}$$

we obtain a differential equation where the first derivative is missing (Problem 4.2):

$$\frac{d^2P}{dr^2} + \left[2\left(E + \frac{Z}{r}\right) - \frac{l(l+1)}{r^2}\right]P = 0. \tag{31}$$

We now study the asymptotic behaviour of $P(r)$ in the two cases where the energy parameter (eigenvalue) E is positive or negative.

(i) $$E > 0 \qquad \sqrt{2E} = \omega. \tag{32}$$

If $r \to \infty$, equation (31) becomes:

$$\frac{d^2P}{dr^2} + \omega^2 P \approx 0 \tag{33}$$

$$P(r) = \exp(\alpha r), \quad \frac{dP}{dr} = P' = \alpha P, \quad \frac{d^2P}{dr^2} = P'' = \alpha^2 P \tag{34}$$

which, upon substitution, gives the characteristic equation determining α:

$$\alpha^2 + \omega^2 = 0 \quad \Longrightarrow \quad \alpha = \pm i\omega, \tag{35}$$

where i is the imaginary unit ($i^2 = -1$). Hence, we get the fundamental integrals:

$$P_1(r) = \exp(i\omega r), \qquad P_2(r) = \exp(-i\omega r) \tag{36}$$

giving the *complex* form for the general integral:

$$P(r) = a\exp(i\omega r) + b\exp(-i\omega r), \tag{37}$$

where a, b are two integration constants. The real form for the general integral is obtained from:

$$\frac{P_1 + P_2}{2} = \cos\omega r, \qquad -i\,\frac{P_1 - P_2}{2} = \sin\omega r, \tag{38}$$

where use has been made of Euler's formula for imaginary exponentials (Problem 4.3):

$$\exp(\pm i\alpha) = \cos\alpha \pm i\,\sin\alpha. \tag{39}$$

By replacing the two integration constants a, b by the amplitude A and the phase ε, the *real* form for the general integral will be given as:

$$P(r) = a\sin\omega r + b\cos\omega r = A\sin(\omega r + \varepsilon) \tag{40}$$

which shows that for $E > 0$ (not quantized energy corresponding to the spectrum of the ionized atom) we obtain an oscillatory solution. By superposing different solutions we get a wave packet corresponding to states of the ionized atom, having a continuous spectrum of energy eigenvalues (all positive values of E are possible). This solution is interesting only in completing the spectrum of the energy eigenvalues of the Hermitian operator $\hat{H}$ ($E > 0$,

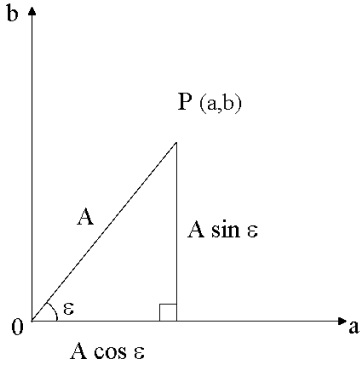

Figure 4.4 Change of integration constants.

continuous part of the spectrum, wave packets; $E < 0$, discrete part of the spectrum, bound states, as we shall see below).

$$\text{(ii)} \qquad E < 0. \tag{41}$$

It is convenient to pose:

$$x = \frac{Z}{n} r \qquad E = -\frac{Z^2}{2n^2}, \tag{42}$$

where we change variable from r to x, and express the negative eigenvalue in terms of the square of a real positive parameter n, to be determined.

The equation in x simplifies to (Problem 4.4):

$$\frac{d^2P}{dx^2} + \left(-1 + \frac{2n}{x} - \frac{l(l+1)}{x^2}\right) P = 0 \quad 0 \le x \le \infty. \tag{43}$$

The asymptotic behaviour of the function $P(x)$ in the two regions will be:

- $x \to \infty$ (*far* from the nucleus)

$$\frac{d^2P}{dx^2} \approx P \quad P(x) = a\exp(-x) + b\exp(x) = a\exp(-x), \tag{44}$$

where a, b are integration constants, and $b = 0$ for the regularity of the function at $x = \infty$.

- $x \to 0$ (*near* to the nucleus)

$$\frac{d^2P}{dx^2} \approx \frac{l(l+1)}{x^2} P \quad P(x) = A\,x^{l+1} + Bx^{-l} = A\,x^{l+1}, \tag{45}$$

where A, B are integration constants, and $B = 0$ for the regularity of the function at $x = 0$ (since $l \ge 0$).

This means that the complete solution $P(x)$ must have the general form:

$$P(x) = \exp(-x)\, x^{l+1}\, F(x), \tag{46}$$

where $F(x)$ is a function which has to be determined and must be regular over the whole interval of x, including $x = 0$ and $x = \infty$. By taking first and second derivatives of $P(x)$, upon substitution in (43), we see that $F(x)$ satisfies the differential equation (Problem 4.5):

$$x\,\frac{d^2F}{dx^2} + [(2l+2) - 2x]\,\frac{dF}{dx} + 2\,(n-l-1)\,F = 0 \tag{47}$$

which can be solved by the power series in x (Taylor):

$$\begin{aligned} F(x) &= \sum_{k=0}^{\infty} a_k\, x^k \\ F'(x) &= \sum_{k=1}^{\infty} k\, a_k\, x^{k-1} \\ F''(x) &= \sum_{k=2}^{\infty} k(k-1)\, a_k\, x^{k-2}. \end{aligned} \tag{48}$$

Upon substitution into the differential equation (47) we obtain an expansion in powers of x, where the coefficients of the different powers must be identically zero:

Coefficient of x^k:

$$k(k+1)\,a_{k+1} + (2l+2)(k+1)\,a_{k+1} - 2k\,a_k + 2(n-l-1)\,a_k = 0 \tag{49}$$

thereby obtaining the 2-term recursion formula for the coefficients:

$$a_{k+1} = \frac{2(k-n+l+1)}{(k+1)(k+2l+2)}\,a_k \quad k = 0, 1, 2, \cdots \tag{50}$$

Since series (48) has infinite terms, we must now study the behaviour of the solution when $k \to \infty$, recalling that we must choose only regular solutions. Using the ratio test for the series:

$$\lim_{k\to\infty} \frac{a_{k+1}\,x^{k+1}}{a_k\,x^k} = x \lim_{k\to\infty} \frac{a_{k+1}}{a_k} \approx x \lim_{k\to\infty} \frac{2}{k} \tag{51}$$

we see that it has the same limit of the function $\exp(2x)$, so that:

$$\sum_{k=0}^{\infty} a_k\, x^k \approx \exp(2x) \tag{52}$$

$$P(x) = \exp(-x)x^{l+1}\sum_{k=0}^{\infty} a_k\, x^k \approx \exp(x)x^{l+1} \tag{53}$$

which must be discarded since it diverges for $x = \infty$. For physically permissible solutions, the series (48) must be truncated to a *finite* polynomial, so we must require that for:

$$a_k \neq 0, \quad a_{k+1} = a_{k+2} = \cdots = 0. \tag{54}$$

For this to be true, it will be sufficient that the numerator of (50) will vanish, so giving the condition:

$$k - n + l + 1 = 0 \implies k_{\text{max}} = n - l - 1, \tag{55}$$

where k_{max} is the maximum order of the resulting polynomial. The physically acceptable polynomial solution of the radial equation will hence be:

$$P(x) = \exp(-x)x^{l+1}\sum_{k=0}^{n-l-1} a_k\, x^k \tag{56}$$

which can be seen to correspond to the usual, sensibly more complicated, solution of equation (47) in terms of associated Laguerre[1] polynomials (Eyring et al., 1944; Abramowitz and Stegun, 1965). Equation (55) determines our so far unknown parameter n:

$$n = k + l + 1 \implies n = l + 1,\, l + 2, \cdots \implies n \geq (l + 1) \tag{57}$$

which is the famous relation between principal and angular quantum numbers n, l.

Going back to our original function $R(x)$, equation (30), we finally get for our radial function ($x = \frac{Z}{n}r$):

$$R_{nl}(x) = \exp(-x)x^{l}\sum_{k=0}^{n-l-1} a_k\, x^k \quad n = 1, 2, 3, \cdots \quad l = 0, 1, 2, \cdots (n-1) \tag{58}$$

with the coefficients determined by the recursion relation (50), the corresponding energy eigenvalue being:

$$E_n = -\frac{Z^2}{2n^2}. \tag{59}$$

Equation (59) can be recognized as the expression in atomic units for the energy levels of the Bohr hydrogen-like atom.

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[1] Laguerre Edmond-Nicolas 1834–1866, French mathematician, artillery officer, Member of the Académie des Sciences.

The un-normalized expressions for the first few radial states have been derived and plotted against x in Problem 4.6, and tested as correct solutions of the corresponding differential equation in Problem 4.7. We notice that the radial functions $R_{nl}(x)$ depend on the quantum numbers n, l and have $(n-l-1)$ nodes (the roots of the polynomial).

4.5 SOLUTION OF THE ANGULAR EQUATION

Now we turn to equation (22):

$$\hat{L}^2\, Y(\theta,\varphi) = \lambda\, Y(\theta,\varphi) \tag{22}$$

$$\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\,\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\varphi^2} + \lambda\right) Y(\theta,\varphi) = 0 \tag{60}$$

which is the equation for the square of the angular momentum operator $\hat{L}^2$. We try to separate the two angular variables θ, φ by posing:

$$Y(\theta,\varphi) = \Theta(\theta)\Phi(\varphi) \tag{61}$$

$$\Phi\left(\frac{\partial^2\Theta}{\partial\theta^2} + \cot\theta\,\frac{\partial\Theta}{\partial\theta} + \lambda\right)\Theta = -\frac{\Theta}{\sin^2\theta}\,\frac{\partial^2\Phi}{\partial\varphi^2}. \tag{62}$$

Multiplying both members through by $\frac{\sin^2\theta}{\Theta\Phi}$, we obtain:

$$\frac{1}{\Theta}\left(\sin^2\theta\,\frac{d^2\Theta}{d\theta^2} + \sin^2\theta\cot\theta\,\frac{d\Theta}{d\theta}\right) + \lambda\sin^2\theta = -\frac{1}{\Phi}\,\frac{d^2\Phi}{d\varphi^2} = m^2, \tag{63}$$

where m^2 is a new separation constant. Equation (22) has hence been separated in two ordinary differential equations:

$$\frac{d^2\Phi}{d\varphi^2} + m^2\Phi = 0 \tag{64}$$

$$\frac{d^2\Theta}{d\theta^2} + \cot\theta\,\frac{d\Theta}{d\theta} + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta = 0. \tag{65}$$

4.5.1 Solution of the Φ-Equation

Equation (64) has the evident normalized solution in *complex* form:

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}\exp(im\varphi) \qquad m = 0, \pm 1, \pm 2, \cdots \tag{66}$$

The regularity condition requires $\Phi(\varphi)$ to be singly-valued:

$$\begin{aligned}
&\Phi(\varphi+2\pi)=\Phi(\varphi)\\
&\exp[im(\varphi+2\pi)]=\exp(im\varphi)\\
&\exp(i2\pi m)=1 \qquad \cos 2\pi m+i\sin 2\pi m=1\\
&\cos 2\pi m=1 \implies m=0,\pm1,\pm2,\cdots \text{ integer.}
\end{aligned} \tag{67}$$

4.5.2 Solution of the Θ-Equation

If we put:

$$x=\cos\theta \qquad -1\le x\le 1 \tag{68}$$

we obtain the differential equation in x (Problem 4.8):

$$(1-x^2)\,\frac{d^2\Theta}{dx^2}-2x\,\frac{d\Theta}{dx}+\left(\lambda-\frac{m^2}{1-x^2}\right)\Theta=0 \tag{69}$$

which shows regular singularities at $|x|=1$.

The asymptotic behaviour of the function $\Theta(x)$ at $|x|=1$ can be obtained by considering the approximate equation:

$$(1-x^2)\,\frac{d^2\Theta}{dx^2}-2x\,\frac{d\Theta}{dx}\approx\frac{m^2}{1-x^2}\Theta. \tag{70}$$

It can be easily shown (Problem 4.9) that the solution of this asymptotic equation is:

$$\Theta(x)=(1-x^2)^{\frac{m}{2}} \qquad m=|m|\ge 0 \tag{71}$$

which is regular for $|x|=1$. The complete solution $\Theta(x)$ must hence have the form:

$$\Theta(x)=(1-x^2)^{\frac{m}{2}}\,G(x), \tag{72}$$

where $G(x)$ has to be determined, with its regularity conditions, over the whole interval $|x|\le 1$. The differential equation for $G(x)$ is (Problem 4.10):

$$(1-x^2)\,\frac{d^2G}{dx^2}-2(m+1)x\,\frac{dG}{dx}+[\lambda-m(m+1)]\,G=0. \tag{73}$$

For $\lambda = l(l+1)$ ($l \geq 0$ integer) this is nothing but the differential equation for the associated Legendre functions $P_l^m(x)$, well known to mathematical physicists in potential theory. We will try again the power series solution for $G(x)$ using the expansion:

$$
\begin{aligned}
G(x) &= \sum_{k=0}^{\infty} a_k\, x^k \\
G'(x) &= \sum_{k=1}^{\infty} k\, a_k\, x^{k-1} \\
G''(x) &= \sum_{k=2}^{\infty} k(k-1)\, a_k\, x^{k-2}.
\end{aligned}
\tag{74}
$$

Proceeding as for the radial solution, we substitute expansions (74) in (73), thereby obtaining:

$$
\begin{aligned}
&\sum_k k(k-1)\, a_k\, x^{k-2} - \sum_k k(k-1)\, a_k\, x^k - 2(m+1) \sum_k k a_k\, x^k \\
&\quad + (\lambda - m(m+1)) \sum_k a_k\, x^k = 0,
\end{aligned}
\tag{75}
$$

where:

Coefficient of x^k:

$$
(k+1)(k+2)\, a_{k+2} - (k-1)k\, a_k - 2(m+1)k\, a_k + (\lambda - m(m+1))\, a_k = 0\,, \tag{76}
$$

so that we obtain the 2-term recursion formula for the coefficients:

$$
a_{k+2} = \frac{(k+m)(k+m+1) - \lambda}{(k+1)(k+2)}\, a_k \quad k = 0, 1, 2, \cdots \tag{77}
$$

According to this recursion formula, we shall obtain this time an *even* series ($k = 0, 2, 4, \cdots$) and an *odd* series ($k = 1, 3, 5, \cdots$), which are characteristic of trigonometric functions. We have now to study the convergence of the series (74) when $k \to \infty$. The ratio test shows that this series has the same asymptotic behaviour of the geometrical series of reason x^2:

$$
S = \sum_{k=0}^{\infty} x^k \tag{78}
$$

with:

$$S_n = 1 + x + x^2 + \cdots + x^{n-1} = \frac{1 - x^n}{1 - x}. \tag{79}$$

Now, $\lim_{n\to\infty} S_n$ does exist if $|x| < 1$, but the series will diverge at $|x| = 1$, since:

$$\lim_{n\to\infty} S_n = \frac{1}{1 - x}. \tag{80}$$

Going back to our series (74), the ratio test says that:

$$\lim_{k\to\infty} \frac{a_{k+2}\, x^{k+2}}{a_k\, x^k} = x^2 \lim_{k\to\infty} \frac{a_{k+2}}{a_k} = x^2 \tag{81}$$

so that:

for $|x| < 1$ the series is absolutely convergent

for $|x| = 1$ the series is divergent.

To get a physically acceptable solution of equation (69) even for $|x| = 1$, the series must reduce to a polynomial, so that:

$$a_k \neq 0, \quad a_{k+2} = a_{k+4} = \cdots = 0 \tag{82}$$

and we obtain the relation:

$$(k + m)(k + m + 1) - \lambda = 0 \tag{83}$$

$$\lambda = (k + m)(k + m + 1) \quad k, m = 0, 1, 2, \cdots \tag{84}$$

Put:

$$k + m = l \quad \text{a non-negative integer } (l \geq 0) \tag{85}$$

$$l = m,\ m + 1,\ m + 2,\ \cdots \tag{86}$$

$$l \geq |m| \quad -l \leq m \leq l \tag{87}$$

and we recover the remaining relation between angular quantum numbers l and m.
Hence we get for the eigenvalue of $\hat{L}^2$:

$$\lambda = l(l + 1) \tag{88}$$

$$l = 0, 1, 2, 3, \cdots (n - 1) \tag{89}$$

$$m = 0, \pm 1, \pm 2, \cdots \pm l \quad (2l+1) \text{ values of } m. \tag{90}$$

The infinite series (74) reduces to a polynomial whose degree is at most:

$$k_{\max} = l - m \quad (\geq 0) \tag{91}$$

giving as complete solution for the angular equation:

$$\Theta_{lm}(x) = (1-x^2)^{\frac{m}{2}} \cdot \left\{ \underbrace{\sum_{k=0}^{\frac{l-m}{2}} a_{2k}\, x^{2k}}_{\substack{\textit{even} \text{ polynomial} \\ (l-m) = \text{even}}} + \underbrace{\sum_{k=0}^{\frac{l-m-1}{2}} a_{2k+1}\, x^{2k+1}}_{\substack{\textit{odd} \text{ polynomial} \\ (l-m) = \text{odd}}} \right\}, \tag{92}$$

where we still use $m = |m|$ for short. The recursion relation for the coefficients is then:

$$a_{k+2} = \frac{(k+m)(k+m+1) - l(l+1)}{(k+1)(k+2)}\, a_k \quad k = 0, 1, 2, \cdots \tag{93}$$

The explicit expressions for the first few angular functions $\Theta_{lm}(x)$ have been derived in Problem 4.11, and tested as correct solutions of the differential equation (69) in Problem 4.12. Our simple polynomial solution $\Theta(x)$ gives a result which is seen to differ from the conventional associated Legendre polynomials $P_l^m(x)$ (Problem 4.13) by a constant factor irrelevant from the standpoint of the differential equation. If $[\cdots]$ stands for "integer part of", we can state that:

$$P_l^m(x) = (-1)^{m + \left[\frac{l+m}{2}\right]}\, \Theta_{lm}(x), \tag{94}$$

where it must be noted that $P_l^m(x)$ is normalized to $\frac{2}{2l+1}\frac{(l+m)!}{(l-m)!}$ and not to 1.

Some of the constant factors occurring between Θ_{lm} and P_l^m are given in Problem 4.14.

4.6 HYDROGEN-LIKE ORBITALS, EIGENVALUES AND QUANTUM NUMBERS

Let us summarize the results obtained so far. The Schroedinger equation for the hydrogen-like system in atomic units:

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right)\psi = E\,\psi \tag{11}$$

has been separated in spherical coordinates into a radial and an angular eigenvalue equation:

$$\left[-\frac{1}{2}\nabla_r^2+\left(\frac{\lambda}{2r^2}-\frac{Z}{r}\right)\right]R(r)=E\,R(r) \tag{21}$$

$$\hat{L}^2\,Y(\theta,\varphi)=\lambda\,Y(\theta,\varphi) \tag{22}$$

having eigenvalues:

$$E_n=-\frac{Z^2}{2n^2}\quad n=1,2,3,\cdots \tag{59}$$

$$\lambda=l(l+1)\quad l=0,1,2,\cdots(n-1) \tag{88}$$

and eigenfunctions (hydrogen-like AOs):

$$\psi_{nlm}(r,\theta,\varphi)=R_{nl}(r)\,Y_{lm}(\theta,\varphi)=|nlm\rangle. \tag{95}$$

Hydrogen-like AOs depend on the three quantum numbers (n,l,m) characterizing the quantum states that the electron can assume in absence of external perturbations ($n=1$, $l=m=0$ is the spherical ground state, all others being excited states). The radial part $R(r)$ depends on n,l, the angular part $Y(\theta,\varphi)$ depends on l,m. We want to underline once more that the radial polynomial solution (a polynomial in $x=\frac{Z}{n}r$ of degree $n-l-1$) is characteristic only of *hydrogen-like* AOs, while the angular part in complex form (the functions Y are known as spherical harmonics) has the same form for *all* AOs, even not hydrogen-like.

Other definitions used for the angular part are (Brink and Satchler, 1993; Stone, 1996):

$$C_{lm}(\theta,\varphi)=C_{lm}(\hat{\mathbf{r}})=\sqrt{\frac{4\pi}{2l+1}}\,Y_{lm}(\hat{\mathbf{r}}) \tag{96}$$

known as modified spherical harmonic,

$$R_{lm}(\mathbf{r})=r^lC_{lm}(\hat{\mathbf{r}}),\quad I_{lm}(\mathbf{r})=r^{-l-1}C_{lm}(\hat{\mathbf{r}}) \tag{97}$$

regular and irregular solid spherical harmonics, respectively.

It is important to notice that AOs in complex form are also eigenfunctions of the operator $\hat{L}_z$ (z-component of the angular momentum operator $\hat{\boldsymbol{L}}$) with eigenvalue m. In fact, in spherical coordinates:

$$\hat{L}_z=-i\,\frac{\partial}{\partial\varphi}\qquad \hat{L}_z\psi=m\psi \tag{98}$$

$$\psi=RY=R\Theta\Phi$$

$$\Phi \propto \exp(im\varphi) \qquad \text{travelling waves eigenfunctions of } \hat{L}^2 \text{ and } \hat{L}_z$$

$$\hat{L}_z\psi = (R\Theta)\,\hat{L}_z\Phi = -i(R\Theta)\,\frac{\partial\Phi}{\partial\varphi} = m(R\Theta\Phi) = m\psi.$$

Φ-functions in *complex* form are usually given with the so called Condon–Shortley phase (Condon and Shortley, 1963; Brink and Satchler, 1993):

$$\begin{cases} \Phi_{+m} = (-1)^m \dfrac{\exp(im\varphi)}{\sqrt{2\pi}} & m > 0 \\ \Phi_{-m} = \dfrac{\exp(-im\varphi)}{\sqrt{2\pi}} = (-1)^m \Phi^*_{+m}. \end{cases} \tag{99}$$

In valence theory it is customary to use *real* Φs, involving trigonometric functions, which are still eigenfunctions of $\hat{L}^2$ but no longer of $\hat{L}_z$. Real Φs are related to complex Φs by the unitary transformation:

$$\begin{cases} \Phi^c_m = \dfrac{\cos m\varphi}{\sqrt{\pi}} = \dfrac{(-1)^m\,\Phi_{+m} + \Phi_{-m}}{\sqrt{2}} \\ \Phi^s_m = \dfrac{\sin m\varphi}{\sqrt{\pi}} = -i\,\dfrac{(-1)^m\,\Phi_{+m} - \Phi_{-m}}{\sqrt{2}}. \end{cases} \tag{100}$$

Real Φs are eigenfunctions of $\hat{L}^2$ only and can be visualized as standing waves. The inverse transformation (from real to complex form) is given by:

$$\begin{cases} \Phi_{+m} = (-1)^m \dfrac{\Phi^c_m + i\Phi^s_m}{\sqrt{2}} \\ \Phi_{-m} = \dfrac{\Phi^c_m - i\Phi^s_m}{\sqrt{2}}. \end{cases} \tag{101}$$

These transformations can be immediately verified by recalling Euler's formula (39) for imaginary exponentials. In matrix form:

$$(\Phi^c_m\ \Phi^s_m) = (\Phi_{+m}\ \Phi_{-m}) \underbrace{\begin{pmatrix} (-1)^m \dfrac{1}{\sqrt{2}} & (-1)^m \dfrac{-i}{\sqrt{2}} \\ \dfrac{1}{\sqrt{2}} & \dfrac{i}{\sqrt{2}} \end{pmatrix}}_{\mathbf{U}} \tag{102}$$

with the inverse transformation ($\mathbf{U}^{-1} = \mathbf{U}^\dagger$):

$$(\Phi_{+m}\ \Phi_{-m}) = (\Phi^c_m\ \Phi^s_m) \begin{pmatrix} (-1)^m \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} \\ (-1)^m \dfrac{i}{\sqrt{2}} & \dfrac{-i}{\sqrt{2}} \end{pmatrix}. \tag{103}$$

The unitary transformation preserves normalization, so that:

$$\begin{aligned}
&\Phi_m^c = \frac{\cos m\varphi}{\sqrt{\pi}} \qquad \Phi_m^s = \frac{\sin m\varphi}{\sqrt{\pi}} \quad m > 0 \\
&\Phi_{+m} = (-1)^m \frac{\exp(im\varphi)}{\sqrt{2\pi}} \qquad \Phi_{-m} = \frac{\exp(-im\varphi)}{\sqrt{2\pi}} = (-1)^m \, \Phi_{+m}^*.
\end{aligned} \tag{104}$$

All Φ functions, either real or complex, are normalized to 1 and mutually orthogonal. Spherical harmonics in real form are also known as tesseral harmonics (Mac Robert, 1947), and are given in un-normalized form as:

$$Y_{l0},\ Y_{lm}^c \sim \Theta_{lm} \cos m\varphi, \qquad Y_{lm}^s \sim \Theta_{lm} \sin m\varphi \quad (m > 0). \tag{105}$$

The first few (un-normalized) hydrogen-like AOs in real form are hence simply given by:

$$\begin{aligned}
&1s \propto \exp(-cr) \quad (c = Z) \\
&2s \propto \exp(-cr)(1 - cr) \quad (2c = Z) \\
&2p_z \propto \exp(-cr)\, z \\
&2p_x \propto \exp(-cr)\, x \\
&2p_y \propto \exp(-cr)\, y \\
&3s \propto \exp(-cr)\left(1 - 2cr + \frac{2}{3}c^2r^2\right) \quad (3c = Z) \\
&3p_z \propto \exp(-cr)\left(1 - \frac{1}{2}cr\right) z \\
&3p_x \propto \exp(-cr)\left(1 - \frac{1}{2}cr\right) x \\
&3p_y \propto \exp(-cr)\left(1 - \frac{1}{2}cr\right) y \\
&3d_{z^2} \propto \exp(-cr)\, \frac{3z^2 - r^2}{2} \\
&3d_{zx} \propto \exp(-cr)\, zx \\
&3d_{yz} \propto \exp(-cr)\, yz \\
&3d_{x^2-y^2} \propto \exp(-cr)(x^2 - y^2) \\
&3d_{xy} \propto \exp(-cr)\, xy,
\end{aligned} \tag{106}$$

where x, y, z are given by equations (13). We see that our AOs have the same transformation properties of (x, y, z)-coordinates or of their combinations.

Hydrogen-like AOs in their complex form simultaneously satisfy the following three eigenvalue equations:

$$\begin{cases} \hat{H}\,\psi_{nlm} = E_n\,\psi_{nlm} \\ \hat{L}^2\,\psi_{nlm} = l(l+1)\,\psi_{nlm} \\ \hat{L}_z\psi_{nlm} = m\,\psi_{nlm}, \end{cases} \tag{107}$$

where:

$$\begin{aligned} &n = 1, 2, 3, \cdots \quad \text{principal quantum number} \\ &l = 0, 1, 2, 3, \cdots (n-1) \quad \text{angular (orbital) quantum number} \\ &m = 0, \pm 1, \pm 2, \cdots \pm l \quad \text{magnetic quantum number.} \end{aligned} \tag{108}$$

• Comments

1. For the 1-electron atom the energy eigenvalues depend only on n. For the many-electron atom, orbital energies do depend on n and l.
2. Each ψ_{nlm} AO is at a time eigenfunction of three different operators ($\hat{H}, \hat{L}^2, \hat{L}_z$). A fundamental theorem of Quantum Mechanics (Eyring et al., 1944) then says that the three operators do commute with each other:

   $$[\hat{H}, \hat{L}^2] = [\hat{H}, \hat{L}_z] = [\hat{L}^2, \hat{L}_z] = 0 \tag{109}$$

   what physically means that, in state ψ_{nlm}, energy, total angular momentum, and z-component of angular momentum, all have a definite value: in other words, we can measure each of these physical quantities with arbitrary precision, without altering the remaining two. Quantities commuting with the Hamiltonian are said to be constants of the motion. Quantities whose operators do not commute cannot be measured at the same time with arbitrary precision, because of Heisenberg's uncertainty principle (e.g., x, $\hat{p}_x$ or y, $\hat{p}_y$ or z, $\hat{p}_z$; $\hat{L}_x, \hat{L}_y$ or $\hat{L}_y, \hat{L}_z$ or $\hat{L}_z, \hat{L}_x$).
3. Since energy eigenvalues do depend only on n, the energy levels of the 1-electron atom are strongly degenerate, the number g of different eigenstates for a given value of n being:

   $$g = \sum_{l=0}^{n-1}(2l+1) = n + 2\sum_{l=0}^{n-1} l = n + 2\,\frac{n(n-1)}{2} = n^2. \tag{110}$$

4. The first states of the 1-electron atom are given in Table 4.1, while in Figure 4.5 is the diagram of the corresponding energy levels (orbital energies).

Table 4.1.

First states of the hydrogen-like electron

n	l	m	E_n	$\|nlm\rangle$	
1	0	0	E_1	$\|100\rangle$	1s
2	0	0	E_2	$\|200\rangle$	2s
	1	1		$\|211\rangle$	2p
	1	0		$\|210\rangle$	
	1	-1		$\|21\bar{1}\rangle$	
3	0	0	E_3	$\|300\rangle$	3s
	1	1		$\|311\rangle$	3p
	1	0		$\|310\rangle$	
	1	-1		$\|31\bar{1}\rangle$	
	2	2		$\|322\rangle$	3d
	2	1		$\|321\rangle$	
	2	0		$\|320\rangle$	
	2	-1		$\|31\bar{1}\rangle$	
	2	-2		$\|32\bar{2}\rangle$	
		...			

5. Electron density distribution.

We recall from first principles that:

$$\begin{aligned} |\psi_{nlm}(\mathbf{r})|^2\, d\mathbf{r} &= [R_{nl}(r)]^2\, |Y_{lm}(\theta,\varphi)|^2 d\varphi \sin\theta d\theta\, r^2 dr \\ &= |Y_{lm}(\Omega)|^2 d\Omega \cdot [R_{nl}(r)]^2\, r^2 dr \\ &= \text{probability of finding in } d\mathbf{r} \text{ the electron in state } \psi_{nlm}. \end{aligned} \tag{111}$$

Here Ω is a shorthand for θ, φ. Upon integration over all angles, we find the *radial probability*, i.e. the probability of finding the electron in a spherical shell of thickness dr, independently of angles θ, φ. If the spherical harmonics Y_{lm} are normalized to 1, we are left with:

$$\int_\Omega d\Omega\, |Y_{lm}(\Omega)|^2 \cdot [R_{nl}(r)]^2\, r^2 dr = [R_{nl}(r)]^2\, r^2 dr = P_{nl}(r) dr, \tag{112}$$

where:

$$P_{nl}(r) = [R_{nl}(r)]^2\, r^2 \tag{113}$$

is the radial probability density.

Figure 4.6 gives the radial probability densities for the first few states of the H atom ($Z = 1$).

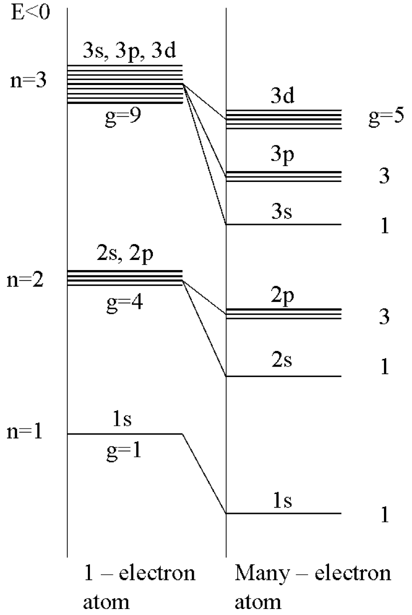


Figure 4.5 Diagram of orbital energies for the hydrogen-like atom compared to that of the many-electron atom (not in scale).

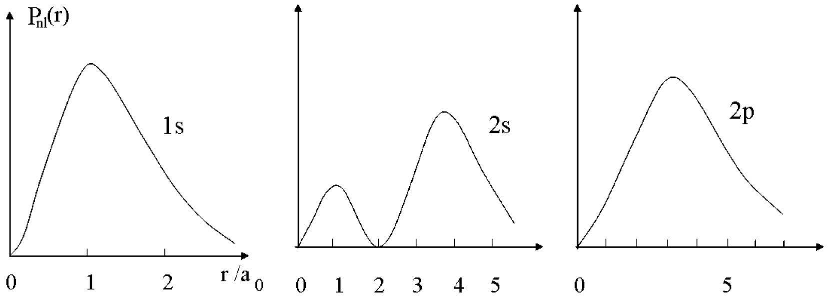


Figure 4.6 Radial probability densities for the H atom.

4.7 PROPERTIES OF GROUND AND EXCITED STATES

4.7.1 1*s* Ground State

The normalized hydrogen-like AO for the 1*s* ground state is:

$$\psi_{1s} = |100\rangle = 1s = \left(\frac{c^3}{\pi}\right)^{1/2} \exp(-cr) \quad c = Z. \tag{114}$$

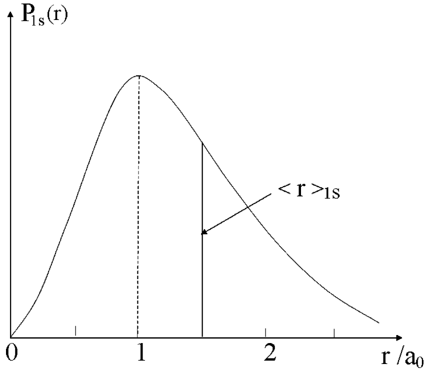


Figure 4.7 Radial probability density for H(1*s*).

1. Radial probability density of state 1*s*.

$$P(r) = \exp(-2cr)\,r^2$$

$$\frac{dP(r)}{dr} = \exp(-2cr)(2r - 2cr^2)$$

$$\frac{d^2P(r)}{dr^2} = \exp(-2cr)(2 - 8cr + 4c^2r^2).$$

2. Find the value of r for which we have the maximum probability density.

$$\frac{dP}{dr} = 0 \Longrightarrow cr = 1 \Longrightarrow r = \frac{1}{c}$$

$$\left(\frac{d^2P}{dr^2}\right)_{cr=1} = \exp(-2)(2 - 8 + 4) = -2\exp(-2) < 0.$$

Since the second derivative is negative, $cr = 1$ is a true maximum. For the H atom, $c = Z = 1$, $r_{\text{max}} = 1$ which is the Bohr radius.

3. Average distance of the 1*s*-electron from the nucleus.

$$\langle r\rangle_{1s} = \langle 1s|r|1s\rangle = \frac{c^3}{\pi}\cdot 4\pi\int_0^{\infty} dr\,r^2\cdot r\exp(-2cr) = \frac{3}{2c}.$$

In the H-atom ground state, the probability density has a maximum for $a_0 = 1$ (Bohr radius), while the average electron radius is larger, $1.5\,a_0$. The radial probability density for H(1*s*) is plotted against r in Figure 4.7.

4.7.2 Excited $2p$ State

The normalized hydrogen-like excited $2p$ state is:

$$\psi_{2p_z} = |210\rangle = \left(\frac{c^5}{\pi}\right)^{1/2} \exp(-cr) r \cos\theta \quad 2c = Z. \tag{115}$$

1. Radial probability density of state $2p$.

$$\begin{aligned}
&P(r) = \exp(-2cr)\, r^4 \\
&\frac{dP}{dr} = \exp(-2cr)(4r^3 - 2cr^4) \\
&\frac{d^2P}{dr^2} = \exp(-2cr)(12r^2 - 16cr^3 + 4c^2r^4) \\
&\frac{dP}{dr} = 0 \Longrightarrow cr = 2 \Longrightarrow r = \frac{2}{c}.
\end{aligned}$$

For the H atom, $2c = Z = 1$, $r_{\text{max}} = 4$, so that the greatest probability of finding the electron in state $2p$ is at $r = 4a_0$, i.e. 4 times larger than the ground state value.

2. Average distance of the $2p$ electron from the nucleus.

$$\begin{aligned}
\langle r\rangle_{2p} = \langle 2p|r|2p\rangle &= \frac{c^5}{\pi} \cdot 2\pi \int_{-1}^{1} dx\, x^2 \int_0^\infty dr\, r^2 \cdot r \cdot \exp(-2cr)\, r^2 \\
&= 2c^5 \cdot \frac{2}{3} \int_0^\infty dr r^5 \exp(-2cr) = \frac{4}{3} c^5 \cdot \frac{5!}{(2c)^6} = \frac{5}{2c},
\end{aligned}$$

where we have put, as usual, $\cos\theta = x$ in the integral over θ.

In the H atom, the average distance from the nucleus of the electron in the excited $2p$ state is $5a_0$, larger than the most probable distance, $4a_0$ (Figure 4.8).

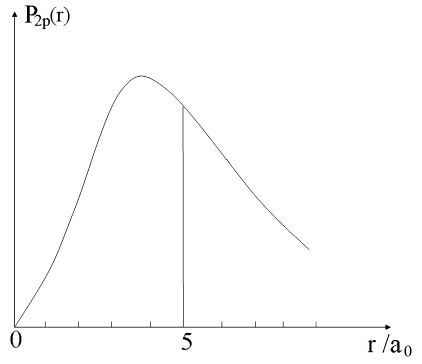


Figure 4.8 Radial probability density for H($2p$).

4.8 EXPECTATION VALUES FOR GROUND AND FIRST EXCITED STATES

Some expectation values (in atomic units) for ground and excited states of the hydrogen-like atom have been collected in Table 4.2.

• Comments

1. In the ground state, the average distance of the electron from the nucleus is greater than its most probable distance ($=1/Z$).
2. In the excited states, the average distance of the electron from the nucleus is greater than that of the ground state.
3. On the average, the electron is nearer to the nucleus in the $2p$ rather than in the $2s$ state.
4. Increasing Z, the electron is nearer to the nucleus for any state.
5. Diamagnetic susceptibility is proportional to $\langle r^2\rangle$. In the excited states it is hence much greater than in the ground state (e.g., in the $2p$ state it is ten times larger than in the $1s$ state).
6. Nuclear attraction is proportional to the nuclear charge, and in the ground state it is four times larger than in the first excited state.
7. Average kinetic energy is repulsive, and in the ground state it is four times larger than in the first excited state.
8. The virial theorem holds:

$$E=-\langle T\rangle=\frac{1}{2}\langle V\rangle.$$

9. We notice that while average values of positive powers of r are different for excited states of different symmetry, the average value of the reciprocal of the distance of the electron from the nucleus is the same for states $2s$ and $2p$. This is due to the fact that $\langle r^{-1}\rangle$ appears in the potential energy expression, whose average value is related to total energy through the virial theorem 8, and the total energy is degenerate for $n=2$ (i.e. *different* states have the *same* energy, hence the same average nuclear attraction).

Table 4.2.

Some expectation values (a.u.) for the H atom

State	$\langle r\rangle$	$\langle r^2\rangle$	$\langle r^{-1}\rangle$	$\langle V\rangle$	$\langle T\rangle$	E
$1s=\lvert 100\rangle$	$\frac{3}{2Z}$	$\frac{3}{Z^2}$	Z	$-Z^2$	$\frac{Z^2}{2}$	$-\frac{Z^2}{2}$
$2s=\lvert 200\rangle$	$\frac{6}{Z}$	$\frac{42}{Z^2}$	$\frac{Z}{4}$	$-\frac{Z^2}{4}$	$\frac{Z^2}{8}$	$-\frac{Z^2}{8}$
$2p=\lvert 210\rangle$	$\frac{5}{Z}$	$\frac{30}{Z^2}$	$\frac{Z}{4}$	$-\frac{Z^2}{4}$	$\frac{Z^2}{8}$	$-\frac{Z^2}{8}$

10. On the average, nuclear attraction overcomes repulsion due to kinetic energy (in a ratio determined by the virial theorem), and the electron is bound either in the ground state or in the first $2s$ and $2p$ excited states.

4.9 SLATER AND GAUSSIAN ATOMIC ORBITALS

The great majority of quantum chemical calculations on atoms and molecules is based on the use of a basis of atomic orbitals (AOs) which have a radial dependence which is different from that of the hydrogenic AOs we have seen so far. They can be distinguished in two classes according if their decay with the radial variable r is exponential (Slater-type orbitals, STOs) or Gaussian (Gaussian-type orbitals, GTOs). We now give some general definitions of both kinds of AOs and some simple atomic (1-centre) 1-electron integrals which will be needed in the next Chapter.

4.9.1 Slater Orbitals (STOs)

STOs were introduced long ago by Slater (1930) and Zener (1930), and extensively used by Roothaan (1951b) in developing his fundamental work on molecular integrals. Slater showed that for many purposes only the term with the highest power of r in the hydrogen-like $R_{nl}(r)$ is of importance for practical calculations. Zener suggested replacing the hydrogenic orbital exponent $c = Z/n$ by an effective nuclear charge $(Z - s)$ seen by the electron, and which is less than the true nuclear charge Z by a quantity s called the screening constant. This gives AOs which are more diffuse than the original hydrogen-like AOs. The Zener approach has today been replaced by the variational determination of the orbital exponents c, as we shall see in the next Chapter. One of the major difficulties of STOs is that the excited STOs within a given angular symmetry are no longer orthogonal to their lowest terms. As we shall see, this is particularly troublesome for ns orbitals ($n > 1$), which lack the cusp which is characteristic of all s orbitals. Furthermore, multicentre integrals over STOs are difficult to evaluate.

Retaining only the highest $(n - l - 1)$ power of r in the polynomial (58) defining $R_{nl}(r)$, the dependence on l is lost and we obtain for the general STO in *real* form:

$$\chi_{nlm}(r,\theta,\varphi) = |nlm\rangle = Nr^{n-1}\exp(-cr)\,Y_{lm}^{c,s}(\theta,\varphi) = R_n(r)\,Y_{lm}^{c,s}(\theta,\varphi), \tag{116}$$

where N is a normalization factor. Here:

$$R_n(r) = N_n r^{n-1}\exp(-cr) \quad (c > 0) \tag{117}$$

is the normalized radial part,

$$Y_{lm}^{c,s}(\theta,\varphi) = N_\Omega P_l^m(x)\begin{cases}\cos m\varphi \\ \sin m\varphi\end{cases} \quad m \geq 0 \tag{118}$$

the normalized angular part in *real* form. As usual, we use Ω to denote the couple of angular variables θ, φ.

Separate normalization of radial and angular part gives:

$$N_n = \left(\frac{(2c)^{2n+1}}{(2n)!}\right)^{1/2}, \qquad N_\Omega = \left(\frac{2l+1}{2\pi(1+\delta_{0m})}\,\frac{(l-m)!}{(l+m)!}\right)^{1/2} \tag{119}$$

so that the overall normalization factor for the general STO (116) will be:

$$N = N_n N_\Omega = \left[\frac{(2c)^{2n+1}}{(2n)!}\cdot\frac{1}{\pi(1+\delta_{0m})}\cdot\frac{2l+1}{2}\,\frac{(l-m)!}{(l+m)!}\right]^{1/2}. \tag{120}$$

We must remember that:

$$\int_0^\infty dr\, r^n \exp(-ar) = \frac{n!}{a^{n+1}} \tag{121}$$

with $n =$ non-negative integer and $a =$ real positive;

$$\int_0^{2\pi} d\varphi \begin{matrix}\cos^2 m\varphi\\ \sin^2 m\varphi\end{matrix} = \pi(1+\delta_{0m}) \tag{122}$$

$$\int_{-1}^{1} dx\, [P_l^m(x)]^2 = \frac{2}{2l+1}\,\frac{(l+m)!}{(l-m)!} \qquad m = |m| \geq 0. \tag{123}$$

The off-diagonal matrix element over STOs of the atomic 1-electron hydrogenic Hamiltonian is:

$$\begin{aligned} h_{\chi'\chi} &= \left\langle R'Y' \left| -\frac{1}{2}\nabla^2 - \frac{Z}{r} \right| RY \right\rangle \\ &= S_{n'l'm',nlm} \left\{ \frac{l(l+1) - n(n-1)}{(n+n')(n+n'-1)}\,\frac{(c+c')^2}{2} \right. \\ &\qquad \left. + \,(nc - Z)\,\frac{c+c'}{n+n'} - \frac{c^2}{2} \right\}, \end{aligned} \tag{124}$$

where $S_{n'l'm',nlm}$ is the non-orthogonality integral given by:

$$\begin{aligned} S_{n'l'm',nlm} &= \langle n'l'm' | nlm \rangle \\ &= \delta_{ll'}\,\delta_{mm'}\,\frac{(n+n')!}{\sqrt{(2n)!\,(2n')!}}\left(\frac{c}{c'}\right)^{\frac{n-n'}{2}}\left(\frac{2(cc')^{1/2}}{c+c'}\right)^{n+n'+1}. \end{aligned} \tag{125}$$

The diagonal element of the Hamiltonian is:

$$h_{\chi\chi} = \left\langle RY \left| -\frac{1}{2}\nabla^2 - \frac{Z}{r} \right| RY \right\rangle = \frac{c^2}{2} \frac{n + 2l(l+1)}{n(2n-1)} - \frac{Zc}{n}. \tag{126}$$

For $c = \frac{Z}{n}$ (hydrogenic AOs):

$$h_{\chi\chi} = -\frac{Z^2}{2n^2} \frac{4n^2 - 3n - 2l(l+1)}{n(2n-1)}, \tag{127}$$

where the last factor on the right is 1 only for the lowest AOs of each symmetry ($l = 0, 1, 2, \cdots$), since in this case STOs and hydrogenic AOs coincide.

4.9.2 Gaussian Orbitals (GTOs)

Gaussian orbitals (GTOs) are largely used today in atomic and molecular computations because of their greater simplicity in computing multicentre molecular integrals. GTOs were originally introduced by Boys (1950) and McWeeny (1950) mostly for computational reasons. In today molecular calculations it is customary to fit STOs in terms of GTOs, which requires rather lengthy expansions (see the variety of Pople's bases in Chapter 7), or to minimize the deviation between STOs and GTOs as done by Huzinaga (1965). Some failures of GTOs with respect to STOs are discussed briefly in the next Chapter.
The most common Gaussian orbitals are given in the form of spherical or Cartesian functions. We shall give here some formulae which are of interest to us, while for details the reader is referred to elsewhere (Cook, 1974; Saunders, 1975, 1983).

(i) Spherical Gaussians.

For spherical GTOs it will be sufficient to consider the radial part of the orbital, since the angular part is the same as that for STOs.

$$R_n(r) = N_n r^{n-1} \exp(-cr^2) \quad (c > 0) \tag{128}$$

$$N_n = \left(\frac{2^{n+1}(2c)^{n+\frac{1}{2}}}{(2n-1)!!\sqrt{\pi}} \right)^{1/2}, \tag{129}$$

where:

$$\begin{aligned} &(2n-1)!! = (2n-1)(2n-3)\cdots 3\cdot 1 = \frac{(2n)!}{2^n n!} = \frac{(2n)!}{(2n)!!} \\ &(-1)!! = 0!! = 1 \end{aligned} \tag{130}$$

is the double factorial.

The normalization factor (129) is easily derived from the general integral:

$$\int_0^\infty dr\, r^n \exp(-ar^2) = \frac{(n-1)!!}{(2a)^{\frac{n+1}{2}}} \sigma(n), \tag{131}$$

where:

$$\sigma(n) = \sqrt{\frac{\pi}{2}} \quad \text{for} \quad n = \text{even}, \qquad \sigma(n) = 1 \quad \text{for} \quad n = \text{odd}. \tag{132}$$

The normalized spherical Gaussian orbital will then be written as:

$$|nlm\rangle = G(nlm, c) = N r^{n-1} \exp(-cr^2)\, Y_{lm}^{c,s}(\theta, \varphi), \tag{133}$$

where the normalization factor is:

$$N = N_n N_\Omega \tag{134}$$

with N_n given by (129) and N_Ω by (119).

The general matrix element of the atomic 1-electron hydrogenic Hamiltonian is:

$$\begin{aligned} h_{G'G} &= \left\langle G'(n'l'm', c') \left| -\frac{1}{2}\nabla^2 - \frac{Z}{r} \right| G(nlm, c) \right\rangle \\ &= \delta_{ll'}\, \delta_{mm'} \frac{(2c + 2c')^{-1}}{\sqrt{(2n-1)!!\,(2n'-1)!!}} \\ &\quad \times \left[\frac{2}{\pi} \left(\frac{c}{c'} \right)^{\frac{n-n'}{2}} \left(\frac{2(cc')^{1/2}}{c + c'} \right)^{n+n'+1} \right]^{1/2} \\ &\quad \times \big\{ \big[2\,(l(l+1) - n(n-1))\,(n + n' - 3)!!\,(c + c')^2 \\ &\quad + 2(2n+1)(n + n' - 1)!!\, c(c + c') \\ &\quad - 2(n + n' + 1)!!\, c^2 \big] \sigma(n + n') \\ &\quad - 2\sqrt{2}\, Z(n + n' - 2)!!\,(c + c')^{3/2} \sigma(n + n' - 1) \big\} \end{aligned} \tag{135}$$

a rather complicated unsymmetrical formula, with the diagonal element ($c' = c$):

$$\begin{aligned} h_{GG} &= \left\langle G(nlm, c) \left| -\frac{1}{2}\nabla^2 - \frac{Z}{r} \right| G(nlm, c) \right\rangle \\ &= \frac{1}{\sqrt{2\pi}}\, \frac{c}{(2n-1)!!} \left\{ [4\,(l(l+1) - n(n-1))\,(2n-3)!! \right. \\ &\quad \left. +\ (2n+1)!!] \sqrt{\frac{\pi}{2}} - 4Z(2n-2)!!\, c^{-1/2} \right\}. \end{aligned} \tag{136}$$

For spherical GTOs there is no longer proportionality between matrix elements of the atomic 1-electron hydrogenic Hamiltonian $\hat{h}$ and non-orthogonality integral S.

For $1s$ spherical GTOs with different orbital exponents formula (135) gives:

$$n = n' = 1 \qquad l = m = 0$$

$$h_{G'G} = \langle G(100, c')|\,\hat{h}\,|G(100, c)\rangle$$

$$= \sqrt{\frac{2^3 \cdot 3^2\,(cc')^{7/2}}{(c+c')^5}} - Z\sqrt{\frac{2^5(cc')^{3/2}}{(c+c')^2\pi}} \tag{137}$$

and, if $c' = c$:

$$h_{GG} = \left\langle G(100, c)\left|-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right|G(100, c)\right\rangle = \frac{3}{2}\,c - Z\left(\frac{8c}{\pi}\right)^{1/2}. \tag{138}$$

(ii) Cartesian Gaussians.

Un-normalized Cartesian Gaussians are best written as:

$$G_{uvw}(c) = x^u y^v z^w \exp(-cr^2) = x^u y^v z^w \exp\bigl[-c(x^2 + y^2 + z^2)\bigr], \tag{139}$$

where u, v, w are non-negative integers, the non-orthogonality integral between GTOs being:

$$S_{u'v'w',uvw} = \langle G'_{u'v'w'}(c')|G_{uvw}(c)\rangle$$

$$= \frac{(2U-1)!!\,(2V-1)!!\,(2W-1)!!}{(2c+2c')^{U+V+W}}\left(\frac{\pi}{c+c'}\right)^{3/2}, \tag{140}$$

where:

$$2U = u + u', \qquad 2V = v + v', \qquad 2W = w + w'. \tag{141}$$

The normalization factor of GTO (139) is then:

$$N = \left[\frac{(4c)^{U+V+W}}{(2U-1)!!\,(2V-1)!!\,(2W-1)!!}\left(\frac{2c}{\pi}\right)^{3/2}\right]^{1/2}. \tag{142}$$

4.10 PROBLEMS 4

4.1. Find the transformation for the two-particle Hamiltonian from Cartesian to centre-of-mass and internal coordinates.

Answer:

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_X^2 - \frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}, \tag{3}$$

where: $M = m_1 + m_2$ is the total mass, $m = \frac{m_1 m_2}{m_1 + m_2}$ the reduced mass of the nucleus + electron system, ∇_X^2 and ∇^2 the Laplacian operators in the centre-of mass (X, Y, Z) and internal (x, y, z) coordinate systems.

Hint:
Find the relations between the Cartesian coordinates $(x_1, y_1, z_1;\ x_2, y_2, z_2)$ of the two particles and the coordinates (X, Y, Z) of the centre-of-mass and (x, y, z) of the electron relative to the nucleus.

4.2. Find the differential equation for $P(r)$.

Answer:

$$\frac{d^2P}{dr^2} + \left[2\left(E + \frac{Z}{r}\right) - \frac{l\,(l+1)}{r^2}\right]P = 0. \tag{31}$$

Hint:
From $R(r) = r^{-1}P(r)$, evaluate first and second derivatives of $R(r)$ with respect to r, then substitute into the differential equation (29).

4.3. Give an elementary derivation of Euler's formula.

Answer:

$$\exp(i\alpha) = \cos\alpha + i\ \sin\alpha.$$

Hint:
Use series expansions for exponential and trigonometric functions.

4.4. Find the differential equation for $P(x)$.

Answer:

$$\frac{d^2P}{dx^2} + \left(-1 + \frac{2n}{x} - \frac{l(l+1)}{x^2}\right)P = 0. \tag{43}$$

Hint:
Change variable to $x = \frac{Z}{n} r$, pose $E = -\frac{Z^2}{2n^2} < 0$, and evaluate first and second derivatives of $P(r)$, recalling that $\frac{d}{dr} = \frac{d}{dx}\frac{dx}{dr}$, $\frac{d^2}{dr^2} = \frac{d}{dx}\left(\frac{d}{dx}\frac{dx}{dr}\right)\left(\frac{dx}{dr}\right)$.

4.5. Find the differential equation satisfied by $F(x)$.

Answer:

$$x\,\frac{d^2F}{dx^2} + [(2l+2) - 2x]\,\frac{dF}{dx} + 2(n-l-1)F = 0. \tag{47}$$

Hint:
Evaluate first and second derivatives of (46).

4.6. Find the radial functions $R_{nl}(x)$ of the hydrogen-like system up to $n = 3$ and $l = 2$, and draw the corresponding plots of R_{nl} against x.

Answer:

$$R_{10} = \exp(-x)a_0 \qquad R_{20} = \exp(-x)(1-x)a_0$$
$$R_{30} = \exp(-x)\left(1 - 2x + \frac{2}{3}x^2\right)a_0$$
$$R_{21} = \exp(-x)xa_0 \qquad R_{31} = \exp(-x)x\left(1 - \frac{1}{2}x\right)a_0$$
$$R_{32} = \exp(-x)x^2a_0.$$

Hint:
Use equation (58) for the different values of the principal quantum number n and the angular quantum number l.

4.7. Verify that the first few radial solutions $R_{nl}(x)$ for $n = 1, 2$ and $l = 0, 1$ do satisfy the corresponding differential equation in x.

4.8. Find the differential equation for $\Theta(x)$.

Answer:

$$(1-x^2)\,\frac{d^2\Theta}{dx^2} - 2x\,\frac{d\Theta}{dx} + \left(\lambda - \frac{m^2}{1-x^2}\right)\Theta = 0. \tag{69}$$

Hint:
Evaluate first and second derivatives of $\Theta(x)$, by recalling that $\frac{d}{d\theta} = \frac{d}{dx}\frac{dx}{d\theta}$, and $\frac{d^2}{d\theta^2} = \frac{d}{dx}\left(\frac{d}{dx}\frac{dx}{d\theta}\right)\left(\frac{dx}{d\theta}\right)$.

4.9. Verify the asymptotic solution for $\Theta(x)$.

Answer:

$$\Theta(x) = (1-x^2)^{\frac{m}{2}} \quad m = |m| \geq 0. \tag{71}$$

Hint:
Evaluate first and second derivatives of $\Theta(x)$, then substitute into the differential equation (70).

4.10. Find the differential equation for $G(x)$.

Answer:

$$(1-x^2)\,\frac{d^2G}{dx^2} - 2(m+1)x\,\frac{dG}{dx} + (\lambda - m(m+1))\,G = 0. \tag{73}$$

Hint:
Evaluate first and second derivatives of $\Theta(x)$ in equation (72).

4.11. Find the angular functions $\Theta_{lm}(x)$ up to $l = m = 3$.

Answer:

$$\Theta_{00} = a_0 \qquad \Theta_{10} = x\,a_1 \qquad \Theta_{20} = (1-3x^2)a_0 \qquad \Theta_{30} = \left(x - \tfrac{5}{3}x^3\right)a_1$$
$$\Theta_{11} = (1-x^2)^{1/2}a_0 \qquad \Theta_{21} = (1-x^2)^{1/2}x\,a_1$$
$$\Theta_{31} = (1-x^2)^{1/2}(1-5x^2)a_0$$
$$\Theta_{22} = (1-x^2)a_0 \qquad \Theta_{32} = (1-x^2)x\,a_1$$
$$\Theta_{33} = (1-x^2)^{3/2}a_0.$$

Hint:
Use equations (92) and (93) for the different values of the angular quantum numbers l and $m = |m|$.

4.12. Verify that the first few angular functions $\Theta_{lm}(x)$ for $l = 1, 2$ and $m = 0, 1, 2$ do satisfy the differential equation (69) with $\lambda = l(l+1)$.

4.13. Find the first few Legendre and associated Legendre polynomials.

Hint:
Start from the definitions of Legendre ($m = 0$) and associated Legendre ($m \neq 0$) polynomials $P_l^m(x)$.

4.14. Find the corresponding factors between $\Theta_{lm}(x)$ and $P_l^m(x)$ for Θ_{20}, Θ_{30} and Θ_{21}.

Answer:

$$\begin{aligned} &l = 2, \quad m = 0 \qquad a_0 = -\frac{1}{2} \\ &l = 3, \quad m = 0 \qquad a_1 = -\frac{3}{2} \\ &l = 2, \quad m = 1 \qquad a_1 = 3. \end{aligned}$$

Hint:
Use equation (94) and the normalization condition.

4.11 SOLVED PROBLEMS

4.1. The transformation for the two-particle system is:

$$(x_1, y_1, z_1;\ x_2, y_2, z_2) \longrightarrow (X, Y, Z;\ x, y, z),$$

where the first set on the r.h.s. denotes centre-of-mass coordinates, and the second gives the Cartesian coordinates of the electron with respect to the nucleus taken as origin of the second coordinate system. We have further:

$$M = m_1 + m_2 \quad \text{total mass of the system}$$

$$m = \frac{m_1 m_2}{m_1 + m_2} \quad \text{reduced mass of the system.}$$

For the x-component we can write:

$$x = x_2 - x_1 \qquad MX = m_1 x_1 + m_2 x_2.$$

The inverse transformations are hence derived from the inhomogeneous system:

$$\begin{cases} m_1 x_1 + m_2 x_2 = MX \\ -x_1 + \quad x_2 = x \end{cases} \qquad D = \begin{vmatrix} m_1 & m_2 \\ -1 & 1 \end{vmatrix} = m_1 + m_2 = M,$$

where D is the determinant of the coefficients. Solutions are obtained by use of Cramer's rule:

$$x_1 = \frac{1}{M}\begin{vmatrix} MX & m_2 \\ x & 1 \end{vmatrix} = X - \frac{m_2}{M}\,x$$

$$x_2 = \frac{1}{M}\begin{vmatrix} m_1 & MX \\ -1 & x \end{vmatrix} = X + \frac{m_1}{M}\,x.$$

Then:

$$\begin{aligned} T &= \frac{m_1}{2}\,\dot{x}_1^2 + \frac{m_2}{2}\,\dot{x}_2^2 = \frac{m_1}{2}\left(\dot{X} - \frac{m_2}{M}\,\dot{x}\right)^2 + \frac{m_2}{2}\left(\dot{X} + \frac{m_1}{M}\,\dot{x}\right)^2 \\ &= \frac{m_1+m_2}{2}\,\dot{X}^2 + \frac{m_1 m_2(m_1+m_2)}{2M^2}\,\dot{x}^2 = \frac{M}{2}\,\dot{X}^2 + \frac{m}{2}\,\dot{x}^2. \end{aligned}$$

The same is true for the remaining y and z-components, so that the classical kinetic energy in the r.h.s. system of coordinates will be:

$$T = \frac{M}{2}\left(\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2\right) + \frac{m}{2}\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right) = \frac{1}{2M}\,P_X^2 + \frac{1}{2m}\,p^2$$

which is the kinetic energy of a particle of mass M placed in the centre-of-mass plus the kinetic energy of a particle of mass m in internal coordinates.

Introducing the momentum operators:

$$\hat{\mathbf{P}} = -\,i\,\hbar\,\nabla_X, \qquad \hat{\mathbf{p}} = -\,i\,\hbar\,\nabla$$

we obtain for the Hamiltonian operator of the two-particle nucleus+electron system:

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_X^2 - \frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\,\frac{Ze^2}{r},$$

where the last term is the Coulomb attraction of the electron by the nucleus in SI units.

4.2. The differential equation for $P(r)$.

We put:

$$R(r) = r^{-1}P(r).$$

We take first and second derivatives of $R(r)$:

$$\begin{aligned}
\frac{dR}{dr} &= r^{-1}\frac{dP}{dr} - r^{-2}P = R' \\
\frac{d^2R}{dr^2} &= r^{-1}\frac{d^2P}{dr^2} - r^{-2}\frac{dP}{dr} - r^{-2}\frac{dP}{dr} + 2r^{-3}P \\
&= r^{-1}\frac{d^2P}{dr^2} - 2r^{-2}\frac{dP}{dr} + 2r^{-3}P = R''.
\end{aligned}$$

Therefore, substituting into equation (29):

$$R'' + 2r^{-1}R' + \left[2\left(E + \frac{Z}{r}\right) - \frac{l\,(l+1)}{r^2}\right]R = 0$$

we obtain:

$$\begin{aligned}
&r^{-1}P'' - 2r^{-2}P' + 2r^{-3}P + 2r^{-2}P' - 2r^{-3}P \\
&\quad + \left[2\left(E + \frac{Z}{r}\right) - \frac{l\,(l+1)}{r^2}\right]r^{-1}P = 0 \\
&P'' + \left[2\left(E + \frac{Z}{r}\right) - \frac{l\,(l+1)}{r^2}\right]P = 0
\end{aligned}$$

which is the required equation (31).

4.3. Euler's formula.

We use the series expansions for $\exp(i\alpha)$, $\cos\alpha$, $\sin\alpha$:

$$\begin{aligned}
\exp(i\alpha) &= 1 + i\,\alpha + \frac{(i\,\alpha)^2}{2!} + \frac{(i\,\alpha)^3}{3!} + \frac{(i\,\alpha)^4}{4!} + \cdots \\
&= 1 + i\,\alpha - \frac{\alpha^2}{2!} - i\,\frac{\alpha^3}{3!} + \frac{\alpha^4}{4!} + \cdots \\
&= \left(1 - \frac{\alpha^2}{2!} + \frac{\alpha^4}{4!} + \cdots\right) + i\left(\alpha - \frac{\alpha^3}{3!} + \frac{\alpha^5}{5!} + \cdots\right) \\
&= \cos\alpha + i\,\sin\alpha.
\end{aligned}$$

4.4. Differential equation for $P(x)$.

The differential equation (31):

$$\frac{d^2P}{dr^2} + \left[2\left(E + \frac{Z}{r}\right) - \frac{l\,(l+1)}{r^2}\right]P = 0$$

can be simplified by posing:

$$x = \frac{Z}{n} r \qquad \frac{dx}{dr} = \frac{Z}{n} = \text{constant.}$$

Then:

$$\frac{d}{dr} = \frac{d}{dx}\frac{dx}{dr} = \frac{Z}{n}\frac{d}{dx}$$

$$\frac{d^2}{dr^2} = \frac{d}{dx}\left(\frac{d}{dx}\frac{dx}{dr}\right)\left(\frac{dx}{dr}\right) = \left(\frac{dx}{dr}\right)^2 \frac{d^2}{dx^2} = \frac{Z^2}{n^2}\frac{d^2}{dx^2}.$$

Substituting we find the differential equation in x:

$$\frac{Z^2}{n^2}\frac{d^2P(x)}{dx^2} + \left[2E + \frac{Z^2}{n^2}\cdot\frac{2n}{x} - \frac{Z^2}{n^2}\frac{l(l+1)}{x^2}\right]P(x) = 0.$$

By posing $2E = -\frac{Z^2}{n^2} < 0$, we obtain:

$$\frac{Z^2}{n^2}\frac{d^2P(x)}{dx^2} + \left[-\frac{Z^2}{n^2} + \frac{Z^2}{n^2}\cdot\frac{2n}{x} - \frac{Z^2}{n^2}\frac{l(l+1)}{x^2}\right]P(x) = 0$$

so that we can finally obtain equation (43):

$$\frac{d^2P}{dx^2} + \left[-1 + \frac{2n}{x} - \frac{l(l+1)}{x^2}\right]P = 0.$$

4.5. Differential equation for $F(x)$.

We calculate first and second derivatives of equation (46):

$$P(x) = \exp(-x)\,x^{l+1}\,F(x)$$

$$P'(x) = \exp(-x)\{x^{l+1}\,F' + [(l+1)x^l - x^{l+1}]F\}$$

$$\begin{aligned} P''(x) = \exp(-x)\{&x^{l+1}\,F'' + [(2l+2)x^l - 2x^{l+1}]F' \\ &+ [x^{l+1} - (2l+2)x^l + l(l+1)x^{l-1}]F\}. \end{aligned}$$

Substituting into differential equation (43) and eliminating $\exp(-x)\,x^l$, we find:

$$x\,F'' + [(2l+2) - 2x]\,F' + 2\,(n-l-1)\,F = 0$$

which is the required equation (47).

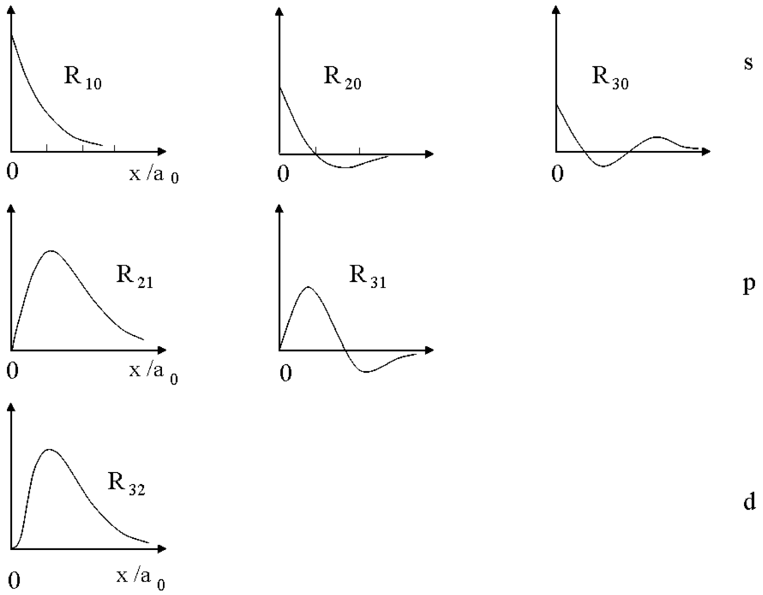


Figure 4.9 Plots of the first $R_{nl}(x)$ radial functions.

4.6. First radial functions for the hydrogen-like atom.

Equation (58) gives for the different values of n and l:

$$n = 1, \quad l = 0 \qquad R_{10} = \exp(-x)a_0$$

$$n = 2, \quad l = 0 \qquad a_1 = -a_0 \qquad \begin{aligned} R_{20} &= \exp(-x)(a_0 + a_1 x) \\ &= \exp(-x)(1 - x)a_0 \end{aligned}$$

$$n = 3, \quad l = 0 \qquad a_1 = -2a_0, \qquad a_2 = -\frac{1}{3}a_1 = \frac{2}{3}a_0$$

$$R_{30} = \exp(-x)(a_0 + a_1 x + a_2 x^2) = \exp(-x)\left(1 - 2x + \frac{2}{3}x^2\right)a_0$$

which are the radial functions for ns, and a_0 is a normalization factor.

$$n = 2, \quad l = 1 \qquad R_{21} = \exp(-x)x\, a_0$$

$$n = 3, \quad l = 1 \qquad a_1 = -\frac{1}{2}a_0$$

$$R_{31} = \exp(-x)x(a_0 + a_1 x) = \exp(-x)x\left(1 - \frac{1}{2}x\right)a_0$$

which are the radial functions for np.

$$n=3, \quad l=2 \qquad R_{32}=\exp(-x)x^2a_0 \qquad 3d \text{ function.}$$

We notice that all ns functions are characterized by a cusp at the origin.

4.7. Using $x=\frac{Z}{n}r$ and $E=-\frac{Z^2}{2n^2}$, equation (29) transforms to:

$$\frac{d^2R}{dx^2}+\frac{2}{x}\frac{dR}{dx}+\left[-1+\frac{2n}{x}-\frac{l\,(l+1)}{x^2}\right]R=0.$$

It will then be sufficient to evaluate first and second derivatives of *un-normalized* R_{10}, R_{20} and R_{21} found in Problem 4.6 and substitute into the differential equation above.

4.7.1 $n=1,\ l=0$

$$R_{10}=\exp(-x) \qquad R'=-\exp(-x) \qquad R''=\exp(-x).$$

Substituting into the differential equation and getting rid of $\exp(-x)$:

$$1-\frac{2}{x}+\left(-1+\frac{2}{x}\right)=0.$$

4.7.2 $n=2,\ l=0$

$$R_{20}=\exp(-x)(1-x) \qquad R'=\exp(-x)(-2+x) \qquad R''=\exp(-x)(3-x)$$

$$\begin{aligned}&(3-x)+\frac{2}{x}(-2+x)+\left(-1+\frac{4}{x}\right)(1-x)\\&\quad=(3-x)+\left(-\frac{4}{x}+2\right)+\left(-1+\frac{4}{x}+x-4\right)=0.\end{aligned}$$

4.7.3 $n=2,\ l=1$

$$R_{21}=\exp(-x)x \qquad R'=\exp(-x)(1-x) \qquad R''=\exp(-x)(-2+x)$$

$$\begin{aligned}&(-2+x)+\frac{2}{x}(1-x)+\left(-1+\frac{4}{x}-\frac{2}{x^2}\right)x\\&=(-2+x)+\left(\frac{2}{x}-2\right)+\left(-x+4-\frac{2}{x}\right)=0.\end{aligned}$$

4.8. Differential equation for $\Theta(x)$.

The differential equation (65) for $\Theta(\theta)$:

$$\frac{d^2\Theta}{d\theta^2}+\cot\theta\,\frac{d\Theta}{d\theta}+\left(\lambda-\frac{m^2}{\sin^2\theta}\right)\Theta=0$$

is usually transformed into an equation for $\Theta(x)$ by posing:

$$x = \cos\theta \qquad \Theta(\theta) \to \Theta(x) \quad \frac{dx}{d\theta} = -(1-x^2)^{1/2} \quad -1 \le x \le 1.$$

Now:

$$\begin{aligned}
\frac{d}{d\theta} &= \frac{d}{dx}\frac{dx}{d\theta} = -(1-x^2)^{1/2}\frac{d}{dx} \\
\frac{d^2}{d\theta^2} &= \frac{d}{dx}\left(\frac{d}{dx}\frac{dx}{d\theta}\right)\left(\frac{dx}{d\theta}\right) \\
&= -(1-x^2)^{1/2}\left\{\left(\frac{dx}{d\theta}\right)\frac{d^2}{dx^2} + \frac{d}{dx}\left[\frac{d}{dx}\left(-(1-x^2)^{1/2}\right)\right]\right\} \\
&= -(1-x^2)^{1/2}\left\{-(1-x^2)^{1/2}\frac{d^2}{dx^2} - \frac{1}{2}(1-x^2)^{-1/2}(-2x)\frac{d}{dx}\right\} \\
&= (1-x^2)\frac{d^2}{dx^2} - x\frac{d}{dx}.
\end{aligned}$$

Hence equation (65) becomes:

$$\begin{aligned}
&(1-x^2)\frac{d^2\Theta}{dx^2} - x\frac{d\Theta}{dx} + x(1-x^2)^{-1/2}\left\{-(1-x^2)^{1/2}\frac{d}{dx}\right\}\Theta \\
&\quad + \left(\lambda - \frac{m^2}{1-x^2}\right)\Theta = 0
\end{aligned}$$

so finally giving:

$$(1-x^2)\frac{d^2\Theta}{dx^2} - 2x\frac{d\Theta}{dx} + \left(\lambda - \frac{m^2}{1-x^2}\right)\Theta = 0$$

which is the required equation (69). We notice that $x = \pm 1$ are regular singular points of the differential equation.

We open here a short digression on singular points (Ince, 1963). Given the ordinary second-order differential equation:

$$P(x)\,y'' + Q(x)\,y' + R(x)\,y = 0,$$

if $x - x_0$ is a factor of $P(x)$ but not of $Q(x)$ and $R(x)$, $x - x_0$ is said to be a singular point (or singularity) of the equation. If it is possible to reduce the differential equation to the form:

$$(x-x_0)^2 P_1(x)\,y'' + (x-x_0)Q_1(x)\,y' + R_1(x)\,y = 0$$

with $P_1(x_0) \neq 0$ and $P_1(x)$, $Q_1(x)$, $R_1(x)$ finite for $x = x_0$, then we can write:

$$y = (x - x_0)^\alpha\, F(x) = (x - x_0)^\alpha \sum_{k=0}^{\infty} a_k\, (x - x_0)^k,$$

where $x - x_0$ is now a *regular* singularity, and $F(x)$ can be expanded as a Taylor series in $x - x_0$. To determine α, we calculate first and second derivatives of y, substitute into the differential equation, and equating to zero the coefficient of $(x - x_0)^\alpha$ $(k = 0)$ we are left with the so called indicial equation:

$$\alpha(\alpha - 1)\, P_1(x) + \alpha\, Q_1(x) + R_1(x) = 0$$

which for $x = x_0$ gives the quadratic equation in α:

$$P_1(x_0)\, \alpha^2 - \{P_1(x_0) - Q_1(x_0)\}\, \alpha + R_1(x_0) = 0$$

whose roots give the two possible values of α.

4.9. Asymptotic solution for $\Theta(x)$.

It can be easily seen that the asymptotic equation for $\Theta(x)$:

$$(1 - x^2)\, \Theta'' - 2x\, \Theta' \approx \frac{m^2}{1 - x^2}\, \Theta, \tag{70}$$

where $|x| = 1$ is a regular singularity, has a solution:

$$\Theta(x) = (1 - x^2)^{\frac{m}{2}} \quad m = |m| > 0$$

which is finite for $|x| = 1$. Taking first and second derivatives of $\Theta(x)$:

$$\begin{aligned}
\Theta'(x) &= \frac{m}{2}\, (1 - x^2)^{\frac{m}{2}-1}(-2x) = -\frac{mx}{1 - x^2}\, \Theta \\
\Theta''(x) &= -m\, (1 - x^2)^{\frac{m}{2}-1} - mx\left(\frac{m}{2} - 1\right)(1 - x^2)^{\frac{m}{2}-2}(-2x) \\
&= \frac{m^2 x^2 - m x^2 - m}{(1 - x^2)^2}\, \Theta
\end{aligned}$$

so that:

$$-2x\Theta' = \frac{2mx^2}{1 - x^2}\, \Theta \qquad (1 - x^2)\Theta'' = \frac{m^2 x^2 - m x^2 - m}{1 - x^2}\, \Theta.$$

Substituting into (70) and simplifying, we find:

$$m^2 x^2 + m x^2 - m \approx m^2$$

which is true for $|x| = 1$.

4.10. Differential equation for $G(x)$.

From:

$$\Theta(x) = (1-x^2)^{\frac{m}{2}}\,G(x) \tag{72}$$

taking first and second derivatives of $\Theta(x)$:

$$\begin{aligned}
\Theta' &= \frac{m}{2}\,(1-x^2)^{\frac{m}{2}-1}(-2x)\,G + (1-x^2)^{\frac{m}{2}}\,G' \\
&= (1-x^2)^{\frac{m}{2}}\left\{G' - mx(1-x^2)^{-1}G\right\}
\end{aligned}$$

$$\begin{aligned}
\Theta'' &= \frac{m}{2}\,(1-x^2)^{\frac{m}{2}-1}(-2x)\left\{G' - mx(1-x^2)^{-1}G\right\} \\
&\quad +(1-x^2)^{\frac{m}{2}}\left\{G'' - m(1-x^2)^{-1}G\right. \\
&\quad \left. -mx\left[-(1-x^2)^{-2}(-2x)\right]G - mx(1-x^2)^{-1}G'\right\} \\
&= (1-x^2)^{\frac{m}{2}}\left\{G'' - 2mx(1-x^2)^{-1}G'\right. \\
&\quad \left. +\,(m^2x^2 - mx^2 - m)(1-x^2)^{-2}G\right\}.
\end{aligned}$$

Substituting into (69) and dividing through by $(1-x^2)^{\frac{m}{2}}$, we obtain:

$$\begin{aligned}
&(1-x^2)G'' - 2mxG' + (m^2x^2 - mx^2 - m)(1-x^2)^{-1}G \quad \text{from } \Theta'' \\
&\qquad\qquad\qquad - 2xG' + 2mx^2(1-x^2)^{-1}G \quad \text{from } \Theta' \\
&\qquad\qquad\qquad + \left\{\lambda - m^2(1-x^2)^{-1}\right\}G \quad \text{from } \Theta \\
&= (1-x^2)G'' - 2(m+1)xG' \\
&\quad + \left\{\lambda - (1-x^2)^{-1}(m^2 - 2mx^2 - m^2x^2 + mx^2 + m)\right\}G \\
&= (1-x^2)G'' - 2(m+1)xG' + \{\lambda - m(m+1)\}\,G = 0
\end{aligned}$$

which is the required equation (73).

4.11. Angular functions $\Theta_{lm}(x)$ up to $l = m = 3$.

We use equations (92) and (93) of our polynomial method for the different values of $l, m = |m|$.

$$\begin{array}{lllll}
l=0, & m=0 & l-m=0 & \Theta_{00}=a_0 & a_0=1 \\
l=1, & m=0 & l-m=1 & \Theta_{10}\sim xa_1\sim\cos\theta & a_1=1 \\
l=2, & m=0 & l-m=2 & a_2=-\dfrac{2\cdot 3}{1\cdot 2}\,a_0=-3a_0 & \\
\multicolumn{4}{l}{\Theta_{20}=a_0+a_2x^2=(1-3x^2)a_0} & a_0=-\dfrac{1}{2} \\
l=3, & m=0 & l-m=3 & a_3=\dfrac{1\cdot 2-3\cdot 4}{2\cdot 3}\,a_1=-\dfrac{5}{3}\,a_1 & \\
\multicolumn{4}{l}{\Theta_{30}=a_1x+a_3x^3=\left(x-\dfrac{5}{3}x^3\right)a_1} & a_1=-\dfrac{3}{2} \\
l=1, & m=1 & l-m=0 & \Theta_{11}=(1-x^2)^{1/2}a_0\sim\sin\theta & a_0=1 \\
l=2, & m=1 & l-m=1 & \Theta_{21}=(1-x^2)^{1/2}xa_1 & a_1=3 \\
 & & & \quad\sim\sin\theta\cos\theta & \\
l=3, & m=1 & l-m=2 & a_2=\dfrac{1\cdot 2-3\cdot 4}{1\cdot 2}\,a_0=-5\,a_0 & \\
\multicolumn{4}{l}{\Theta_{31}=(1-x^2)^{1/2}(a_0+a_2x^2)=(1-x^2)^{1/2}(1-5x^2)a_0} & a_0=-\dfrac{3}{2} \\
l=2, & m=2 & l-m=0 & \Theta_{22}=(1-x^2)a_0\sim\sin^2\theta & a_0=3 \\
l=3, & m=2 & l-m=1 & \Theta_{32}=(1-x^2)xa_1 & a_1=15 \\
l=3, & m=3 & l-m=0 & \Theta_{33}=(1-x^2)^{3/2}a_0\sim\sin^3\theta & a_0=15
\end{array}$$

The values of a_0 and a_1 are the factors giving identity between $\Theta_{lm}(x)$ and $P_l^m(x)$.

4.12. We can easily verify by direct substitution that Θ_{00}, Θ_{10}, Θ_{20} and Θ_{11} do satisfy the differential equation (69) with $\lambda = l(l+1)$:

$$(1-x^2)\,\frac{d^2\Theta}{dx^2}-2x\,\frac{d\Theta}{dx}+\left(l(l+1)-\frac{m^2}{1-x^2}\right)\Theta=0. \tag{69}$$

We evaluate first and second derivatives of the un-normalized Θ-functions found in Problem 4.11.

4.12.1 $l=0,\ m=0$

$$\Theta_{00}=a_0 \qquad \Theta'=\Theta''=0$$

will evidently satisfy equation (69).

4.12.2 $l = 1,\ m = 0$

$$\Theta_{10} = x \qquad \Theta' = 1 \qquad \Theta'' = 0 \qquad -2x + 2x = 0.$$

4.12.3 $l = 2,\ m = 0$

$$\Theta_{20} = 1 - 3x^2 \qquad \Theta' = -6x \qquad \Theta'' = -6$$

$$-6(1 - x^2) + 12x^2 + 6(1 - 3x^2) = 0.$$

4.12.4 $l = 1,\ m = 1$

$$\Theta_{11} = (1 - x^2)^{1/2} \qquad \Theta' = -x(1 - x^2)^{-1/2} \qquad \Theta'' = -(1 - x^2)^{-3/2}$$

$$-(1 - x^2)^{-1/2} + 2x^2(1 - x^2)^{-1/2} + \left(2 - \frac{1}{1 - x^2}\right)(1 - x^2)^{1/2}$$

$$= (1 - x^2)^{-1/2}(-1 + 2x^2) + (1 - 2x^2)(1 - x^2)^{-1/2} = 0.$$

4.13. Legendre polynomials.

We start from the definitions (Hobson, 1965):

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} \left(x^2 - 1\right)^l \tag{143}$$

$$P_l^m(x) = (1 - x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} P_l(x) \tag{144}$$

where:

$$x = \cos\theta \qquad m = |m| \geq 0 \qquad l - m \geq 0.$$

Equation (143) is the definition of the Legendre polynomial (degree l) and (144) of the associated Legendre polynomial (degree l and order m). Associated Legendre polynomials are orthogonal in the interval $-1 \leq x \leq 1$ and normalized to:

$$\int_{-1}^{1} dx\, P_l^m(x) P_{l'}^{m'}(x) = \delta_{ll'}\, \delta_{mm'} \frac{2}{2l + 1} \frac{(l + m)!}{(l - m)!}. \tag{145}$$

4.13.1 First few Legendre polynomials up to $l = 5$.

$$\left.\begin{array}{llll} P_0 = 1 & P_1 = x & P_2 = \dfrac{3x^2-1}{2} & P_3 = \dfrac{5x^3-3x}{2} \\ P_4 = \dfrac{35x^4-30x^2+3}{8} & & P_5 = \dfrac{63x^5-70x^3+15x}{8} & \end{array}\right\} m = 0.$$

4.13.2 First few associated Legendre polynomials up to $l = m = 5$.

$$\left.\begin{array}{lll} P_1^1 = (1-x^2)^{1/2} & P_2^1 = (1-x^2)^{1/2}3x & P_3^1 = (1-x^2)^{1/2}\dfrac{3}{2}(5x^2-1) \\ P_4^1 = (1-x^2)^{1/2}\dfrac{5}{2}(7x^3-3x) & P_5^1 = (1-x^2)^{1/2}\dfrac{15}{8}(21x^4-14x^2+1) & \end{array}\right\} m = 1$$

$$\left.\begin{array}{lll} P_2^2 = (1-x^2)3 & P_3^2 = (1-x^2)15x & P_4^2 = (1-x^2)\dfrac{15}{2}(7x^2-1) \\ P_5^2 = (1-x^2)\dfrac{105}{2}(3x^3-x) & & \end{array}\right\} m = 2$$

$$\left.\begin{array}{ll} P_3^3 = (1-x^2)^{3/2}15 & P_4^3 = (1-x^2)^{3/2}105x \\ P_5^3 = (1-x^2)^{3/2}\dfrac{105}{2}(9x^2-1) & \end{array}\right\} m = 3$$

$$\left.P_4^4 = (1-x^2)^2 105 \qquad P_5^4 = (1-x^2)^2 945x\right\} m = 4$$

$$\left.P_5^5 = (1-x^2)^{5/2}945\right\} m = 5.$$

4.14. Corresponding factors between $\Theta_{lm}(x)$ and $P_l^m(x)$ for Θ_{20}, Θ_{30} and Θ_{21}. Using equations (94) and (145) we find:

4.14.1 $\quad \Theta_{20} = (1-3x^2)a_0 \quad a_0 = -\dfrac{1}{2}$

$$\begin{aligned} \langle\Theta_{20}|\Theta_{20}\rangle &= a_0^2\int_{-1}^{1} dx\big(1-3x^2\big)^2 = a_0^2\int_{-1}^{1} dx\big(1-6x^2+9x^4\big) \\ &= a_0^2\left(2-6\cdot\frac{2}{3}+9\cdot\frac{2}{5}\right) = 2a_0^2\left(\frac{9}{5}-1\right) = \frac{8}{5}a_0^2 = \frac{2}{5} \\ 4a_0^2 = 1 &\Longrightarrow a_0 = \frac{1}{2}, \end{aligned}$$

where we have taken into account the phase factor arising from (94).

4.14.2 $\Theta_{30} = \left(x - \frac{5}{3}x^3\right)a_1 \quad a_1 = -\frac{3}{2}$

$$\begin{aligned}\langle\Theta_{30}|\Theta_{30}\rangle &= \frac{1}{9}\,a_1^2\int_{-1}^{1}dx\left(3x-5x^3\right)^2 = \frac{1}{9}\,a_1^2\int_{-1}^{1}dx\left(9x^2-30x^4+25x^6\right)\\ &= \frac{1}{9}\,a_1^2\left(9\cdot\frac{2}{3}-30\cdot\frac{2}{5}+25\cdot\frac{2}{7}\right) = \frac{2}{9}\,a_1^2\left(\frac{25}{7}-3\right) = \frac{8}{7\cdot 9}\,a_1^2\\ &= \frac{2}{7}\end{aligned}$$

$$\frac{4}{9}\,a_1^2 = 1 \Longrightarrow a_1 = \frac{3}{2}.$$

4.14.3 $\Theta_{21} = (1-x^2)^{1/2}xa_1 \quad a_1 = 3$

$$\begin{aligned}\langle\Theta_{21}|\Theta_{21}\rangle &= a_1^2\int_{-1}^{1}dx(1-x^2)x^2 = a_1^2\int_{-1}^{1}dx\left(x^2-x^4\right)\\ &= a_1^2\left(\frac{2}{3}-\frac{2}{5}\right) = \frac{4}{3\cdot 5}\,a_1^2 = \frac{2}{5}\cdot 3! = \frac{3\cdot 4}{5}\end{aligned}$$

$$\frac{1}{9}\,a_1^2 = 1 \Longrightarrow a_1 = 3.$$

– 5 –

The Variation Method

5.1 INTRODUCTION

At the beginning of Chapter 3 we have seen that the Schroedinger equation can be solved exactly only for a few physical systems, and we have studied in detail the case of the particle in a box and of the hydrogen-like system. For other applications, we must resort to methods which enable us to evaluate *approximations* to the energy of some states of the system. They are essentially two: (i) the variation method due to Rayleigh, and (ii) the perturbation method introduced by Schroedinger and known as Rayleigh–Schroedinger (RS) perturbation theory. While we postpone discussion of RS perturbation theory until Chapters 11 and 12, where we shall find it particularly adapted to deal with the problem of electric properties of molecules and intermolecular forces, we shall be mostly concerned here with the variation method, which is extremely powerful in finding *bounds* to the energy of ground and excited states of atomic and molecular systems. In Section 7 of this Chapter we shall briefly outline (iii) the principles of the so called Wentzel–Kramers–Brillouin method, which is mostly of interest in establishing in a direct way the connection between classical and quantum mechanics.

5.2 THE VARIATION METHOD

It is based on variational principles due to Rayleigh and allows us to find variational approximations to energy and wavefunction of ground and excited states of the system.

5.2.1 Variational Principles

Let φ be a normalizable (Q-class) trial (or variational) function. The φ-dependent functional:

$$\varepsilon[\varphi] = \frac{\langle\varphi|\hat{H}|\varphi\rangle}{\langle\varphi|\varphi\rangle}, \tag{1}$$

where $\hat{H}$ is the Hamiltonian of the system, is called the Rayleigh ratio. Then:

$$\varepsilon[\varphi] \geq E_0 \tag{2}$$

is the Rayleigh variational principle for the ground state, E_0 being the true ground state energy of the system;

$$\varepsilon[\varphi] \geq E_1 \quad \text{provided} \quad \langle\psi_0|\varphi\rangle = 0 \tag{3}$$

is the Rayleigh variational principle for the first excited state (orthogonal to the true ground state ψ_0), E_1 being the true energy of the first excited state, and so on. So, evaluation of the integrals in (1) under suitable constraints gives *upper bounds* to the energy of ground and excited states. Inequalities (2) and (3) can be easily proved by a formal expansion of the trial function φ into eigenstates $\{\psi_k\}$ of $\hat{H}$.

(i)
$$\varphi = \sum_k \psi_k C_k \quad C_k = \langle\psi_k|\varphi\rangle \tag{4}$$

with:

$$\hat{H}\psi_k = E_k\psi_k \quad \langle\psi_k|\psi_{k'}\rangle = \delta_{kk'}. \tag{5}$$

Then:

$$\begin{aligned}\varepsilon - E_0 = \langle\varphi|\hat{H} - E_0|\varphi\rangle &= \sum_k\sum_{k'} C_k^* C_{k'}\langle\psi_k|\hat{H} - E_0|\psi_{k'}\rangle \\ &= \sum_k\sum_{k'} C_k^* C_{k'}(E_{k'} - E_0)\delta_{kk'} = \sum_k |C_k|^2(E_k - E_0) \geq 0\end{aligned} \tag{6}$$

which proves inequality (2).

(ii)
$$\varphi=\sum_k \psi_k C_k=\psi_0\langle\psi_0|\varphi\rangle+\sum_k{}' \psi_k C_k=\sum_k{}' \psi_k C_k, \tag{7}$$

where the dash means that we must exclude from the expansion the term with $k=0$. Then:

$$\begin{aligned}\varepsilon-E_1&=\langle\varphi|\hat{H}-E_1|\varphi\rangle=\sum_k{}'\sum_{k'}{}' C_k^* C_{k'}\langle\psi_k|\hat{H}-E_1|\psi_{k'}\rangle\\&=\sum_k{}'\sum_{k'}{}' C_k^* C_{k'}(E_{k'}-E_1)\delta_{kk'}=\sum_k{}'|C_k|^2(E_k-E_1)\geq 0\end{aligned} \tag{8}$$

which proves inequality (3).

5.2.2 Properties of the Variational Solutions

(i) If:

$$\varphi=\psi_0 \qquad \varepsilon[\varphi]=E_0 \tag{9}$$

and the equality sign holds (the *true* lowest eigenvalue of $\hat{H}$).

(ii) If:

$$\varphi=\psi_0+\delta \tag{10}$$

namely, if the variational function differs from the true ψ_0 by a *small* first-order function δ, then:

$$\varepsilon-E_0=\langle\delta|\hat{H}-E_0|\delta\rangle=O(\delta^2)\geq 0, \tag{11}$$

that is the variational energy differs from the true energy by a second-order quantity. In fact:

$$\begin{aligned}\varepsilon-E_0&=\langle\varphi|\hat{H}-E_0|\varphi\rangle=\langle\psi_0+\delta|\hat{H}-E_0|\psi_0+\delta\rangle\\&=\langle\psi_0|\hat{H}-E_0|\psi_0\rangle+2\langle\delta|\hat{H}-E_0|\psi_0\rangle+\langle\delta|\hat{H}-E_0|\delta\rangle\\&=\langle\delta|\hat{H}-E_0|\delta\rangle=O(\delta^2)\geq 0\end{aligned} \tag{12}$$

which means that, in variational approximations, energy is better approximated than function.

(iii) Being based on the average value of the energy, the variational method privileges the space regions *near* to the nucleus, where the potential energy is larger (r small). Use of variationally optimized wavefunctions can give poor results for operators different from $\hat{H}$ (like the dipole moment operator $\boldsymbol{\mu}=e\mathbf{r}$, which takes large values *far* from the nucleus).

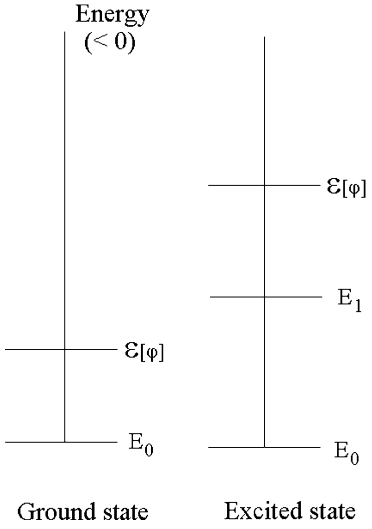


Figure 5.1 Energy upper bounds to ground and excited states.

5.2.3 Variational Approximations

The functional $\varepsilon[\varphi]$ gives an upper bound to E_0 or E_1 (Figure 5.1). The variation method consists in applying the Rayleigh variational principles to the determination of approximations to the energy and the wavefunction. Even if in some cases (see Problems 5.1 and 5.2) it is possible to get bounds to the true energy simply by imposing the boundary conditions on the variational wavefunction, usually we shall introduce in the trial function φ a number of variational parameters $\{c\}$ and minimize the energy ε with respect to these parameters:

$$\varepsilon[\varphi] = \frac{\langle\varphi|\hat{H}|\varphi\rangle}{\langle\varphi|\varphi\rangle} \frac{\int dx\varphi^*(x;c)\hat{H}\varphi(x;c)}{\int dx\varphi^*(x;c)\varphi(x;c)} = \varepsilon(c). \tag{13}$$

In this way, by evaluating the integrals in (13), the functional of φ is changed into an ordinary function of the variational parameters $\{c\}$. For a single parameter, we have a plot like that given in Figure 5.2, $\varepsilon_{\min} = \varepsilon(c_{\min})$ being then the *best* variational approximation arising from the given form of the trial function $\varphi(c)$. The best value of the parameter c (hence, of ε and φ) is found by *minimizing* the variational energy, i.e. by solving the equation arising as necessary condition for the minimum of ε:

$$\frac{\partial\varepsilon}{\partial c} = 0 \Longrightarrow c_{\min}, \text{ provided } \left(\frac{\partial^2\varepsilon}{\partial c^2}\right)_{c_{\min}} > 0. \tag{14}$$

Increasing the number of variational parameters increases the flexibility of the variational wavefunction, and so increases the accuracy of the variational approximation.

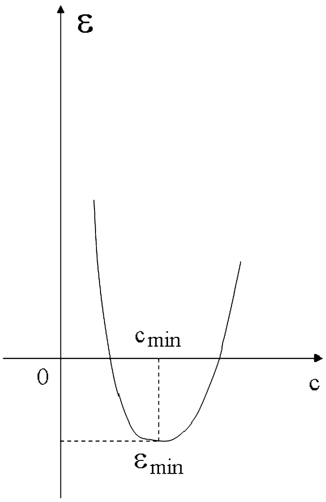


Figure 5.2 Schematic plot of the variational energy around the minimum.

5.2.4 Basis Functions and Variational Parameters

In molecular theory the variational wavefunctions are usually expressed in terms of a basis of atomic orbitals (STOs or GTOs, see Section 4.9 of the previous Chapter), possibly orthonormal or anyway orthogonalizable by the Schmidt method:

$$\chi_{nlm}(r,\Omega) = R_n(r)Y_{lm}(\Omega), \tag{15}$$

where the radial part is:

$$R_n(r) \propto \underset{\text{STO}}{r^{n-1}\exp(-cr)} \qquad \text{or} \qquad \underset{\text{GTO}}{r^{n-1}\exp(-cr^2)} \quad c>0. \tag{16}$$

Flexibility in the variational wavefunction is introduced through the so called variational parameters, which can be of two types:

$$\begin{matrix}\text{variational}\\ \text{parameters}\end{matrix}\begin{cases}\text{non-linear}\\ \text{(orbital exponents)}\\ \text{linear}\\ \text{(coefficients of the} \Longrightarrow \text{Ritz method}\\ \text{linear combination)}\end{cases}. \tag{17}$$

The Ritz method is more systematic and yields typical secular equations which can be solved by standard matrix techniques (see Chapter 2), while careful optimization of non-linear parameters is more difficult (see Problem 5.5 for the simple Ransil method applied to the case of a single parameter).

Table 5.1.

Variational approximations to the ground state of the hydrogen-like system

φ	$\langle r\rangle_\varphi$	$\varepsilon(c)$	$c_{\min}$	$\varepsilon_{\min}$
1. $\exp(-cr)$	$\frac{3}{2c}$	$\frac{c^2}{2}-Zc$	Z	$-\frac{Z^2}{2}$
2. $\exp(-cr)r$	$\frac{5}{2c}$	$\frac{c^2}{6}-\frac{Zc}{2}$	$\frac{3}{2}Z$	$-\frac{3}{8}Z^2$
3. $\exp(-cr^2)$	$\left(\frac{2}{\pi c}\right)^{1/2}$	$\frac{3}{2}c-Z\left(\frac{8c}{\pi}\right)^{1/2}$	$\frac{8}{9\pi}Z^2$	$-\frac{4}{3\pi}Z^2$

5.3 NON-LINEAR PARAMETERS

We shall now apply the variational techniques for finding approximations to energy and wavefunctions of ground and excited states of the hydrogen-like system, for which exact solutions were found in Chapter 4. This allows us to compare the results with the true solutions, unequivocally judging for the accuracy of the numerical results. We start by considering approximate functions of non-linear parameters. Short applications to ground and excited states of the harmonic oscillator will be given later in this Chapter as Problems 5.3 and 5.4.

5.3.1 The 1*s* Ground State of the Hydrogenic System

We look for the best variational energy and average distance of the electron from the nucleus for the ground state of the hydrogenic system arising from the three (un-normalized) variational functions depending on the single non-linear parameter c.

$$\left.\begin{array}{lll} 1. & \varphi=\exp(-cr) & 1s\text{-STO} \\ 2. & \varphi=\exp(-cr)r & 2s\text{-STO} \\ 3. & \varphi=\exp(-cr^2) & 1s\text{-GTO} \end{array}\right\}, \tag{18}$$

where $c>0$ is the adjustable orbital exponent. The necessary integrals are easily obtained from the general formulae given in Chapter 4, and we obtain variational approximations to the ground state of the hydrogen-like system (Table 5.1).

Putting $Z=1$ we find the following numerical values for the H atom (Table 5.2).

Function 1 gives for $c=1$ the exact value for either the energy eigenvalue or the average distance of the electron from the nucleus (the function φ_1 is the *exact* eigenfunction, the energy corresponding to the equality sign in Rayleigh principle (2)). The reasons of the poor behavior at the origin of functions 2 ($\varphi=0$) and 3 ($d\varphi/dr=0$) become apparent from the plot (Figure 5.3) giving the dependence of the three (normalized) functions on the radial variable r. The numerical values were taken from Table 5.3 (functions 2 and 3 lack of the requested cusp at the origin). It is important to notice how function $2G$ improves by about 12% the energy eigenvalue but not at all the eigenfunction (next paragraph).

Table 5.2.

Variational approximations to the H-atom ground state

φ	$c_{\min}$	$\varepsilon(c)/E_h$	$\langle r\rangle_\varphi/a_0$
1. $\exp(-cr)$	1	−0.5	1.5
2. $\exp(-cr)r$	1.5	−0.375	1.67
3. $\exp(-cr^2) = 1G$	0.2829	−0.4244	1.5
4. $2G^a$	$\begin{cases} a = 1.3296 \\ b = 0.2014 \end{cases}$	−0.4858	1.48

[a] $2G = A\exp(-ar^2) + B\exp(-br^2)$ with: $A = 0.2425$, $B = 0.1759$.

Table 5.3.

Radial dependence of the three (normalized) variational functions

r/a_0	$\varphi_1 = \dfrac{\exp(-r)}{\sqrt{\pi}}$	$\varphi_2 = \left(\dfrac{(1.5)^5}{3\pi}\right)^{1/2} \exp(-1.5r)r$	$\varphi_3 = \left(\dfrac{0.5658}{\pi}\right)^{3/4} \exp(-0.2829r^2)$
0	0.564	0	0.276
0.25	0.439	0.154	0.272
0.5	0.342	0.212	0.258
0.75	0.267	0.219	0.236
1	0.208	0.200	0.208
2	0.0763	0.0893	0.0892
3	0.0281	0.0299	0.0217
4	0.0103	0.0089	0.0030
5	0.0038	0.0025	0.0002

Comments. φ_1 is the point-by-point exact function. φ_2 is zero at the origin, has a maximum of 0.220 at $r = 0.67a_0$, being always smaller than φ_1 in the region 0.25–$1a_0$, greater in 2–$3a_0$, then decreases. φ_3 has a zero derivative at the origin, changes slowly at small values of r being always smaller than φ_1, coincides with φ_1 at $r = 1a_0$, then decreases rapidly with r.

- Gaussian bases

A more detailed comparison of different N-GTO approximations (Van Duijneveldt, 1971) to the exact $1s$ results for the H-atom ground state is given in Table 5.4 for different values of N. In the first column is the number N of optimized $1s$ GTOs, in the second the overlap with the exact $1s$ eigenfunction, in the third the error in the eigenvalue $\Delta\varepsilon = \varepsilon_{NG} - E_0$, in the last column the quadratic average error (the variance) defined as $\langle(\hat{H} - \varepsilon)\varphi|(\hat{H} - \varepsilon)\varphi\rangle = \langle\hat{H}\varphi|\hat{H}\varphi\rangle - \varepsilon^2$.

We may see from the Table 5.4 that, in going from $N = 4$ to $N = 10$, the error $\Delta\varepsilon$ reduces by a factor 1000 (from about $1mE_h$ to $1\mu E_h$), whereas the quadratic error (last

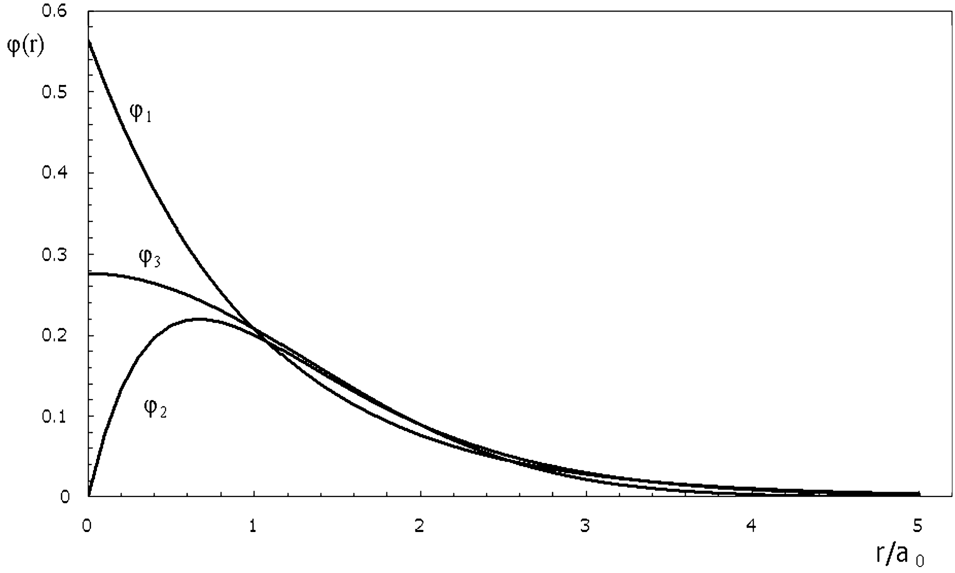


Figure 5.3 Plot of the (normalized) variational 1*s* functions against *r*.

Table 5.4.

Errors arising from optimized Gaussian 1*s* functions

N	$\langle\psi_0\vert\varphi\rangle$	$\Delta\varepsilon/10^{-3}E_h$	$\langle\hat{H}\varphi\vert\hat{H}\varphi\rangle-\varepsilon^2/E_h^2$
1	0.9782	75.58	0.2912
2	0.9966	14.19	0.2857
3	0.9994	3.02	0.2032
4	0.9998	0.72	0.1347
5	0.9999_7	0.19	0.0887
10	0.9999_{999}	$0.00_1=1\mu E_h$	0.0134

column) reduces by just 10 times. This means that the Van Duijneveldt NG is still point-by-point very different from the true ψ_0, even for large values of N. As already observed, this is due to the lack of cusp in the 1*s* GTO, which persists even increasing the number of GTOs. To remove this error, Klopper and Kutzelnigg (KK) (1986) have suggested to represent the 1*s* H orbital by means of a linear combination of n Gaussian functions having *different* and systematically increasing principal quantum numbers: 1*s*, 2*s*, 3*s*, ..., even with a single orbital exponent. Then:

$$\varphi=\exp(-cr^2)(1+c_1r+c_2r^2+\cdots) \tag{19}$$

$$\frac{d\varphi}{dc}=\exp(-cr^2)[c_1+2c_2r+\cdots-2cr(1+c_1r+\cdots)] \tag{20}$$

Table 5.5.

Comparison of different Gaussian functions with cusped Gaussians

φ	Variational parameters	$\Delta\varepsilon/10^{-9}E_h$	$\langle\hat{H}\varphi\vert\hat{H}\varphi\rangle - \varepsilon^2/E_h^2$
	Linear/Non-linear		
VD[a]	10/10	755.3	1.3×10^{-2}
WM[b]	32/2	0.2	3.2×10^{-4}
K10[c]	10/1 ($c = 0.11181$)	216.2	7.8×10^{-6}
K15[c]	15/1 ($c = 0.08761$)	0.0	3.4×10^{-9}

[a] Van Duijneveldt (1971) (VD).
[b] Wheatley and Meath (1993) (WM).
[c] Magnasco et al. (1995) (KN).

$$\lim_{r\to 0}\frac{d\varphi}{dc} = c_1 \neq 0 \tag{21}$$

and φ can now account for the cusp at $r = 0$. In Table 5.5 we have collected some results obtained from different Gaussian functions.

KN denotes Kutzelnigg-like "cusped" GTOs with a single orbital exponent. We may notice the improvement in the variance already obtained by K10 (which has the same number of linear parameters as VD, but only *one* optimized non-linear parameter). The "cusped" K15, still with a single non-linear parameter for a basis set whose dimensions are about half of those of the "uncusped" WM, is seen to give an ε value exact to ten decimal figures and a variance exceedingly small. This means that K15 with $c = 0.08761$ is practically point-by-point coincident with the exact $1s$ eigenfunction.

5.3.2 The First $2s$, $2p$ Excited States of the Hydrogenic System

We now look for the best variational approximations to the first excited state of the hydrogen-like atom using STOs of the appropriate symmetry.

(i) Excited $2s$ state.

The spherical function $s = (\frac{c^5}{3\pi})^{1/2} r\exp(-cr)$ (normalized and nodeless $2s$ STO) cannot be used as such in a variational calculation for state $2s$ (the first excited state having the same spherical symmetry of the ground state $\psi_0 = 1s$) since it is not orthogonal to ψ_0. We have already seen that optimizing such a function with respect to the orbital exponent c, we find a poor approximation to the true energy of the ground state. A convenient variational function for the first excited state of spherical symmetry will hence be obtained by Schmidt orthogonalizing s against ψ_0:

$$\varphi = \frac{s - S\psi_0}{\sqrt{1 - S^2}} \quad \langle\psi_0\vert\varphi\rangle = 0, \tag{22}$$

where $S = \langle \psi_0 | s \rangle \neq 0$. The variation theorem for excited states of the *same* symmetry can now be applied and gives:

$$\begin{aligned}
\varepsilon_\varphi &= \left\langle \varphi \middle| -\frac{1}{2}\nabla^2 - \frac{Z}{r} \middle| \varphi \right\rangle \\
&= (1 - S^2)^{-1}(h_{ss} + S^2 h_{\psi_0\psi_0} - 2S h_{s\psi_0}) \\
&= h_{ss} + \frac{S^2(h_{\psi_0\psi_0} + h_{ss}) - 2S h_{s\psi_0}}{1 - S^2} \\
&= h_{ss} + E_{\text{pn}} \geq E_{2s},
\end{aligned} \tag{23}$$

where the term:

$$E_{\text{pn}} = \frac{S^2(h_{\psi_0\psi_0} + h_{ss}) - 2S h_{s\psi_0}}{1 - S^2} > 0 \tag{24}$$

which arises from the non-orthogonality between s and ψ_0 ($S \neq 0$), gives a repulsive contribution avoiding the excited $2s$ electron to collapse onto the inner $1s$ state. We call this term penetration energy correction, and we shall see that it is of great importance whenever problems of non-orthogonality or overlap arise for interacting systems. We see from (23) that the variational energy ε_φ differs from h_{ss} just by this correction term (which is always repulsive, i.e. positive). We can evaluate the necessary integrals with the formulae given in Chapter 4, and we find:

$$\begin{aligned}
h_{\psi_0\psi_0} &= \frac{c_0^2}{2} - Z c_0 \qquad h_{ss} = \frac{c^2}{6} - \frac{Zc}{2} \\
h_{s\psi_0} &= \frac{S}{3}\left[(c_0 - Z)(c_0 + c) - \frac{3}{2}c_0^2\right] \\
S &= \sqrt{3}\frac{c}{c_0 + c}\left(\frac{2(c_0 c)^{1/2}}{c_0 + c}\right)^3.
\end{aligned} \tag{25}$$

All matrix elements can now be evaluated as functions of the variational parameter c assuming $c_0 = Z = 1$. The results (atomic units) are collected in Table 5.6 and plotted against c in Figure 5.4.

The variational optimization of c by the Ransil method (Problem 5.5) yields $c = 0.4222$ ($Z = 1$), and the energy upper bound:

$$\varepsilon_\varphi = -0.1234 E_h \tag{26}$$

which is within 98.7% of the exact value ($-0.125 E_h$). For $c = 0.5$ (unoptimized orbital exponent in the STO, corresponding to the hydrogenic value $c = Z/n$), the Schmidt orthogonalized STO (22) gives the fair value $\varepsilon_\varphi = -0.1192 E_h$, which is still within 95% of the correct value. This clearly illustrates the importance of orthogonalization in establishing correct upper bounds to the variational energy of the excited states.

Table 5.6.

Variational results (E_h) for H($2s$)

c	h_{ss}	E_{pn}	ε_φ
0.2	−0.0933	0.0059	−0.0874
0.3	−0.1350	0.0221	−0.1129
0.4	−0.1733	0.0502	−0.1231
0.5	−0.2083	0.0891_5	−0.1192
0.6	−0.24	0.1385	−0.1015
0.7	−0.2683	0.1994	−0.0689
0.8	−0.2933	0.2750	-0.0183_5

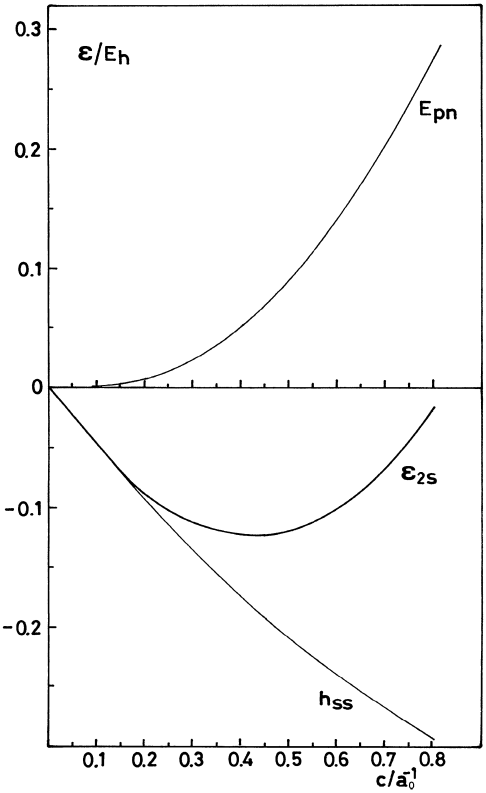


Figure 5.4 Variational energy components for H($2s$) plotted vs c.

(ii) Excited $2p$ state.

As a variational function of the appropriate symmetry we take the normalized $2p_z$-STO:

$$\varphi = \left(\frac{c^5}{\pi}\right)^{1/2} \exp(-cr) r \cos\theta, \tag{27}$$

which is now orthogonal to ψ_0 by symmetry:

$$\langle \psi_0 | \varphi \rangle = 0. \tag{28}$$

Using the formulae of Chapter 4 for the necessary integrals we find:

$$\varepsilon(c) = \left\langle \varphi \middle| -\frac{1}{2}\nabla^2 - \frac{Z}{r} \middle| \varphi \right\rangle = \frac{1}{2}\left(c^2 - Zc\right) \tag{29}$$

$$\frac{d\varepsilon}{dc} = c - \frac{Z}{2} = 0 \Longrightarrow c = \frac{Z}{2} \qquad \left(\frac{d^2\varepsilon}{dc^2}\right)_{c=\frac{Z}{2}} = 1 > 0 \tag{30}$$

$$\varepsilon_{\min} = \frac{1}{2}\left(\frac{Z^2}{4} - \frac{Z^2}{2}\right) = -\frac{Z^2}{8} \tag{31}$$

as it must be. The optimization of the orbital exponent c gives in this case the *exact* answer ($Z = 1$ for the H atom).

5.3.3 The $1s^2$ Ground State of the He-Like System

The 2-electron He-like atom (Figure 5.5) has the Hamiltonian (atomic units):

$$\hat{H}(1,2) = \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}}$$

$$\hat{h} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \quad \text{1-electron hydrogenic Hamiltonian} \tag{32}$$

$$\frac{1}{r_{12}} \quad \text{electron repulsion (2-electron operator),}$$

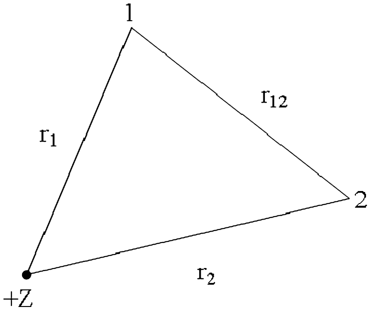


Figure 5.5 The atomic 2-electron system.

where, for different values of the nuclear charge Z:

$$Z = \begin{matrix} 1, & 2, & 3, & 4, & \cdots \\ \text{H}^- & \text{He} & \text{Li}^+ & \text{Be}^{2+} & \end{matrix} \tag{33}$$

we have the *isoelectronic* series of the atomic 2-electron system.

If we could not to take into account electronic repulsion, the 2-electron Schroedinger equation would be separable into two 1-electron hydrogenic equations, one for each electron, by posing:

$$\varphi(1,2) = \varphi_1\varphi_2. \tag{34}$$

Then:

$$\hat{H}(1,2)\varphi(1,2) = E\varphi(1,2) \tag{35}$$

$$(\hat{h}_1\varphi_1)\varphi_2 + \varphi_1(\hat{h}_2\varphi_2) = E\varphi_1\varphi_2$$

$$\underset{\substack{\text{depends}\\ \text{only on 1}}}{\frac{\hat{h}_1\varphi_1}{\varphi_1}} = E - \underset{\substack{\text{depends}\\ \text{only on 2}}}{\frac{\hat{h}_2\varphi_2}{\varphi_2}} = \varepsilon_1 \quad \text{separation constant} \tag{36}$$

giving:

$$\hat{h}_1\varphi_1 = \varepsilon_1\varphi_1 \qquad \hat{h}_2\varphi_2 = \varepsilon_2\varphi_2 \qquad \varepsilon_2 = E - \varepsilon_1. \tag{37}$$

The presence of the electron repulsion term in the complete Hamiltonian (32) gives, however, a non-separable 2-electron Schroedinger equation (35), which does not admit an exact solution. Approximations can however be found using the variational method, the simplest being by choosing as trial function the product (34) of two $1s$ STOs, one for each electron, containing just a simple variational parameter c (the orbital exponent):

$$\varphi(1,2) = \varphi_1(1)\varphi_2(2) = N\exp(-cr_1)\cdot\exp(-cr_2), \tag{38}$$

where:

$$N = \frac{c^3}{\pi} \tag{39}$$

is a normalization factor. Then:

$$\begin{aligned}\varepsilon(c) &= \left\langle \varphi_1\varphi_2 \middle| \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \middle| \varphi_1\varphi_2 \right\rangle \\ &= 2h_{1s1s} + (1s^2|1s^2) \\ &= 2\left(\frac{c^2}{2} - Zc\right) + \frac{5}{8}c = c^2 - 2\left(Z - \frac{5}{16}\right)c,\end{aligned} \tag{40}$$

where the new 2-electron repulsion integral in charge density notation $(1s^2|1s^2)$ is calculated in Section 5 of Chapter 13. We then get as stationarity condition:

$$\frac{d\varepsilon}{dc} = 2c - 2\left(Z - \frac{5}{16}\right) = 0 \tag{41}$$

giving:

$$c_{\min} = Z - \frac{5}{16}. \tag{42}$$

The optimized orbital exponent is the nuclear charge Z diminished by the quantity $s = 5/16$, the screening constant (Zener) arising from the effect of the second electron. For the best energy we find:

$$\varepsilon_{\min} = \varepsilon\left(c_{\min} = Z - \frac{5}{16}\right) = -\left(Z - \frac{5}{16}\right)^2 \tag{43}$$

and, for $Z = 2$ (He atom):

$$\varepsilon_{\min} = -2.847\,65 E_h \tag{44}$$

which is within 98% of the correct value $-2.903\,72 E_h$ (Pekeris, 1958). The hydrogenic approximation (without the screening effect) with $c = Z = 2$ would give:

$$\varepsilon(c = 2) = -2.75 E_h \tag{45}$$

which is within 95% of the correct value. This justifies the hypothesis of the screening effect suggested by Zener (1930) in proposing reasonable, but not variational, values for the screening constant s (Chapter 4).

It is worth noting that the effective potential for electron 1 in presence of the second electron is:

$$V_{\text{eff}}(r) = -\frac{Z}{r} + J_{1s}(r) = -\frac{Z_{\text{eff}}}{r}, \tag{46}$$

where the first term is the bare nuclear attraction and the second the electrostatic repulsive potential at r due to the second electron (Section 4 of Chapter 13). The effective nuclear charge felt by the electron is then given by:

$$Z_{\text{eff}}(r) = (Z - 1) + \exp(-2cr)(1 + cr). \tag{47}$$

Hence:

(i) $r =$ small (electron *near* to the nucleus)

$$\exp(-2cr) \approx 1 - 2cr, \qquad Z_{\text{eff}} \approx Z. \tag{48}$$

Table 5.7.

Errors in energy and ionization potential for He ($Z = 2$)

Approximation	% error in ε	% error in I
$c = Z = 2$ (hydrogen-like)	5	11
$c = 1.6875$ (1 non-linear parameter)	2	6
$c_1 = 2.183, c_2 = 1.188$ (2 non-linear parameters)	1	3

For $r \to 0$ the electron sees the whole (unscreened) nuclear charge Z.

(ii) $r =$ large (electron *far* from the nucleus)

$$\exp(-2cr) \approx 0, \qquad Z_{\text{eff}} \approx Z - 1. \tag{49}$$

For $r \to \infty$ the electron sees the nuclear charge as it was fully screened by the other electron acting as a point-like negative charge. Therefore, Z_{eff} depends on r, being Z near to the nucleus and $(Z - 1)$ far from it. The variation theorem averages between these two cases, with a larger weight for the regions near to the nucleus (hence, $Z_{\text{eff}} \approx 1.7$ closer to 2 rather than to 1).

Using different orbital exponents for different electrons and symmetrizing the resulting function:

$$\varphi(1,2) = N[\exp(-c_1r_1) \cdot \exp(-c_2r_2) + \exp(-c_2r_1) \cdot \exp(-c_1r_2)] \tag{50}$$

Eckart (1930) has obtained a sensibly better variational value for the energy, the value for He being $\varepsilon = -2.875\,66E_h$ ($c_1 = 2.18, c_2 = 1.19$), which differs by 1% from the accurate Pekeris value. This is due to the "splitting" of the spherical shells of the electrons, which introduces some radial correlation into the wavefunction. The physics of the problem does suggest how to improve the wavefunction. Details of the calculation are given in Problem 5.6. By increasing the flexibility of the variational wavefunction we improve the accuracy of the variational result. Comparison with experimental results is possible through the calculation of the first ionization potential I. For He:

$$I = \varepsilon(\text{He}^+) - \varepsilon(\text{He}) = -2 - \varepsilon(\text{He}). \tag{51}$$

Accurate values for the ground state He atom are $\varepsilon = -2.903\,72E_h$ and $I = 0.903\,72E_h = 24.6$ eV. The errors resulting for different variational wavefunctions are collected in Table 5.7 for He.

The greater error in I is due to the fact that the ionization potential is smaller in absolute value than the corresponding energy.

5.4 LINEAR PARAMETERS AND THE RITZ METHOD

We now consider the variational approximation due to Ritz (Pauling and Wilson, 1935) consisting in the linear combination of a basis of given functions, where flexibility is introduced in the wavefunction by the coefficients of the linear combination. This method is more systematic than that involving non-linear parameters, and optimization of the linear coefficients yields now to secular equations whose roots are upper bounds to ground and excited states of the system. Molecular orbital (MO) and valence bond (VB) approximations are typical applications of the Ritz method in valence theory, where the variational wavefunction is expressed in terms of a given basis of AOs or VB structures, respectively. As we shall see, the Ritz method is intimately connected with the problem of matrix diagonalization of Chapter 2.

5.4.1 Orthonormal Basis

(i) We start by considering the Rayleigh ratio (2) written in the form:

$$\varepsilon = HM^{-1}, \tag{2}$$

where:

$$H = \langle \varphi | \hat{H} | \varphi \rangle, \qquad M = \langle \varphi | \varphi \rangle. \tag{52}$$

We introduce a basis of N orthonormal functions $\boldsymbol{\chi}$ written as a row vector and a column of N variational coefficients $\mathbf{c}$:

$$\varphi = \boldsymbol{\chi}\mathbf{c} \tag{53}$$

$$\boldsymbol{\chi} = (\chi_1 \chi_2 \cdots \chi_N) \qquad \mathbf{c} = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix}. \tag{54}$$

Then:

$$H = \mathbf{c}^\dagger \boldsymbol{\chi}^\dagger \hat{H} \boldsymbol{\chi} \mathbf{c} = \mathbf{c}^\dagger \mathbf{H} \mathbf{c}, \tag{55}$$

where $\mathbf{H}$ is the Hermitian matrix representative of the Hamiltonian operator in the $\boldsymbol{\chi}$ basis, with elements:

$$H_{\mu\nu} = \langle \chi_\mu | \hat{H} | \chi_\nu \rangle, \tag{56}$$

and $\mathbf{M}$ the metric of the $\boldsymbol{\chi}$ basis, the identity matrix for an orthonormal set:

$$M = \mathbf{c}^\dagger \boldsymbol{\chi}^\dagger \boldsymbol{\chi} \mathbf{c} = \mathbf{c}^\dagger \mathbf{M} \mathbf{c} = \mathbf{c}^\dagger \mathbf{1} \mathbf{c} \tag{57}$$

$$M_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle = \delta_{\mu\nu}. \tag{58}$$

(ii) An infinitesimal *first* variation in the linear coefficients will induce an infinitesimal variation in the energy functional given by:

$$\delta\varepsilon = \delta H \cdot M^{-1} - H \cdot M^{-1-1} \delta M = M^{-1}(\delta H - \varepsilon \delta M), \tag{59}$$

where, to first order in $\delta\mathbf{c}$:

$$\delta H = \delta\mathbf{c}^\dagger \mathbf{H}\mathbf{c} + \mathbf{c}^\dagger \mathbf{H} \delta\mathbf{c} \tag{60}$$

$$\delta M = \delta\mathbf{c}^\dagger \mathbf{1}\mathbf{c} + \mathbf{c}^\dagger \mathbf{1} \delta\mathbf{c} \tag{61}$$

$\delta\mathbf{c}$ being a column of infinitesimal variations of the coefficients. The stationarity condition for the functional $\varepsilon[\varphi]$ against arbitrary infinitesimal changes in the coefficients will be:

$$\delta\varepsilon = 0 \Longrightarrow \delta H - \varepsilon \delta M = 0. \tag{62}$$

In terms of matrices $\mathbf{H}$, $\mathbf{1}$ we can write:

$$\delta\mathbf{c}^\dagger (\mathbf{H} - \varepsilon \mathbf{1})\mathbf{c} + \mathbf{c}^\dagger (\mathbf{H} - \varepsilon \mathbf{1}) \delta\mathbf{c} = 0. \tag{63}$$

Since $\mathbf{H}^\dagger = \mathbf{H}$ (Hermitian), the second term in (63) is the complex conjugate of the first, so that the condition of stationarity for ε takes the matrix form ($\delta\mathbf{c}^\dagger =$ arbitrary):

$$(\mathbf{H} - \varepsilon \mathbf{1})\mathbf{c} = \mathbf{0} \qquad \mathbf{H}\mathbf{c} = \varepsilon \mathbf{c} \tag{64}$$

which is nothing but the eigenvalue equation for matrix $\mathbf{H}$. The homogeneous system (64) of N algebraic linear equations in the N unknowns $\mathbf{c}$ (the variational coefficients) has hence acceptable solutions if and only if:

$$|\mathbf{H} - \varepsilon \mathbf{1}| = 0, \tag{65}$$

namely only for those ε values which are solutions of an algebraic equation of degree N in ε, having the N (real) ordered roots:

$$\varepsilon_1 \le \varepsilon_2 \le \cdots \le \varepsilon_N \quad \text{eigenvalues} \tag{66}$$

$$\mathbf{c}_1, \mathbf{c}_2, \cdots, \mathbf{c}_N \quad \text{eigenvectors} \tag{67}$$

$$\varphi_1, \varphi_2, \cdots, \varphi_N \quad \text{eigenfunctions (pseudostates).} \tag{68}$$

As shown in Chapter 2 (explicitly for the case $N = 2$), the eigenvectors are obtained by the ordered substitution of each eigenvalue ε_μ in turn into the homogeneous system (64), then solving the system with respect to $\mathbf{c}_\mu$ under the normalization condition $\mathbf{c}_\mu^\dagger \mathbf{c}_\mu = 1$.

(iii) To find the linear combination of the orthonormal basis functions which minimizes the variational energy is therefore equivalent to solve the eigenvalue equation (64) for the **H** matrix or, as it is usually said, to diagonalize **H**. In fact, the complete set of eigenvalues and eigenvectors of matrix **H** is given by the full eigenvalue matrix:

$$\mathbf{HC} = \mathbf{C}\boldsymbol{\mathcal{E}}, \tag{69}$$

where **C** is now the square matrix of the complete eigenvectors (the row matrix of the single column eigenvectors):

$$\mathbf{C} = (\mathbf{c}_1|\mathbf{c}_2|\cdots|\mathbf{c}_N) = \left(\begin{array}{c|c|c|c} c_{11} & c_{12} & \dots & c_{1N} \\ c_{21} & c_{22} & \dots & c_{2N} \\ \vdots & \vdots & \dots & \vdots \\ c_{N1} & c_{N2} & \dots & c_{NN} \end{array}\right) \tag{70}$$

and $\boldsymbol{\mathcal{E}}$ the diagonal matrix collecting the N eigenvalues:

$$\boldsymbol{\mathcal{E}} = \begin{pmatrix} \varepsilon_1 & 0 & \cdots & 0 \\ 0 & \varepsilon_2 & \cdots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \cdots & \varepsilon_N \end{pmatrix}. \tag{71}$$

Since matrix **C** is unitary:

$$\mathbf{CC}^\dagger = \mathbf{C}^\dagger\mathbf{C} = \mathbf{1} \Longrightarrow \mathbf{C}^{-1} = \mathbf{C}^\dagger, \tag{72}$$

the Hermitian matrix **H** can be brought to diagonal form through the unitary transformation with the complete matrix of its eigenvectors:

$$\mathbf{C}^\dagger\mathbf{HC} = \boldsymbol{\mathcal{E}}. \tag{73}$$

The inverse transformation:

$$\mathbf{H} = \mathbf{C}\boldsymbol{\mathcal{E}}\mathbf{C}^\dagger \tag{74}$$

allows us to express **H** in terms of its eigenvalues and eigenvectors and will be useful in what follows.

(iv) Let us now consider the *second* variation of the functional ε:

$$\delta^2 H = \delta^2\mathbf{c}^\dagger\mathbf{Hc} + \mathbf{c}^\dagger\mathbf{H}\delta^2\mathbf{c} + 2\delta\mathbf{c}^\dagger\mathbf{H}\delta\mathbf{c} \tag{75}$$

$$\delta^2 M = \delta^2\mathbf{c}^\dagger\mathbf{1c} + \mathbf{c}^\dagger\mathbf{1}\delta^2\mathbf{c} + 2\delta\mathbf{c}^\dagger\mathbf{1}\delta\mathbf{c}, \tag{76}$$

where $\delta^2\mathbf{c}$ is a column of infinitesimal second variations of the coefficients, so that:

$$\begin{aligned} \delta^2\varepsilon &= M^{-1}(\delta^2 H - \varepsilon\delta^2 M - \delta\varepsilon\cdot\delta M) - M^{-2}\delta M(\delta H - \varepsilon\delta M) \\ \delta^2\varepsilon &= M^{-1}(\delta^2 H - \varepsilon\delta^2 M) \end{aligned} \tag{77}$$

since $\delta\varepsilon = 0$ and $\delta H - \varepsilon\delta M = 0$ at the stationary point. In matrix form:

$$\begin{aligned}
\delta^2\varepsilon &= M^{-1}[\delta^2\mathbf{c}^\dagger(\mathbf{H}-\varepsilon\mathbf{1})\mathbf{c} + \mathbf{c}^\dagger(\mathbf{H}-\varepsilon\mathbf{1})\delta^2\mathbf{c} + 2\delta\mathbf{c}^\dagger(\mathbf{H}-\varepsilon\mathbf{1})\delta\mathbf{c}] \\
\delta^2\varepsilon &= 2M^{-1}\delta\mathbf{c}^\dagger(\mathbf{H}-\varepsilon\mathbf{1})\delta\mathbf{c} = 2M^{-1}\delta\mathbf{c}^\dagger\mathbf{C}(\boldsymbol{\mathcal{E}}-\varepsilon\mathbf{1})\mathbf{C}^\dagger\delta\mathbf{c},
\end{aligned} \tag{78}$$

where use has been made of equation (74). By posing:

$$\underset{N\times N}{\mathbf{C}^\dagger}\ \underset{N\times 1}{\delta\mathbf{c}} = \underset{N\times 1}{\delta\mathbf{c}'} \qquad \underset{1\times N}{\delta\mathbf{c}^\dagger}\ \underset{N\times N}{\mathbf{C}} = \underset{1\times N}{\delta\mathbf{c}'^\dagger}, \tag{79}$$

where $\delta\mathbf{c}'$ is a new column of variations, the second variation in ε can be written as:

$$\delta^2\varepsilon = 2M^{-1}\delta\mathbf{c}'^\dagger(\boldsymbol{\mathcal{E}}-\varepsilon\mathbf{1})\delta\mathbf{c}' \tag{80}$$

and, in components:

$$\begin{aligned}
\delta^2\varepsilon &= 2M^{-1}\sum_{\mu,\nu}\delta c'^\dagger_\mu(\varepsilon_{\mu\nu}-\varepsilon\delta_{\mu\nu})\delta c'_\nu \\
&= 2M^{-1}\sum_{\mu,\nu}\delta c'^\dagger_\mu(\varepsilon_\mu-\varepsilon)\delta_{\mu\nu}\delta c'_\nu \\
&= 2M^{-1}\sum_{\mu}|\delta c'_\mu|^2(\varepsilon_\mu-\varepsilon).
\end{aligned} \tag{81}$$

There follows that for the lowest eigenvalue ε_1 of $\mathbf{H}$ $\delta^2\varepsilon$ is positive, and $\delta\varepsilon = 0$ corresponds to a true minimum in the energy:

$$(\delta^2\varepsilon)_{\varepsilon=\varepsilon_1} = 2M^{-1}\sum_{\mu=1}^{N}|\delta c'_\mu|^2(\varepsilon_\mu-\varepsilon_1) > 0. \tag{82}$$

We can do the same for all the remaining eigenvalues of $\mathbf{H}$, so that we conclude by saying that all the ordered roots of the secular equation (65) give true minima for the variational energy ordered in a crescent way.

(v) McDonald (1933, 1934) has further shown the important result that each eigenvalue ε_μ gives an upper bound to the corresponding true eigenvalue E_μ of the Hamiltonian $\hat{H}$:

$$\varepsilon_1 \geq E_1, \quad \varepsilon_2 \geq E_2, \quad \cdots, \quad \varepsilon_N \geq E_N. \tag{83}$$

McDonald's theorem does not include the case of degenerate eigenvalues. Davies (1960) has discussed the problem of the separation of degenerate eigenvalues in variational calculations. He showed that the occurrence of degenerate eigenvalues does not prevent the determination of upper bounds to exact eigenvalues in physical problems.

5.4.2 Non-Orthogonal Basis

Let us now consider the case (Chapter 2, Section 2.3.3) where the basis functions $\boldsymbol{\chi}'$ are normalized but *not* orthogonal with metric:

$$\mathbf{M}' = \boldsymbol{\chi}'^{\dagger}\boldsymbol{\chi}' = \mathbf{1} + \mathbf{S} \quad \mathbf{S} \neq \mathbf{0}, \tag{84}$$

where $\mathbf{S}$ is a traceless matrix of non-orthogonalities. Minimization of the functional ε with respect to the linear parameters $\mathbf{c}'$ yields now to:

$$(\mathbf{H}' - \varepsilon\mathbf{M}')\mathbf{c}' = \mathbf{0} \qquad \mathbf{H}'\mathbf{c}' = \varepsilon\mathbf{M}'\mathbf{c}', \tag{85}$$

where the latter is known as the *pseudoeigenvalue equation* for the Hermitian matrix $\mathbf{H}'$. The rather more complicated pseudosecular equation is now:

$$|\mathbf{H}' - \varepsilon\mathbf{M}'| = 0. \tag{86}$$

The problem is best dealt with by doing a simultaneous diagonalization of matrices $\mathbf{H}'$ and $\mathbf{M}'$ with a linear invertible (not unitary) transformation with a matrix $\mathbf{V}$:

$$\mathbf{V}^{\dagger}\mathbf{H}'\mathbf{V} = \boldsymbol{\mathcal{E}} \quad \boldsymbol{\mathcal{E}} = \begin{pmatrix} \varepsilon_1 & 0 & \cdots & 0 \\ 0 & \varepsilon_2 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \varepsilon_N \end{pmatrix} \tag{87}$$

$$\mathbf{V}^{\dagger}\mathbf{M}'\mathbf{V} = \mathbf{1} \quad \mathbf{1} = \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & 1 \end{pmatrix}. \tag{88}$$

To do this, we first orthogonalize basis χ' through matrix $\mathbf{T}$ (Schmidt or Löwdin):

$$\boldsymbol{\chi} = \boldsymbol{\chi}'\mathbf{T}, \tag{89}$$

then transform matrices $\mathbf{H}'$ and $\mathbf{M}'$ to the orthonormal basis $\boldsymbol{\chi}$:

$$\mathbf{H}_{\chi} = \mathbf{T}^{\dagger}\mathbf{H}'\mathbf{T}, \qquad \mathbf{M}_{\chi} = \mathbf{T}^{\dagger}\mathbf{M}'\mathbf{T} = \mathbf{1}, \tag{90}$$

finally solving the ordinary eigenvalue equation for $\mathbf{H}_{\chi}$:

$$|\mathbf{H}_{\chi} - \varepsilon\mathbf{1}| = 0. \tag{91}$$

The complete matrix of the eigenvectors $\mathbf{C}$ is now unitary, and matrix $\mathbf{V}$ is given by:

$$\mathbf{V} = \mathbf{TC}. \tag{92}$$

The functions obtained by the transformation:

$$\boldsymbol{\psi} = \boldsymbol{\chi}\mathbf{C} \qquad \mathbf{C}\mathbf{C}^{\dagger} = \mathbf{C}^{\dagger}\mathbf{C} = \mathbf{1} \tag{93}$$

are known as *pseudostates*.

5.5 ATOMIC APPLICATIONS OF THE RITZ METHOD

In the following, we shall apply the Ritz method to the study of the first excited states of the He-like atom, (i) the $1s2s$ state of spherical symmetry, and (ii) the $1s2p$ state.

5.5.1 The First $1s2s$ Excited State of the He-Like System

The 2-electron basis functions are:

$$\chi_1 = 1s_1 2s_2, \qquad \chi_2 = 2s_1 1s_2 \tag{94}$$

which are orthonormal if the 1-electron basis $(1s2s)$ is orthonormal, what we assume. The secular equation is then:

$$\begin{vmatrix} H_{11}-\varepsilon & H_{12} \\ H_{12} & H_{22}-\varepsilon \end{vmatrix} = 0 \tag{95}$$

with the matrix elements (electrons in dictionary order):

$$\begin{aligned} H_{11} &= \left\langle \overset{1}{1s}\overset{2}{2s} \left| \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \right| \overset{1}{1s}\overset{2}{2s} \right\rangle = h_{1s1s} + h_{2s2s} + (1s^2|2s^2) \\ &= E_0 + J = H_{22} \end{aligned} \tag{96}$$

$$\begin{aligned} H_{12} = H_{21} &= \left\langle \overset{1}{1s}\overset{2}{2s} \left| \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \right| \overset{1}{2s}\overset{2}{1s} \right\rangle = \left\langle \overset{1}{1s}\overset{2}{2s} \left| \frac{1}{r_{12}} \right| \overset{1}{2s}\overset{2}{1s} \right\rangle \\ &= (1s2s|1s2s) = K, \end{aligned} \tag{97}$$

where:

$$E_0 = h_{1s1s} + h_{2s2s} \tag{98}$$

is the 1-electron energy,

$$J = (1s^2|2s^2) \tag{99}$$

the 2-electron Coulomb integral, and

$$K = (1s2s|1s2s) \tag{100}$$

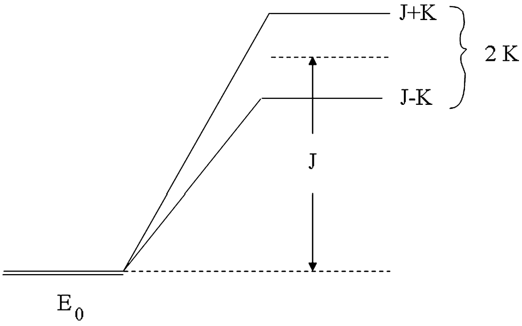


Figure 5.6 Schematic diagram of the energy levels for the excited S $(1s2s)$ state of the He-like atom.

the 2-electron exchange integral, both given in charge density notation (see Chapter 13).

Roots are:

$$\varepsilon_+ = H_{11} + H_{12} = E_0 + J + K \tag{101}$$

$$\varepsilon_- = H_{11} - H_{12} = E_0 + J - K, \tag{102}$$

with the corresponding eigenfunctions:

$$\varphi_+ = \frac{1}{\sqrt{2}}(1s2s + 2s1s) \tag{103}$$

$$\varphi_- = \frac{1}{\sqrt{2}}(1s2s - 2s1s) \tag{104}$$

which are, respectively, symmetric and antisymmetric in the electron interchange.

The schematic diagram of the energy levels for the $1s2s$ state is given in Figure 5.6.

Electron repulsion *couples* the two physically identical states $1s2s$ and $2s1s$ (through the off-diagonal term H_{12}), removing the double degeneracy of the atomic level $H_{11} = H_{22} = E_0 + J$, and originates two distinct levels (a doublet) whose *splitting* is $2K$. So, the experimental measurement of the splitting gives directly the value of the exchange integral K.

We notice that the (unoptimized) hydrogenic AOs give a wrong order of the excited levels because they overestimate electron repulsion. Using as $2s$ the function:

$$2s = (1 - S^2)^{-1/2}(s - Sk) \quad S = \langle k|s\rangle \tag{105}$$

$$s = \left(\frac{c_s^5}{3\pi}\right)^{1/2} \exp(-c_s r) r \tag{106}$$

$$k = \left(\frac{c_0^3}{\pi}\right)^{1/2} \exp(-c_0 r), \tag{107}$$

variational optimization of ε_+ against c_s (for $c_0 = 1.6875$)[1] gives:

$$c_s = 0.4822 \tag{108}$$

$$\varepsilon_+ = -2.09374 E_h \qquad \varepsilon_- = -2.12168 E_h \tag{109}$$

with excitation energies (from the ground state) which are within 99.7% of the experimentally observed values (Moore, 1949):

$$\begin{array}{lll} \Delta\varepsilon & 0.7539 & 0.7260 \\ \text{Exptl.} & 0.7560 & 0.7282 \end{array} \tag{110}$$

and a splitting $(2K)$ which is within 95.5% of the experiment:

$$\begin{array}{ll} 2K & 0.0279 \\ \text{Exptl.} & 0.0292. \end{array} \tag{111}$$

Optimization of the orbital exponent of the orthogonalized $2s$ function gives not only the correct order of the atomic levels, but also results that are quantitatively satisfactory in view of the simplicity of our variational approximation. Notice that the best value of c_s is less than half of the hydrogenic value $c = Z/n = 1$, so that electron repulsion is strongly reduced.

5.5.2 The First $1s2p$ Excited State of the He-Like System

Because of space degeneracy there are now six states belonging to the $1s2p$ configuration:

$$\begin{array}{cccccc} 1s2p_z, & 2p_z1s, & 1s2p_x, & 2p_x1s, & 1s2p_y, & 2p_y1s \\ 1 & 2 & 3 & 4 & 5 & 6 \end{array} \tag{112}$$

giving a basis of 6 functions. Functions belonging to different (x, y, z) components are orthogonal and not interacting with respect to $\hat{H}$ by symmetry. Functions belonging to the same symmetry can interact through electron repulsion. All functions are also orthogonal and not interacting with respect to all S states.

---

[1] We optimize the root having the *same* symmetry of the ground state.

The 6×6 secular equation has a block-diagonal form and factorizes into three 2×2 secular equations each corresponding to a given coordinate axis (x, y, z):

$$\begin{vmatrix} \begin{vmatrix} H_{11}-\varepsilon & H_{12} \\ H_{12} & H_{22}-\varepsilon \end{vmatrix} \sim z & & 0 \\ & \begin{vmatrix} H_{33}-\varepsilon & H_{34} \\ H_{34} & H_{44}-\varepsilon \end{vmatrix} \sim x & \\ 0 & & \begin{vmatrix} H_{55}-\varepsilon & H_{56} \\ H_{56} & H_{66}-\varepsilon \end{vmatrix} \sim y \end{vmatrix} = 0 \, . \tag{113}$$

So, it will be sufficient to consider the 2×2 secular equation:

$$\begin{vmatrix} H_{11}-\varepsilon & H_{12} \\ H_{12} & H_{22}-\varepsilon \end{vmatrix} = 0 \tag{114}$$

whose roots are spatially triply degenerate (a degeneracy that can only be removed by including spin). Matrix elements are:

$$H_{11} = H_{22} = h_{1s1s} + h_{2p2p} + (1s^2|2p^2) = E'_0 + J' \tag{115}$$

$$H_{12} = H_{21} = (1s2p|1s2p) = K', \tag{116}$$

with the triply degenerate roots:

$$\varepsilon_+ = H_{11} + H_{12} = E'_0 + J' + K' \tag{117}$$

$$\varepsilon_- = H_{11} - H_{12} = E'_0 + J' - K', \tag{118}$$

and the corresponding eigenfunctions:

$$\varphi_+ = \frac{1}{\sqrt{2}}(1s2p + 2p1s) \tag{119}$$

$$\varphi_- = \frac{1}{\sqrt{2}}(1s2p - 2p1s) \tag{120}$$

which are, respectively, symmetric and antisymmetric in the electron interchange ($2p = 2p_z, 2p_x, 2p_y$).

The schematic diagram of the energy levels for the $1s2p$ state is qualitatively similar to that given in Figure 5.6, but now each level is triply degenerate.

Table 5.8.

Variational calculation of ground and excited states in He

Electron configuration	$1s^2$	$1s2s$	$1s2s$	$1s2p$	$1s2p$
State	1^1S	2^3S	2^1S	2^3P	2^1P
ε/E_h	$-2.847\,65$	$-2.121\,68$	$-2.093\,74$	$-2.082\,26$	$-2.072\,37$
$\Delta\varepsilon/E_h$	0	0.7260	0.7539	0.7654	0.7753
Exptl.		0.7282	0.7560	0.7703	0.7796
% error		99.7	99.7	99.4	99.4
$2K/10^{-3}E_h$		27.94		9.89	
Exptl.		29.26		9.33	
Orbital exponents	c_0	c_s		c_p	
c/a_0^{-1} (optimized)	1.6875	0.4822		0.4761	
Hydrogenic	2	1		1	

Using a variational function $2p = (\frac{c_p^5}{\pi})^{1/2}\exp(-c_p r)r\cos\theta$, orthogonal by symmetry to $k = 1s$, optimization of ε_+ against the non-linear parameter c_p gives:

$$c_p = 0.4761 \tag{121}$$

$$\varepsilon_+ = -2.072\,37E_h \qquad \varepsilon_- = -2.082\,26E_h \tag{122}$$

with excitation energies (from the ground state) which are within 99.4% of the experimentally observed values (Moore, 1949):

$$\begin{array}{lll} \Delta\varepsilon & 0.7753 & 0.7654 \\ \text{Exptl.} & 0.7796 & 0.7703 \end{array} \tag{123}$$

and a splitting ($2K'$) which is 6% larger than experiment:

$$\begin{array}{ll} 2K' & 0.0099 \\ \text{Exptl.} & 0.0093. \end{array} \tag{124}$$

All these results are collected in Table 5.8.

We can notice the satisfactory agreement with the experimental results for the calculated excitation energies $\Delta\varepsilon$ and, also, for the splittings $2K$ and $2K'$, which are much more difficult to evaluate. The variational orbital exponents give AOs which are sensibly more diffuse than the hydrogenic ones.

Table 5.9.

Variational calculation of ground and excited $1s2s$ and $1s2p$ states in He using hydrogenic AOs

Electron configuration	$1s^2$	$1s2s$	$1s2p$	$1s2s$	$1s2p$
State	1^1S	^3S	^3P	^1S	^1P
ε/E_h	−2.75	−2.124 14	−2.048 54	−2.036 35	−1.980 26
$\Delta\varepsilon/E_h$	0	0.6259	0.7015	0.7136	0.7697
$\Delta K/10^{-3}E_h$		87.79	68.28		

5.5.3 Results for Hydrogenic AOs

Using the normalized hydrogenic AOs:

$$1s = \left(\frac{c_0^3}{\pi}\right)^{1/2} \exp(-c_0 r) \equiv \psi_0 \quad c_0 = Z \tag{125}$$

$$2s = \left(\frac{c^3}{\pi}\right)^{1/2} \exp(-cr)(1-cr) = k - \sqrt{3}s \quad 2c = Z, \tag{126}$$

where k and s are STOs with identical orbital exponents c:

$$k = \left(\frac{c^3}{\pi}\right)^{1/2} \exp(-cr), \qquad s = \left(\frac{c^5}{3\pi}\right)^{1/2} \exp(-cr)r,$$

$$S = \langle k|s\rangle = \frac{\sqrt{3}}{2} \tag{127}$$

the resulting order of levels is *wrong* and the splittings are much too large. Table 5.9 collects the results of such calculations.

We observe the inversion in the order of the levels $1s2p(^3P)$ and $1s2s(^1S)$, the excitation energies are too small, the splittings too large, more than 3 and 7 times, respectively. As we have already said, this is due to the overestimation of the electronic repulsion due to the sensible overestimation of the hydrogenic orbital exponents ($c = 1$ instead of ≈ 0.5).

5.6 MOLECULAR APPLICATIONS OF THE RITZ METHOD

The Ritz method will now be applied to the study of the ground and first excited state of the hydrogen molecule-ion H_2^+.

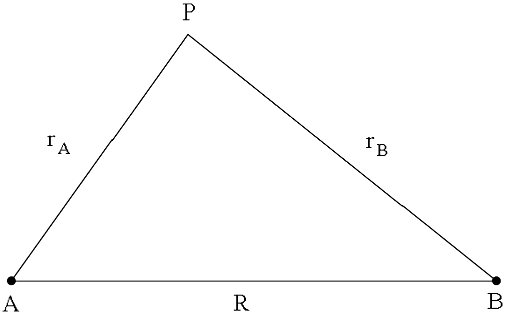


Figure 5.7 Interparticle distances in the H_2^+ molecular ion

5.6.1 The Ground and First Excited State of the H_2^+ Molecular Ion

The electron is at point P, in A,B are the two protons a fixed distance R apart. In atomic units, the 1-electron molecular Hamiltonian of H_2^+ will be:

$$\hat{H} = \hat{h} + \frac{1}{R} = \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B}\right) + \frac{1}{R}. \tag{128}$$

As a first approximation to the variational wavefunction we choose the 1-electron molecular orbital (MO) arising from the linear combination of the two $1s$ AOs centred at A and B, respectively:

$$\varphi = ac_1 + bc_2 \tag{129}$$

$$a = 1s_A = \frac{1}{\sqrt{\pi}}\exp(-r_A), \qquad b = 1s_B = \frac{1}{\sqrt{\pi}}\exp(-r_B) \tag{130}$$

$$\langle a|a\rangle = \langle b|b\rangle = 1 \qquad \langle a|b\rangle = \langle b|a\rangle = S, \tag{131}$$

where S is the overlap between the AOs. At variance with the atomic cases considered so far, we observe that the two AOs onto different centres are non-orthogonal. The Ritz method for two non-orthogonal functions gives the 2 × 2 pseudosecular equation:

$$\begin{vmatrix} H_{aa} - \varepsilon & H_{ab} - \varepsilon S \\ H_{ab} - \varepsilon S & H_{bb} - \varepsilon \end{vmatrix} = 0. \tag{132}$$

Because of the nuclear symmetry we must have:

$$H_{aa} = H_{bb}, \qquad H_{ba} = H_{ab} \tag{133}$$

so that expansion of the secular determinant gives:

$$(H_{aa}-\varepsilon)^2=(H_{ab}-\varepsilon S)^2$$

$$H_{aa}-\varepsilon=\pm(H_{ab}-\varepsilon S) \tag{134}$$

with the two roots:

$$\varepsilon_+=\frac{H_{aa}+H_{ab}}{1+S}=H_{aa}+\frac{H_{ba}-SH_{aa}}{1+S} \tag{135}$$

$$\varepsilon_-=\frac{H_{aa}-H_{ab}}{1-S}=H_{aa}-\frac{H_{ba}-SH_{aa}}{1-S} \tag{136}$$

the first corresponding to the ground state, the second to the first excited state of the H_2^+ molecular ion.

We now evaluate the best value for the coefficients of the linear combination for the ground state. From the homogeneous system, we have for the first eigenvalue:

$$\varepsilon_+=\frac{H_{aa}+H_{ba}}{1+S} \tag{135}$$

$$\begin{cases}\left(H_{aa}-\dfrac{H_{aa}+H_{ba}}{1+S}\right)c_1+\left(H_{ba}-\dfrac{H_{aa}+H_{ba}}{1+S}S\right)c_2=0\\ c_1^2+c_2^2+2c_1c_2S=1,\end{cases} \tag{137}$$

where the last equation is the normalization condition for non-orthogonal AOs. We obtain:

$$\begin{aligned}\left(\frac{c_2}{c_1}\right)_+&=\lambda_+=-\frac{H_{aa}+SH_{aa}-H_{aa}-H_{ba}}{1+S}\,\frac{1+S}{H_{ba}+SH_{ba}-H_{aa}S-SH_{ba}}\\&=\frac{H_{ba}-SH_{aa}}{H_{ba}-SH_{aa}}=1\end{aligned} \tag{138}$$

$$c_1^2\left[1+\left(\frac{c_2}{c_1}\right)_+^2+2\left(\frac{c_2}{c_1}\right)_+S\right]=1\Longrightarrow c_1=c_2=(2+2S)^{-1/2} \tag{139}$$

giving the *bonding* MO:

$$\varphi_+=\frac{a+b}{\sqrt{2+2S}}. \tag{140}$$

Proceeding likely, we have for the remaining root:

$$\left(\frac{c_1}{c_2}\right)_-=\lambda_-=-\frac{H_{ba}-SH_{aa}}{H_{ba}-SH_{aa}}=-1 \tag{141}$$

$$c_2 = (2-2S)^{-1/2}, \qquad c_1 = -(2-2S)^{-1/2}, \tag{142}$$

giving the *antibonding* MO:

$$\varphi_- = \frac{b-a}{\sqrt{2-2S}}. \tag{143}$$

We notice that, while φ_+ has no nodes, φ_- has a nodal plane occurring at the midpoint of AB (it is like a $2p_z$ AO). We notice, too, that in both cases the LCAO coefficients are completely determined by symmetry.

We now evaluate the matrix elements of $\hat{H}$ over the two basis functions:

$$\begin{aligned} H_{aa} &= \left\langle a \middle| \hat{h} + \frac{1}{R} \middle| a \right\rangle = h_{aa} + \frac{1}{R} = \left\langle a \middle| -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} \middle| a \right\rangle + \frac{1}{R} \\ &= E_A + (a^2| - r_B^{-1}) + \frac{1}{R}, \end{aligned} \tag{144}$$

where:

$$E_A = \left\langle a \middle| -\frac{1}{2}\nabla^2 - \frac{1}{r_A} \middle| a \right\rangle \tag{145}$$

is the energy of the isolated A atom ($= -1/2E_h$), and we have used the charge density notation:

$$\left\langle a \middle| -\frac{1}{r_B} \middle| a \right\rangle = (a^2| - r_B^{-1}), \tag{146}$$

the attraction by the B-nucleus of the electron described by the density a^2 centred on A.

In the same way:

$$\begin{aligned} H_{ba} &= \left\langle b \middle| \hat{h} + \frac{1}{R} \middle| a \right\rangle = h_{ba} + \frac{1}{R}S = \left\langle b \middle| -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} \middle| a \right\rangle + \frac{1}{R}S \\ &= E_A S + (ab| - r_B^{-1}) + \frac{1}{R}S. \end{aligned} \tag{147}$$

We therefore obtain for the ground state:

$$\begin{aligned} \varepsilon_+ &= H_{aa} + \frac{H_{ba} - SH_{aa}}{1+S} \\ &= E_A + \left\{ (a^2| - r_B^{-1}) + \frac{1}{R} \right\} + \frac{(ab| - r_B^{-1}) - S(a^2| - r_B^{-1})}{1+S}, \end{aligned} \tag{148}$$

and for the first excited state:

$$\varepsilon_- = H_{aa} - \frac{H_{ba} - SH_{aa}}{1-S}$$

$$= E_A + \left\{(a^2|-r_B^{-1}) + \frac{1}{R}\right\} - \frac{(ab|-r_B^{-1}) - S(a^2|-r_B^{-1})}{1-S}. \tag{149}$$

5.6.2 The Interaction Energy and Its Components

Even if the matter will be discussed to a greater extent in Chapter 12, we see from equations (148) and (149) that the interaction energy, defined as the difference between ε_+ (or ε_-) and the energy E_A of the isolated H atom, can be written as:

$$\Delta E(^2\Sigma_g^+) = \varepsilon_+ - E_A = \Delta E^{\text{cb}} + \Delta E^{\text{exch-ov}}(^2\Sigma_g^+) \tag{150}$$

$$\Delta E(^2\Sigma_u^+) = \varepsilon_- - E_A = \Delta E^{\text{cb}} + \Delta E^{\text{exch-ov}}(^2\Sigma_u^+). \tag{151}$$

The interaction energy is seen to depend on the electronic states of H_2^+, naturally resulting from the sum of the two components:

$$\Delta E^{\text{cb}} = (a^2|-r_B^{-1}) + \frac{1}{R}, \tag{152}$$

the semiclassical electrostatic energy (which is the *same* for the two states), and:

$$\Delta E^{\text{exch-ov}}(^2\Sigma_g^+) = \frac{(ab - Sa^2|-r_B^{-1})}{1+S} \tag{153}$$

$$\Delta E^{\text{exch-ov}}(^2\Sigma_u^+) = -\frac{(ab - Sa^2|-r_B^{-1})}{1-S} \tag{154}$$

the quantum mechanical components arising from the exchange-overlap density $(ab - Sa^2)$, which has the property:

$$\int d\mathbf{r}\big[a(\mathbf{r})b(\mathbf{r}) - Sa^2(\mathbf{r})\big] = S - S = 0. \tag{155}$$

As can be seen from (153) and (154), at variance with ΔE^{cb}, $\Delta E^{\text{exch-ov}}$ depends on the symmetry of the wavefunction and is *different* for ground (attractive) and excited state (repulsive). These components and their corrections occurring in higher orders of perturbation theory will be examined in detail in Chapter 12.

The 1-electron 2-centre integrals occurring in the present calculation are evaluated in Chapter 13. For completeness, however, we give here their analytic form as a function of the internuclear distance R ($c_0 = 1$):

$$S = (ab|1) = \exp(-R)\left(1 + R + \frac{R^2}{3}\right) \tag{156}$$

$$(ab|r_B^{-1}) = \exp(-R)(1+R) \tag{157}$$

$$(a^2|r_B^{-1}) = \frac{1}{R} - \frac{\exp(-2R)}{R}(1+R). \tag{158}$$

Their values to 7 significant figures have been collected in Table 5.10 as a function of R.

Even if in molecular computations the energy is usually evaluated in terms of molecular integrals (Chapter 13), in this simple case it is easily possible to obtain the analytic expressions for the components of the interaction energy as a function of R as:

$$\Delta E^{\mathrm{cb}} = \frac{\exp(-2R)}{R}(1+R) \tag{159}$$

$$\begin{aligned}\Delta E^{\mathrm{exch-ov}}({}^2\Sigma_g^+) = (1+S)^{-1}\Bigg\{ & \frac{\exp(-R)}{R}\left(1-\frac{2}{3}R^2\right) \\ & - \frac{\exp(-3R)}{R}\left(1+2R+\frac{4}{3}R^2+\frac{1}{3}R^3\right)\Bigg\}.\end{aligned} \tag{160}$$

These expressions allow us for the *direct* calculation of the interaction energy in H_2^+, avoiding the "round-off errors" which increase with increasing R (see the difference between R^{-1} and $(a^2|r_B^{-1})$, which differ by charge-overlap terms, in Table 5.10).

Table 5.11 gives the calculated interaction energy and its components ($10^{-3}E_h$) for the ground state $H_2^+({}^2\Sigma_g^+)$, while Table 5.12 gives the same quantities for the excited state

Table 5.10.

Numerical values of the 2-centre integrals ($c_0 = 1$) occurring in the H_2^+ calculation as a function of R (energy integrals in E_h)

R/a_0	R^{-1}	S	$(a^2\|r_B^{-1})$	$(ab\|r_B^{-1})$
1.0	1	$8.583\,854 \times 10^{-1}$	$7.293\,294 \times 10^{-1}$	$7.357\,589 \times 10^{-1}$
1.2	$8.333\,333 \times 10^{-1}$	$8.072\,005 \times 10^{-1}$	$6.670\,171 \times 10^{-1}$	$6.626\,273 \times 10^{-1}$
1.4	$7.142\,857 \times 10^{-1}$	$7.529\,427 \times 10^{-1}$	$6.100\,399 \times 10^{-1}$	$5.918\,327 \times 10^{-1}$
1.6	6.250×10^{-1}	$6.972\,160 \times 10^{-1}$	$5.587\,614 \times 10^{-1}$	$5.249\,309 \times 10^{-1}$
1.8	$5.555\,556 \times 10^{-1}$	$6.413\,597 \times 10^{-1}$	$5.130\,520 \times 10^{-1}$	$4.628\,369 \times 10^{-1}$
2.0	5.0×10^{-1}	$5.864\,529 \times 10^{-1}$	$4.725\,265 \times 10^{-1}$	$4.060\,059 \times 10^{-1}$
2.5	4.0×10^{-1}	$4.583\,079 \times 10^{-1}$	$3.905\,669 \times 10^{-1}$	$2.872\,975 \times 10^{-1}$
3.0	$3.333\,333 \times 10^{-1}$	$3.485\,095 \times 10^{-1}$	$3.300\,283 \times 10^{-1}$	$1.991\,483 \times 10^{-1}$
3.5	$2.857\,143 \times 10^{-1}$	$2.591\,942 \times 10^{-1}$	$2.845\,419 \times 10^{-1}$	$1.358\,882 \times 10^{-1}$
4.0	2.5×10^{-1}	$1.892\,616 \times 10^{-1}$	$2.495\,807 \times 10^{-1}$	$9.157\,819 \times 10^{-2}$
4.5	$2.222\,222 \times 10^{-1}$	$1.360\,852 \times 10^{-1}$	$2.220\,714 \times 10^{-1}$	$6.109\,948 \times 10^{-2}$
5.0	2.0×10^{-1}	$9.657\,724 \times 10^{-2}$	$1.999\,455 \times 10^{-1}$	$4.042\,768 \times 10^{-2}$
5.5	$1.818\,182 \times 10^{-1}$	$6.777\,229 \times 10^{-2}$	$1.817\,984 \times 10^{-1}$	$2.656\,401 \times 10^{-2}$
6.0	$1.666\,667 \times 10^{-1}$	$4.709\,629 \times 10^{-2}$	$1.666\,595 \times 10^{-1}$	$1.735\,127 \times 10^{-2}$
7.0	$1.428\,571 \times 10^{-1}$	$2.218\,913 \times 10^{-2}$	$1.428\,562 \times 10^{-1}$	$7.295\,056 \times 10^{-3}$
8.0	1.25×10^{-1}	$1.017\,570 \times 10^{-2}$	$1.249\,999 \times 10^{-1}$	$3.019\,164 \times 10^{-3}$

Table 5.11.

$^2\Sigma_g^+$ ground state of H_2^+. Interaction energy and its components ($10^{-3}E_h$) for the simple MO wavefunction ($c_0 = 1$)

R/a_0	ΔE^{cb}	$\Delta E^{exch-ov}(^2\Sigma_g^+)$	$\Delta E(^2\Sigma_g^+)$	Accurate[a]
1.0	270.67	−59.037	211.634	48.21
1.2	166.31	−68.731	97.579	
1.4	104.25	−75.591	28.659	
1.6	66.239	−79.750	−13.511	
1.8	42.504	−81.509	−39.005	
2.0	27.473	−81.245	−53.772	−102.63
2.5	9.433_1	-74.262_5	−64.829	−93.82
3.0	3.305_0	−62.388	−59.083	−77.56
3.5	1.172_4	−49.346	−48.174	−60.85
4.0	4.193×10^{-1}	−37.285	−36.866	−46.08
4.5	1.508×10^{-1}	−27.180	−27.029	−33.94
5.0	5.448×10^{-2}	−19.258	−19.204	−24.42
5.5	1.974×10^{-2}	−13.339	−13.319	−17.23
6.0	7.168×10^{-3}	−9.075	−9.068	−11.97
7.0	9.503×10^{-4}	−4.036	−4.035	−5.59
8.0	1.266×10^{-4}	−1.730	−1.729	−2.57

[a] Peek (1965).

($^2\Sigma_u^+$). Figure 5.8 gives the plots vs R of the interaction energies $\Delta E(10^{-3}E_h)$ for the two electronic states.

Comments to Tables 5.11 and 5.12 are as follows:

(i) $^2\Sigma_g^+$ ground state.

While ΔE^{cb} is always *repulsive* (classically it is not possible to form any chemical bond between H and H^+), the quantum mechanical component $\Delta E^{exch-ov}(^2\Sigma_g^+)$ is always *attractive* (going to zero as $R \to 0$) and appears as the main factor determining the formation of the 1-electron bond in H_2^+. $\Delta E^{exch-ov}$ has its minimum near to $R = 2a_0$, the distance of the chemical bond. The minimum in the potential energy curve for ground state H_2^+ occurs near $R = 2.5a_0$, i.e. for a value of R which is about 25% larger than the experimental value ($2a_0$). The true minimum of the simple MO wavefunction of Table 5.11 occurs at $R_e = 2.493a_0$ and is $\Delta E = -64.84 \times 10^{-3}E_h$. Even if the simple MO wavefunction of Table 5.11 gives a qualitatively correct behavior of the potential energy curve for ground state H_2^+, the quantitative error is still very large, the calculated bond energy at $R = 2a_0$ being no more than 52% of the correct value.

(ii) $^2\Sigma_u^+$ excited state.

The components of ΔE are now both *repulsive* (Table 5.12) and, to this level of approximation (rigid AOs), the excited $^2\Sigma_u^+$ state is *repulsive* (a *scattering* state). The polarization of the H atom by the proton H^+ (see Chapter 12) yields at large distances ($R = 12.5a_0$) a weak Van der Waals bond with $\Delta E = -60.8 \times 10^{-6}E_h$. It is interesting

Table 5.12.

${}^2\Sigma_u^+$ excited state of H_2^+. Interaction energy and its components ($10^{-3}E_h$) for the simple MO wavefunction ($c_0 = 1$)

R/a_0	$\Delta E^{\text{exch-ov}}({}^2\Sigma_u^+)$	$\Delta E({}^2\Sigma_u^+)$	Accurate[a]
1.0	774.73	1045.4	935.19
1.2	644.25	810.56	
1.4	536.34	640.59	
1.6	447.03	513.27	
1.8	373.04	415.54	
2.0	311.67	339.15	332.47
2.5	199.92	209.36	207.93
3.0	129.14	132.44	131.91
3.5	83.877	85.049	84.50
4.0	54.693	55.112	54.45
4.5	35.743	35.894	35.17
5.0	23.375	23.430	22.71
5.5	15.279	15.298	14.62
6.0	9.972	9.979	9.36
7.0	4.219	4.220	3.73
8.0	1.765	1.765	1.40

[a] Peek (1965).

to note (Figure 5.8) that the simple MO results for the excited state are much in better agreement with the accurate Peek values than those of the ground state.

Systematically improving the quality of the basic AOs gives the improved results collected in Table 5.13.

We make few comments on the nature of the basic AOs.

1. The *undistorted* H atom AOs ($c_0 = 1$) do not allow to find the correct bond length (the bond is 25% too long, since bond energy is insufficient).
2. Optimization of the orbital exponent c_0 in the $1s$ STO functions allows us to introduce a great part of the spherical distortion (polarization) of the H atom by the proton H^+: the bond length R_e is now correct and the bond energy ΔE improved by over 30%.
3. Dipole distortion of $1s$ (sp hybridization) improves ΔE by a further 13%, giving a result within 2% of the accurate value (Peek, 1965).
4. Use of a 2-centre AO (GZ, see the Eckart split-shell for He) allows us to reproduce nearly entirely the polarization of the H atom by the proton H^+, with a result which is now within 0.2% of the accurate value. The 2-centre GZ orbital is tantamount to including in the basis functions onto A *all* polarization functions with $l = 0, 1, 2, 3, 4, \ldots$ (spherical, dipole, quadrupole, octupole, hexadecapole, ...). GZ is the simplest variational function containing two optimizable non-linear parameters.

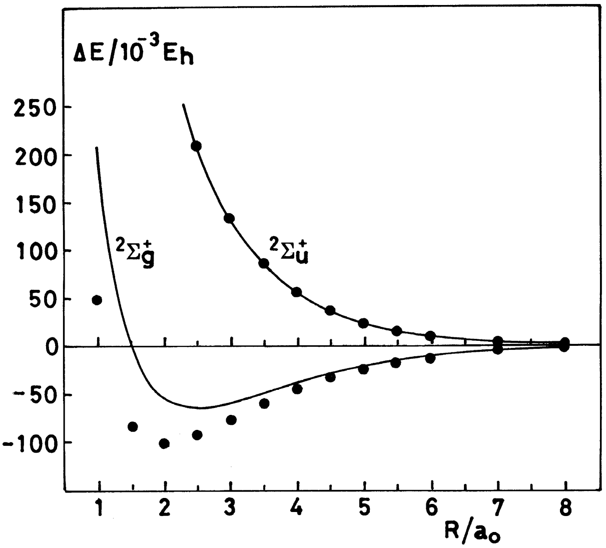


Figure 5.8 Plot of the MO interaction energies ΔE vs R for the two states of H_2^+ ($c_0 = 1$). The black points are the accurate results by Peek (1965).

Table 5.13.

$^2\Sigma_g^+$ ground state of H_2^+. Effect of improving the basic AO a in the MO wavefunction on the bond energy ΔE at $R = 2a_0$, and residual error with respect to the accurate value

	a	Basic AO	$\Delta E/10^{-3}E_h$	Residual error/$10^{-3}E_h$
1.	$1s_A \propto \exp(-r_A)$ ($c_0 = 1$)	H $1s^a$	−53.77	48.86
2.	$1s_A \propto \exp(-c_0 r_A)$ ($c_0 = 1.2387$)	STO $1s^b$ (optimized)	−86.51	16.12
3.	$1s_A + \lambda 2p\sigma_A$ ($c_0 = 1.2458$, $c_p = 1.4824$, $\lambda = 0.1380$)	Dipole polarized AO (sp hybrid)^c	−100.36	2.27
4.	$\exp(-\alpha r_A - \beta r_B)$ ($\alpha = 1.1365$, $\beta = 0.2174$)	2-centre GZ AO^d	−102.44	0.19
5.	Accurate	^{e}	−102.63	0

[a] Pauling (1928).

[b] Finkelstein and Horowitz (1928).

[c] Dickinson (1933).

[d] Guillemin and Zener (1929) (GZ).

[e] Peek (1965).

5.7 THE WENTZEL–KRAMERS–BRILLOUIN (WKB) METHOD

The following considerations are mostly taken from Pauling and Wilson (1935). In the development of quantum mechanics, the Bohr–Sommerfeld quantization rules of the old quantum theory (not considered in this book) give a connection between classical and quantum mechanics. The Wentzel–Kramers–Brillouin (WKB) method gives an approximate treatment of the Schroedinger wave equation that shows its connection with the quantization rules. It is based on an asymptotic expansion of the wavefunction in powers of $\hbar$ which is useful for finding approximate solutions to quantum mechanical problems whose wave equation can be separated into one or more total differential equations each involving a single independent variable. The first term of the expansion then gives the *classical* result, the second term the *old quantum theory* result, the higher order terms introducing the effects characteristic of the *new quantum mechanics* (based on the famous Erwin Schroedinger (1926) paper entitled "Quantizierung als Eigenwertproblem").

It can be easily verified that a solution $\psi(x)$ of the one-dimensional Schroedinger equation:

$$\frac{1}{\psi}\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}(E - V) \tag{161}$$

can be written in the form:

$$\psi(x) \propto \exp\left[\frac{i}{\hbar}\int y\,dx\right], \tag{162}$$

where:

$$y(x) = -i\hbar\left(\frac{1}{\psi}\frac{d\psi}{dx}\right) = -i\hbar\frac{d\ln\psi}{dx}. \tag{163}$$

We remark that in equation (161):

$$E - V = T = \frac{p^2}{2m} \tag{164}$$

is the kinetic energy of the particle. Then:

$$\begin{aligned}\frac{dy}{dx} &= -i\hbar\left\{\frac{d\psi}{dx}\left(-\psi^{-2}\frac{d\psi}{dx}\right) + \psi^{-1}\frac{d^2\psi}{dx^2}\right\}\\ &= -i\hbar\left\{\frac{1}{\hbar^2}\left(-i\hbar\frac{1}{\psi}\frac{d\psi}{dx}\right)^2 + \frac{1}{\psi}\frac{d^2\psi}{dx^2}\right\}\\ &= -i\hbar\left\{\frac{y^2}{\hbar^2} - \frac{2m}{\hbar^2}(E - V)\right\}\\ &= -\frac{i}{\hbar}\left\{y^2 - 2m(E - V)\right\}.\end{aligned} \tag{165}$$

Multiplying both members of (165) by $(-i\hbar)$ we get the basic WKB equation:

$$-i\hbar\frac{dy}{dx} = p^2 - y^2, \tag{166}$$

where:

$$p = \pm\sqrt{2m(E-V)} = \pm\sqrt{2mT} \tag{167}$$

is the classical momentum of the particle. From a mathematical standpoint, the basic WKB equation (166) is a Riccati first-order differential equation (Ince, 1963).

We now expand $y(x)$ into powers of $(-i\hbar)$:

$$y(x) = y_0 + (-i\hbar)y_1 + (-i\hbar)^2 y_2 + \cdots \tag{168}$$

$$\frac{dy}{dx} = \frac{dy_0}{dx} + (-i\hbar)\frac{dy_1}{dx} + (-i\hbar)^2\frac{dy_2}{dx} + \cdots, \tag{169}$$

where we must remark that (168) is a semiconvergent or *asymptotic* expansion (Erdèlyi, 1956), accurate far from the "turning points" where $E = V$. Then:

$$\begin{aligned}
&(-i\hbar)\frac{dy_0}{dx} + (-i\hbar)^2\frac{dy_1}{dx} + (-i\hbar)^3\frac{dy_2}{dx} + \cdots \\
&\quad = p^2 - \left\{y_0 + (-i\hbar)y_1 + (-i\hbar)^2 y_2 + (-i\hbar)^3 y_3 + \cdots\right\}^2 \\
&\quad = p^2 - y_0^2 - (-i\hbar)^2 y_1^2 - 2(-i\hbar)y_0y_1 - 2(-i\hbar)^2 y_0y_2 \\
&\quad - 2(-i\hbar)^3 y_1y_2 - 2(-i\hbar)^3 y_0y_3 + \cdots
\end{aligned} \tag{170}$$

and, collecting terms corresponding to same power of $(-i\hbar)^n$:

$$(-i\hbar)^0 \qquad p^2 - y_0^2 = 0 \tag{171}$$

$$(-i\hbar) \qquad \frac{dy_0}{dx} + 2y_0y_1 = 0 \tag{172}$$

$$(-i\hbar)^2 \qquad \frac{dy_1}{dx} + y_1^2 + 2y_0y_2 = 0 \tag{173}$$

$$(-i\hbar)^3 \qquad \frac{dy_2}{dx} + 2y_1y_2 + 2y_0y_3 = 0 \tag{174}$$

$$\cdots$$

Therefore we obtain the equations determining the various coefficients of the expansion (168):

$$y_0 = p = \pm\sqrt{2m(E-V)} = \pm\sqrt{2mT} \tag{175}$$

$$y_1 = -\frac{1}{2}\frac{1}{y_0}\frac{dy_0}{dx} = -\frac{1}{2}\frac{1}{p}\frac{dp}{dx} = -\frac{1}{2}\frac{d\ln p}{dx} \tag{176}$$

$$y_2 = -\frac{1}{2y_0}\left(y_1^2 + \frac{dy_1}{dx}\right) \tag{177}$$

$$\dots$$

Equation (175) is the *classical* result expressing the momentum of the particle, (176) gives the first quantum correction, (177) the second correction, and so on. In terms of the potential energy V (characterizing the system) and its first and second derivatives, V' and V'', we can write (see Problem 5.7):

$$y_1 = \frac{V'}{4(E-V)} \tag{178}$$

$$y_2 = \frac{1}{32}(2m)^{-1/2}(E-V)^{-5/2}\left\{5(V')^2 + 4(E-V)V''\right\}. \tag{179}$$

Now:

$$\exp\left[\int y_0 dx\right] = \exp\left[\int \sqrt{2m(E-V)}dx\right] \tag{180}$$

$$\begin{aligned}\int y_1 dx &= \int dx \frac{V'}{4(E-V)} = -\frac{1}{4}\int \frac{d(E-V)}{E-V} \\ &= -\frac{1}{4}\int d\ln(E-V) = \ln(E-V)^{-1/4}\end{aligned} \tag{181}$$

$$\exp\left[\int y_1 dx\right] = \exp\left[\ln(E-V)^{-1/4}\right] = (E-V)^{-1/4}, \tag{182}$$

giving as the first 2-term approximation:

$$\begin{aligned}\exp\left[\int y dx\right] &\cong \exp\left[\int y_0 dx\right]\cdot\exp\left[\int y_1 dx\right] \\ &= (E-V)^{-1/4}\exp\left[\int \sqrt{2m(E-V)}dx\right]\end{aligned} \tag{183}$$

$$\begin{aligned}\psi(x) &\propto \exp\left[\frac{i}{\hbar}\int y dx\right] \\ &\cong N(E-V)^{-1/4}\exp\left[\frac{i}{\hbar}\int \sqrt{2m(E-V)}dx\right]\end{aligned} \tag{184}$$

with the probability distribution:

$$|\psi|^2 = N^2(E - V)^{-1/2} \approx \text{constant} \times \frac{1}{p} \tag{185}$$

that coincides with the *classical* result.

Quantization will result when we try to extend the wavefunction into the region where $E < V$ (imaginary kinetic energy). The restriction imposed on E demands that:

$$\oint y dx = nh \quad n = 0, 1, 2, \cdots, \tag{186}$$

where the cyclic integral (the *action* integral) can be calculated only for conditionally periodic systems, and n is a positive integer.

If we insert in (186) the first term of the series (168) for y, $y = y_0 = p$, we obtain the condition of the *old* quantum theory:

$$\oint p dx = nh \quad n = 0, 1, 2, \cdots \tag{187}$$

while the second term introduces the half-quantum numbers characteristic of the *new* quantum theory:

$$-i\hbar \oint y_1 dx = -\frac{h}{2} \tag{188}$$

$$\oint (y_0 - i\hbar y_1) dx = \oint p dx - \frac{h}{2} = nh \tag{189}$$

so that:

$$\oint p dx = \left(n + \frac{1}{2}\right) h \tag{190}$$

to the second approximation.

In deriving (188) use has been made of the contour integration techniques in the complex plane (Problem 5.8).

5.8 PROBLEMS 5

5.1. Find a simple variational approximation to the ground state of the particle in a box of side a with impenetrable walls.

Answer:

$$\varphi = N x (a - x)$$

$$\varepsilon_\varphi = \frac{5}{a^2}.$$

Hint:
Use a trial function satisfying the boundary conditions.

5.2. Find a variational approximation to the first excited state of the particle in a box of side a with impenetrable walls.

Answer:

$$\varphi = Nx(a-x)\left(\frac{a}{2}-x\right)$$

$$\varepsilon_\varphi = \frac{21}{a^2}.$$

Hint:
Follow the same suggestions of Problem 5.1.

5.3. Find a simple variational approximation to the ground state of the 1-dimensional harmonic oscillator.

Answer:

$$\varphi = N\exp(-cx^2)$$

$$\varepsilon(c) = \frac{c}{2} + \frac{k}{8}c^{-1},$$

where k is the force constant. Optimization of the orbital exponent in φ gives as best variational values:

$$c_{\min} = \frac{1}{2}\sqrt{k}$$

$$\varepsilon_{\min} = \frac{1}{2}\sqrt{k}.$$

Hint:
Evaluate all necessary integrals over the Gaussian functions using the general formulae given in Section 9.2 of Chapter 4.

5.4. Find a variational approximation to the first excited state of the 1-dimensional harmonic oscillator.

Answer:

$$\varphi = Nx\exp(-cx^2), \quad \langle\psi_0|\varphi\rangle = 0$$

$$\varepsilon(c) = \frac{c}{2}c + \frac{3}{8}kc^{-1}.$$

Optimization of the orbital exponent c gives as best variational values:

$$c_{\text{min}} = \frac{1}{2}\sqrt{k}$$

$$\varepsilon_{\text{min}} = \frac{3}{2}\sqrt{k}.$$

Hint:
Follow the suggestions of Problem 5.3.

5.5. Find a simple method allowing to minimize the energy as a function of a single variable parameter c.

Answer:
The Ransil method.

Hint:
Expand the function $\varepsilon(c)$ in powers of c according to Taylor.

5.6. Perform Eckart's calculation for He($1s^2$) and find the best variational values for energy and orbital exponents.

Answer:

$$\varepsilon = -2.875\,661\,E_h$$

$$c_1 = 2.183\,171, c_2 = 1.188\,531.$$

Hint:
Evaluate the necessary matrix elements and integrals, transform to variables $x = \dfrac{c_1 + c_2}{2}$ and $S = x^{-3}(c_1c_2)^{3/2}$, find the relation between x and S, then optimize ε against the single parameter S using Ransil's method.

5.7. Find the expressions of y_1 and y_2 in the series expansion of the action $y(x)$.

Answer:

$$y_1 = \frac{V'}{4(E-V)}$$

$$y_2 = -\frac{1}{32}(2m)^{-1/2}(E-V)^{-5/2}\{5(V')^2 + 4(E-V)V''\}.$$

where:

$$V' = \frac{dV}{dx}, \qquad V'' = \frac{d^2V}{dx^2}.$$

Hint:
Integrate the differential equations (176) and (177).

5.8. Evaluate the phase integral (188).

Answer:

$$-i\hbar \oint y_1 dx = -\frac{h}{2}$$

where h is the Planck constant.

Hint:
Use contour integration in the complex plane.

5.9 SOLVED PROBLEMS

5.1. Variational approximation to the ground state of the particle in a box of side a.

We see that the simple function:

$$\varphi = Nx(a-x) = N(ax - x^2)$$

is a correct variational wavefunction not containing any adjustable parameter but satisfying the boundary conditions of the problem at $x = 0$ and $x = a$ ($\varphi = 0$).

Normalization factor:

$$\langle\varphi|\varphi\rangle = N^2 \int_0^a dx (ax - x^2)^2 = N^2 \frac{a^5}{30} = 1 \Rightarrow N = \left(\frac{30}{a^5}\right)^{1/2}.$$

Derivatives evaluation:

$$\frac{d\varphi}{dx} = N(a-2x), \qquad \frac{d^2\varphi}{dx^2} = -2N$$

$$\left\langle \varphi \middle| \frac{d^2\varphi}{dx^2} \right\rangle = -2N^2 \int_0^a dx (ax - x^2) = -\frac{10}{a^2}$$

thereby giving:

$$\varepsilon_\varphi = \langle T\rangle_\varphi = \left\langle \varphi \left| -\frac{1}{2}\frac{d^2\varphi}{dx^2} \right| \varphi \right\rangle = \frac{5}{a^2}.$$

Since the exact value for the ground state is (Chapter 3):

$$E_1 = \frac{\pi^2}{2a^2} = 4.934802\frac{1}{a^2}$$

the variational result exceeds the correct value by 1.32%.

5.2. Variational approximation to the first excited state of the particle in a box of side a.

In this case, we must construct a variational function satisfying the boundary conditions at $x = 0$, $x = a/2$ and $x = a$ ($\varphi = 0$) and orthogonal to the ground state function. A trial function satisfying all these conditions is:

$$\varphi = Nx(a-x)\left(\frac{a}{2} - x\right) = \frac{N}{2}(a^2x - 3ax^2 + 2x^3).$$

It can be easily shown that such a function is orthogonal to either φ_1 or to the true ground state ψ_1. This is easily shown for φ_1, since:

$$\begin{aligned}\langle\varphi_1|\varphi\rangle &\propto \langle ax - x^2|a^2x - 3ax^2 + 2x^3\rangle \\ &= \int_0^a dx(a^3x^2 - 4a^2x^3 + 5ax^4 - 2x^5) \\ &= a^6\left(\frac{1}{3} - 1 + 1 - \frac{2}{6}\right) = 0,\end{aligned}$$

while a little longer calculation shows that the chosen variational wavefunction for the first excited state is orthogonal to the true ground state wavefunction $\psi_1 \propto \sin\alpha x$ with $\alpha = \pi/a$ for $n = 1$. The skill student may do this calculation by himself using the general integral (Gradshteyn and Ryzhik, 1980, p. 183):

$$\int dx x^n \sin\alpha x = -\sum_{k=0}^{n} k!\binom{n}{k}\frac{x^{n-k}}{\alpha^{k+1}}\cos\left(\alpha x + k\frac{\pi}{2}\right).$$

Turning to our starting function φ, we now evaluate all necessary integrals.

Normalization factor:

$$\begin{aligned}\langle\varphi|\varphi\rangle &= \frac{N^2}{4}\int_0^a dx x^2(a^2 - 3ax + 2x^2)^2 \\ &= \frac{N^2}{4}\int_0^a dx(a^4x^2 - 6a^3x^3 + 13a^2x^4 - 12ax^5 + 4x^6)\end{aligned}$$

$$= N^2\frac{a^7}{4}\left(\frac{1}{3}-\frac{3}{2}+\frac{13}{5}-2+\frac{4}{7}\right) = N^2\frac{a^7}{840} = 1 \Rightarrow N = \left(\frac{840}{a^7}\right)^{1/2}.$$

Derivatives evaluation:

$$\frac{d\varphi}{dx} = \frac{N}{2}(a^2 - 6ax + 6x^2)$$

$$\frac{d^2\varphi}{dx^2} = 3N(-a+2x)$$

$$\left\langle \varphi \middle| \frac{d^2\varphi}{dx^2} \right\rangle = \frac{3}{2}N^2 \int_0^a dx(-a^3x + 5a^2x^2 - 8ax^3 + 4x^4) = -\frac{42}{a^2}$$

thereby giving:

$$\varepsilon_\varphi = \langle T \rangle_\varphi = \left\langle \varphi \middle| -\frac{1}{2}\frac{d^2\varphi}{dx^2} \middle| \varphi \right\rangle = \frac{21}{a^2}.$$

Since the exact value for the first excited state is:

$$E_2 = 4\frac{\pi^2}{2a^2} = \frac{2\pi^2}{a^2} = 19.739209\frac{1}{a^2}$$

the variational result exceeds by 6.4% the exact value.

So, the approximation is worst than that for the ground state, but it must not be forgotten that φ has *no* variational parameters in it.

The following two problems illustrate the equality sign in equations (2) and (3) of Section 5.2.1 in the case of the first two states of the harmonic oscillator, which we have not treated in this book, but of which good account is given, for instance in Eyring et al. (1944). We summarize here the main exact results for comparison.

$$a = \frac{\beta}{2}, \quad 2a = \beta = \sqrt{k} \quad k = \text{force constant}$$

$$\psi_0(x) = \left(\frac{2a}{\pi}\right)^{1/4} \exp(-ax^2) = \left(\frac{\beta}{\pi}\right)^{1/4} \exp(-\frac{\beta}{2}x^2), \quad E_0 = \frac{1}{2}\beta = \frac{1}{2}\sqrt{k}$$

$$\psi_1(x) = \left(4a\sqrt{\frac{2a}{\pi}}\right)^{1/2} x\exp(-ax^2) = \left(2\beta\sqrt{\frac{\beta}{\pi}}\right)^{1/2} x\exp\left(-\frac{\beta}{2}x^2\right)$$

$$E_1 = \frac{3}{2}\beta = \frac{3}{2}\sqrt{k}.$$

5.3. Variational calculation for the ground state of the harmonic oscillator in one dimension.

As a convenient variational function, satisfying all regularity conditions, we choose the Gaussian:

$$\varphi = N\exp(-cx^2),$$

where $c > 0$ is a non-linear variation parameter. Using the general integral over Gaussian functions given by equations (131) and (132) of Chapter 4, the following results are easily obtained.

Normalization factor:

$$\begin{aligned}\langle\varphi|\varphi\rangle &= N^2\int_{-\infty}^{\infty} dx\exp(-2cx^2) = 2N^2\int_0^{\infty} dx\exp(-2cx^2)\\ &= N^2\left(\frac{\pi}{2c}\right)^{1/2} = 1 \Rightarrow N = \left(\frac{2c}{\pi}\right)^{1/4}.\end{aligned}$$

Average kinetic energy:

$$\frac{d\varphi}{dx} = N\exp(-cx^2)(-2cx), \qquad \frac{d^2\varphi}{dx^2} = -2c(1-2cx^2)\varphi$$

$$\begin{aligned}\langle\varphi|x^2|\varphi\rangle &= N^2\int_{-\infty}^{\infty} dx x^2\exp(-2cx^2) = 2N^2\int_0^{\infty} dx x^2\exp(-2cx^2)\\ &= 2N^2\frac{1}{8c}\left(\frac{\pi}{2c}\right)^{1/2} = 2\left(\frac{2c}{\pi}\right)^{1/2}\frac{1}{8c}\left(\frac{\pi}{2c}\right)^{1/2} = \frac{1}{4c}\end{aligned}$$

$$\begin{aligned}\left\langle\varphi\middle|\frac{d^2\varphi}{dx^2}\right\rangle &= -2c\langle\varphi|1-2cx^2|\varphi\rangle\\ &= -2c\{1-2c\langle\varphi|x^2|\varphi\rangle\} = -2c\left(1-2c\frac{1}{4c}\right) = -c\end{aligned}$$

$$\langle T\rangle = \left\langle\varphi\middle|-\frac{1}{2}\frac{d^2\varphi}{dx^2}\middle|\varphi\right\rangle = \frac{c}{2}.$$

Average potential energy:

$$\langle V\rangle = \left\langle\varphi\middle|\frac{kx^2}{2}\middle|\varphi\right\rangle = \frac{k}{2}\frac{1}{4c} = \frac{k}{8c}.$$

Total energy:

$$\varepsilon(c) = \langle T\rangle + \langle V\rangle = \frac{c}{2} + \frac{k}{8}c^{-1}$$

$$\frac{d\varepsilon}{dc}=\frac{1}{2}-\frac{k}{8}c^{-2}=0\Rightarrow c^2=\frac{k}{4}\Rightarrow c_{\min}=\frac{\sqrt{k}}{2}$$

$$\frac{d^2\varepsilon}{dc^2}=\frac{k}{4}c^{-3}\qquad\left(\frac{d^2\varepsilon}{dc^2}\right)_{c=\frac{\sqrt{k}}{2}}=\frac{2}{\sqrt{k}}>0$$

ensuring the existence of a true minimum. Therefore:

$$\varepsilon_{\min}=\frac{\sqrt{k}}{4}+\frac{k}{8}\frac{2}{\sqrt{k}}=2\frac{\sqrt{k}}{4}=\frac{\sqrt{k}}{2}=E_0$$

$$\varphi_{\text{best}}=N\exp\left(-\frac{\sqrt{k}}{2}x^2\right)=\left(\frac{\beta}{\pi}\right)^{1/4}\exp\left(-\frac{\beta}{2}x^2\right)=\psi_0$$

which are, respectively, the *exact* energy and wavefunction for the ground state. So, in this case, the equality sign holds in the variation principle for the ground state.

5.4. Variational calculation for the first excited state of the harmonic oscillator in one dimension.

We choose the function:

$$\varphi=Nx\exp(-cx^2),$$

where $c>0$ is the non-linear variation parameter. This function satisfies the regularity conditions and is orthogonal to ψ_0 by symmetry:

$$\langle\psi_0|\varphi\rangle\propto\langle\textit{even}\text{ function}|\textit{odd}\text{ function}\rangle=0$$

as can be easily verified. In fact, consider the integral:

$$\int_{-\infty}^{\infty}dx\,x\exp(-2cx^2)=\int_{-\infty}^{0}dx\,x\exp(-2cx^2)+\int_{0}^{\infty}dx\,x\exp(-2cx^2).$$

In the first integral of the right-hand-side, change $x\to -x$ obtaining:

$$\int_{-\infty}^{0}dx\,x\exp(-2cx^2)=\int_{\infty}^{0}dx\,x\exp(-2cx^2)=-\int_{0}^{\infty}dx\,x\exp(-2cx^2)$$

so that:

$$\int_{-\infty}^{\infty}dx\,x\exp(-2cx^2)=-\int_{0}^{\infty}dx\,x\exp(-2cx^2)+\int_{0}^{\infty}dx\,x\exp(-2cx^2)=0.$$

We then easily obtain the following results.

Normalization factor:

$$\begin{aligned}\langle\varphi|\varphi\rangle &= N^2\int_{-\infty}^{\infty}dx\,x^2\exp(-2cx^2) = 2N^2\int_0^{\infty}dx\,x^2\exp(-2cx^2)\\ &= 2N^2\frac{1}{8c}\left(\frac{\pi}{2c}\right)^{1/2} = N^2\frac{1}{4c}\left(\frac{\pi}{2c}\right)^{1/2} = 1 \Rightarrow N = \left(4c\sqrt{\frac{2c}{\pi}}\right)^{1/2}.\end{aligned}$$

Average kinetic energy:

$$\frac{d\varphi}{dx} = N\exp(-cx^2)(1-2cx^2), \qquad \frac{d^2\varphi}{dx^2} = -2c(3-2cx^2)\varphi$$

$$\begin{aligned}\langle\varphi|x^2|\varphi\rangle &= 2N^2\int_0^{\infty}dx\,x^4\exp(-2cx^2)\\ &= 2N^2\frac{3}{2^5c^2}\left(\frac{\pi}{2c}\right)^{1/2} = 4c\left(\frac{2c}{\pi}\right)^{1/2}\frac{3}{16c^2}\left(\frac{\pi}{2c}\right)^{1/2} = \frac{3}{4c}\end{aligned}$$

$$\begin{aligned}\left\langle\varphi\left|\frac{d^2\varphi}{dx^2}\right.\right\rangle &= -2c\langle\varphi|3-2cx^2|\varphi\rangle\\ &= -2c\{3-2c\langle\varphi|x^2|\varphi\rangle\} = -2c\left(3-2c\frac{3}{4c}\right) = -3c\end{aligned}$$

$$\langle T\rangle = \left\langle\varphi\left|-\frac{1}{2}\frac{d^2\varphi}{dx^2}\right|\varphi\right\rangle = \frac{3}{2}c.$$

Average potential energy:

$$\langle V\rangle = \left\langle\varphi\left|\frac{kx^2}{2}\right|\varphi\right\rangle = \frac{k}{2}\frac{3}{4c} = 3\frac{k}{8c}.$$

Total energy:

$$\varepsilon(c) = \langle T\rangle + \langle V\rangle = \frac{3}{2}c + \frac{3}{8}kc^{-1}$$

$$\frac{d\varepsilon}{dc} = \frac{3}{2} - \frac{3}{8}kc^{-2} = 0 \Rightarrow c^2 = \frac{k}{4} \Rightarrow c_{\min} = \frac{\sqrt{k}}{2}$$

$$\frac{d^2\varepsilon}{dc^2} = \frac{3}{4}kc^{-3} \qquad \left(\frac{d^2\varepsilon}{dc^2}\right)_{c=\frac{\sqrt{k}}{2}} = \frac{6}{\sqrt{k}} > 0$$

ensuring the existence of a true minimum. Therefore:

$$\varepsilon_{\min} = \frac{3}{2}\frac{\sqrt{k}}{2} + \frac{3}{8}k\frac{2}{\sqrt{k}} = 2\frac{3}{4}\sqrt{k} = \frac{3}{2}\sqrt{k} = E_1$$

$$\varphi_{\text{best}} = Nx\exp\left(-\frac{\sqrt{k}}{2}x^2\right) = \left(2\beta\sqrt{\frac{\beta}{\pi}}\right)^{1/2} x\exp(-\frac{\beta}{2}x^2) = \psi_1$$

so that the best variational results coincide with the *exact* results for energy and first excited wavefunction. In this case, again, the equality sign holds in the variation principle for the first excited state.

5.5. The Ransil method.

Ransil (1960a) suggested an elementary method that allows for the 3-point numerical minimization of a function having a parabolic behaviour near the minimum. By restricting ourselves to a function of a single parameter c, we expand $\varepsilon(c)$ around c_0 in the Taylor power series:

$$\varepsilon(c) = \varepsilon(c_0) + \left(\frac{d\varepsilon}{dc}\right)_{c_0}\Delta c + \frac{1}{2}\left(\frac{d^2\varepsilon}{dc^2}\right)_{c_0}(\Delta c)^2 + \cdots,$$

where:

$$\Delta c = c - c_0$$

with c_0 a convenient starting point (better near to the minimum). At the minimum point we must have:

$$\frac{d\varepsilon}{d\Delta c} = \left(\frac{d\varepsilon}{dc}\right)_{c_0} + \left(\frac{d^2\varepsilon}{dc^2}\right)_{c_0}\Delta c = 0$$

so that the first correction will be:

$$\Delta c = -\frac{\left(\frac{d\varepsilon}{dc}\right)_{c_0}}{\left(\frac{d^2\varepsilon}{dc^2}\right)_{c_0}}.$$

By choosing as a new starting point $c_0 + \Delta c$, the process can be iterated until a predetermined threshold is reached. This usually happens provided the iteration process converges if the starting point c_0 is well chosen. First and second derivatives can be evaluated numerically starting from the definitions:

$$\left(\frac{d\varepsilon}{dc}\right)_{c_0} = \frac{\varepsilon(c_0+\Delta c) - \varepsilon(c_0-\Delta c)}{2\Delta c} \tag{191}$$

$$\left(\frac{d^2\varepsilon}{dc^2}\right)_{c_0} = \frac{\varepsilon(c_0+\Delta c)+\varepsilon(c_0-\Delta c)-2\varepsilon(c_0)}{(\Delta c)^2}. \tag{192}$$

As a starting increment it is convenient to choose a small value for Δc, say $\Delta c = 0.01$. For convenience, the second derivative is evaluated from the incremental ratio of the first derivatives taken in $c_0 + \frac{\Delta c}{2}$ and $c_0 - \frac{\Delta c}{2}$, respectively:

$$\left(\frac{d\varepsilon}{dc}\right)_{c_0+\frac{\Delta c}{2}} = \frac{\varepsilon\left(c_0+\frac{\Delta c}{2}+\frac{\Delta c}{2}\right)-\varepsilon\left(c_0+\frac{\Delta c}{2}-\frac{\Delta c}{2}\right)}{2\cdot\frac{\Delta c}{2}} = \frac{\varepsilon(c_0+\Delta c)-\varepsilon(c_0)}{\Delta c}.$$

Similarly:

$$\left(\frac{d\varepsilon}{dc}\right)_{c_0-\frac{\Delta c}{2}} = \frac{\varepsilon(c_0)-\varepsilon(c_0-\Delta c)}{\Delta c}$$

so that:

$$\begin{aligned}\left(\frac{d^2\varepsilon}{dc^2}\right)_{c_0} &= \frac{\left(\frac{d\varepsilon}{dc}\right)_{c_0+\frac{\Delta c}{2}}-\left(\frac{d\varepsilon}{dc}\right)_{c_0-\frac{\Delta c}{2}}}{\Delta c}\\ &= \frac{\varepsilon(c_0+\Delta c)+\varepsilon(c_0-\Delta c)-2\varepsilon(c_0)}{(\Delta c)^2}\end{aligned}$$

which is the result given in (192).

5.6. Eckart's calculation on He.

Eckart' split-shell approach to the ground state of the He-like atom was revisited by Figari (1991), who introduces a variable transformation allowing to optimize the variational energy with respect to just the non-orthogonality integral S between φ_1 and φ_2. Let:

$$\varphi_1 = \left(\frac{c_1^3}{\pi}\right)^{1/2}\exp(-c_1 r), \qquad \varphi_2 = \left(\frac{c_2^3}{\pi}\right)^{1/2}\exp(-c_2 r)$$

be the normalized $1s$ STOs having the non-orthogonality integral:

$$S = \langle\varphi_1|\varphi_2\rangle = \left(\frac{2(c_1c_2)^{1/2}}{c_1+c_2}\right)^3.$$

The symmetrized 2-electron trial function containing *two* non-linear variational parameters (an *atomic* "split-shell" function) in its normalized form is:

$$\varphi(1,2) = N[\varphi_1(1)\varphi_2(2)+\varphi_2(1)\varphi_1(2)]$$

$$N = (2+2S^2)^{-1/2}$$

and is reminiscent of the Heitler–London wavefunction for ground state H_2, the corresponding *molecular* "split-shell" function.

After integration, the energy functional $\varepsilon[\varphi]$ becomes a function of c_1 and c_2:

$$\begin{aligned}\varepsilon[\varphi] &= \left\langle \varphi \middle| \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \middle| \varphi \right\rangle \\ &= \frac{h_{11} + h_{22} + 2Sh_{12} + (\varphi_1^2|\varphi_2^2) + (\varphi_1\varphi_2|\varphi_1\varphi_2)}{1+S^2} = \varepsilon(c_1, c_2)\end{aligned}$$

since all matrix elements depend on c_1 and c_2:

$$h_{11} = \frac{c_1^2}{2} - Zc_1, \qquad h_{22} = \frac{c_2^2}{2} - Zc_2, \qquad h_{12} = \frac{S}{2}\big[c_1c_2 - Z(c_1+c_2)\big]$$

$$(\varphi_1^2|\varphi_2^2) = \frac{c_1c_2}{c_1+c_2}\left\{1 + \frac{c_1c_2}{(c_1+c_2)^2}\right\}, \qquad (\varphi_1\varphi_2|\varphi_1\varphi_2) = 20\frac{(c_1c_2)^3}{(c_1+c_2)^5}.$$

Transforming from variables c_1, c_2 to the new variables x, S defined as:

$$x = \frac{c_1+c_2}{2}, \qquad S = x^{-3}(c_1c_2)^{3/2}$$

the variational energy becomes:

$$\begin{aligned}\varepsilon(x, S) &= -2Zx + S^{2/3}x^2 \\ &\quad + \frac{2(1-S^{2/3})x^2 + \left(\frac{1}{2}S^{2/3} + \frac{1}{8}S^{4/3} + \frac{5}{8}S^2\right)x}{1+S^2}.\end{aligned}$$

The stationarity condition of ε against x:

$$\left(\frac{\partial \varepsilon}{\partial x}\right)_S = -2Z + 2S^{2/3}x + \frac{4(1-S^{2/3})x + \left(\frac{1}{2}S^{2/3} + \frac{1}{8}S^{4/3} + \frac{5}{8}S^2\right)x}{1+S^2} = 0$$

gives:

$$x = \frac{Z - \frac{1}{4}S^{2/3} - \frac{1}{16}S^{4/3} + \left(Z - \frac{5}{16}\right)S^2}{2 - S^{2/3} + S^{8/3}},$$

a relation which allows us to optimize ε with respect to the *single* variable S. For any given value of S in the range $0 \le S \le 1$, the best x is obtained from the relation above. For $S = 1$, $c_1 = c_2$ and $x = Z - 5/16$, the well known variational result for the single orbital exponent. When ε has been minimized with respect to S (e.g. by the Ransil method of Problem 5.5), from the relations:

$$c_1 + c_2 = 2x \qquad c_1c_2 = x^2S^{2/3},$$

the best values of the orbital exponents c_1 and c_2 are obtained by the inverse relations:

$$c_1 = x\left\{1 + \left(1 - S^{2/3}\right)^{1/2}\right\}, \qquad c_2 = x\left\{1 - \left(1 - S^{2/3}\right)^{1/2}\right\}.$$

The best value of ε:

$$\varepsilon = -2.875\,661\,331\,E_h$$

is obtained for:

$$S = 0.872\,348\,108, \quad x = 1.685\,850\,852$$

giving as best values for the orbital exponents of the optimized Eckart function:

$$c_1 = 2.183\,170\,865, \qquad c_2 = 1.188\,530\,839.$$

The "splitting" of the orbital exponents from their average value $x = 1.6858$ (not far from the best value for the single orbital exponent, 1.6875) accounts for some "radial" correlation ($l = 0$) between the electrons, yielding a lowering in the electronic energy of about $28 \times 10^{-3} E_h$. Improvement upon Eckart result might be obtained by further introducing the "angular" correlation ($l \neq 0$) between the electrons, i.e. using Eckart-like wavefunctions involving $p, d, f, g, \cdots$ optimized orbitals.

5.7. Coefficients y_1 and y_2 in the WKB series expansion of $y(x)$.
Equation (175) for the momentum p gives (apart from the signs in front)

$$\ln p = \frac{1}{2}\ln(2mE - 2mV)$$

$$\frac{d\ln p}{dx} = \frac{1}{2}\frac{-2mV'}{2mE - 2mV} = -\frac{V'}{2(E - V)}$$

so that equation (176) gives for y_1:

$$y_1 = -\frac{1}{2}\frac{d\ln p}{dx} = \frac{V'}{4(E - V)}$$

which is the required equation (178). Then:

$$(y_1)^2 = \frac{1}{16}(V')^2(E - V)^{-2}$$

$$\frac{dy_1}{dx} = \frac{1}{4}V''(E - V)^{-1} - \frac{1}{4}V'(E - V)^{-2}(-V')$$

$$= \frac{1}{4}(E - V)^{-2}\left\{(V')^2 + (E - V)V''\right\},$$

and, from equation (177):

$$\begin{aligned} y_2 &= -\frac{1}{2p}\left\{\frac{1}{16}(E-V)^{-2}(V')^2 \right. \\ &\quad \left. + \frac{1}{4}(E-V)^{-2}(V')^2 + \frac{1}{4}(E-V)^{-1}V''\right\} \\ &= -\frac{1}{2p}(E-V)^{-2}\left\{\frac{5}{16}(V')^2 + \frac{1}{4}(E-V)(V'')\right\} \\ &= -\frac{1}{32p}(E-V)^{-2}\{5(V')^2 + 4(E-V)(V'')\}, \end{aligned}$$

which, upon substituting:

$$p^{-1} = \{2m(E-V)\}^{-1/2} = (2m)^{-1/2}(E-V)^{-1/2}$$

gives the required equation (179).

5.8. The cyclic integral.

As far as integral (188) is concerned, we notice that from (178):

$$\oint y_1 dx = \oint dx \frac{V'}{4(E-V)} = -\frac{1}{4}\oint \frac{d(E-V)}{E-V}.$$

Introduce now the complex plane of Figure 5.9, and pose the complex variable:

$$E - V = z = \rho \exp(i\varphi).$$

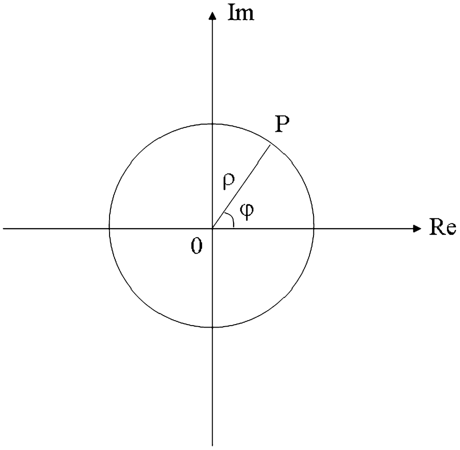


Figure 5.9 Integration path for the complex variable z.

Then:

$$dz = i\rho \exp(i\varphi) d\varphi$$

giving:

$$\oint \frac{dz}{z} = \oint \frac{i\rho \exp(i\varphi) d\varphi}{\rho \exp(i\varphi)} = i \oint d\varphi = 2\pi i,$$

so that:

$$\oint y_1 dx = -\frac{1}{4} \cdot 2 \oint \frac{dz}{z} = -i\pi.$$

Hence, we finally obtain:

$$-i\hbar \oint y_1 dx = -i\hbar(-i\pi) = -\frac{h}{2}$$

which is the required result (188).

– 6 –

The Electron Spin

6.1 INTRODUCTION

The three quantum numbers we found in Chapter 3 from the exact solution of the 1-electron atomic problem are not enough for a complete physical description of the electron states. The lines observed in the atomic spectrum of hydrogen under high resolution show a fine structure which cannot be explained in terms of the simple theory we have presented so far. It is observed that in a magnetic field even the non-degenerate $1s$ ground state of the H atom splits into two lines whose separation is many orders of magnitude smaller than that of the spectroscopic lines arising from the optical transitions from ground to excited states. The explanation of this fact was first given by Uhlenbeck and Goudsmit (1925, 1926) and then formalized by Pauli (1926) in terms of a new property of the electron, its intrinsic angular momentum or electron spin.

After a short introduction of the Zeeman effect for a non-degenerate 1-electron level giving a physical basis to the Pauli hypothesis of the two-state electron spin, we shall formally develop the theory of 1-electron and 2-electron spin, giving an indication on how to proceed in treating the many-electron problem. It will be seen in the next Chapter that the latter is connected to the permutational symmetry of the many-electron wavefunction. We shall treat explicitly spin states alone, since the formalism derived is in one-to-one correspondence with that of the spin-orbitals needed for the correct description of many-electron wavefunctions in the Slater method (Chapter 7).

Connection of spin with the properties of the symmetric group of $N!$ permutations will be briefly mentioned in Chapter 8, devised to symmetry and group theory. As a last point, we stress that all we can say for electron spin $1/2$ is equally valid for nuclei of spin $1/2$, like ^{1}H and ^{13}C.

6.2 ELECTRON SPIN ACCORDING TO PAULI AND THE ZEEMAN EFFECT

In the absence of a magnetic field the 1*s* ground state of the H atom shows a twofold spin degeneracy. A magnetic field removes this degeneracy, and for a field of 1 Tesla (10^4 Gauss) the Zeeman splitting is about 10^5 times smaller than the separation observed between the first orbital levels (Figure 6.1). We recall that transitions between stationary energy levels produce the spectral lines observed for atoms.

The orbital magnetic moment μ_L of an electron of charge $-e/c$ (in electromagnetic units) moving in a circular orbit of radius r with tangential velocity v is elementarily given by:

$$\begin{aligned}\mu_L &= \text{involved surface} \times \text{current intensity circulating in the orbit}\\ &= \pi r^2 \times \frac{-e/c}{\frac{2\pi r}{v}} = -\frac{e}{2mc}(mvr) = -\frac{e}{2mc}L,\end{aligned} \tag{1}$$

where L is the value of the orbital angular momentum. Since according to quantum mechanics the permissible values of L are $\hbar\sqrt{l(l+1)}$, the corresponding quantum mechanical operator will be:

$$\hat{\boldsymbol{\mu}}_L = -\frac{e\hbar}{2mc}\hat{\boldsymbol{L}} = -\beta_e\hat{\boldsymbol{L}}, \tag{2}$$

where:

$$\hat{\boldsymbol{L}} = \mathbf{i}\hat{L}_x + \mathbf{j}\hat{L}_y + \mathbf{k}\hat{L}_z \tag{3}$$

is the orbital angular momentum vector operator, and:

$$\beta_e = \frac{e\hbar}{2mc} = 9.274015 \times 10^{-24} \quad \frac{\text{J}}{\text{Tesla}} \tag{4}$$

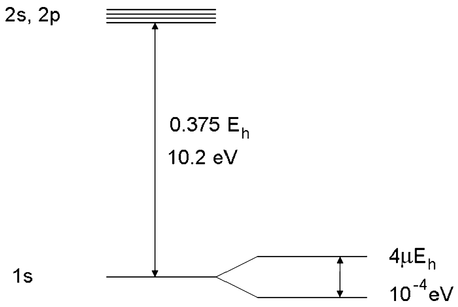


Figure 6.1 Zeeman splitting for the ground state H atom in a magnetic field of 1 Tesla (not in scale).

the Bohr magneton (the unit of magnetic moment). We assume for the spin magnetic moment:

$$\hat{\boldsymbol{\mu}}_S = -g_e \beta_e \hat{\mathbf{S}}, \tag{5}$$

where:

$$\hat{\mathbf{S}} = \mathbf{i}\hat{S}_x + \mathbf{j}\hat{S}_y + \mathbf{k}\hat{S}_z \tag{6}$$

is the electron spin vector operator, and $g_e \approx 2$ the intrinsic electron g-factor[1], the so called spin anomaly. In the atomic LS-coupling g_J is the Landé g-factor and is given by (Eyring et al., 1944; Herzberg, 1944):

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}. \tag{7}$$

For the simple s-electron, $L = 0$, $S = 1/2$, $J = L + S = 1/2$ and $g_J = 2$.

The electron with spin in the uniform magnetic field $\mathbf{B}$ ($B_x = B_y = 0$, $B_z = B$) acquires the potential energy:

$$V = -\hat{\boldsymbol{\mu}}_S \cdot \mathbf{B} = g_e \beta_e B \hat{S}_z. \tag{8}$$

so that the total Hamiltonian (including spin) will be:

$$\hat{h}(\mathbf{r}, s) = \hat{h}_0(\mathbf{r}) + g_e \beta_e B \hat{S}_z. \tag{9}$$

From now on, we shall use $\mathbf{r}$ to denote a space variable, s the *formal* spin variable, $\mathbf{x} = \mathbf{r}s$ the space-spin variable. Pauli (1926) postulates for the electron the existence of two (orthonormal) spin states α, β:

$$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1 \qquad \langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0, \tag{10}$$

where in terms of the *formal* spin variable s we assume:

$$\langle\alpha|\beta\rangle = \int ds\alpha^*(s)\beta(s). \tag{11}$$

α, β are assumed to satisfy the eigenvalue equation for the z-component of spin, $\hat{S}_z$:

$$\hat{S}_z\alpha = \frac{1}{2}\alpha, \qquad \hat{S}_z\beta = -\frac{1}{2}\beta. \tag{12}$$

---

[1] $g_e = 2$ (Dirac), but, according to quantum-electrodynamics, $g_e = 2.002\,342$ (Schwinger, 1948). There is also the g-factor in molecular ESR and the g-tensor in solid state ESR, etc. (Atkins, 1983).

Generally speaking, instead of the space orbital $\chi_\lambda(\mathbf{r})$ we must consider the two spin-orbitals (SOs):

$$\psi_\lambda(\mathbf{x}) = \psi_\lambda(\mathbf{r}, s) = \chi_\lambda(\mathbf{r})\alpha(s) \tag{13}$$

$$\overline{\psi}_\lambda(\mathbf{x}) = \overline{\psi}_\lambda(\mathbf{r}, s) = \chi_\lambda(\mathbf{r})\beta(s) \tag{14}$$

which satisfy the eigenvalue equations:

$$\hat{h}_0\psi_\lambda = \varepsilon_\lambda\psi_\lambda \qquad \hat{h}_0\overline{\psi}_\lambda = \varepsilon_\lambda\overline{\psi}_\lambda \tag{15}$$

$$\hat{S}_z\psi_\lambda = \frac{1}{2}\psi_\lambda \qquad \hat{S}_z\overline{\psi}_\lambda = -\frac{1}{2}\overline{\psi}_\lambda \tag{16}$$

so that, in absence of magnetic field, the energy eigenvalue ε_λ is twofold degenerate.

The energy of the electron in presence of the magnetic field B (Zeeman effect) is readily evaluated by the Ritz method by considering the matrix representative of the Hamiltonian $\hat{h}(\mathbf{r}, s)$ over the two spin-orbital functions $(\psi_\lambda\overline{\psi}_\lambda)$:

$$\mathbf{h} = \begin{pmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix}, \tag{17}$$

where:

$$h_{11} = \langle\psi_\lambda|\hat{h}|\psi_\lambda\rangle = \langle\chi_\lambda\alpha|\hat{h}_0 + g_e\beta_e B\hat{S}_z|\chi_\lambda\alpha\rangle = \varepsilon_\lambda + \frac{1}{2}g_e\beta_e B \tag{18}$$

$$h_{22} = \langle\overline{\psi}_\lambda|\hat{h}|\overline{\psi}_\lambda\rangle = \langle\chi_\lambda\beta|\hat{h}_0 + g_e\beta_e B\hat{S}_z|\chi_\lambda\beta\rangle = \varepsilon_\lambda - \frac{1}{2}g_e\beta_e B \tag{19}$$

and

$$h_{12} = h_{21} = 0 \tag{20}$$

because the spin-orbitals are orthogonal. Hence, matrix $\mathbf{h}$ is already diagonal and the secular equation:

$$\begin{vmatrix} h_{11} - \varepsilon & 0 \\ 0 & h_{22} - \varepsilon \end{vmatrix} = 0 \tag{21}$$

has the roots:

$$\varepsilon_1 = h_{11} = \varepsilon_\lambda + \frac{1}{2}g_e\beta_e B \tag{22}$$

$$\varepsilon_2 = h_{22} = \varepsilon_\lambda - \frac{1}{2}g_e\beta_e B, \tag{23}$$

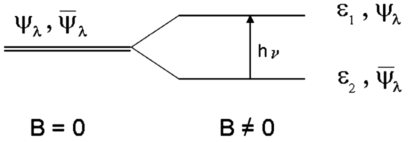


Figure 6.2 Zeeman splitting for a twofold degenerate level and origin of an ESR line.

giving a Zeeman splitting linear in the field B:

$$\Delta\varepsilon = \varepsilon_1 - \varepsilon_2 = g_e\beta_e B. \tag{24}$$

Since:

$$\Delta\varepsilon = h\nu \tag{25}$$

by the Planck law, transition between these two states is allowed by magnetic dipole radiation (Dixon, 1965), provided the magnetic vector of the electromagnetic wave has a component perpendicular to the static magnetic field (magnetic transition moment $\neq 0$). The electron spin can hence be re-oriented by a photon of energy:

$$h\nu = g_e\beta_e B \tag{26}$$

a process which is known as electron spin resonance (ESR). The frequency of the transition is proportional to B and, for a free electron, the constant of proportionality is:

$$\frac{g_e\beta_e}{h} \cong 2.8 \times 10^6 \text{ sec}^{-1}\,\text{Gauss}^{-1} = 2.8\ \text{MHz}\,\text{Gauss}^{-1}. \tag{27}$$

For a nucleus of spin $I = 1/2$, the nuclear spin functions α, β satisfy to:

$$\hat{I}_z\alpha = \frac{1}{2}\alpha \qquad \hat{I}_z\beta = -\frac{1}{2}\beta \tag{28}$$

and the nuclear spin Hamiltonian is:

$$\hat{h}_N = -g_N\beta_N B\hat{I}_z, \tag{29}$$

where for ^{1}H:

$$\beta_N = \frac{e\hbar}{2m_Pc} = \frac{1}{1836}\frac{e\hbar}{2mc} = \frac{1}{1836}\beta_e \tag{30}$$

is the nuclear magneton, and $g_N = 5.585$. The theory of the Zeeman effect reverses now the levels originating the splitting (state α being now the lowest), so that:

$$\varepsilon_2 - \varepsilon_1 = g_N\beta_N B = h\nu. \tag{31}$$

Magnetic dipole radiation gives now a transition whose frequency is still proportional to B, with a proportionality constant $g_N\beta_N/h$ which is about 4.258 kHz Gauss^{-1} for ^{1}H, and 1.070 kHz Gauss^{-1} for ^{13}C. Usually resonance is reached, for a given frequency, by varying the strength of the external field B. The process is known as nuclear magnetic resonance (NMR), mostly based on ^{1}H or ^{13}C. High resolution studies show hyperfine structure due to the coupling of nuclear spin. It is interesting to notice that, for a field of 1 Tesla = 10^4 Gauss, (i) the frequency of an ESR absorption is about $\nu \approx 2.8 \times 10^{10}$ Hz, corresponding to a wave length of:

$$\lambda = \frac{c}{\nu} \approx 1 \text{ cm} = 10^8 \text{ Å},$$

while (ii) the frequency of a proton NMR absorption is about $\nu \approx 4.3 \times 10^7$ Hz, corresponding to a wave length of:

$$\lambda = \frac{c}{\nu} \approx 700 \text{ cm} = 7 \times 10^{10} \text{ Å},$$

so that either absorptions occur in the radiofrequency region ($\lambda > 1$ cm, $\nu < 3 \times 10^{10}$ Hz).

6.3 THEORY OF 1-ELECTRON SPIN

Even if the Pauli postulate of the existence of two spin states α, β is sufficient to explain the origin of the linear Zeeman splitting, we do not know anything as yet about the components $\hat{S}_x$ and $\hat{S}_y$ of $\hat{\mathbf{S}}$. The equations pertaining to $\hat{S}_x$ and $\hat{S}_y$ are the consequence (i) of the commutation properties of the spin operators, which we take in analogy to those of the orbital angular momentum operator, and (ii) of the fact that the spin ladder for the single electron has only *two* steps. Assuming the magnetic field along z, we shall find that the components of the spin angular momentum operator do satisfy the following equations (in atomic units):

$$\begin{aligned} &\hat{S}_x\alpha = \frac{1}{2}\beta \qquad \hat{S}_y\alpha = \frac{1}{2}i\beta \qquad \hat{S}_z\alpha = \frac{1}{2}\alpha \\ &\hat{S}_x\beta = \frac{1}{2}\alpha \qquad \hat{S}_y\beta = -\frac{1}{2}i\alpha \qquad \hat{S}_z\beta = -\frac{1}{2}\beta, \end{aligned} \tag{32}$$

where i is the imaginary unit ($i^2 = -1$). Equations (32) are known as Pauli equations for spin 1/2. So, for $\hat{S}_z$ we have eigenvalue equations but the remaining components have the effect of permuting state α with state β after multiplication by suitable constants.

Under these assumptions, we can now easily show that the spin states α, β have the same eigenvalue $\frac{3}{4}$ with respect to $\hat{S}^2$:

$$\hat{S}^2\alpha = \frac{1}{2}\left(\frac{1}{2}+1\right)\alpha \qquad \hat{S}^2\beta = \frac{1}{2}\left(\frac{1}{2}+1\right)\beta \tag{33}$$

with $S = \frac{1}{2}$. In fact if:

$$\begin{aligned}\hat{S}^2 &= \hat{\mathbf{S}} \cdot \hat{\mathbf{S}} = (\mathbf{i}\hat{S}_x + \mathbf{j}\hat{S}_y + \mathbf{k}\hat{S}_z) \cdot (\mathbf{i}\hat{S}_x + \mathbf{j}\hat{S}_y + \mathbf{k}\hat{S}_z) \\ &= \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \end{aligned} \tag{34}$$

is the operator for the square of the spin angular momentum, repeated application of (32) immediately gives:

$$\begin{aligned}\hat{S}^2\alpha &= \hat{S}_x^2\alpha + \hat{S}_y^2\alpha + \hat{S}_z^2\alpha = \hat{S}_x(\hat{S}_x\alpha) + \hat{S}_y(\hat{S}_y\alpha) + \hat{S}_z(\hat{S}_z\alpha) \\ &= \hat{S}_x\left(\frac{1}{2}\beta\right) + \hat{S}_y\left(\frac{1}{2}i\beta\right) + \hat{S}_z\left(\frac{1}{2}\alpha\right) \\ &= \frac{1}{2}\left(\frac{1}{2}\alpha\right) + \frac{1}{2}i\left(-\frac{1}{2}i\alpha\right) + \frac{1}{2}\left(\frac{1}{2}\alpha\right) \\ &= \left(\frac{1}{4} + \frac{1}{4} + \frac{1}{4}\right)\alpha = \frac{3}{4}\alpha = \frac{1}{2}\left(\frac{1}{2} + 1\right)\alpha \end{aligned} \tag{35}$$

and similarly for $\hat{S}^2\beta$. Spin states α, β have hence the same eigenvalue with respect to $\hat{S}^2$ (they belong to the doublet $S = 1/2$, with spin multiplicity $2S + 1 = 2$) and opposed eigenvalue with respect to $\hat{S}_z$ ($M_S = 1/2$, $M_S = -1/2$).

- Spin ladder operators.

The spin ladder operators:

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y \qquad \hat{S}_- = \hat{S}_x - i\hat{S}_y \tag{36}$$

have the same commutation properties of the orbital angular momentum operators (Chapters 1 and 9).

Pauli equations for spin $1/2$ can be immediately derived from the fact that the ladder for the single electron has two steps only (the states α and β, postulated from experimental evidence):

$$\underset{\text{(top)}}{\hat{S}_+\alpha = 0} \qquad \hat{S}_-\alpha = \beta \tag{37}$$

$$\hat{S}_+\beta = \alpha \qquad \underset{\text{(bottom)}}{\hat{S}_-\beta = 0}. \tag{38}$$

Then:

$$\begin{aligned}&(\hat{S}_+ + \hat{S}_-)\alpha = \beta \qquad (\hat{S}_x + i\hat{S}_y + \hat{S}_x - i\hat{S}_y)\alpha = \beta \Longrightarrow \hat{S}_x\alpha = \frac{1}{2}\beta \\ &(\hat{S}_+ - \hat{S}_-)\alpha = -\beta \qquad (\hat{S}_x + i\hat{S}_y - \hat{S}_x + i\hat{S}_y)\alpha = -\beta \Longrightarrow \hat{S}_y\alpha = \frac{1}{2}i\beta \end{aligned} \tag{39}$$

$$\begin{aligned} &(\hat{S}_+ + \hat{S}_-)\beta = \alpha \qquad (\hat{S}_x + i\hat{S}_y + \hat{S}_x - i\hat{S}_y)\beta = \alpha \Longrightarrow \hat{S}_x\beta = \frac{1}{2}\alpha \\ &(\hat{S}_+ - \hat{S}_-)\beta = \alpha \qquad (\hat{S}_x + i\hat{S}_y - \hat{S}_x + i\hat{S}_y)\beta = \alpha \Longrightarrow \hat{S}_y\beta = -\frac{1}{2}i\alpha, \end{aligned} \tag{40}$$

and we recover Pauli's equations for the components $\hat{S}_x$ and $\hat{S}_y$ for spin $1/2$.

- Commutation properties of spin operators.

  It is easily seen that:

$$\begin{aligned} [\hat{S}_x, \hat{S}_y]\alpha &= \hat{S}_x\hat{S}_y\alpha - \hat{S}_y\hat{S}_x\alpha \\ &= \hat{S}_x\left(\frac{1}{2}i\beta\right) - \hat{S}_y\left(\frac{1}{2}\beta\right) = \frac{1}{2}i\left(\frac{1}{2}\alpha\right) - \frac{1}{2}\left(-\frac{1}{2}i\alpha\right) \\ &= \left(\frac{1}{4} + \frac{1}{4}\right)i\alpha = \frac{1}{2}i\alpha = i\hat{S}_z\alpha \end{aligned}$$

so that:

$$[\hat{S}_x, \hat{S}_y] = i\hat{S}_z. \tag{41}$$

Likely, it is found:

$$[\hat{S}_y, \hat{S}_z] = i\hat{S}_x \tag{42}$$

$$[\hat{S}_z, \hat{S}_x] = i\hat{S}_y. \tag{43}$$

For the ladder operators:

$$\begin{aligned} [\hat{S}_z, \hat{S}_+] &= \hat{S}_z\hat{S}_+ - \hat{S}_+\hat{S}_z = \hat{S}_z(\hat{S}_x + i\hat{S}_y) - (\hat{S}_x + i\hat{S}_y)\hat{S}_z \\ &= [\hat{S}_z, \hat{S}_x] - i[\hat{S}_y, \hat{S}_z] = i\hat{S}_y - i(i\hat{S}_x) = \hat{S}_x + i\hat{S}_y = \hat{S}_+ \end{aligned} \tag{44}$$

$$\begin{aligned} [\hat{S}_z, \hat{S}_-] &= \hat{S}_z\hat{S}_- - \hat{S}_-\hat{S}_z = \hat{S}_z(\hat{S}_x - i\hat{S}_y) - (\hat{S}_x - i\hat{S}_y)\hat{S}_z \\ &= [\hat{S}_z, \hat{S}_x] + i[\hat{S}_y, \hat{S}_z] = i\hat{S}_y + i(i\hat{S}_x) = -(\hat{S}_x - i\hat{S}_y) = -\hat{S}_- \end{aligned} \tag{45}$$

and, for the square of the spin operator:

$$\begin{aligned} [\hat{S}^2, \hat{S}_x]\alpha &= (\hat{S}^2\hat{S}_x - \hat{S}_x\hat{S}^2)\alpha \\ &= \hat{S}^2\left(\frac{1}{2}\beta\right) - \hat{S}_x\left(\frac{3}{4}\alpha\right) = \frac{1}{2}\cdot\frac{3}{4}\beta - \frac{3}{4}\cdot\frac{1}{2}\beta = 0 \end{aligned} \tag{46}$$

so that $\hat{S}^2$ commutes with $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$.

Summarizing all these results, we have the commutation rules for spin operators:

$$\begin{aligned}
&[\hat{S}_x, \hat{S}_y] = i\hat{S}_z \qquad [\hat{S}_y, \hat{S}_z] = i\hat{S}_x \qquad [\hat{S}_z, \hat{S}_x] = i\hat{S}_y \\
&[\hat{S}_z, \hat{S}_+] = \hat{S}_+ \qquad [\hat{S}_z, \hat{S}_-] = -\hat{S}_- \\
&[\hat{S}^2, \hat{S}_x] = [\hat{S}^2, \hat{S}_y] = [\hat{S}^2, \hat{S}_z] = 0 \\
&[\hat{S}^2, \hat{S}_\pm] = 0.
\end{aligned} \tag{47}$$

- Properties of spin ladder operators

Let us now study the effect of the spin ladder operators on a spin function $\eta(M_S)$ belonging to the step M_S of the ladder specified by S:

$$\hat{S}_z\eta(M_S) = M_S\eta(M_S) \qquad \hat{S}^2\eta(M_S) = S(S+1)\eta(M_S). \tag{48}$$

$$\begin{aligned}
\hat{S}_z\big(\hat{S}_+\eta(M_S)\big) &= \hat{S}_+\big(\hat{S}_z\eta(M_S)\big) + \big(\hat{S}_+\eta(M_S)\big) \\
&= \big(M_S+1\big)\big(\hat{S}_+\eta(M_S)\big) \propto \eta\big(M_S+1\big)
\end{aligned} \tag{49}$$

$$\begin{aligned}
\hat{S}_z\big(\hat{S}_-\eta(M_S)\big) &= \hat{S}_-\big(\hat{S}_z\eta(M_S)\big) - \big(\hat{S}_-\eta(M_S)\big) \\
&= (M_S-1)\big(\hat{S}_-\eta(M_S)\big) \propto \eta(M_S-1)
\end{aligned} \tag{50}$$

while:

$$\hat{S}^2\big(\hat{S}_\pm\eta(M_S)\big) = \hat{S}_\pm\big(\hat{S}^2\eta(M_S)\big) = S(S+1)\big(\hat{S}_\pm\eta(M_S)\big) \tag{51}$$

so that it is evident the step-up effect of $\hat{S}_+\eta(M_S)$ and the step-down effect of $\hat{S}_-\eta(M_S)$ within the same ladder (specified by S).

We can now normalize the function $\hat{S}_+\eta(M_S)$. We recall that:

$$\begin{aligned}
\hat{S}^2 &= \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \\
&= \hat{S}_-\hat{S}_+ + \hat{S}_z(\hat{S}_z+1) = \hat{S}_+\hat{S}_- + \hat{S}_z(\hat{S}_z-1).
\end{aligned} \tag{52}$$

Then, assuming $\eta(M_S)$ normalized to 1:

$$\hat{S}_+\eta(M_S) = N\eta(M_S+1) \tag{53}$$

$$\begin{aligned}
\langle\eta(M_S)|\hat{S}^2|\eta(M_S)\rangle &= \langle\eta(M_S)|\hat{S}_-\hat{S}_+ + \hat{S}_z(\hat{S}_z+1)|\eta(M_S)\rangle \\
&= \langle\hat{S}_+\eta(M_S)|\hat{S}_+\eta(M_S)\rangle + M_S(M_S+1)\langle\eta(M_S)|\eta(M_S)\rangle \\
&= S(S+1)\langle\eta(M_S)|\eta(M_S)\rangle
\end{aligned} \tag{54}$$

and we finally obtain:

$$\begin{aligned}\langle \hat{S}_+\eta(M_S)|\hat{S}_+\eta(M_S)\rangle &= [S(S+1)-M_S(M_S+1)]\langle \eta(M_S)|\eta(M_S)\rangle \\ &= N^2\langle \eta(M_{S+1})|\eta(M_{S+1})\rangle.\end{aligned} \tag{55}$$

Since:

$$\langle \eta(M_S)|\eta(M_S)\rangle = \langle \eta(M_{S+1})|\eta(M_{S+1})\rangle = 1 \tag{56}$$

it follows that:

$$\begin{aligned}&N^2 = S(S+1)-M_S(M_S+1)\\ &N = [S(S+1)-M_S(M_S+1)]^{1/2}.\end{aligned} \tag{57}$$

Taking into account normalization, the complete expressions of the spin functions $\hat{S}_\pm\eta$ are hence the following:

$$\begin{aligned}&\hat{S}_+\eta(M_S) = [S(S+1)-M_S(M_S+1)]^{1/2}\eta(M_S+1) \quad \text{step-up}\\ &\hat{S}_-\eta(M_S) = [S(S+1)-M_S(M_S-1)]^{1/2}\eta(M_S-1) \quad \text{step-down.}\end{aligned} \tag{58}$$

Examples.

(i) On the top of the ladder:

$$\begin{aligned}&\hat{S}_+\eta_{\frac{1}{2}} = \left[\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}+1\right)\right]^{1/2}\eta_{\frac{3}{2}} = 0\\ &\hat{S}_+\eta_{-\frac{1}{2}} = \left[\frac{1}{2}\left(\frac{1}{2}+1\right)-\left(-\frac{1}{2}\right)\left(-\frac{1}{2}+1\right)\right]^{1/2}\eta_{\frac{1}{2}} = \eta_{\frac{1}{2}}\end{aligned} \tag{59}$$

(ii) On the bottom of the ladder:

$$\begin{aligned}&\hat{S}_-\eta_{\frac{1}{2}} = \left[\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}-1\right)\right]^{1/2}\eta_{-\frac{1}{2}} = \eta_{-\frac{1}{2}}\\ &\hat{S}_-\eta_{-\frac{1}{2}} = \left[\frac{1}{2}\left(\frac{1}{2}+1\right)-\left(-\frac{1}{2}\right)\left(-\frac{1}{2}-1\right)\right]^{1/2}\eta_{-\frac{3}{2}} = 0.\end{aligned} \tag{60}$$

In this way, the results obtained from the commutation rules confirm the results intuitively assumed for the two-step ladder.

6.4 MATRIX REPRESENTATION OF SPIN OPERATORS

If we represent the basis of the two spin states as the row matrix:

$$\boldsymbol{\eta} = (\alpha\beta) \tag{61}$$

the Pauli spin operators are given by the 2 × 2 matrix representatives:

$$\mathbf{S}_x = \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \qquad \mathbf{S}_y = \begin{pmatrix} 0 & -\frac{1}{2}i \\ \frac{1}{2}i & 0 \end{pmatrix} \qquad \mathbf{S}_z = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \tag{62}$$

which are the 2 × 2 Pauli matrices for spin 1/2. In fact:

$$\begin{aligned} \mathbf{S}_x = \boldsymbol{\eta}^\dagger \hat{S}_x \boldsymbol{\eta} &= \begin{pmatrix} \alpha^* \\ \beta^* \end{pmatrix} (\hat{S}_x\alpha \ \hat{S}_x\beta) = \begin{pmatrix} \langle\alpha|\hat{S}_x|\alpha\rangle & \langle\alpha|\hat{S}_x|\beta\rangle \\ \langle\beta|\hat{S}_x|\alpha\rangle & \langle\beta|\hat{S}_x|\beta\rangle \end{pmatrix} \\ &= \begin{pmatrix} \frac{1}{2}\langle\alpha|\beta\rangle & \frac{1}{2}\langle\alpha|\alpha\rangle \\ \frac{1}{2}\langle\beta|\beta\rangle & \frac{1}{2}\langle\beta|\alpha\rangle \end{pmatrix} = \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \end{aligned} \tag{63}$$

and so on.

In this matrix representation, state α is represented by the column $\binom{1}{0} = \boldsymbol{\alpha}$, state β by the column $\binom{0}{1} = \boldsymbol{\beta}$. Then:

$$\begin{aligned} \mathbf{S}_x \begin{pmatrix} 1 \\ 0 \end{pmatrix} &= \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{1}{2} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ \mathbf{S}_x \begin{pmatrix} 0 \\ 1 \end{pmatrix} &= \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \end{aligned} \tag{64}$$

$$\mathbf{S}_y \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2}i \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad \mathbf{S}_y \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{1}{2}i \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{65}$$

$$\mathbf{S}_z \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \mathbf{S}_z \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -\frac{1}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{66}$$

as it must be.

For the matrix representatives of the ladder operators we have:

$$\begin{aligned} \mathbf{S}_+ = \mathbf{S}_x + i\mathbf{S}_y &= \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} + i \begin{pmatrix} 0 & -\frac{1}{2}i \\ \frac{1}{2}i & 0 \end{pmatrix} \\ &= \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} + \begin{pmatrix} 0 & \frac{1}{2} \\ -\frac{1}{2} & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \end{aligned} \tag{67}$$

$$\mathbf{S}_- = \mathbf{S}_x - i\mathbf{S}_y = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{68}$$

so that:

$$\left.\begin{aligned}\mathbf{S}_+\boldsymbol{\alpha} &= \begin{pmatrix}0 & 1\\0 & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}0\\0\end{pmatrix}\\ \mathbf{S}_+\boldsymbol{\beta} &= \begin{pmatrix}0 & 1\\0 & 0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}1\\0\end{pmatrix} = \boldsymbol{\alpha}\end{aligned}\right\} \quad \text{top} \tag{69}$$

$$\left.\begin{aligned}\mathbf{S}_-\boldsymbol{\alpha} &= \begin{pmatrix}0 & 0\\1 & 0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}0\\1\end{pmatrix} = \boldsymbol{\beta}\\ \mathbf{S}_-\boldsymbol{\beta} &= \begin{pmatrix}0 & 0\\1 & 0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}0\\0\end{pmatrix}\end{aligned}\right\} \quad \text{bottom} \tag{70}$$

as it must be.

We can now give the commutation relations in matrix form.

$$\begin{aligned}[\mathbf{S}_x, \mathbf{S}_y] &= \mathbf{S}_x\mathbf{S}_y - \mathbf{S}_y\mathbf{S}_x\\ &= \begin{pmatrix}0 & \frac{1}{2}\\ \frac{1}{2} & 0\end{pmatrix}\begin{pmatrix}0 & -\frac{1}{2}i\\ \frac{1}{2}i & 0\end{pmatrix} - \begin{pmatrix}0 & -\frac{1}{2}i\\ \frac{1}{2}i & 0\end{pmatrix}\begin{pmatrix}0 & \frac{1}{2}\\ \frac{1}{2} & 0\end{pmatrix}\\ &= \begin{pmatrix}\frac{1}{4}i & 0\\ 0 & -\frac{1}{4}i\end{pmatrix} - \begin{pmatrix}-\frac{1}{4}i & 0\\ 0 & \frac{1}{4}i\end{pmatrix} = \begin{pmatrix}\frac{1}{2}i & 0\\ 0 & -\frac{1}{2}i\end{pmatrix} = i\mathbf{S}_z\end{aligned} \tag{71}$$

and, likely:

$$[\mathbf{S}_y, \mathbf{S}_z] = i\mathbf{S}_x \tag{72}$$

$$[\mathbf{S}_z, \mathbf{S}_x] = i\mathbf{S}_y. \tag{73}$$

Furthermore:

$$\begin{aligned}\mathbf{S}^2 &= \mathbf{S}_x^2 + \mathbf{S}_y^2 + \mathbf{S}_z^2\\ &= \begin{pmatrix}0 & \frac{1}{2}\\ \frac{1}{2} & 0\end{pmatrix}\begin{pmatrix}0 & \frac{1}{2}\\ \frac{1}{2} & 0\end{pmatrix} + \begin{pmatrix}0 & -\frac{1}{2}i\\ \frac{1}{2}i & 0\end{pmatrix}\begin{pmatrix}0 & -\frac{1}{2}i\\ \frac{1}{2}i & 0\end{pmatrix}\\ &\quad + \begin{pmatrix}\frac{1}{2} & 0\\ 0 & -\frac{1}{2}\end{pmatrix}\begin{pmatrix}\frac{1}{2} & 0\\ 0 & -\frac{1}{2}\end{pmatrix}\\ &= \begin{pmatrix}\frac{1}{4} & 0\\ 0 & \frac{1}{4}\end{pmatrix} + \begin{pmatrix}\frac{1}{4} & 0\\ 0 & \frac{1}{4}\end{pmatrix} + \begin{pmatrix}\frac{1}{4} & 0\\ 0 & \frac{1}{4}\end{pmatrix} = \frac{3}{4}\mathbf{1}\end{aligned} \tag{74}$$

so that:

$$[\mathbf{S}^2, \mathbf{S}_x] = [\mathbf{S}^2, \mathbf{S}_y] = [\mathbf{S}^2, \mathbf{S}_z] = \mathbf{0}. \tag{75}$$

6.5 THEORY OF 2-ELECTRON SPIN

For $N = 2$ we have $2^2 = 4$ spin product functions, out of which we must construct suitable spin eigenstates. Taking electrons always in dictionary order, the product functions are:

$$\alpha\alpha, \alpha\beta, \beta\alpha, \beta\beta. \tag{76}$$

We now look at the behaviour of these products under the action of operators $\hat{S}_z$ and $\hat{S}^2$.

$$\text{(i)} \quad \hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2} \tag{77}$$

$$\hat{S}_z(\alpha_1\alpha_2) = (\hat{S}_{z1}\alpha_1)\alpha_2 + \alpha_1(\hat{S}_{z2}\alpha_2) = \left(\frac{1}{2} + \frac{1}{2}\right)\alpha_1\alpha_2 \quad M_S = 1$$

$$\hat{S}_z(\alpha_1\beta_2) = (\hat{S}_{z1}\alpha_1)\beta_2 + \alpha_1(\hat{S}_{z2}\beta_2) = \left(\frac{1}{2} - \frac{1}{2}\right)\alpha_1\beta_2 \quad M_S = 0$$

so that the product functions are eigenstates of $\hat{S}_z$ with eigenvalues:

$$\begin{array}{rcccc} & \alpha_1\alpha_2 & \alpha_1\beta_2 & \beta_1\alpha_2 & \beta_1\beta_2 \\ M_S = & 1 & 0 & 0 & -1 \end{array}, \tag{78}$$

where:

$$M_S = \frac{N_\alpha - N_\beta}{2} \quad N_\alpha + N_\beta = N, \tag{79}$$

N_α being the number of electrons with spin α, N_β that of electrons with spin β, and N the total number of electrons.

$$\text{(ii)} \quad \hat{S}^2 = \hat{\mathbf{S}} \cdot \hat{\mathbf{S}} = (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2) \cdot (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2) = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2, \tag{80}$$

where $\hat{S}_1^2$ and $\hat{S}_2^2$ are 1-electron spin operators, while $\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$ is a 2-electron spin operator. We have for the scalar product:

$$\begin{aligned} \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 &= (\mathbf{i}\hat{S}_{x1} + \mathbf{j}\hat{S}_{y1} + \mathbf{k}\hat{S}_{z1}) \cdot (\mathbf{i}\hat{S}_{x2} + \mathbf{j}\hat{S}_{y2} + \mathbf{k}\hat{S}_{z2}) \\ &= \hat{S}_{x1}\hat{S}_{x2} + \hat{S}_{y1}\hat{S}_{y2} + \hat{S}_{z1}\hat{S}_{z2} \end{aligned} \tag{81}$$

so that:

$$\begin{aligned} (\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2)\alpha_1\beta_2 &= (\hat{S}_{x1}\alpha_1)(\hat{S}_{x2}\beta_2) + (\hat{S}_{y1}\alpha_1)(\hat{S}_{y2}\beta_2) + (\hat{S}_{z1}\alpha_1)(\hat{S}_{z2}\beta_2) \\ &= \left(\frac{1}{2}\beta_1\right)\left(\frac{1}{2}\alpha_2\right) + \left(\frac{1}{2}i\beta_1\right)\left(-\frac{1}{2}i\alpha_2\right) + \left(-\frac{1}{2}\beta_2\right) \\ &= \left(\frac{1}{4} + \frac{1}{4}\right)\beta_1\alpha_2 - \frac{1}{4}\alpha_1\beta_2 \end{aligned} \tag{82}$$

$$
\begin{aligned}
\hat{S}^2\alpha_1\beta_2 &= (\hat{S}_1^2\alpha_1)\beta_2 + \alpha_1(\hat{S}_2^2\beta_2) + 2(\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2)\alpha_1\beta_2 \\
&= \left(\frac{3}{4}+\frac{3}{4}-\frac{2}{4}\right)\alpha_1\beta_2 + 2\left(\frac{1}{4}+\frac{1}{4}\right)\beta_1\alpha_2 = \alpha_1\beta_2+\beta_1\alpha_2.
\end{aligned}
\tag{83}
$$

We hence obtain:

$$\hat{S}^2 = \hat{I} + \hat{P}_{12}, \tag{84}$$

where $\hat{P}_{12}$ is an operator which interchanges spin coordinates only, or, leaving electrons in dictionary order, interchanges spin state α with spin state β. Formula (84) is known as Dirac's formula, and allows us to express $\hat{S}^2$ in terms of the identity operator $\hat{I}$ and the spin permutation operator $\hat{P}_{12}$. To find the eigenstates of $\hat{S}^2$ we must construct and diagonalize its matrix representative over the basis of the four product functions. Then:

$$\hat{S}^2\alpha\alpha = 2\alpha\alpha \qquad \hat{S}^2\alpha\beta = \alpha\beta+\beta\alpha \qquad \hat{S}^2\beta\alpha = \beta\alpha+\alpha\beta \qquad \hat{S}^2\beta\beta = 2\beta\beta \tag{85}$$

so that we have the matrix elements:

$$
\begin{array}{llll}
\langle\alpha\alpha|\hat{S}^2|\alpha\alpha\rangle = 2 & \langle\alpha\alpha|\hat{S}^2|\alpha\beta\rangle = 0 & \langle\alpha\alpha|\hat{S}^2|\beta\alpha\rangle = 0 & \langle\alpha\alpha|\hat{S}^2|\beta\beta\rangle = 0 \\
\langle\alpha\beta|\hat{S}^2|\alpha\alpha\rangle = 0 & \langle\alpha\beta|\hat{S}^2|\alpha\beta\rangle = 1 & \langle\alpha\beta|\hat{S}^2|\beta\alpha\rangle = 1 & \langle\alpha\beta|\hat{S}^2|\beta\beta\rangle = 0 \\
\langle\beta\alpha|\hat{S}^2|\alpha\alpha\rangle = 0 & \langle\beta\alpha|\hat{S}^2|\alpha\beta\rangle = 1 & \langle\beta\alpha|\hat{S}^2|\beta\alpha\rangle = 1 & \langle\beta\alpha|\hat{S}^2|\beta\beta\rangle = 0 \\
\langle\beta\beta|\hat{S}^2|\alpha\alpha\rangle = 0 & \langle\beta\beta|\hat{S}^2|\alpha\beta\rangle = 0 & \langle\beta\beta|\hat{S}^2|\beta\alpha\rangle = 0 & \langle\beta\beta|\hat{S}^2|\beta\beta\rangle = 2,
\end{array}
$$

giving the 4 × 4 Hermitian matrix $\mathbf{S}^2$ whose eigenvalues are $\lambda = S(S+1)$ in the block diagonal form:

$$
\mathbf{S}^2 = \left(\begin{array}{c|cc|c}
2 & 0 & 0 & 0 \\
\hline
0 & 1 & 1 & 0 \\
0 & 1 & 1 & 0 \\
\hline
0 & 0 & 0 & 2
\end{array}\right). \tag{86}
$$

It will be sufficient to diagonalize the inner 2 × 2 block with the secular equation:

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0 \quad x = 1-\lambda \tag{87}$$

having the roots:

$$x = \pm 1. \tag{88}$$

Hence, we obtain for the eigenvalues:

$$\lambda = 1-1 = 0 \Longrightarrow S = 0 \quad \text{(singlet)} \tag{89}$$

$$\lambda = 1 + 1 = 2 \Longrightarrow S = 1 \quad \text{(triplet)}. \tag{90}$$

We now evaluate the eigenvectors.

- Eigenvalue $x = 1$ (singlet)

$$\begin{cases} c_1 + c_2 = 0 & c_2 = -c_1 \\ c_1^2 + c_2^2 = 1 & 2c_1^2 = 1 \Longrightarrow c_1 = \dfrac{1}{\sqrt{2}}, \; c_2 = -\dfrac{1}{\sqrt{2}} \end{cases} \tag{91}$$

- Eigenvalue $x = -1$ (triplet)

$$\begin{cases} -c_1 + c_2 = 0 & c_2 = c_1 \\ c_1^2 + c_2^2 = 1 & 2c_1^2 = 1 \Longrightarrow c_1 = c_2 = \dfrac{1}{\sqrt{2}}. \end{cases} \tag{92}$$

The spin eigenstates for $N = 2$ are therefore:

Eigenstates η	S	M_S		
$\alpha\alpha$	1	1	*Symmetric* spin	
$\frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$	1	0	eigenfunctions with	(93)
$\beta\beta$	1	-1	$2S + 1 = 3$ (triplet)	
			Antisymmetric spin	
$\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)$	0	0	eigenfunction with	(94)
			$2S + 1 = 1$ (singlet)	

At variance with the simple product functions (76), we see that the spin eigenfunctions have a definite symmetry (symmetric or antisymmetric) with respect to electron interchange.

6.6 THEORY OF N-ELECTRON SPIN

If $N = N_\alpha + N_\beta$ is the total number of electrons (or spin) with N_α the number of α-electrons, N_β the number of β-electrons, we shall have 2^N product functions like

$(\cdots\alpha_\kappa\cdots\beta_\lambda\cdots)$, where the notation means that electron κ is in spin state α and electron λ in spin state β. We again look for the action of $\hat{S}_z$ and $\hat{S}^2$ on these product functions.

$$\text{(i)}\quad \hat{S}_z=\sum_{\kappa=1}^{N}\hat{S}_{z\kappa} \tag{95}$$

$$\hat{S}_z(\cdots\alpha_\kappa\cdots)=\sum_{\lambda=1}^{N}\hat{S}_{z\lambda}(\cdots\alpha_\kappa\cdots)=\sum_{\lambda=1}^{N}m_{s\lambda}(\cdots\alpha_\kappa\cdots)=M_S(\cdots\alpha_\kappa\cdots), \tag{96}$$

where:

$$M_S=\sum_{\lambda=1}^{N}m_{s\lambda}=\frac{N_\alpha-N_\beta}{2}. \tag{97}$$

All product functions are eigenstates of $\hat{S}_z$ with eigenvalue M_S.

$$\begin{aligned}\text{(ii)}\quad \hat{S}^2&=(\hat{\mathbf{S}}_1+\hat{\mathbf{S}}_2+\cdots+\hat{\mathbf{S}}_N)\cdot(\hat{\mathbf{S}}_1+\hat{\mathbf{S}}_2+\cdots+\hat{\mathbf{S}}_N)\\&=\sum_{\kappa=1}^{N}\hat{S}_\kappa^2+2\sum_{\kappa<\lambda}\hat{\mathbf{S}}_\kappa\cdot\hat{\mathbf{S}}_\lambda,\end{aligned} \tag{98}$$

where the first single sum of 1-electron operators has N terms, the second double sum of 2-electron operators $N(N-1)/2$ terms, the number of distinct pairs. Now:

$$\hat{S}_\kappa^2(\cdots\alpha_\kappa\cdots\beta_\lambda\cdots)=\frac{3}{4}(\cdots\alpha_\kappa\cdots\beta_\lambda\cdots) \tag{99}$$

$$\begin{aligned}&(\hat{S}_{x\kappa}\hat{S}_{x\lambda}+\hat{S}_{y\kappa}\hat{S}_{y\lambda}+\hat{S}_{z\kappa}\hat{S}_{z\lambda})(\cdots\alpha_\kappa\cdots\beta_\lambda\cdots)\\&\quad=\left(-\frac{1}{4}\hat{I}+2\frac{1}{4}\hat{P}_{\kappa\lambda}\right)(\cdots\alpha_\kappa\cdots\beta_\lambda\cdots).\end{aligned} \tag{100}$$

Adding all contributions altogether we get:

$$\begin{aligned}&\hat{S}^2(\cdots\alpha_\kappa\cdots\beta_\lambda\cdots)\\&\quad=\Bigg\{\underbrace{\left(\frac{3}{4}+\frac{3}{4}+\cdots+\frac{3}{4}\right)}_{N\text{-times}}\hat{I}-\underbrace{\left(\frac{2}{4}+\frac{2}{4}+\cdots+\frac{2}{4}\right)}_{\frac{N(N-1)}{2}\text{-times}}\hat{I}\\&\qquad+\sum_{\kappa<\lambda}\hat{P}_{\kappa\lambda}\Bigg\}(\cdots\alpha_\kappa\cdots\beta_\lambda\cdots)\end{aligned} \tag{101}$$

namely, since the result is independent of $(\cdots\alpha_\kappa\cdots\beta_\lambda\cdots)$:

$$\hat{S}^2 = \frac{3}{4}N\hat{I} - \frac{2}{4}\frac{N(N-1)}{2}\hat{I} + \sum_{\kappa<\lambda}\hat{P}_{\kappa\lambda} \tag{102}$$

$$\hat{S}^2 = \frac{N}{4}(4-N)\hat{I} + \sum_{\kappa<\lambda}\hat{P}_{\kappa\lambda} \tag{103}$$

which is the Dirac formula (1929; see also Löwdin, 1955a) for the N-electron system. Using this formula it is possible to calculate in a simple way the effect of $\hat{S}^2$ on a many-electron wavefunction, even if, at least in an elementary way, the spin-part is not separable from the space part as it happens for $N \geqslant 3$. We can then construct the matrix $\mathbf{S}^2$ over the basis of the N-electron product functions, whose diagonalization gives the eigenvalues $S(S+1)$ and the correct linear combinations of product functions (eigenvectors), which are the eigenstates of $\hat{S}^2$ for the different eigenvalues. These eigenstates of $\hat{S}^2$ are states of definite total spin S satisfying simultaneously the two eigenvalue equations:

$$\hat{S}^2\eta = S(S+1)\eta \qquad \hat{S}_z\eta = M_S\eta, \tag{104}$$

where:

$$S = 0, 1, 2, \cdots \frac{N}{2} \qquad \text{for } N = \text{even} \tag{105}$$

$$S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots \frac{N}{2} \qquad \text{for } N = \text{odd} \tag{106}$$

$$M_S = \frac{N_\alpha - N_\beta}{2}. \tag{107}$$

In terms of the spin multiplicity $2S+1$, i.e. the number of linearly independent spin eigenstates of given S, we have:

$$N = \text{even} \Rightarrow \text{singlets, triplets, quintets, } \ldots \tag{108}$$

$$N = \text{odd} \Rightarrow \text{doublets, quartets, sextets, } \ldots \tag{109}$$

We notice that the product functions involving all α or β spin are already eigenstates of $\hat{S}^2$ with eigenvalue $S = |M_S|$. The total number f_S^N of linearly independent spin eigenstates of given S, M_S does depend only on S and is given by:

(i) The Wigner formula

$$f_S^N = \binom{N}{\frac{N}{2}-S} - \binom{N}{\frac{N}{2}-S-1} = \frac{(2S+1)N!}{(\frac{N}{2}-S)!(\frac{N}{2}+S+1)!} \tag{110}$$

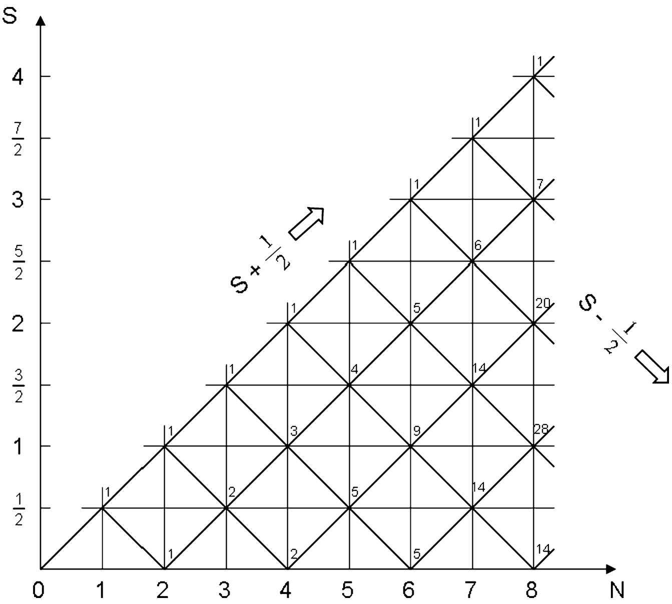


Figure 6.3 Kotani branching diagram.

or (ii) The Kotani branching diagram (Figure 6.3).

The numbers on the intersection points of the Kotani branching diagram are the number f_S^N of linearly independent *spin states* of given S for each value of N. It is true that:

$$f_S^N = f_{S+\frac{1}{2}}^{N-1} + f_{S-\frac{1}{2}}^{N-1}, \tag{111}$$

and that, adding by columns:

$$\sum_S (2S+1) f_S^N = 2^N. \tag{112}$$

Examples.

(i) $N = 3$ $\qquad 2^3 = 8$ spin states

$$\begin{array}{ccccc} 1 \text{ quartet}\left(S = \dfrac{3}{2}\right) & + & 2 \text{ doublets}\left(S = \dfrac{1}{2}\right) & & \\ 4 & + & 4 & = 8 & \end{array} \tag{113}$$

(ii) $N = 4$ $\qquad 2^4 = 16$ spin states

$$\begin{array}{cccccc} 1 \text{ quintet}(S = 2) & + & 3 \text{ triplets}(S = 1) & + & 2 \text{ singlets}(S = 0) & \\ 5 & + & 9 & + & 2 & = 16 \end{array} \tag{114}$$

(iii) $N = 5 \qquad 2^5 = 32$ spin states

$$\begin{array}{ccccccc} 1\text{ sextet}\left(S=\dfrac{5}{2}\right) & + & 4\text{ quartets}\left(S=\dfrac{3}{2}\right) & + & 5\text{ doublets}\left(S=\dfrac{1}{2}\right) & & \\ 6 & + & 16 & + & 10 & = & 32 \end{array} \tag{115}$$

6.7 THE KOTANI SYNTHETIC METHOD

Kotani (Kotani et al., 1963) has proposed a *synthetic* method to construct the N-electron spin eigenfunctions, starting from the spin functions for the single electron ($\eta = \alpha$ for $M_S = \frac{1}{2}$, $\eta = \beta$ for $M_S = -\frac{1}{2}$) and building-up the N-electron function by coupling the spins successively according to the usual rules for angular momenta in quantum mechanics (Chapter 9) with reference to the branching diagram. The vector coupling formula, with the adoption of standard phases, for the spin eigenfunction of N electrons can be written as:

$$\begin{aligned} \eta^N_{SM_S;k} = &-\sqrt{\frac{S-M_S+1}{2S+2}}\,\eta^{N-1}_{S+\frac{1}{2},M_S-\frac{1}{2};k}(s_1,s_2,\cdots,s_{N-1})\alpha(s_N) \\ &+\sqrt{\frac{S+M_S+1}{2S+2}}\,\eta^{N-1}_{S+\frac{1}{2},M_S+\frac{1}{2};k}(s_1,s_2,\cdots,s_{N-1})\beta(s_N) \end{aligned} \tag{116}$$

$$\begin{aligned} \eta^N_{SM_S;k} = &\sqrt{\frac{S+M_S}{2S}}\,\eta^{N-1}_{S-\frac{1}{2},M_S-\frac{1}{2};k}(s_1,s_2,\cdots,s_{N-1})\alpha(s_N) \\ &+\sqrt{\frac{S-M_S}{2S}}\,\eta^{N-1}_{S-\frac{1}{2},M_S+\frac{1}{2};k}(s_1,s_2,\cdots,s_{N-1})\beta(s_N), \end{aligned} \tag{117}$$

where we have omitted for short the arguments in η^N. The coefficients in equations (116) and (117) are the appropriate Clebsch–Gordan coefficients (Brink and Satchler, 1993). The index k on each function $\eta^N_{SM_S;k}$ must be interpreted as a series of *partial resultant spins*:

$$k = (S_1 S_2 \ldots S_\mu \ldots S_{N-1}), \tag{118}$$

where S_μ is the resultant spin of the function after coupling μ electrons. S_1 is, of course, always equal to $\frac{1}{2}$, while there is no need to specify S_N since this is just the total resultant spin S. The spin eigenfunctions obtained in this way are known as Young–Yamanouchi or Kotani basis, or "standard" functions. They have a permutational symmetry that follows directly from their definitions by equations (116) and (117), but we shall not examine this aspect here (see Gerratt, 1971). The considerations of this Section will be of importance in presenting some recent formulations of valence bond (VB) theories (Chapter 10), where space and spin parts of the wavefunction are sometimes treated separately according to a suggestion by Wigner (1959).

6.8 LÖWDIN SPIN PROJECTION OPERATORS

An *analytic* method for constructing spin eigenfunctions of given S by acting on product functions with suitable projection operators was proposed by Löwdin (1959). It is based on the successive annihilation of each unwanted component in the expansion of the spin product η in eigenstates of $\hat{S}^2$:

$$\eta = \sum_{SM_S} \eta_{SM_S} C_{SM_S}. \tag{119}$$

From:

$$\hat{S}^2 \eta_{SM_S} = S(S+1)\eta_{SM_S} \tag{120}$$

it follows:

$$[\hat{S}^2 - S(S+1)\hat{I}]\eta_{SM_S} = 0 \tag{121}$$

so that the operator $\hat{O}_k = [\hat{S}^2 - S(S+1)\hat{I}]$ acts as an *annihilator* for the component of total spin $k = S$. Mathematically speaking, $\hat{O}_k$ has the property of resolving an arbitrary vector η into its component along the k-axis, in other words it is a "projection operator (or projector)" which satisfies the three characteristic properties of idempotency, mutual exclusivity, and completeness:

$$\hat{O}_k \hat{O}_l = \hat{O}_k \delta_{kl} \qquad \sum_k \hat{O}_k = \hat{I}. \tag{122}$$

The last expression is known in mathematics as the "resolution of the identity" for a finite Hilbert space. For N-electron spin, the Löwdin spin projector must be generalized to:

$$\hat{O}_k = \prod_{S(\neq k)} \frac{\hat{S}^2 - S(S+1)}{k(k+1) - S(S+1)}, \tag{123}$$

where $\hat{O}_k$ removes from the product functions all spin components except that having $S = k$, and the denominator has been chosen merely for reasons of convenience.

These properties are easily verified for $N = 2$. The possible spin states have $S = 0, 1$ and we have a singlet and a triplet. Löwdin projectors are:

$$\hat{O}_0 = \frac{\hat{S}^2 - 1(1+1)}{-1(1+1)} = \frac{2 - \hat{S}^2}{2} = \frac{2 - (\hat{I} + \hat{P}_{12})}{2} = \frac{\hat{I} - \hat{P}_{12}}{2} \tag{124}$$

(annihilates the triplet component)

$$\hat{O}_1 = \frac{\hat{S}^2 - 0(0+1)}{1(1+1) - 0(0+1)} = \frac{\hat{I} + \hat{P}_{12}}{2}. \tag{125}$$

(annihilates the singlet component)

Then:

(i) For the singlet:

$$\hat{O}_0\alpha\beta = \frac{\hat{I} - \hat{P}_{12}}{2}\alpha\beta = \frac{\alpha\beta - \beta\alpha}{2} \tag{126}$$

the (un-normalized) antisymmetrical function.

(ii) For the triplet:

$$\hat{O}_1\alpha\beta = \frac{\hat{I} + \hat{P}_{12}}{2}\alpha\beta = \frac{\alpha\beta + \beta\alpha}{2} \tag{127}$$

the (un-normalized) symmetrical function, as it must be. Furthermore:

(iii) Idempotency:

$$\hat{O}_0^2 = \frac{\hat{I} - \hat{P}_{12}}{2} \cdot \frac{\hat{I} - \hat{P}_{12}}{2} = \frac{\hat{I} - 2\hat{P}_{12} + \hat{P}_{12}^2}{4} = \frac{\hat{I} - \hat{P}_{12}}{2} = \hat{O}_0 \tag{128}$$

$$\hat{O}_1^2 = \frac{\hat{I} + \hat{P}_{12}}{2} \cdot \frac{\hat{I} + \hat{P}_{12}}{2} = \frac{\hat{I} + 2\hat{P}_{12} + \hat{P}_{12}^2}{4} = \frac{\hat{I} + \hat{P}_{12}}{2} = \hat{O}_1. \tag{129}$$

(iv) Mutual exclusivity:

$$\hat{O}_0\hat{O}_1 = \frac{\hat{I} - \hat{P}_{12}}{2} \cdot \frac{\hat{I} + \hat{P}_{12}}{2} = \frac{\hat{I} - \hat{P}_{12}^2}{4} = \frac{\hat{I} - \hat{I}}{4} = 0. \tag{130}$$

(v) Completeness (resolution of the identity):

$$\hat{O}_0 + \hat{O}_1 = \frac{\hat{I} - \hat{P}_{12}}{2} + \frac{\hat{I} + \hat{P}_{12}}{2} = \hat{I}. \tag{131}$$

For $N = 3$, we have $S = 1/2$ (twice, *two* doublets), $S = 3/2$ (one quartet), and Löwdin un-normalized projectors are:

$$\hat{O}_{\frac{1}{2}} \propto \hat{S}^2 - \frac{15}{4}\hat{I} \quad \text{(removes the quartet component)} \tag{132}$$

$$\hat{O}_{\frac{3}{2}} \propto \hat{S}^2 - \frac{3}{4}\hat{I} \quad \text{(removes the doublet component).} \tag{133}$$

The *two* doublets are recovered by acting with $\hat{O}_{\frac{1}{2}}$ on at least two different spin products and removing possible linear dependences through Schmidt orthogonalization.

6.9 PROBLEMS 6

6.1. Find the spin eigenstates for $N = 3$ using the matrix method.

Answer:

$$\begin{array}{lrcl}
 & M_S & S & \\
\begin{array}{l} \eta_1 = \frac{1}{\sqrt{6}}(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha) \\[2ex] \eta_2 = \frac{1}{\sqrt{6}}(\beta\beta\alpha + \beta\alpha\beta - 2\alpha\beta\beta) \end{array} & \left.\begin{array}{r} \frac{1}{2} \\[2ex] -\frac{1}{2} \end{array}\right\} & \frac{1}{2} & \text{First doublet} \\[4ex]
\begin{array}{l} \eta_3 = \frac{1}{\sqrt{2}}(\alpha\alpha\beta - \alpha\beta\alpha) \\[2ex] \eta_4 = \frac{1}{\sqrt{2}}(\beta\beta\alpha - \beta\alpha\beta) \end{array} & \left.\begin{array}{r} \frac{1}{2} \\[2ex] -\frac{1}{2} \end{array}\right\} & \frac{1}{2} & \text{Second doublet} \\[4ex]
\begin{array}{l} \eta_5 = \alpha\alpha\alpha \\[2ex] \eta_6 = \frac{1}{\sqrt{3}}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha) \\[2ex] \eta_7 = \frac{1}{\sqrt{3}}(\beta\beta\alpha + \beta\alpha\beta + \alpha\beta\beta) \\[2ex] \eta_8 = \beta\beta\beta \end{array} & \left.\begin{array}{r} \frac{3}{2} \\[2ex] \frac{1}{2} \\[2ex] -\frac{1}{2} \\[2ex] -\frac{3}{2} \end{array}\right\} & \frac{3}{2} & \text{Quartet}
\end{array}$$

Hint:
Construct the representative $\mathbf{S}^2$ over the eight product functions and solve the related eigenvalue problem.

6.2. Solve the $N = 3$ spin problem by use of the Löwdin projection operators method.

Answer:
Same as in Problem 6.1.

Hint:
Use spin projectors $\hat{O}_{\frac{1}{2}}$ and $\hat{O}_{\frac{3}{2}}$ on suitable product functions and normalize the results for linearly independent functions.

6.3. Solve the spin problem for $N = 4$.

Answer:

	M_S	S	
$\eta_1 = \frac{1}{2}(\alpha\beta\alpha\beta - \beta\alpha\alpha\beta + \beta\alpha\beta\alpha - \alpha\beta\beta\alpha)$	0	0	Two singlets
$\eta_2 = \frac{1}{\sqrt{12}}(2\alpha\alpha\beta\beta - \alpha\beta\alpha\beta - \beta\alpha\alpha\beta + 2\beta\beta\alpha\alpha - \beta\alpha\beta\alpha - \alpha\beta\beta\alpha)$	0		
$\eta_3 = \frac{1}{2}(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$	1	1	First triplet
$\eta_4 = \frac{1}{\sqrt{2}}(\alpha\beta\alpha\beta - \beta\alpha\beta\alpha)$	0		
$\eta_5 = \frac{1}{2}(\beta\beta\beta\alpha + \beta\beta\alpha\beta - \beta\alpha\beta\beta - \alpha\beta\beta\beta)$	-1		
$\eta_6 = \frac{1}{\sqrt{2}}(\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha)$	1	1	Second triplet
$\eta_7 = \frac{1}{\sqrt{2}}(\alpha\alpha\beta\beta - \beta\beta\alpha\alpha)$	0		
$\eta_8 = \frac{1}{\sqrt{2}}(\beta\beta\beta\alpha - \beta\beta\alpha\beta)$	-1		
$\eta_9 = \frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$	1	1	Third triplet
$\eta_{10} = \frac{1}{\sqrt{2}}(\beta\alpha\alpha\beta - \alpha\beta\beta\alpha)$	0		
$\eta_{11} = \frac{1}{\sqrt{2}}(\beta\alpha\beta\beta - \alpha\beta\beta\beta)$	-1		
$\eta_{12} = \alpha\alpha\alpha\alpha$	2	2	Quintet
$\eta_{13} = \frac{1}{2}(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha + \alpha\beta\alpha\alpha + \beta\alpha\alpha\alpha)$	1		
$\eta_{14} = \frac{1}{\sqrt{6}}(\alpha\alpha\beta\beta + \alpha\beta\alpha\beta + \beta\alpha\alpha\beta + \beta\beta\alpha\alpha + \beta\alpha\beta\alpha + \alpha\beta\beta\alpha)$	0		
$\eta_{15} = \frac{1}{2}(\beta\beta\beta\alpha + \beta\beta\alpha\beta + \beta\alpha\beta\beta + \alpha\beta\beta\beta)$	-1		
$\eta_{16} = \beta\beta\beta\beta$	-2		

Hint:
Use Löwdin spin projectors $\hat{O}_0$, $\hat{O}_1$ and $\hat{O}_2$ for $N = 4$, and normalize the resulting linearly independent functions.

6.4. Construct the Kotani standard spin functions for $N = 3$ and $S = M_S = \frac{1}{2}$.

Answer:

$$\eta_1' = \frac{1}{\sqrt{6}}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$$

$$\eta_3' = \frac{1}{\sqrt{2}}(\alpha\beta\alpha - \beta\alpha\alpha)$$

Hint:
Construct the two coupling schemes for $N = 3$ and $S = \frac{1}{2}$, then use Kotani's formulae (116) for $k_1 = (\frac{1}{2}\ 1)$ and (117) for $k_2 = (\frac{1}{2}\ 0)$.

6.5. Find the orthogonal transformation **U** connecting Löwdin and Kotani spin eigenfunctions for $N = 3$ and $S = M_S = \frac{1}{2}$.

Answer:

$$\mathbf{U} = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}.$$

Hint:
Write the orthogonal transformation and determine the coefficients by simple inspection.

6.6. Construct the Kotani standard spin functions for $N = 3$ and $S = M_S = \frac{1}{2}$ by an elementary way.

Answer:
The same of Problem 6.4.

Hint:
Couple first the *triplet* functions with $N = 2$ to α_3 and β_3, then choose that linear combination of the two functions having $M_S = \frac{1}{2}$ which gives $S = \frac{1}{2}$. Do the same by coupling next the *singlet* function with $N = 2$ to α_3 and β_3.

6.7. Find the two singlets ($S = M_S = 0$) for $N = 4$ using the elementary way of the preceding Problem.

Answer:

$$\eta_1' = \frac{1}{\sqrt{12}}(2\alpha\alpha\beta\beta - \alpha\beta\alpha\beta - \beta\alpha\alpha\beta + 2\beta\beta\alpha\alpha - \beta\alpha\beta\alpha - \alpha\beta\beta\alpha)$$

$$\eta_2' = \frac{1}{2}(\alpha\beta\alpha\beta - \beta\alpha\alpha\beta + \beta\alpha\beta\alpha - \alpha\beta\beta\alpha)$$

Hint:
Construct the spin coupling schemes for $N = 4$, then use the elementary algebraic technique described in Problem 6.6 for the case $S = 0$.

6.10 SOLVED PROBLEMS

6.1. Spin eigenstates for $N = 3$ by the matrix method.
We have the eight product functions:

$$\begin{array}{rcccccccc} & \alpha\alpha\alpha, & \alpha\alpha\beta, & \alpha\beta\alpha, & \beta\alpha\alpha, & \beta\beta\alpha, & \beta\alpha\beta, & \alpha\beta\beta, & \beta\beta\beta \\ M_S = & \frac{3}{2}, & \frac{1}{2}, & \frac{1}{2}, & \frac{1}{2}, & -\frac{1}{2}, & -\frac{1}{2}, & -\frac{1}{2}, & -\frac{3}{2} \end{array}$$

$$\hat{S}^2 = \frac{3}{4}\hat{I} + \hat{P}_{12} + \hat{P}_{13} + \hat{P}_{23}.$$

Then, limiting ourselves to $M_S > 0$:

$$\hat{S}^2\alpha\alpha\alpha = \left(\frac{3}{4} + 3\right)\alpha\alpha\alpha = \frac{15}{4}\alpha\alpha\alpha$$

$$\hat{S}^2\alpha\alpha\beta = \frac{7}{4}\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha$$

$$\hat{S}^2\alpha\beta\alpha = \alpha\alpha\beta + \frac{7}{4}\alpha\beta\alpha + \beta\alpha\alpha$$

$$\hat{S}^2\beta\alpha\alpha = \alpha\alpha\beta + \alpha\beta\alpha + \frac{7}{4}\beta\alpha\alpha$$

giving for $\mathbf{S}^2$ the block-diagonal form:

$$\mathbf{S}^2 = \left(\begin{array}{c|ccc} \frac{15}{4} & 0 & 0 & 0 \\ \hline 0 & \frac{7}{4} & 1 & 1 \\ 0 & 1 & \frac{7}{4} & 1 \\ 0 & 1 & 1 & \frac{7}{4} \end{array}\right) \qquad \lambda = S(S+1).$$

The secular equation for the right lower block:

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0 \quad x = \frac{7}{4} - \lambda$$

factorizes to:

$$(x-1)(x^2+x-2)=(x-1)^2(x+2)=0$$

having the roots:

$$x=1 \quad \text{twice}$$
$$x=-2.$$

We then obtain for the eigenvalues:

$$\lambda=\frac{7}{4}-\frac{4}{4}=\frac{3}{4}\Longrightarrow S=\frac{1}{2} \quad \text{twice (two doublets)}$$
$$\lambda=\frac{7}{4}+\frac{8}{4}=\frac{15}{4}\Longrightarrow S=\frac{3}{2} \quad \text{single (one quartet).}$$

We now evaluate the eigenvectors.

- Eigenvalue $x=1$

$$\begin{cases} c_1+c_2+c_3=0 \\ c_1^2+c_2^2+c_3^2=1. \end{cases}$$

We have 2 equations and 3 unknowns, so that one of the unknowns can be chosen in an arbitrary way.

(i) First assumption:

- $$c_2=c_1 \qquad 2c_1+c_3=0 \qquad c_3=-2c_1$$

  $$2c_1^2+4c_1^2=1 \qquad 6c_1^2=1\Longrightarrow c_1=c_2=\frac{1}{\sqrt{6}}, \quad c_3=-\frac{2}{\sqrt{6}}$$

  $$\eta_1=\frac{1}{\sqrt{6}}(\alpha\alpha\beta+\alpha\beta\alpha-2\beta\alpha\alpha) \quad \text{first doublet}$$

- $$c_3=0 \qquad c_2=-c_1$$

  $$2c_1^2=1\Longrightarrow c_1=\frac{1}{\sqrt{2}}, \quad c_2=-\frac{1}{\sqrt{2}}$$

  $$\eta_3=\frac{1}{\sqrt{2}}(\alpha\alpha\beta-\alpha\beta\alpha) \quad \text{second doublet}$$

Since $\langle\eta_1|\eta_3\rangle=0$ the two functions are linearly independent.

(ii) *Different* choice for the arbitrary unknown:

- $$c_1 = 0 \qquad c_3 = -c_2 \qquad 2c_2^2 = 1 \Longrightarrow c_2 = \frac{1}{\sqrt{2}}, \quad c_3 = -\frac{1}{\sqrt{2}}$$

$$\eta_1' = \frac{1}{\sqrt{2}}(\alpha\beta\alpha - \beta\alpha\alpha)$$

- $$c_3 = 0 \qquad c_2 = -c_1 \qquad 2c_1^2 = 1 \Longrightarrow c_1 = \frac{1}{\sqrt{2}}, \quad c_2 = -\frac{1}{\sqrt{2}}$$

$$\eta_3 = \frac{1}{\sqrt{2}}(\alpha\alpha\beta - \alpha\beta\alpha).$$

Since:

$$\langle \eta_1' | \eta_3 \rangle = -\frac{1}{2} = S \ (\neq 0)$$

the functions are not linearly independent. We can however orthogonalize η_1' to η_3 by the Schmidt method, obtaining:

$$\eta_3' = \frac{1}{\sqrt{2}}(\alpha\alpha\beta - \alpha\beta\alpha) = \eta_3$$

$$\begin{aligned}\eta_1'' &= \frac{\eta_1' - S\eta_3}{\sqrt{1-S^2}} = \frac{2}{\sqrt{3}} \cdot \frac{1}{2\sqrt{2}}(2\alpha\beta\alpha - 2\beta\alpha\alpha + \alpha\alpha\beta - \alpha\beta\alpha) \\ &= \frac{1}{\sqrt{6}}(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha) = \eta_1\end{aligned}$$

which is the linearly independent function of the first doublet we have found before.

- Eigenvalue $x = -2$

We have the system:

$$\begin{cases} -2c_1 + c_2 + c_3 = 0 \\ c_1 - 2c_2 + c_3 = 0 \\ c_1 + c_2 - 2c_3 = 0 \\ c_1^2 + c_2^2 + c_3^2 = 1 \end{cases}$$

Subtracting equation 2 from equation 1 gives:

$$-3c_1 + 3c_2 = 0 \qquad c_2 = c_1$$

while, from equation 3:

$$2c_1 - 2c_3 = 0 \qquad c_3 = c_1$$

$$3c_1^2 = 1 \Longrightarrow c_1 = c_2 = c_3 = \frac{1}{\sqrt{3}}$$

so that we have:

$$\eta_6 = \frac{1}{\sqrt{3}}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)$$

which is the quartet function with $M_S = 1/2$.

The remaining spin eigenstates are readily found by interchanging $\alpha \leftrightarrow \beta$ in the previous functions, while $\alpha\alpha\alpha$ and $\beta\beta\beta$ are already eigenstates belonging to $S = 3/2$ with $M_S = \pm 3/2$, respectively.

6.2. Spin eigenstates for $N = 3$ by the Löwdin projector method.

For our present purposes it will be sufficient to use Löwdin projectors for $N = 3$ in the form given by (132) and (133). Acting with $\hat{O}_{\frac{1}{2}}$ on the product function $\beta\alpha\alpha$ we obtain:

$$\begin{aligned}\hat{O}_{\frac{1}{2}}\beta\alpha\alpha &= \left(\hat{S}^2 - \frac{15}{4}\hat{I}\right)\beta\alpha\alpha = \left(\frac{3}{4} + \frac{4}{4} - \frac{15}{4}\right)\beta\alpha\alpha + \alpha\beta\alpha + \alpha\alpha\beta \\ &= \alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha\end{aligned}$$

that normalized gives:

$$\eta_1 = \frac{1}{\sqrt{6}}(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha)$$

which is the component with $M_S = 1/2$ of the first doublet $S = 1/2$. For the second doublet we may act with $\hat{O}_{\frac{1}{2}}$ on another product, say $\alpha\beta\alpha$:

$$\begin{aligned}\hat{O}_{\frac{1}{2}}\alpha\beta\alpha &= \left(\frac{3}{4} + \frac{4}{4} - \frac{15}{4}\right)\alpha\beta\alpha + \beta\alpha\alpha + \alpha\alpha\beta \\ &= \alpha\alpha\beta - 2\alpha\beta\alpha + \beta\alpha\alpha\end{aligned}$$

giving the normalized function:

$$\eta = \frac{1}{\sqrt{6}}(\alpha\alpha\beta - 2\alpha\beta\alpha + \beta\alpha\alpha).$$

This function however does depend linearly on η_1 since:

$$\langle\eta_1|\eta\rangle = \frac{1}{6}(1 - 2 - 2) = -\frac{1}{2} = S(\neq 0).$$

By Schmidt orthogonalization of η against η_1 we obtain:

$$\eta' = \frac{\eta - S\eta_1}{\sqrt{1-S^2}} = \frac{2}{\sqrt{3}} \cdot \frac{1}{2\sqrt{6}}(2\alpha\alpha\beta - 4\alpha\beta\alpha + 2\beta\alpha\alpha + \alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha)$$
$$= \frac{1}{\sqrt{2}}(\alpha\alpha\beta - \alpha\beta\alpha) \equiv \eta_3$$

which is the correct component with $M_S = 1/2$ of the second doublet.

To get the quartet function ($S = 3/2$) belonging to $M_S = 1/2$, we act with the projector (133) on the same product function $\beta\alpha\alpha$:

$$\hat{O}_{\frac{3}{2}}\beta\alpha\alpha = \left(\hat{S}^2 - \frac{3}{4}\hat{I}\right)\beta\alpha\alpha = \left(\frac{3}{4} - \frac{3}{4} + \frac{4}{4}\right)\beta\alpha\alpha + \alpha\beta\alpha + \alpha\alpha\beta$$
$$= \alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha$$

and normalization gives:

$$\eta_6 = \frac{1}{\sqrt{3}}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)$$

the correct spin eigenfunction with $S = 3/2$, $M_S = 1/2$. By the interchange $\alpha \leftrightarrow \beta$ all remaining spin eigenfunctions of the $N = 3$ problem are immediately derived.

6.3. The spin problem for $N = 4$.

Because of its length we shall not treat the problem of $N = 4$ completely, but shall limit ourselves to consideration of the spin states having $M_S = 0$ as a further example of application of Löwdin projection technique. For $N = 4$ the possible spin states are $2^4 = 16$ with $f_0^4 = 2$ (singlets), $f_1^4 = 3$ (triplets), $f_2^4 = 1$ (quintet) as can be seen from the Wigner formula or from the Kotani branching diagram. The 16 product functions are:

	M_S
$\alpha\alpha\alpha\alpha$	2
$\alpha\alpha\alpha\beta, \alpha\alpha\beta\alpha, \alpha\beta\alpha\alpha, \beta\alpha\alpha\alpha$	1
$\left.\begin{matrix}\alpha\alpha\beta\beta, \alpha\beta\alpha\beta, \beta\alpha\alpha\beta \\ \beta\beta\alpha\alpha, \beta\alpha\beta\alpha, \alpha\beta\beta\alpha\end{matrix}\right\}$	0
$\beta\beta\beta\alpha, \beta\beta\alpha\beta, \beta\alpha\beta\beta, \alpha\beta\beta\beta$	-1
$\beta\beta\beta\beta$	-2

The Dirac formula for $N = 4$ gives:

$$\hat{S}^2 = \hat{P}_{12} + \hat{P}_{13} + \hat{P}_{14} + \hat{P}_{23} + \hat{P}_{24} + \hat{P}_{34}.$$

By constructing the matrix representative of $\hat{S}^2$ over the product functions we can find the various spin eigenstates by diagonalizing suitable blocks of given $M_S \geqslant 0$ (the corresponding eigenstates for $M_S < 0$ are then simply obtained by the interchange $\alpha \leftrightarrow \beta$ in the resulting expressions). This gives the set of (normalized) linearly independent spin eigenstates for the $N = 4$ problem given previously. All these formulae can be easily checked by acting with $\hat{S}^2$ and verifying that:

$$\hat{S}^2\eta_\mu = S(S+1)\eta_\mu, \qquad \hat{S}_z\eta_\mu = M_S\eta_\mu \quad \mu = 1, 2, \cdots 16.$$

We now turn to use of Löwdin projectors. The projectors selecting, respectively, the singlet ($S = 0$), triplet ($S = 1$) and quintet ($S = 2$) components of the $N = 4$ problem are from (123):

$$\hat{O}_0 = \frac{\hat{S}^2 - 1(1+1)}{0(0+1) - 1(1+1)} \cdot \frac{\hat{S}^2 - 2(2+1)}{0(0+1) - 2(2+1)} = \frac{1}{12}(\hat{S}^2 \cdot \hat{S}^2 - 8\hat{S}^2 + 12\hat{I})$$

$$\hat{O}_1 = \frac{\hat{S}^2 - 0(0+1)}{1(1+1) - 0(0+1)} \cdot \frac{\hat{S}^2 - 2(2+1)}{1(1+1) - 2(2+1)} = -\frac{1}{8}(\hat{S}^2 \cdot \hat{S}^2 - 6\hat{S}^2)$$

$$\hat{O}_2 = \frac{\hat{S}^2 - 0(0+1)}{2(2+1) - 0(0+1)} \cdot \frac{\hat{S}^2 - 1(1+1)}{2(2+1) - 1(1+1)} = \frac{1}{24}(\hat{S}^2 \cdot \hat{S}^2 - 2\hat{S}^2).$$

(i) Singlets ($S = 0$)

Acting with $\hat{S}^2$ and $\hat{S}^2 \cdot \hat{S}^2$ (twice) on the first product function with $M_S = 0$ and orderly collecting all resulting terms, it is easily found (after normalizing the result):

$$\hat{O}_0\alpha\alpha\beta\beta = \frac{1}{\sqrt{12}}(2\alpha\alpha\beta\beta - \alpha\beta\alpha\beta - \beta\alpha\alpha\beta + 2\beta\beta\alpha\alpha - \beta\alpha\beta\alpha - \alpha\beta\beta\alpha) \equiv \eta_2$$

namely, the function of the second singlet given before.

Applying $\hat{O}_0$ to the second product function with $M_S = 0$, it is found after normalization:

$$\hat{O}_0\alpha\beta\alpha\beta = \frac{1}{\sqrt{12}}(-\alpha\alpha\beta\beta + 2\alpha\beta\alpha\beta - \beta\alpha\alpha\beta - \beta\beta\alpha\alpha + 2\beta\alpha\beta\alpha - \alpha\beta\beta\alpha) = \eta,$$

but now:

$$\langle\eta|\eta_2\rangle = -\frac{6}{12} = -\frac{1}{2} = S(\neq 0)$$

so that η is *not* orthogonal to η_2, and has a linear dependence. If we Schmidt-orthogonalize η against η_2, we immediately find the function of the first singlet:

$$\eta' = \frac{\eta - S\eta_2}{\sqrt{1 - S^2}} = \frac{1}{2}(\alpha\beta\alpha\beta - \beta\alpha\alpha\beta + \beta\alpha\beta\alpha - \alpha\beta\beta\alpha) \equiv \eta_1.$$

(ii) Triplets ($S = 1$)

In the same way, acting with $\hat{O}_1$ on the first product function with $M_S = 0$ and normalizing:

$$\hat{O}_1\alpha\alpha\beta\beta = \frac{1}{\sqrt{2}}(\alpha\alpha\beta\beta - \beta\beta\alpha\alpha) \equiv \eta_7$$

which is the component with $M_S = 0$ of the second triplet.

Acting on the second product function:

$$\hat{O}_1\alpha\beta\alpha\beta = \frac{1}{\sqrt{2}}(\alpha\beta\alpha\beta - \beta\alpha\beta\alpha) \equiv \eta_4$$

the component with $M_S = 0$ of the first triplet.

Acting on the third product function:

$$\hat{O}_1\beta\alpha\alpha\beta = \frac{1}{\sqrt{2}}(\beta\alpha\alpha\beta - \alpha\beta\beta\alpha) \equiv \eta_{10}$$

we find the component with $M_S = 0$ of the third triplet. In this way, all the components with $M_S = 0$ of the 3 triplets have been correctly recovered.

(iii) Quintet ($S = 2$)

Acting with $\hat{O}_2$ on one of the product functions with $M_S = 0$, say the second one $\alpha\beta\alpha\beta$, and normalizing the result, we find:

$$\hat{O}_2\alpha\beta\alpha\beta = \frac{1}{\sqrt{6}}(\alpha\alpha\beta\beta + \alpha\beta\alpha\beta + \beta\alpha\alpha\beta + \beta\beta\alpha\alpha + \beta\alpha\beta\alpha + \alpha\beta\beta\alpha) \equiv \eta_{14}$$

namely, the component with $M_S = 0$ of the quintet spin eigenstate given previously.

Proceeding in the same way with the appropriate projectors, we may find all the remaining components with $M_S = 1$ of the triplets and quintet, so completing the solution of the problem of finding the spin eigenstates for $N = 4$ by the Löwdin projection method.

6.4. The Kotani standard spin functions for $N = 3$, $S = M_S = \frac{1}{2}$.

For $N = 3$, $S = \frac{1}{2}$, $f^3_{\frac{1}{2}} = \frac{2\cdot 3!}{3!1!} = 2$, we have two linearly independent doublets with the coupling schemes of Figure 6.4.

We then have from the Kotani formulae for $S = M_S = \frac{1}{2}$:

(i) for $k_1 = (\frac{1}{2}\ 1)$ from (116):

$$\eta^3_{\frac{1}{2}\frac{1}{2};k_1} = -\sqrt{\frac{\frac{1}{2} - \frac{1}{2} + 1}{3}}\,\eta^2_{10;k_1}\alpha + \sqrt{\frac{\frac{1}{2} + \frac{1}{2} + 1}{3}}\,\eta^2_{11;k_1}\beta$$

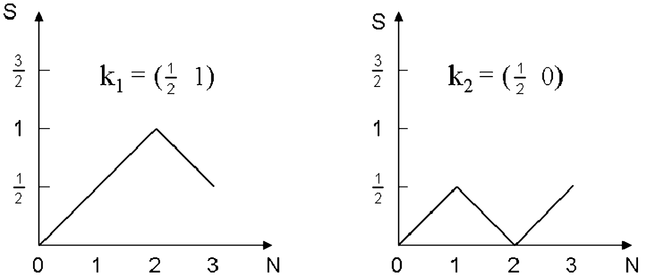


Figure 6.4 The two coupling schemes for $N = 3$, $S = \frac{1}{2}$.

$$
\begin{aligned}
&= -\frac{1}{\sqrt{3}} \cdot \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)\alpha + \frac{\sqrt{2}}{\sqrt{3}}\alpha\alpha\beta \\
&= \frac{1}{\sqrt{6}}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha) = \eta_1'
\end{aligned}
$$

(ii) for $k_2 = (\frac{1}{2}\ 0)$ from $(117)^2$:

$$
\begin{aligned}
\eta^3_{\frac{1}{2}\frac{1}{2};k_2} &= \sqrt{\frac{\frac{1}{2}+\frac{1}{2}}{1}}\,\eta^2_{00;k_2}\alpha \\
&= \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)\alpha = \frac{1}{\sqrt{2}}(\alpha\beta\alpha - \beta\alpha\alpha) = \eta_3'.
\end{aligned}
$$

We note that:

$$
\langle \eta_1' | \eta_3' \rangle \propto \langle 2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha | \alpha\beta\alpha - \beta\alpha\alpha \rangle = 0
$$

so that the two doublet functions found by the Kotani synthetic method are orthogonal, i.e. linearly independent. Since η_1' and η_3' are *different* from η_1 and η_3 found in Problems 6.1 and 6.2, the two sets of functions are *equivalent*, so that they must be related by a unitary (orthogonal) transformation.

6.5. Orthogonal transformation connecting Löwdin to Kotani spin functions for $N = 3$ and $S = M_S = \frac{1}{2}$.

---

[2] It must be recalled that all functions with $|M_S| > S$ are identically zero.

For the two spin doublets occurring for $N = 3$ and $S = M_S = \frac{1}{2}$ we have obtained the following results:

$$\begin{array}{ll}
\text{Löwdin (analytic)} & \text{Kotani (synthetic)} \\
\eta_1 = \dfrac{1}{\sqrt{6}}(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha) & \eta'_1 = \dfrac{1}{\sqrt{6}}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha) \\
\eta_3 = \dfrac{1}{\sqrt{2}}(\alpha\alpha\beta - \alpha\beta\alpha) & \eta'_3 = \dfrac{1}{\sqrt{2}}(\alpha\beta\alpha - \beta\alpha\alpha)
\end{array}$$

The functions within each set are eigenfunctions of $\hat{S}^2$ with $S = M_S = \frac{1}{2}$, orthogonal to each other and linearly independent, so that they must be connected by some unitary transformation (orthogonal, since the functions are *real*). A general orthogonal transformation (rotation) can be written as:

$$(\eta_1\ \eta''_3) = (\eta'_1\ \eta'_3)\begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}$$

giving:

$$\eta_1 = \eta'_1 \cos\theta - \eta'_3 \sin\theta \qquad \eta''_3 = \eta'_1 \sin\theta + \eta'_3 \cos\theta.$$

Upon substitution, simple inspection shows that:

$$\begin{aligned}
&\text{Coefficient of } \alpha\alpha\beta\text{: } 1 = 2\cos\theta \quad \Rightarrow \quad \cos\theta = \frac{1}{2} \\
&\text{Coefficient of } \alpha\beta\alpha\text{: } 1 = -\cos\theta - \sqrt{3}\sin\theta \quad \Rightarrow \quad \sin\theta = -\frac{\sqrt{3}}{2} \\
&\text{Coefficient of } \beta\alpha\alpha\text{: } -2 = -\cos\theta + \sqrt{3}\sin\theta = -\frac{1}{2} - \frac{3}{2} = -\frac{4}{2}
\end{aligned}$$

giving:

$$\mathbf{U}' = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}.$$

The last transformed function, $\eta''_3 = -\frac{1}{\sqrt{2}}(\alpha\beta\alpha - \alpha\alpha\beta)$, differs by an irrelevant -1 phase factor from Löwdin's η_3. To get complete coincidence we do the further transformation:

$$(\eta_1\ \eta_3) = (\eta_1\ \eta''_3)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

giving the (symmetrical) orthogonal transformation (reflection) connecting the two sets as the matrix:

$$\mathbf{U}=\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}=\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

$$\det\mathbf{U}=-\frac{1}{4}-\frac{3}{4}=-1$$

as it must be for an orthogonal matrix.

6.6. Elementary derivation of the spin coupling problem for $N=3$ and $S=M_S=\frac{1}{2}$.

For $N=2$ there is a *triplet* ($S=1$) and a *singlet* ($S=0$) whose functions are well known. We must couple the triplet functions for $N=2$ ($\alpha\alpha$, $\frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha)$, $\beta\beta$) with $S_3=\frac{1}{2}$ for the third electron so as to form a first doublet ($S=\frac{1}{2}$) corresponding to the coupling scheme $k_1=(\frac{1}{2}\ 1)$ on the branching diagram. Next, we couple the singlet function for $N=2$, $\frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha)$, with $S_3=\frac{1}{2}$ for the third electron so as to form the second doublet ($S=\frac{1}{2}$) corresponding to the coupling scheme $k_2=(\frac{1}{2}\ 0)$. The two doublets obtained in this way must be linearly independent, which means orthogonal to each other.

1. Coupling the triplet for $N=2$ to the doublet for $N=1$:

$$\begin{array}{lcll} & & & M_S \\ \left.\begin{array}{c} \alpha\alpha \\[2ex] \frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha) \\[2ex] \beta\beta \end{array}\right\}\alpha & \Longrightarrow & \begin{array}{c} \alpha\alpha\alpha \\[2ex] \frac{1}{\sqrt{2}}(\alpha\beta\alpha+\beta\alpha\alpha) \\[2ex] \beta\beta\alpha \end{array} & \begin{array}{c} \frac{3}{2} \\[2ex] \frac{1}{2} \\[2ex] -\frac{1}{2} \end{array} \\[6ex] \left.\begin{array}{c} \alpha\alpha \\[2ex] \frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha) \\[2ex] \beta\beta \end{array}\right\}\beta & \Longrightarrow & \begin{array}{c} \alpha\alpha\beta \\[2ex] \frac{1}{\sqrt{2}}(\alpha\beta\beta+\beta\alpha\beta) \\[2ex] \beta\beta\beta \end{array} & \begin{array}{c} \frac{1}{2} \\[2ex] -\frac{1}{2} \\[2ex] -\frac{3}{2} \end{array} \end{array}$$

To get a doublet $S=\frac{1}{2}$ with $M_S=\frac{1}{2}$ we must take a linear combination of functions 2 and 4, and determine the coefficients so as to satisfy:

$$\hat{S}^2\eta_1'=\frac{1}{2}\left(\frac{1}{2}+1\right)\eta_1', \qquad \hat{S}_z\eta_1'=\frac{1}{2}\eta_1'$$

using for $\hat{S}^2$ the Dirac expression for $N = 3$:

$$\hat{S}^2 = \frac{3}{4}\hat{I} + \hat{P}_{12} + \hat{P}_{13} + \hat{P}_{23}.$$

Take:

$$\eta_1' = A\frac{1}{\sqrt{2}}(\alpha\beta\alpha + \beta\alpha\alpha) + B\alpha\alpha\beta.$$

Then:

$$\hat{S}^2\eta_1' = \left(2\frac{A}{\sqrt{2}} + \frac{7}{4}B\right)\alpha\alpha\beta + \left(\frac{11}{4}\frac{A}{\sqrt{2}} + B\right)(\alpha\beta\alpha + \beta\alpha\alpha) = \frac{3}{4}\eta_1'.$$

From the identity above it follows:

$$2\frac{A}{\sqrt{2}} + \frac{7}{4}B = \frac{3}{4}B$$

$$\frac{11}{4}\frac{A}{\sqrt{2}} + B = \frac{3}{4}\frac{A}{\sqrt{2}}$$

giving:

$$2\frac{A}{\sqrt{2}} + B = 0 \Rightarrow B = -\sqrt{2}A.$$

Hence we obtain after normalization $\left(A = -\frac{1}{\sqrt{3}}\right)$:

$$\eta_1' = \frac{1}{\sqrt{6}}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$$

which is the first Kotani's function.

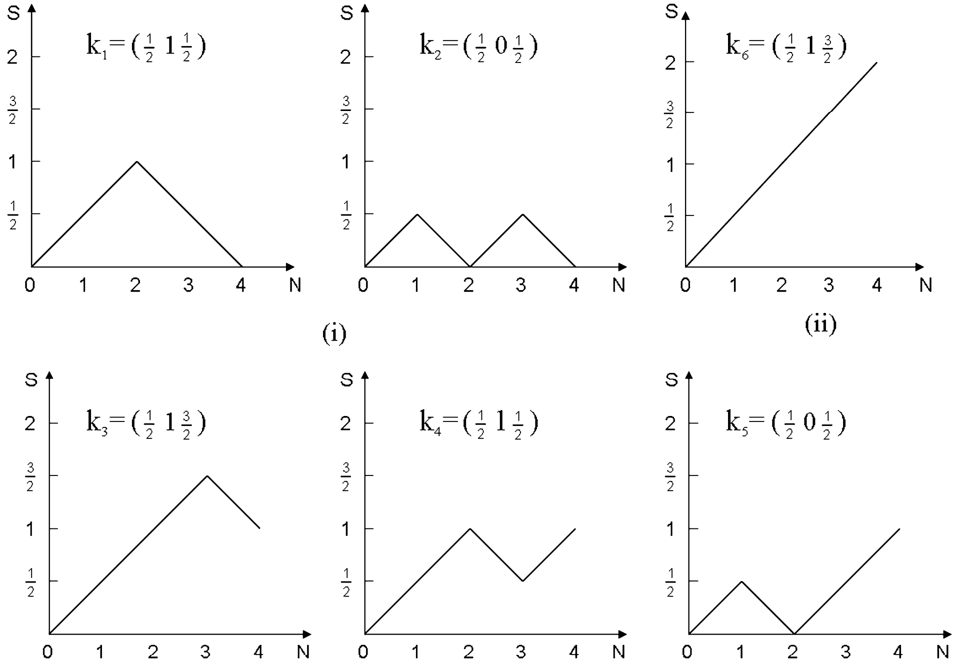
2. Coupling the singlet for $N = 2$ to the doublet for $N = 1$:

$$\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)\alpha \quad \Longrightarrow \quad \frac{1}{\sqrt{2}}(\alpha\beta\alpha - \beta\alpha\alpha) \qquad M_S = \frac{1}{2}$$

$$\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)\beta \quad \Longrightarrow \quad \frac{1}{\sqrt{2}}(\alpha\beta\beta - \beta\alpha\beta) \qquad M_S = -\frac{1}{2}$$

Hence, the second doublet for $N = 3$, $S = M_S = \frac{1}{2}$ will be:

$$\eta_3' = \frac{1}{\sqrt{2}}(\alpha\beta\alpha - \beta\alpha\alpha) \qquad \hat{S}^2\eta_3' = \frac{1}{2}\left(\frac{1}{2} + 1\right)\eta_3'$$



(i)

(ii)

(iii)

Figure 6.5 The coupling schemes for $N = 4$. (i) Singlets ($S = 0$), (ii) quintet ($S = 2$), (iii) triplets ($S = 1$).

which is the second Kotani's function. Hence, by the elementary coupling procedure we obtained the two doublets for $N = 3$:

$$\eta_1' = \frac{1}{\sqrt{6}}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$$

$$\eta_3' = \frac{1}{\sqrt{2}}(\alpha\beta\alpha - \beta\alpha\alpha)$$

which are the Kotani spin standard functions. The algebraic procedure is fully equivalent to Kotani's technique, which is however more valuable for more complex cases.

6.7. Construction of the two singlets ($S = 0$) for $N = 4$ using the elementary way of Problem 6.6. The coupling schemes for $N = 4$ and $S = 2, 1, 0$ are given in Figure 6.5.

We follow the lines of Problem 6.6 using the results obtained there. With reference to the first row (i) of Figure 6.5, we must couple the two doublets $\left(S = \frac{1}{2}\right)$ corresponding to the two coupling schemes $k_1 = \left(\frac{1}{2}\ 1\ \frac{1}{2}\right)$ and $k_2 = \left(\frac{1}{2}\ 0\ \frac{1}{2}\right)$ to the doublet for $N = 1$ to get the two singlets ($S = 0$).

1. Coupling the first doublet $\left(S=\frac{1}{2}\right)$ for $N=3$ to the doublet for $N=1$ to get the first singlet ($S=0$):

$$\left.\begin{array}{l}\frac{1}{\sqrt{6}}(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)\\ \frac{1}{\sqrt{6}}(2\beta\beta\alpha-\beta\alpha\beta-\alpha\beta\beta)\end{array}\right\}\alpha \implies \begin{array}{lc} & M_S\\ \frac{1}{\sqrt{6}}(2\alpha\alpha\beta\alpha-\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha) & 1\\ \frac{1}{\sqrt{6}}(2\beta\beta\alpha\alpha-\beta\alpha\beta\alpha-\alpha\beta\beta\alpha) & 0\end{array}$$

$$\left.\begin{array}{l}\frac{1}{\sqrt{6}}(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)\\ \frac{1}{\sqrt{6}}(2\beta\beta\alpha-\beta\alpha\beta-\alpha\beta\beta)\end{array}\right\}\beta \implies \begin{array}{lc} & M_S\\ \frac{1}{\sqrt{6}}(2\alpha\alpha\beta\beta-\alpha\beta\alpha\beta-\beta\alpha\alpha\beta) & 0\\ \frac{1}{\sqrt{6}}(2\beta\beta\alpha\beta-\beta\alpha\beta\beta-\alpha\beta\beta\beta) & -1\end{array}$$

To get the first singlet we must take a linear combination of functions 3 and 2 ($M_S=0$) which must be eigenfunctions of $\hat{S}^2$ with eigenvalue $S=0$:

$$\hat{S}^2\eta'_1=0(0+1)\eta'_1, \qquad \hat{S}_z\eta'_1=0\eta'_1$$

By taking:

$$\eta'_1=A\frac{1}{\sqrt{6}}(2\alpha\alpha\beta\beta-\alpha\beta\alpha\beta-\beta\alpha\alpha\beta)+B\frac{1}{\sqrt{6}}(2\beta\beta\alpha\alpha-\beta\alpha\beta\alpha-\alpha\beta\beta\alpha)$$

acting with $\hat{S}^2$ on η'_1 we are led to the conclusion that:

$$\frac{A}{\sqrt{6}}-\frac{B}{\sqrt{6}}=0\Rightarrow B=A$$

giving, after normalization, the first singlet as:

$$\eta'_1=\frac{1}{\sqrt{12}}(2\alpha\alpha\beta\beta-\alpha\beta\alpha\beta-\beta\alpha\alpha\beta+2\beta\beta\alpha\alpha-\beta\alpha\beta\alpha-\alpha\beta\beta\alpha).$$

2. Coupling the second doublet $\left(S=\frac{1}{2}\right)$ for $N=3$ to the doublet for $N=1$ to get the second singlet ($S=0$):

$$\begin{array}{lcll} & & & M_S \\ \left.\begin{array}{l} \frac{1}{\sqrt{2}}(\alpha\beta\alpha-\beta\alpha\alpha) \\ \frac{1}{\sqrt{2}}(\beta\alpha\beta-\alpha\beta\beta) \end{array}\right\}\alpha & \Longrightarrow & \begin{array}{l} \frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha-\beta\alpha\alpha\alpha) \\ \frac{1}{\sqrt{2}}(\beta\alpha\beta\alpha-\alpha\beta\beta\alpha) \end{array} & \begin{array}{c} 1 \\ 0 \end{array} \end{array}$$

$$\begin{array}{lcll} \left.\begin{array}{l} \frac{1}{\sqrt{2}}(\alpha\beta\alpha-\beta\alpha\alpha) \\ \frac{1}{\sqrt{2}}(\beta\alpha\beta-\alpha\beta\beta) \end{array}\right\}\beta & \Longrightarrow & \begin{array}{l} \frac{1}{\sqrt{2}}(\alpha\beta\alpha\beta-\beta\alpha\alpha\beta) \\ \frac{1}{\sqrt{2}}(\beta\alpha\beta\beta-\alpha\beta\beta\beta) \end{array} & \begin{array}{c} 0 \\ -1 \end{array} \end{array}$$

Take:

$$\eta_2' = A\frac{1}{\sqrt{2}}(\alpha\beta\alpha\beta-\beta\alpha\alpha\beta)+B\frac{1}{\sqrt{2}}(\beta\alpha\beta\alpha-\alpha\beta\beta\alpha)$$

and determine A and B so as:

$$\hat{S}^2\eta_2' = 0(0+1)\eta_2', \qquad \hat{S}_z\eta_2' = 0\eta_2.$$

Again we find that the necessary condition that must be satisfied is:

$$\frac{A}{\sqrt{2}}-\frac{B}{\sqrt{2}}=0 \Rightarrow B=A$$

giving, after normalization, the second singlet as:

$$\eta_2' = \frac{1}{2}(\alpha\beta\alpha\beta-\beta\alpha\alpha\beta+\beta\alpha\beta\alpha-\alpha\beta\beta\alpha).$$

We see that $\eta_1' = \eta_2$ and $\eta_2' = \eta_1$, so that the present results coincide with those of our previous Löwdin and matrix method except for the interchange of the two functions. We can proceed systematically in the same way to determine the functions belonging to the three triplets ($S=1$) and the quintet ($S=2$). The results coincide with those obtained from Kotani's formulae. However, the triplets are different from those found previously by

Löwdin or matrix method. As far as the three triplets are concerned, we have the comparison table between the different sets:

Löwdin (analytic)	Algebraic (or Kotani)	M_S
$\eta_3 = \frac{1}{2}(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$	$\eta'_3 = \frac{1}{\sqrt{12}}(3\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$	1
$\eta_4 = \frac{1}{\sqrt{2}}(\alpha\beta\alpha\beta - \beta\alpha\beta\alpha)$	$\eta'_4 = \frac{1}{\sqrt{6}}(\alpha\alpha\beta\beta + \alpha\beta\alpha\beta + \beta\alpha\alpha\beta - \beta\beta\alpha\alpha - \beta\alpha\beta\alpha - \alpha\beta\beta\alpha)$	0
$\eta_6 = \frac{1}{\sqrt{2}}(\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha)$	$\eta'_6 = \frac{1}{\sqrt{6}}(2\alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$	1
$\eta_7 = \frac{1}{\sqrt{2}}(\alpha\alpha\beta\beta - \beta\beta\alpha\alpha)$	$\eta'_7 = \frac{1}{\sqrt{12}}(2\alpha\alpha\beta\beta - \alpha\beta\alpha\beta - \beta\alpha\alpha\beta - 2\beta\beta\alpha\alpha + \beta\alpha\beta\alpha + \alpha\beta\beta\alpha)$	0
$\eta_9 = \frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$	$\eta'_9 = \frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$	1
$\eta_{10} = \frac{1}{\sqrt{2}}(\beta\alpha\alpha\beta - \alpha\beta\beta\alpha)$	$\eta'_{10} = \frac{1}{2}(\alpha\beta\alpha\beta - \beta\alpha\alpha\beta - \beta\alpha\beta\alpha + \alpha\beta\beta\alpha)$	0

The two sets having $M_S = 1$ are related by the orthogonal symmetric transformation whose elements can be easily found by inspection:

$$(\eta_3\ \eta_6\ \eta_9) = (\eta'_3\ \eta'_6\ \eta'_9)\mathbf{U}$$

$$\mathbf{U} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{\sqrt{2}}{\sqrt{3}} & 0 \\ \frac{\sqrt{2}}{\sqrt{3}} & -\frac{1}{\sqrt{3}} & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \det \mathbf{U} = -\frac{1}{3} - \frac{2}{3} = -1$$

The orthogonal transformation connecting the $M_S = 0$ components of the three triplets is a bit more complicated since it is not symmetrical. Straightforward but lengthy calculation shows that:

$$(\eta_4\ \eta_7\ \eta_{10}) = (\eta'_4\ \eta'_7\ \eta'_{10})\mathbf{U}$$

$$\mathbf{U} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{6}} & \frac{\sqrt{2}}{\sqrt{3}} & -\frac{1}{\sqrt{6}} \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{pmatrix} \qquad \det \mathbf{U} = -\frac{1}{3} - \frac{2}{3} = -1$$

We can easily check the first transformed function. We have:

$$\begin{aligned}
\eta_4 &= \eta_4' U_{11} + \eta_7' U_{21} + \eta_{10}' U_{31} \\
&= \frac{1}{\sqrt{3}} \cdot \frac{1}{\sqrt{6}} (\alpha\alpha\beta\beta + \alpha\beta\alpha\beta + \beta\alpha\alpha\beta - \beta\beta\alpha\alpha - \beta\alpha\beta\alpha - \alpha\beta\beta\alpha) \\
&\quad - \frac{1}{\sqrt{6}} \cdot \frac{1}{\sqrt{12}} (2\alpha\alpha\beta\beta - \alpha\beta\alpha\beta - \beta\alpha\alpha\beta - 2\beta\beta\alpha\alpha + \beta\alpha\beta\alpha + \alpha\beta\beta\alpha) \\
&\quad + \frac{1}{\sqrt{2}} \cdot \frac{1}{2} (\alpha\beta\alpha\beta - \beta\alpha\alpha\beta - \beta\alpha\beta\alpha + \alpha\beta\beta\alpha) \\
&= \frac{1}{\sqrt{2}} \cdot \frac{1}{3} (\cdots) - \frac{1}{\sqrt{2}} \cdot \frac{1}{6} (\cdots) + \frac{1}{\sqrt{2}} \cdot \frac{1}{2} (\cdots) \\
&= \frac{1}{\sqrt{2}} \cdot \frac{1}{6} (2\alpha\alpha\beta\beta + 2\alpha\beta\alpha\beta + 2\beta\alpha\alpha\beta - 2\beta\beta\alpha\alpha - 2\beta\alpha\beta\alpha - 2\alpha\beta\beta\alpha \\
&\quad - 2\alpha\alpha\beta\beta + \alpha\beta\alpha\beta + \beta\alpha\alpha\beta + 2\beta\beta\alpha\alpha - \beta\alpha\beta\alpha - \alpha\beta\beta\alpha \\
&\quad + 3\alpha\beta\alpha\beta - 3\beta\alpha\alpha\beta - 3\beta\alpha\beta\alpha + 3\alpha\beta\beta\alpha) \\
&= \frac{1}{\sqrt{2}} (\alpha\beta\alpha\beta - \beta\alpha\beta\alpha)
\end{aligned}$$

as it must be.

– 7 –

Many-Electron Wavefunctions: Slater, Hartree–Fock and Related Methods

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7.1 INTRODUCTION

We shall examine in this Chapter how a many-electron wavefunction satisfying the Pauli principle can be constructed starting from an orbital basis. We shall follow the classical work by Slater (1929), where such a wavefunction is built in terms of a determinant (Slater det) of orthonormal spin-orbitals. Reduction from the $4N$-dimensional configuration space of the wavefunction to the ordinary 3-dimensional space + spin is then considered in terms of 1-particle and 2-particle density matrices, whose diagonal elements determine the probability of finding clusters of one and two particles. This allows us to discuss electron and spin densities, and the correlation problem. Hartree–Fock theory is next introduced as the best independent particle model to treat many-electron systems, being the central step of an ideal ladder having uncorrelated approaches below it, from Hückel's topological theory to the LCAO-MO-SCF approach by Hall (1951) and Roothaan (1951a), and correlated approaches above it, such as CI and MC-SCF techniques, to many-body perturbation methods, among which particular attention is devoted to Møller–Plesset MP2, which gives directly a second-order evaluation of the correlation energy. Some space is deserved to methods including explicitly the interelectronic distance r_{12} in the wavefunction. Finally, a short outline of second quantization techniques is presented as alternative to Slater and Harteee–Fock methods, and of the density functional approach which is widely used today in the applications. Many problems are presented and discussed, as usual, at the end of the Chapter.

7.2 ANTISYMMETRY OF THE ELECTRONIC WAVEFUNCTION AND THE PAULI PRINCIPLE

7.2.1 Two-Electron Wavefunctions

Let $\mathbf{x}_1$ and $\mathbf{x}_2$ be two *fixed* points in the space-spin space, and $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ a normalized two-electron wavefunction. Then, because of the indistinguishability of the electrons:

$$
\begin{aligned}
&|\Psi(\mathbf{x}_1, \mathbf{x}_2)|^2 \, d\mathbf{x}_1 \, d\mathbf{x}_2 \\
&\quad = \text{probability of finding electron 1 at } d\mathbf{x}_1 \text{ and electron 2 at } d\mathbf{x}_2 \\
&\quad = |\Psi(\mathbf{x}_2, \mathbf{x}_1)|^2 \, d\mathbf{x}_1 \, d\mathbf{x}_2 \\
&\quad = \text{probability of finding electron 2 at } d\mathbf{x}_1 \text{ and electron 1 at } d\mathbf{x}_2.
\end{aligned}
$$

Therefore it follows:

$$|\Psi(\mathbf{x}_2,\mathbf{x}_1)|^2 = |\Psi(\mathbf{x}_1,\mathbf{x}_2)|^2 \implies \Psi(\mathbf{x}_2,\mathbf{x}_1) = \pm\Psi(\mathbf{x}_1,\mathbf{x}_2) \tag{1}$$

and the wavefunction must be symmetric (+ sign) or antisymmetric (− sign) in the interchange of the space-spin coordinates of the two electrons.

Pauli principle states that, in nature, electrons are described only by antisymmetric wavefunctions:

$$\Psi(\mathbf{x}_2,\mathbf{x}_1) = -\Psi(\mathbf{x}_1,\mathbf{x}_2), \tag{2}$$

which is the *Pauli antisymmetry principle* in the form given by Dirac.

This formulation includes the *exclusion principle* for electrons in the *same* orbital with the *same* spin:

$$\Psi(\mathbf{x}_1,\mathbf{x}_2) = \psi_\lambda(\mathbf{x}_1)\psi_\lambda(\mathbf{x}_2) - \psi_\lambda(\mathbf{x}_1)\psi_\lambda(\mathbf{x}_2) = 0, \tag{3}$$

where we always take electrons in dictionary order, and interchange spin-orbitals only. Instead, it is allowable to put two electrons in the *same* orbital with *different* spin:

$$\begin{aligned}\Psi(\mathbf{x}_1,\mathbf{x}_2) &= \psi_\lambda(\mathbf{x}_1)\overline{\psi}_\lambda(\mathbf{x}_2) - \overline{\psi}_\lambda(\mathbf{x}_1)\,\psi_\lambda(\mathbf{x}_2)\\ &= \begin{vmatrix}\psi_\lambda(\mathbf{x}_1) & \overline{\psi}_\lambda(\mathbf{x}_1)\\ \psi_\lambda(\mathbf{x}_2) & \overline{\psi}_\lambda(\mathbf{x}_2)\end{vmatrix} = |\psi_\lambda(\mathbf{x}_1)\overline{\psi}_\lambda(\mathbf{x}_2)|\end{aligned} \tag{4}$$

where the wavefunction is written as a 2 × 2 Slater determinant of the occupied spin-orbitals (SOs, recall the notation where ψ_λ is associated to spin α, and $\overline{\psi}_\lambda$ to spin β). Hence, the antisymmetry requirement of the Pauli principle for a pair of different SOs is automatically met by writing the 2-electron wavefunction as a *determinant* having electrons as rows and spin-orbitals as columns. Such a determinant is called a Slater det, since Slater (1929, 1931) was the first who suggested this approach, avoiding in this way the difficulties connected with older work which was mostly based on use of group theoretical techniques.

If the SOs are orthonormal, $\langle\psi_\lambda|\psi_\lambda\rangle = \langle\overline{\psi}_\lambda|\overline{\psi}_\lambda\rangle = 1$ and $\langle\psi_\lambda|\overline{\psi}_\lambda\rangle = \langle\overline{\psi}_\lambda|\psi_\lambda\rangle = 0$, the det is normalized by the factor $1/\sqrt{2}$, and it is usually assumed to represent the *normalized* det as:

$$\Psi(\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{\sqrt{2}}|\psi_\lambda\,\overline{\psi}_\lambda| = \|\psi_\lambda(\mathbf{x}_1)\overline{\psi}_\lambda(\mathbf{x}_2)\|. \tag{5}$$

7.2.2 Three-Electron Wavefunctions

The permutations of $N = 3$ electrons (*identical* particles) are $3! = 6$. The permutations are:

$$\begin{matrix} 123, & 213, & 321, & 132, & 312, & 231\\ I & P_{12} & P_{13} & P_{23} & P_{12}P_{13} & P_{12}P_{23}\end{matrix}\,, \tag{6}$$

where, in the case of multiple permutations, we recall that the inner permutation must act first, then the outer. Since for each permutation (interchange) we must change sign in order to satisfy Pauli's principle, we can construct the antisymmetrizing operator (the antisymmetrizer):

$$\hat{A} \propto \hat{I} - \hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} + \hat{P}_{12}\hat{P}_{13} + \hat{P}_{12}\hat{P}_{23}, \tag{7}$$

which, acting on the *product* function of three SOs $(a\,b\,c)$ transforms it into its antisymmetric component. Let us take as an example the three orthonormal spin-orbitals $a(\mathbf{x})$, $b(\mathbf{x})$, $c(\mathbf{x})$. Acting with the antisymmetrizer $\hat{A}$ it is obtained:

$$\begin{aligned}
\hat{A}\overset{1}{a}\,\overset{2}{b}\,\overset{3}{c} &= \text{keep SOs fixed and permute in all} \\
&\quad\ \text{possible ways the electrons among them} \\
&= \overset{1}{a}\,\overset{2}{b}\,\overset{3}{c} - \overset{2}{a}\,\overset{1}{b}\,\overset{3}{c} - \overset{3}{a}\,\overset{2}{b}\,\overset{1}{c} - \overset{1}{a}\,\overset{3}{b}\,\overset{2}{c} + \overset{3}{a}\,\overset{1}{b}\,\overset{2}{c} + \overset{2}{a}\,\overset{3}{b}\,\overset{1}{c} \\
&= \text{restore dictionary order for the electrons} \\
&= \overset{1}{a}\,\overset{2}{b}\,\overset{3}{c} - b\,a\,c - c\,b\,a - a\,c\,b + b\,c\,a + c\,a\,b,
\end{aligned} \tag{8}$$

so that:

$$\begin{aligned}
\hat{A}\overset{1}{a}\overset{2}{b}\overset{3}{c} &= a(bc - cb) - b(ac - ca) + c(ab - ba) \\
&= \begin{vmatrix} \overset{1}{a} & \overset{1}{b} & \overset{1}{c} \\ \overset{2}{a} & \overset{2}{b} & \overset{2}{c} \\ \overset{3}{a} & \overset{3}{b} & \overset{3}{c} \end{vmatrix} = |\overset{1}{a} \quad \overset{2}{b} \quad \overset{3}{c}|
\end{aligned} \tag{9}$$

a Slater det of order 3. The permutation of the electrons among the spin-orbitals is hence equivalent to the construction of a Slater determinant having space-spin electron coordinates as rows and spin-orbitals as columns.

7.2.3 Many-Electron Wavefunctions and the Slater Method

For an N-electron system (atom or molecule) the wavefunction Ψ is antisymmetric if it is unaltered by an *even* number of permutations of the electrons among the SOs, while it changes sign by an *odd* number of permutations. As an example:

$$\hat{P}_{12}\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3 \cdots \mathbf{x}_N) = \Psi(\mathbf{x}_2, \mathbf{x}_1, \mathbf{x}_3 \cdots \mathbf{x}_N) = -\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3 \cdots \mathbf{x}_N). \tag{10}$$

The N-electron wavefunctions can be constructed from a set, in principle *complete*, of one-electron functions including spin (atomic or molecular spin-orbitals).

If:

$$\{\psi_i(\mathbf{x})\} \quad i = 1, 2, \ldots \quad \mathbf{x} = \mathbf{r}s \tag{11}$$

$$\langle \psi_i | \psi_j \rangle = \int d\mathbf{x}\psi_i^*(\mathbf{x})\psi_j(\mathbf{x}) = \delta_{ij}, \tag{12}$$

we can write:

$$\Psi(\mathbf{x}_1) = \sum_i \psi_i(\mathbf{x}_1)C_i \quad C_i = \langle \psi_i | \Psi \rangle \tag{13}$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i \psi_i(\mathbf{x}_1)C_i(\mathbf{x}_2) = \sum_i \sum_j \psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)C_{ji} \tag{14}$$

$$\ldots$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N) = \sum_{ij\cdots N} \psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\cdots\psi_N(\mathbf{x}_N)C_{N\cdots ji}. \tag{15}$$

The coefficients of the linear combination of the products of spin-orbitals are determined by the fact that the resultant Ψ must be antisymmetric with respect to the interchange of any pair of electrons (Pauli). The simplest way of writing such a function was introduced by Slater (1929, 1931), as we have seen, and consists in writing Ψ in the form of a determinant of order N (Slater det):

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \overset{1}{\psi_1} & \overset{1}{\psi_2} & \cdots & \overset{1}{\psi_N} \\ \overset{2}{\psi_1} & \overset{2}{\psi_2} & \cdots & \overset{2}{\psi_N} \\ & & \cdots & \\ \overset{N}{\psi_1} & \overset{N}{\psi_2} & \cdots & \overset{N}{\psi_N} \end{vmatrix} = \| \overset{1}{\psi_1} \quad \overset{2}{\psi_2} \quad \cdots \quad \overset{N}{\psi_N} \|, \tag{16}$$

where:

$$\begin{aligned} &\text{rows} = \text{space-spin electron coordinates} \\ &\text{columns} = \text{spin-orbital functions.} \end{aligned} \tag{17}$$

If the SOs are orthonormal:

$$\langle \psi_i | \psi_j \rangle = \delta_{ij},$$

then the many-electron wavefunction (16) is normalized to 1:

$$\langle \Psi | \Psi \rangle = 1. \tag{18}$$

- Properties of Slater determinants

(i) The Ψ written in the form of a Slater det is antisymmetric with respect to the interchange of any pair of electrons:

$$\Psi(\mathbf{x}_2, \mathbf{x}_1, \cdots \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \overset{2}{\psi_1} & \overset{2}{\psi_2} & \cdots & \overset{2}{\psi_N} \\ \overset{1}{\psi_1} & \overset{1}{\psi_2} & \cdots & \overset{1}{\psi_N} \\ & & \cdots & \\ \overset{N}{\psi_1} & \overset{N}{\psi_2} & \cdots & \overset{N}{\psi_N} \end{vmatrix} = -\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N), \tag{19}$$

since this is equivalent to interchanging two rows of the determinant, and this changes sign to the function.

(ii) If two spin-orbitals are equal, the determinant has two columns equal and therefore vanishes identically:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \overset{1}{\psi_1} & \overset{1}{\psi_1} & \cdots & \overset{1}{\psi_N} \\ \overset{2}{\psi_1} & \overset{2}{\psi_1} & \cdots & \overset{2}{\psi_N} \\ & & \cdots & \\ \overset{N}{\psi_1} & \overset{N}{\psi_1} & \cdots & \overset{N}{\psi_N} \end{vmatrix} \equiv 0. \tag{20}$$

A function of this kind cannot exist. This is nothing but the Pauli principle in its exclusion form: two atomic SOs cannot have equal the four quantum numbers $|n\, l\, m\, m_s\rangle$. The same is true for molecular SOs, since we cannot have two spatial MOs identical with the same spin.

(iii) The Slater det is unchanged if we orderly interchange rows with columns:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \overset{1}{\psi_1} & \overset{2}{\psi_1} & \cdots & \overset{N}{\psi_1} \\ \overset{1}{\psi_2} & \overset{2}{\psi_2} & \cdots & \overset{N}{\psi_2} \\ & & \cdots & \\ \overset{1}{\psi_N} & \overset{2}{\psi_N} & \cdots & \overset{N}{\psi_N} \end{vmatrix}, \tag{21}$$

where now:

$$\begin{aligned} &\text{rows} = \text{spin-orbital functions} \\ &\text{columns} = \text{space-spin electron coordinates.} \end{aligned} \tag{22}$$

(iv) The probability density (as the Hamiltonian operator) is left *unchanged* after any number of interchanges among the electrons:

$$|\Psi(\mathbf{x}_2, \mathbf{x}_1, \cdots \mathbf{x}_N)|^2 = |\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N)|^2. \tag{23}$$

(v) A single Slater det is sufficient as a first approximation in the case of closed shells (with spin $S = M_S = 0$) or open shells with $|M_S| = S$ (all spins parallel or antiparallel), while in the general open-shell case to get an eigenstate of $\hat{S}^2$ with eigenvalue S (state of *definite* spin) it is necessary to take a linear combination of Slater dets. The effect of the spin operator $\hat{P}_{s_\kappa s_\lambda}$ on a Slater det is equivalent to interchanging the two spin functions η_κ and η_λ among the two columns of the original det, leaving unaltered the orbital part (which is purely spatial). In such a way, the Dirac formula of Chapter 6 can equally well be applied to the Slater dets to verify or to construct determinants which are eigenstates of spin.

(vi) Examples.

• The ground and the first excited states of the He atom are described in terms of Slater dets by:

$$\Psi(1s^2, {}^1S) = \|1s\overline{1s}\| \quad S = M_S = 0$$

$$\Psi(1s\,2s, {}^3S) = \begin{cases} \|1s2s\| & S = 1,\ M_S = 1 \\ \dfrac{1}{\sqrt{2}}\{\|1s\overline{2s}\| + \|\overline{1s}2s\|\} & 0 \\ \|\overline{1s2s}\| & -1 \end{cases}$$

$$\Psi(1s\,2s, {}^1S) = \frac{1}{\sqrt{2}}\{\|1s\overline{2s}\| - \|\overline{1s}2s\|\} \qquad S = M_S = 0$$

$$\Psi(1s2p, {}^3P) = \begin{cases} \|1s2p\| & S = 1,\ M_S = 1 \\ \dfrac{1}{\sqrt{2}}\{\|1s\overline{2p}\| + \|\overline{1s}2p\|\} & 0 \\ \|\overline{1s2p}\| & -1 \end{cases}$$

nine states ($p = x, y, z$),

$$\Psi(1s2p, {}^1P) = \frac{1}{\sqrt{2}}\{\|1s\overline{2p}\| - \|\overline{1s}2p\|\} \quad S = M_S = 0$$

three states ($p = x, y, z$).

Other examples.

$$\bullet \quad \mathrm{Li}(1s^2 2s, {}^2S) = \begin{cases} \|1s\overline{1s}2s\| & S = \dfrac{1}{2},\ M_S = \dfrac{1}{2} \\ \|1s\,\overline{1s}\,\overline{2s}\| & -\dfrac{1}{2} \end{cases}.$$

The ground state of the Li atom is a doublet S.

- $\mathrm{Be}(1s^2 2s^2, {}^1S) = \|1s\overline{1s}\,2s\,\overline{2s}\| \quad S = M_S = 0.$

The ground state of the Be atom is a singlet S.

- $\mathrm{H}_2(\sigma_g^2, {}^1\Sigma_g^+) = \|\sigma_g\overline{\sigma_g}\| \quad S = M_S = 0.$

The ground state of the H_2 molecule is a singlet Σ_g^+ (the bonding MO $\sigma_g = \frac{a+b}{\sqrt{2+2S}}$ is *doubly* occupied).

- $$\mathrm{H}_2(\sigma_g\sigma_u, {}^3\Sigma_u^+) = \begin{cases} \|\sigma_g\,\sigma_u\| & S = 1,\ M_S = 1 \\ \dfrac{1}{\sqrt{2}}\{\|\sigma_g\overline{\sigma_u}\| + \|\overline{\sigma_g}\sigma_u\|\} & 0. \\ \|\overline{\sigma_g}\,\overline{\sigma_u}\| & -1 \end{cases}$$

The excited triplet state of the H_2 molecule has *singly* occupied MOs ($\sigma_u = \frac{b-a}{\sqrt{2-2S}}$ is the antibonding MO).

- $\mathrm{H}_2\mathrm{O}(1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2, {}^1A_1) = \|1a_1\overline{1a}_1 2a_1\overline{2a}_1 \cdots 1b_1\overline{1b}_1\| \quad S = M_S = 0.$

The ground state of the H_2O molecule ($N = 10$) is described by five doubly occupied non-degenerate MOs (see Chapter 8), where $a_1, b_1, b_2, \cdots$ are MOs having the symmetry of the C_{2v} point group (the symmetry group to which the H_2O molecule belongs).

We now verify using Dirac's rule that the ground state wavefunction for H_2 is a singlet ($S = 0$), and that for the excited state a triplet ($S = 1$).

$$\Psi(\sigma_g^2, {}^1\Sigma_g^+) = \|\sigma_g\overline{\sigma}_g\|$$

$$\hat{S}^2 = \hat{I} + \hat{P}_{12}$$

$$\hat{S}^2\Psi = \|\sigma_g\overline{\sigma}_g\| + \|\overline{\sigma}_g\sigma_g\| = \|\sigma_g\overline{\sigma}_g\| - \|\sigma_g\overline{\sigma}_g\| = 0(0+1)\Psi \quad S = 0,\ \text{singlet}$$

$$\Psi(\sigma_g\sigma_u, {}^3\Sigma_u^+) = \frac{1}{\sqrt{2}}\{\|\sigma_g\overline{\sigma}_u\| + \|\overline{\sigma}_g\sigma_u\|\}$$

$$\begin{aligned} \hat{S}^2\Psi &= \frac{1}{\sqrt{2}}\{\|\sigma_g\overline{\sigma}_u\| + \|\overline{\sigma}_g\sigma_u\| + \|\overline{\sigma}_g\sigma_u\| + \|\sigma_g\overline{\sigma}_u\|\} \\ &= 2\cdot\frac{1}{\sqrt{2}}\{\|\sigma_g\overline{\sigma}_u\| + \|\overline{\sigma}_g\sigma_u\|\} = 1(1+1)\Psi \quad S = 1,\ \text{triplet } (M_S = 0). \end{aligned}$$

Other examples for $\mathrm{Li}({}^2S)$ and $\mathrm{Be}({}^1S)$ are given as Problems 7.1 and 7.2.

7.3 ELECTRON DISTRIBUTION FUNCTIONS

The distribution functions determine the distribution of electron "clusters", and allow us to pass from the abstract $4N$-dimensional space of the N-electron wavefunction to the 3-dimensional + spin physical space where experiments are done (McWeeny, 1960).

7.3.1 1-Electron Distribution Functions: General Definitions

Let:

$$\Psi(\mathbf{x}_1,\, \mathbf{x}_2, \cdots \mathbf{x}_N) \quad \text{with} \quad \langle\Psi|\Psi\rangle = 1 \tag{24}$$

be a normalized N-electron wavefunction satisfying the antisymmetry requirement. Then the first principles state that:

$$\begin{aligned}&\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N)\Psi^*(\mathbf{x}_1,\, \mathbf{x}_2, \cdots \mathbf{x}_N) d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N\\ &\quad = \text{probability of finding electron (or particle) 1 at } d\mathbf{x}_1,\\ &\qquad 2 \text{ at } d\mathbf{x}_2, \cdots, N \text{ at } d\mathbf{x}_N,\end{aligned} \tag{25}$$

where $d\mathbf{x}_1$, $d\mathbf{x}_2, \cdots d\mathbf{x}_N$ are *fixed* infinitesimal space-spin volume elements in configuration space.

The probability of finding electron 1 at $d\mathbf{x}_1$ *independently* of the remaining $(N-1)$ electrons will be given by:

$$\left[\int d\mathbf{x}_2 \cdots d\mathbf{x}_N \Psi\Psi^*\right] d\mathbf{x}_1. \tag{26}$$

The probability of finding any one *unspecified* electron at $d\mathbf{x}_1$ will be N times this quantity:

$$\left[N \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N)\Psi^*(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N)\right] d\mathbf{x}_1 = \rho_1(\mathbf{x}_1; \mathbf{x}_1)\, d\mathbf{x}_1, \tag{27}$$

where the bilinear function:

From $\Psi \quad \Psi^*$

$$\rho_1(\mathbf{x}_1\, ;\, \mathbf{x}_1) = N \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N)\Psi^*(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N) \tag{28}$$

is called the 1-electron distribution function. It is the *diagonal* element $(\mathbf{x}_1' = \mathbf{x}_1)$ of the more general mathematical quantity:[1]

$$\rho_1(\mathbf{x}_1; \mathbf{x}_1') = N \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N)\Psi^*(\mathbf{x}_1', \mathbf{x}_2, \cdots \mathbf{x}_N) \tag{29}$$

---

[1] As far as notation is concerned, we shall use ρ for the density (or density matrix) with spin, P for the density (or density matrix) without spin.

which is called the 1-electron density matrix. It is important to stress that (29) has no physical meaning, while its diagonal element (28) is the function determining the physical distribution of the electrons.

The 1-electron distribution function (28) satisfies the conservation relation:

$$\int d\mathbf{x}_1 \rho_1(\mathbf{x}_1;\, \mathbf{x}_1) = N, \tag{30}$$

where N is the total number of electrons.

7.3.2 Electron Density and Spin Density

The most general expression for the 1-electron distribution function as a bilinear function of space-spin variables is:

$$\begin{aligned}\rho_1(\mathbf{x}_1;\mathbf{x}_1) &= \rho_1(\mathbf{r}_1 s_1;\mathbf{r}_1 s_1)\\ &= P_1(\overset{\alpha}{\mathbf{r}_1};\overset{\alpha}{\mathbf{r}_1})\alpha(s_1)\alpha^*(s_1) + P_1(\overset{\beta}{\mathbf{r}_1};\overset{\beta}{\mathbf{r}_1})\beta(s_1)\beta^*(s_1)\\ &\quad + P_1(\overset{\alpha}{\mathbf{r}_1};\overset{\beta}{\mathbf{r}_1})\alpha(s_1)\beta^*(s_1) + P_1(\overset{\beta}{\mathbf{r}_1};\overset{\alpha}{\mathbf{r}_1})\beta(s_1)\alpha^*(s_1),\end{aligned} \tag{31}$$

where the P_1s are purely spatial functions, and we shall sometimes make use of the short notation:

$$P_1(\overset{\alpha}{\mathbf{r}_1};\overset{\alpha}{\mathbf{r}_1}) = P_1^\alpha, \quad \text{etc.} \tag{32}$$

Integrating over the spin variable:

$$\int ds_1\, \rho_1(\mathbf{r}_1 s_1;\mathbf{r}_1 s_1) = P_1(\overset{\alpha}{\mathbf{r}_1};\overset{\alpha}{\mathbf{r}_1}) + P_1(\overset{\beta}{\mathbf{r}_1};\overset{\beta}{\mathbf{r}_1}), \tag{33}$$

where:

$$P_1(\overset{\alpha}{\mathbf{r}_1};\overset{\alpha}{\mathbf{r}_1})d\mathbf{r}_1 = \text{probability of finding at } d\mathbf{r}_1 \text{ an electron with spin } \alpha \tag{34}$$

$$P_1(\overset{\beta}{\mathbf{r}_1};\overset{\beta}{\mathbf{r}_1})d\mathbf{r}_1 = \text{probability of finding at } d\mathbf{r}_1 \text{ an electron with spin } \beta. \tag{35}$$

The two remaining integrals in (31) vanish because of the orthogonality of the spin functions. In terms of the two *spinless* components P_1^α and P_1^β we define:

$$P(\mathbf{r}_1;\mathbf{r}_1) = P_1(\overset{\alpha}{\mathbf{r}_1};\overset{\alpha}{\mathbf{r}_1}) + P_1(\overset{\beta}{\mathbf{r}_1};\overset{\beta}{\mathbf{r}_1}) = P_1^\alpha + P_1^\beta \tag{36}$$

the electron density (as measured from experiment), with:

$$P(\mathbf{r}_1;\mathbf{r}_1)\,d\mathbf{r}_1 = \text{probability of finding at } d\mathbf{r}_1 \text{ an electron with either spin;} \tag{37}$$

$$Q(\mathbf{r}_1;\mathbf{r}_1) = P_1(\overset{\alpha}{\mathbf{r}_1};\overset{\alpha}{\mathbf{r}_1}) - P_1(\overset{\beta}{\mathbf{r}_1};\overset{\beta}{\mathbf{r}_1}) = P_1^{\alpha} - P_1^{\beta} \tag{38}$$

the spin density, with:

$$Q(\mathbf{r}_1;\mathbf{r}_1)\,d\mathbf{r}_1 = \text{probability of finding at } d\mathbf{r}_1 \text{ an excess of spin } \alpha \text{ over spin } \beta. \tag{39}$$

We have the conservation relations:

$$\int d\mathbf{r}_1 P_1(\overset{\alpha}{\mathbf{r}_1};\overset{\alpha}{\mathbf{r}_1}) = N_\alpha \tag{40}$$

the number of electrons with spin α;

$$\int d\mathbf{r}_1 P_1(\overset{\beta}{\mathbf{r}_1};\overset{\beta}{\mathbf{r}_1}) = N_\beta \tag{41}$$

the number of electrons with spin β;

$$\int d\mathbf{r}_1 P(\mathbf{r}_1;\mathbf{r}_1) = N_\alpha + N_\beta = N \tag{42}$$

the total number of electrons;

$$\int d\mathbf{r}_1 Q(\mathbf{r}_1;\mathbf{r}_1) = N_\alpha - N_\beta = 2M_S, \tag{43}$$

where M_S is the eigenvalue of the z-component of the spin operator:

$$\hat{S}_z\eta = M_S\eta. \tag{44}$$

As an example, consider the doubly occupied (normalized) MO $\phi(\mathbf{r})$. The normalized 2-electron wavefunction will be:

$$\Psi = \|\phi\overline{\phi}\| = \frac{1}{\sqrt{2}}\begin{vmatrix} \overset{1}{\phi\alpha} & \overset{1}{\phi\beta} \\ \overset{2}{\phi\alpha} & \overset{2}{\phi\beta} \end{vmatrix} = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\,\frac{1}{\sqrt{2}}\big[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)\big], \tag{45}$$

$$\begin{aligned}
\rho_1(\mathbf{x}_1;\,\mathbf{x}_1) &= 2\int d\mathbf{x}_2\,\Psi(\mathbf{x}_1,\mathbf{x}_2)\Psi^*(\mathbf{x}_1,\mathbf{x}_2) \\
&= 2\int d\mathbf{r}_2\,ds_2 \quad \begin{matrix} \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\dfrac{1}{\sqrt{2}}\big[\alpha(s_1)\beta(s_2)-\beta(s_1)\alpha(s_2)\big] \\ \phi^*(\mathbf{r}_1)\phi^*(\mathbf{r}_2)\dfrac{1}{\sqrt{2}}\big[\alpha^*(s_1)\beta^*(s_2)-\beta^*(s_1)\alpha^*(s_2)\big] \end{matrix} \\
&= \phi(\mathbf{r}_1)\phi^*(\mathbf{r}_1)\big[\alpha(s_1)\alpha^*(s_1)+\beta(s_1)\beta^*(s_1)\big], \qquad (46)
\end{aligned}$$

so that:

$$P_1(\overset{\alpha}{\mathbf{r}_1}\,;\,\overset{\alpha}{\mathbf{r}_1}) = P_1(\overset{\beta}{\mathbf{r}_1}\,;\,\overset{\beta}{\mathbf{r}_1}) = \phi(\mathbf{r}_1)\phi^*(\mathbf{r}_1) = R(\mathbf{r}_1;\mathbf{r}_1) \tag{47}$$

$$P(\mathbf{r}_1;\mathbf{r}_1) = P_1^\alpha + P_1^\beta = 2\phi(\mathbf{r}_1)\phi^*(\mathbf{r}_1) = 2|\phi(\mathbf{r}_1)|^2 \tag{48}$$

$$Q(\mathbf{r}_1;\mathbf{r}_1) = P_1^\alpha - P_1^\beta = 0 \tag{49}$$

provided we remember that, under the action of a differential operator (like ∇^2), the operator acts only on ϕ and *not* on ϕ^* (this is one of the main reasons for using density matrices, where there is a distinction between $\mathbf{r}$ and $\mathbf{r}'$).

In terms of an atomic basis $(\chi_A\ \chi_B)$, where χ_A and χ_B are normalized non-orthogonal AOs with overlap $S = \langle\chi_A|\chi_B\rangle \neq 0$, the MO $\phi(\mathbf{r})$ can be written as:

$$\phi(\mathbf{r}) = \chi_A(\mathbf{r})c_A + \chi_B(\mathbf{r})c_B = \frac{\chi_A + \lambda\chi_B}{\sqrt{1+\lambda^2+2\lambda S}}, \tag{50}$$

where:

$$\lambda = \frac{c_B}{c_A} \tag{51}$$

is the polarity parameter of the MO, and:

$$c_A = (1+\lambda^2+2\lambda S)^{-1/2} \tag{52}$$

the normalization factor.

The electron density can be analyzed into elementary densities coming from equation (50) as:

$$P(\mathbf{r}) = 2|\phi(\mathbf{r})|^2 = q_A\chi_A^2(\mathbf{r}) + q_B\chi_B^2(\mathbf{r}) + q_{AB}\frac{\chi_A(\mathbf{r})\chi_B(\mathbf{r})}{S} + q_{BA}\frac{\chi_B(\mathbf{r})\chi_A(\mathbf{r})}{S}, \tag{53}$$

where $\chi_A^2(\mathbf{r})$, $\chi_B^2(\mathbf{r})$ are atomic densities, $\frac{\chi_A(\mathbf{r})\chi_B(\mathbf{r})}{S}$ and $\frac{\chi_B(\mathbf{r})\chi_A(\mathbf{r})}{S}$ overlap densities, all normalized to 1, while the coefficients:

$$q_A = \frac{2}{1+\lambda^2+2\lambda S}, \qquad q_B = \frac{2\lambda^2}{1+\lambda^2+2\lambda S} \tag{54}$$

are atomic charges, and:

$$q_{AB} = q_{BA} = \frac{2\lambda S}{1+\lambda^2+2\lambda S} \tag{55}$$

overlap charges. They are normalized so that:

$$q_A + q_B + q_{AB} + q_{BA} = \frac{2+2\lambda^2+4\lambda S}{1+\lambda^2+2\lambda S} = 2 \tag{56}$$

the total number of electrons in the bond orbital $\phi(\mathbf{r})$.

For a *homopolar* bond, $\lambda = 1$:

$$q_A = q_B = \frac{1}{1+S}, \qquad q_{AB} = q_{BA} = \frac{S}{1+S}. \tag{57}$$

For a *heteropolar* bond, $\lambda \neq 1$, and we can define *gross* charges on A and B as:

$$Q_A = q_A + q_{AB} = \frac{2+2\lambda S}{1+\lambda^2+2\lambda S} \tag{58}$$

$$Q_B = q_B + q_{BA} = \frac{2\lambda^2+2\lambda S}{1+\lambda^2+2\lambda S}, \tag{59}$$

and *formal* charges on A and B as:

$$\delta_A = 1 - Q_A = \frac{\lambda^2-1}{1+\lambda^2+2\lambda S} \tag{60}$$

$$\delta_B = 1 - Q_B = -\frac{\lambda^2-1}{1+\lambda^2+2\lambda S}. \tag{61}$$

If $\lambda > 1$, $\delta_A = \delta > 0$, $\delta_B = -\delta_A = -\delta < 0$, and we have the dipole $\overset{+\delta}{A}\ \overset{-\delta}{B}$ (e.g. LiH).

Further examples for the ${}^1\Sigma_g^+$ ground state and the ${}^3\Sigma_u^+$ excited triplet state of H_2 are given as Problems 7.3 and 7.4.

7.3.3 2-Electron Distribution Functions: General Definitions

The 2-electron distribution function determines the distribution of the electrons in *pairs*, and is defined as:

$$\begin{aligned}
&\text{From } \Psi \qquad \Psi^* \\
&\rho_2(\mathbf{x}_1, \mathbf{x}_2\,;\, \mathbf{x}_1, \mathbf{x}_2) \\
&\quad = N(N-1) \int d\mathbf{x}_3 \cdots d\mathbf{x}_N \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \cdots \mathbf{x}_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \cdots \mathbf{x}_N).
\end{aligned} \tag{62}$$

Its physical meaning is:

$$\begin{aligned}
&\rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\
&\quad = \text{probability of finding an electron at } d\mathbf{x}_1 \text{ and, simultaneously,} \\
&\quad\quad \text{another electron at } d\mathbf{x}_2.
\end{aligned} \tag{63}$$

From the definition (62) of ρ_2 and the normalization of Ψ, it follows that:

$$\int d\mathbf{x}_2 \rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) = (N-1)\rho_1(\mathbf{x}_1; \mathbf{x}_1) \tag{64}$$

$$\iint d\mathbf{x}_1 d\mathbf{x}_2 \rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) = N(N-1) \tag{65}$$

which is the total number of indistinct pairs of electrons. Equation (65) is the conservation relation for ρ_2, while equation (64) shows that ρ_1 can be obtained from ρ_2 by integration, while, in general, the opposite is not true. As we shall see later in this Chapter, the only exception is the Hartree–Fock theory where ρ_1 determines ρ_2.

7.3.4 Spinless Pair Functions and the Correlation Problem

The most general expression for the 2-electron distribution function is:

$$\begin{aligned}
\rho_2(\mathbf{x}_1, \mathbf{x}_2\,;\, \mathbf{x}_1, \mathbf{x}_2) = {} & P_2(\overset{\alpha}{\mathbf{r}_1}, \overset{\alpha}{\mathbf{r}_2}\,;\, \overset{\alpha}{\mathbf{r}_1}, \overset{\alpha}{\mathbf{r}_2})\alpha(s_1)\alpha(s_2)\alpha^*(s_1)\alpha^*(s_2) \\
& + P_2(\overset{\beta}{\mathbf{r}_1}, \overset{\beta}{\mathbf{r}_2}\,;\, \overset{\beta}{\mathbf{r}_1}, \overset{\beta}{\mathbf{r}_2})\beta(s_1)\beta(s_2)\beta^*(s_1)\beta^*(s_2) \\
& + P_2(\overset{\alpha}{\mathbf{r}_1}, \overset{\beta}{\mathbf{r}_2}\,;\, \overset{\alpha}{\mathbf{r}_1}, \overset{\beta}{\mathbf{r}_2})\alpha(s_1)\beta(s_2)\alpha^*(s_1)\beta^*(s_2) \\
& + P_2(\overset{\beta}{\mathbf{r}_1}, \overset{\alpha}{\mathbf{r}_2}\,;\, \overset{\beta}{\mathbf{r}_1}, \overset{\alpha}{\mathbf{r}_2})\beta(s_1)\alpha(s_2)\beta^*(s_1)\alpha^*(s_2) + \cdots
\end{aligned} \tag{66}$$

By integrating over spin we obtain the *spinless* pair function, which can be written in short as:

$$P_2(\mathbf{r}_1;\mathbf{r}_2) = P_2(\overset{\alpha}{\mathbf{r}_1}\,;\overset{\alpha}{\mathbf{r}_2}) + P_2(\overset{\beta}{\mathbf{r}_1}\,;\overset{\beta}{\mathbf{r}_2}) + P_2(\overset{\alpha}{\mathbf{r}_1}\,;\overset{\beta}{\mathbf{r}_2}) + P_2(\overset{\beta}{\mathbf{r}_1}\,;\overset{\alpha}{\mathbf{r}_2}), \tag{67}$$

where only the diagonal elements appear in the short notation. The physical meaning of each component is self-evident, that for the third component being:

$$\begin{aligned} &P_2(\overset{\alpha}{\mathbf{r}_1}\,;\overset{\beta}{\mathbf{r}_2})d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad = \text{probability of finding an electron at } d\mathbf{r}_1 \text{ with spin } \alpha \text{ and, simultaneously,} \\ &\qquad \text{another electron at } d\mathbf{r}_2 \text{ with spin } \beta\text{, and so on.} \end{aligned} \tag{68}$$

It is useful to introduce a *correlation factor* f (McWeeny, 1960):

$$P_2(\overset{\alpha}{\mathbf{r}_1}\,;\overset{\beta}{\mathbf{r}_2}) = P_1(\overset{\alpha}{\mathbf{r}_1})P_1(\overset{\beta}{\mathbf{r}_2})\big[1 + f(\overset{\alpha}{\mathbf{r}_1}\,;\overset{\beta}{\mathbf{r}_2})\big], \tag{69}$$

where $f(\overset{\alpha}{\mathbf{r}_1}\,;\overset{\beta}{\mathbf{r}_2})$ describes the deviation from the independence ($f = 0$) in the motion of the two electrons due to electron correlation. For antisymmetric functions, if $\mathbf{r}_2 \to \mathbf{r}_1$:

$$f(\overset{\alpha}{\mathbf{r}_1}\,;\overset{\alpha}{\mathbf{r}_2}) = f(\overset{\beta}{\mathbf{r}_1}\,;\overset{\beta}{\mathbf{r}_2}) = -1 \tag{70}$$

namely there is a 100% of negative correlation, so that electrons with the *same* spin cannot be found in the *same* point of space. This is called "Fermi correlation", and it represents the most general formulation of the Pauli principle, being completely independent of the form of the wavefunction.

Let us take as an example the component with $M_S = 1$ of the $1s2s(^3S)$ state of He, to which the only non-zero component of the pair function is associated:

$$\Psi(^3S,\, M_S = 1) = \|1s\,2s\| = \frac{1}{\sqrt{2}}(\overset{\mathbf{r}_1}{1s}\,\overset{\mathbf{r}_2}{2s} - \overset{\mathbf{r}_1}{2s}\,\overset{\mathbf{r}_2}{1s})\overset{s_1}{\alpha}\,\overset{s_2}{\alpha} \tag{71}$$

$$\begin{aligned} \rho_2(\mathbf{x}_1, \mathbf{x}_2\,;\,\mathbf{x}_1, \mathbf{x}_2) &= 2\Psi(\mathbf{x}_1, \mathbf{x}_2)\Psi^*(\mathbf{x}_1, \mathbf{x}_2) \\ &= (\overset{\mathbf{r}_1}{1s}\,\overset{\mathbf{r}_2}{2s}\,\overset{\mathbf{r}_1}{1s^*}\,\overset{\mathbf{r}_2}{2s^*} + \overset{\mathbf{r}_1}{2s}\,\overset{\mathbf{r}_2}{1s}\,\overset{\mathbf{r}_1}{2s^*}\,\overset{\mathbf{r}_2}{1s^*} - \overset{\mathbf{r}_1}{1s}\,\overset{\mathbf{r}_2}{2s}\,\overset{\mathbf{r}_1}{2s^*}\,\overset{\mathbf{r}_2}{1s^*} \\ &\qquad - \overset{\mathbf{r}_1}{2s}\,\overset{\mathbf{r}_2}{1s}\,\overset{\mathbf{r}_1}{1s^*}\,\overset{\mathbf{r}_2}{2s^*})\overset{s_1}{\alpha}\,\overset{s_2}{\alpha}\,\overset{s_1}{\alpha^*}\,\overset{s_2}{\alpha^*}, \end{aligned} \tag{72}$$

where, in the extended notation:

$$P_2(\overset{\beta}{\mathbf{r}_1}, \overset{\beta}{\mathbf{r}_2}\,;\,\overset{\beta}{\mathbf{r}_1}, \overset{\beta}{\mathbf{r}_2}) = P_2(\overset{\alpha}{\mathbf{r}_1}, \overset{\beta}{\mathbf{r}_2}\,;\,\overset{\alpha}{\mathbf{r}_1}, \overset{\beta}{\mathbf{r}_2}) = P_2(\overset{\beta}{\mathbf{r}_1}, \overset{\alpha}{\mathbf{r}_2}\,;\,\overset{\beta}{\mathbf{r}_1}, \overset{\alpha}{\mathbf{r}_2}) = 0 \tag{73}$$

$$
\begin{aligned}
P_2(\overset{\alpha}{\mathbf{r}_1}, \overset{\alpha}{\mathbf{r}_2}\,;\, \overset{\alpha}{\mathbf{r}_1}, \overset{\alpha}{\mathbf{r}_2}) &= 1s2s1s^*2s^* + 2s1s2s^*1s^* - 1s2s2s^*1s^* \\
&\quad - 2s1s1s^*2s^* \qquad (74)
\end{aligned}
$$

$$
\lim_{\mathbf{r}_2 \to \mathbf{r}_1} P_2(\overset{\alpha}{\mathbf{r}_1}\,;\, \overset{\alpha}{\mathbf{r}_2}) = 2\,1s^2(\mathbf{r}_1)2s^2(\mathbf{r}_1) - 21s^2(\mathbf{r}_1)2s^2(\mathbf{r}_1) = 0 \qquad (75)
$$

so that:

$$
f(\overset{\alpha}{\mathbf{r}_1}\,;\, \overset{\alpha}{\mathbf{r}_2}) = -1 \qquad (76)
$$

in the limit $\mathbf{r}_2 \to \mathbf{r}_1$.

The same is true for the component $M_S = 0$ of the triplet:

$$
\Psi(^3S, M_S = 0) = \frac{1}{\sqrt{2}}(1s2s - 2s1s)\frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha) \qquad (77)
$$

$$
\begin{aligned}
\rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) &= 2\Psi(\mathbf{x}_1, \mathbf{x}_2)\Psi^*(\mathbf{x}_1, \mathbf{x}_2) \\
&= \frac{1}{2}(1s2s1s^*2s^* + 2s1s2s^*1s^* \\
&\quad - 1s2s2s^*1s^* - 2s1s1s^*2s^*) \\
&\quad \cdot (\alpha\beta\alpha^*\beta^* + \beta\alpha\beta^*\alpha^* + \cdots), \qquad (78)
\end{aligned}
$$

where we have indicated only the spin terms surviving after integration over spin. Then:

$$
P_2(\overset{\alpha}{\mathbf{r}_1}\,;\, \overset{\alpha}{\mathbf{r}_2}) = P_2(\overset{\beta}{\mathbf{r}_1}\,;\, \overset{\beta}{\mathbf{r}_2}) = 0 \qquad (79)
$$

$$
\begin{aligned}
P_2(\overset{\alpha}{\mathbf{r}_1}\,;\, \overset{\beta}{\mathbf{r}_2}) &= P_2(\overset{\beta}{\mathbf{r}_1}\,;\, \overset{\alpha}{\mathbf{r}_2}) \\
&= \frac{1}{2}(1s2s1s^*2s^* + 2s1s2s^*1s^* - 1s2s2s^*1s^* - 2s1s1s^*2s^*) \qquad (80)
\end{aligned}
$$

$$
\lim_{\mathbf{r}_2 \to \mathbf{r}_1} P_2(\overset{\alpha}{\mathbf{r}_1}\,;\, \overset{\beta}{\mathbf{r}_2}) = \frac{1}{2}\big[2\,1s^2(\mathbf{r}_1)2s^2(\mathbf{r}_1) - 21s^2(\mathbf{r}_1)2s^2(\mathbf{r}_1\big] = 0 \qquad (81)
$$

namely, $\Psi(^3S,\ M_S = 0)$ for the electron configuration $1s2s$ of He describes a 100% of negative correlation in the limit $\mathbf{r}_2 \to \mathbf{r}_1$ for electrons with *opposed* spin with $f(\overset{\alpha}{\mathbf{r}_1}\,;\, \overset{\beta}{\mathbf{r}_2}) = -1$. For $\mathbf{r}_2 \neq \mathbf{r}_1$, $P_2(\overset{\alpha}{\mathbf{r}_1}\,;\, \overset{\beta}{\mathbf{r}_2}) \neq P_1(\overset{\alpha}{\mathbf{r}_1})P_1(\overset{\beta}{\mathbf{r}_2})$, so that $\Psi(^3S, M_S = 0)$ describes some correlation between electrons with different spin in each point of space.

The situation is different for electrons with *different* spin occupying the *same* (atomic or molecular) orbital, and one of the typical problems of advanced quantum mechanics is that of calculating as exactly as possible the correlation factor for different spin $f(\overset{\alpha}{\mathbf{r}_1}\,;\, \overset{\beta}{\mathbf{r}_2})$.

In the simple one-configuration MO theory (Ψ approximated as a single Slater det of doubly occupied MOs), this correlation factor is equal to zero:

$$P_2(\overset{\alpha}{\mathbf{r}_1};\overset{\beta}{\mathbf{r}_2}) = P_2(\overset{\beta}{\mathbf{r}_1};\overset{\alpha}{\mathbf{r}_2}) = P_1(\overset{\alpha}{\mathbf{r}_1})P_1(\overset{\beta}{\mathbf{r}_2}) = P_1(\overset{\beta}{\mathbf{r}_1})P_1(\overset{\alpha}{\mathbf{r}_2}), \tag{82}$$

so that the distribution function of electron pairs with different spin is simply the product of the distribution functions of the single electrons (no correlation). This means that the two electrons can approach each other in a completely arbitrary way, at variance with the physical reality of the Coulomb repulsion of the two electrons which would tend to ∞ as $r_{12} \to 0$. In other words, the single det MO wavefunction does not correlate at all the motion of the electrons (independent particle model, IPM).

Let us take as an example the ground state (${}^1\Sigma_g^+$) of the H_2 molecule described by the single MO determinant wavefunction:

$$\Psi_{\text{MO}}(\mathbf{x}_1,\mathbf{x}_2) = \|\sigma_g\overline{\sigma}_g\| = \overset{\mathbf{r}_1}{\sigma_g}\,\overset{\mathbf{r}_2}{\sigma_g}\,\frac{1}{\sqrt{2}}(\overset{s_1}{\alpha}\,\overset{s_2}{\beta} - \overset{s_1}{\beta}\,\overset{s_2}{\alpha}), \tag{83}$$

where Ψ_{MO} describes a *one*-configuration of molecular SOs. Then:

$$\begin{aligned}\rho_2(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1,\mathbf{x}_2) &= 2\Psi_{\text{MO}}(\mathbf{x}_1,\mathbf{x}_2)\Psi^*_{\text{MO}}(\mathbf{x}_1,\mathbf{x}_2)\\ &= \sigma_g\sigma_g\sigma_g^*\sigma_g^*(\alpha\beta\alpha^*\beta^* + \beta\alpha\beta^*\alpha^* - \alpha\beta\beta^*\alpha^* - \beta\alpha\alpha^*\beta^*)\end{aligned} \tag{84}$$

$$P_2(\overset{\alpha}{\mathbf{r}_1},\overset{\alpha}{\mathbf{r}_2};\overset{\alpha}{\mathbf{r}_1},\overset{\alpha}{\mathbf{r}_2}) = P_2(\overset{\beta}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2};\overset{\beta}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2}) = 0 \tag{85}$$

$$P_2(\overset{\alpha}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2};\overset{\alpha}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2}) = P_2(\overset{\beta}{\mathbf{r}_1},\overset{\alpha}{\mathbf{r}_2};\overset{\beta}{\mathbf{r}_1},\overset{\alpha}{\mathbf{r}_2}) = \sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)\sigma_g^*(\mathbf{r}_1)\sigma_g^*(\mathbf{r}_2), \tag{86}$$

so that:

$$P_2(\overset{\alpha}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2};\overset{\alpha}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2}) = P_1(\overset{\alpha}{\mathbf{r}_1})P_1(\overset{\beta}{\mathbf{r}_2}) \tag{87}$$

$$P_1(\overset{\alpha}{\mathbf{r}_1}) = \sigma_g(\mathbf{r}_1)\sigma_g^*(\mathbf{r}_1), \qquad P_1(\overset{\beta}{\mathbf{r}_2}) = \sigma_g(\mathbf{r}_2)\sigma_g^*(\mathbf{r}_2), \tag{88}$$

the simple product of 1-electron distributions. Therefore, Ψ_{MO} for a closed shell does not describe any correlation (hence, the large error found in describing the dissociation of the H_2 molecule using the simple one-configuration MO wavefunction).

Instead, consider the Heitler–London (HL) wavefunction for ground state H_2:

$$\Psi_{\text{HL}}(\mathbf{x}_1,\mathbf{x}_2) = N\big\{\|a\overline{b}\| + \|b\overline{a}\|\big\} = N(ab+ba)\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha) \tag{89}$$

a *two*-configuration wavefunction of atomic SOs. Then:

$$\begin{aligned}\rho_2(\mathbf{x}_1,\mathbf{x}_2\,;\,\mathbf{x}_1,\mathbf{x}_2) &= 2\Psi_{\mathrm{HL}}(\mathbf{x}_1,\mathbf{x}_2)\,\Psi^*_{\mathrm{HL}}(\mathbf{x}_1,\mathbf{x}_2)\\ &= N^2(aba^*b^* + bab^*a^* + abb^*a^* + baa^*b^*)\\ &\quad\cdot(\alpha\beta\alpha^*\beta^* + \beta\alpha\beta^*\alpha^* - \alpha\beta\beta^*\alpha^* - \beta\alpha\alpha^*\beta^*)\end{aligned} \tag{90}$$

$$P_2(\overset{\alpha}{\mathbf{r}_1},\overset{\alpha}{\mathbf{r}_2}\,;\,\overset{\alpha}{\mathbf{r}_1},\overset{\alpha}{\mathbf{r}_2}) = P_2(\overset{\beta}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2}\,;\,\overset{\beta}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2}) = 0 \tag{91}$$

$$\begin{aligned}P_2(\overset{\alpha}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2}\,;\,\overset{\alpha}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2}) &= P_2(\overset{\beta}{\mathbf{r}_1},\overset{\alpha}{\mathbf{r}_2}\,;\,\overset{\beta}{\mathbf{r}_1},\overset{\alpha}{\mathbf{r}_2})\\ &= N^2(aba^*b^* + bab^*a^* + abb^*a^* + baa^*b^*)\\ &\neq P_1(\overset{\alpha}{\mathbf{r}_1})P_1(\overset{\beta}{\mathbf{r}_2}),\end{aligned} \tag{92}$$

where:

$$\begin{aligned}P_1(\overset{\alpha}{\mathbf{r}_1}) &= \int d\mathbf{r}_2 P_2(\overset{\alpha}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2}\,;\,\overset{\alpha}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2}) = N^2(a^2 + b^2 + 2Sab)\\ = P_1(\overset{\beta}{\mathbf{r}_2}) &= \int d\mathbf{r}_1 P_2(\overset{\alpha}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2}\,;\,\overset{\alpha}{\mathbf{r}_1},\overset{\beta}{\mathbf{r}_2}).\end{aligned} \tag{93}$$

Therefore, at variance of the Ψ_{MO}, Ψ_{HL} introduces some sort of correlation between electrons with different spin. This is due to its molecular "split-shell" structure, which partially prevents the electrons from doubly occupying the same orbital with different spin.

7.4 AVERAGE VALUES OF 1- AND 2-ELECTRON OPERATORS

The electron distribution functions we saw so far (better, their corresponding density matrices) allow one to compute easily the average values of symmerical sums of 1- and 2-electron operators, such as those occurring in evaluating the expectation value for the electronic energy in atomic and molecular systems.

7.4.1 Symmetrical Sums of 1-Electron Operators

$$\begin{aligned}&\left\langle \Psi \left| \sum_{i=1}^{N} \hat{h}_i \right| \Psi \right\rangle\\ &\quad= \sum_i \int \hat{h}_i \Psi(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_N)\Psi^*(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_N)d\mathbf{x}_1\,d\mathbf{x}_2\cdots d\mathbf{x}_N\\ &\quad= \int d\mathbf{x}_1\,\hat{h}_1 \int d\mathbf{x}_2\cdots d\mathbf{x}_N \Psi(\mathbf{x}_1,\,\mathbf{x}_2,\cdots\mathbf{x}_N)\Psi^*(\mathbf{x}_1,\,\mathbf{x}_2,\cdots\mathbf{x}_N)\\ &\qquad+ \int d\mathbf{x}_2\,\hat{h}_2 \int d\mathbf{x}_1\cdots d\mathbf{x}_N \Psi(\mathbf{x}_2,\,\mathbf{x}_1,\cdots\mathbf{x}_N)\Psi^*(\mathbf{x}_2,\,\mathbf{x}_1,\cdots\mathbf{x}_N)\end{aligned}$$

$$
\begin{aligned}
&+\cdots \quad N \text{ terms identical to the first one}\\
&=\int d\mathbf{x}_1\,\hat{h}_1\left\{N\int d\mathbf{x}_2\cdots d\mathbf{x}_N\,\Psi(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_N)\Psi^*(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_N)\right\}\\
&=\int d\mathbf{x}_1\,\hat{h}_1\rho_1(\mathbf{x}_1;\mathbf{x}_1), \qquad (94)
\end{aligned}
$$

where we must take care that $\hat{h}_1$ acts only upon the first set of variables (those coming from Ψ) and *not* on the second (those coming from Ψ^*). It is more correct to write:

$$
\left\langle\Psi\middle|\sum_i\hat{h}_i\middle|\Psi\right\rangle=\int d\mathbf{x}_1\,\hat{h}_1\rho_1(\mathbf{x}_1;\mathbf{x}'_1)|_{\mathbf{x}'_1=\mathbf{x}_1}, \qquad (95)
$$

where $\rho_1(\mathbf{x}_1;\mathbf{x}'_1)$ is the 1-electron density matrix, and the prime is removed before the final integration over $d\mathbf{x}_1$.

In this way, the 4^N-dimensional integration over the N-electron wavefunction Ψ is replaced by a 4-dimensional integration over the 1-electron density matrix. It must be stressed here that, for a Ψ in the form of a single Slater det of order N such as that occurring in the HF theory for closed shells, the matrix element (94) would involve a 4^N-dimensional integration of $(N!)^2$ terms!

7.4.2 Symmetrical Sums of 2-Electron Operators

In the following, we make explicit reference to the electron repulsion operator, but the same holds for any other 2-electron operator, such as those involving spin operators.[2]

$$
\begin{aligned}
&\left\langle\Psi\middle|{\sum_{i,j}}'\frac{1}{r_{ij}}\middle|\Psi\right\rangle\\
&={\sum_{ij}}'\int\frac{1}{r_{ij}}\Psi(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_N)\Psi^*(\mathbf{x}_1,\,\mathbf{x}_2,\cdots\mathbf{x}_N)d\mathbf{x}_1\,d\mathbf{x}_2\cdots d\mathbf{x}_N\\
&=\iint d\mathbf{x}_1\,d\mathbf{x}_2\frac{1}{r_{12}}\int d\mathbf{x}_3\cdots d\mathbf{x}_N\,\Psi(\mathbf{x}_1,\mathbf{x}_2,\,\mathbf{x}_3,\cdots\mathbf{x}_N)\Psi^*(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\cdots\mathbf{x}_N)\\
&\quad+\iint d\mathbf{x}_1\,d\mathbf{x}_3\frac{1}{r_{13}}\int d\mathbf{x}_2\cdots d\mathbf{x}_N\,\Psi(\mathbf{x}_1,\mathbf{x}_3,\,\mathbf{x}_2,\cdots\mathbf{x}_N)\Psi^*(\mathbf{x}_1,\mathbf{x}_3,\mathbf{x}_2,\cdots\mathbf{x}_N)\\
&\quad+\cdots \quad N(N-1) \text{ terms identical to the first one}\\
&=\iint d\mathbf{x}_1\,d\mathbf{x}_2\frac{1}{r_{12}}\left\{N(N-1)\int d\mathbf{x}_3\cdots d\mathbf{x}_N\,\Psi(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\cdots\mathbf{x}_N)\right.\\
&\quad\left.\times\,\Psi^*(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\cdots\mathbf{x}_N)\right\}\\
&=\iint d\mathbf{x}_1\,d\mathbf{x}_2\frac{1}{r_{12}}\,\rho_2(\overset{\Psi}{\mathbf{x}_1},\mathbf{x}_2\;;\;\overset{\Psi^*}{\mathbf{x}_1},\mathbf{x}_2), \qquad (96)
\end{aligned}
$$

where the 2-electron operator $1/r_{12}$ is now a simple multiplier.

---

[2] The $'$ means that the terms $j=i$ are excluded from the summation. There are altogether $N(N-1)$ indistinct terms.

Hence, we conclude that, in general:

$$\left\langle \Psi \middle| \sum_i \hat{O}_i \middle| \Psi \right\rangle = \sum_i \int \hat{O}_i \Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N) d\mathbf{x}_1\, d\mathbf{x}_2 \cdots d\mathbf{x}_N$$

$$= \int d\mathbf{x}_1 \hat{O}_1 \rho_1(\mathbf{x}_1; \mathbf{x}'_1)|_{\mathbf{x}'_1 = \mathbf{x}_1} \tag{97}$$

$$\left\langle \Psi \middle| {\sum_{i,j}}' \hat{O}_{ij} \middle| \Psi \right\rangle$$

$$= {\sum_{i,j}}' \int \hat{O}_{ij} \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \cdots \mathbf{x}_N) \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \cdots \mathbf{x}_N) d\mathbf{x}_1\, d\mathbf{x}_2\, d\mathbf{x}_3 \cdots d\mathbf{x}_N$$

$$= \iint d\mathbf{x}_1\, d\mathbf{x}_2 \hat{O}_{12} \rho_2(\mathbf{x}_1 \mathbf{x}_2; \mathbf{x}_1 \mathbf{x}_2). \tag{98}$$

7.4.3 Average Value of the Electronic Energy

The electronic Hamiltonian in the Born–Oppenheimer approximation (Chapter 10) contains two of such symmetrical sums. Therefore, its average value over the (normalized) many-electron wavefunction Ψ can be written as:

$$E_e = \langle \Psi | \hat{H}_e | \Psi \rangle = \left\langle \Psi \middle| \sum_i \hat{h}_i + \frac{1}{2} {\sum_{i,j}}' \frac{1}{r_{ij}} \middle| \Psi \right\rangle$$

$$= \int d\mathbf{x}_1\, \hat{h}_1 \rho_1(\mathbf{x}_1; \mathbf{x}'_1)|_{\mathbf{x}'_1 = \mathbf{x}_1} + \frac{1}{2} \iint d\mathbf{x}_1\, d\mathbf{x}_2 \frac{1}{r_{12}} \rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) \tag{99}$$

$$= \int d\mathbf{x}_1 \left\{ -\frac{1}{2} \nabla_1^2 \rho_1(\mathbf{x}_1; \mathbf{x}'_1) \right\}_{\mathbf{x}'_1 = \mathbf{x}_1} \tag{100}$$

$$+ \int d\mathbf{x}_1 V_1 \rho_1(\mathbf{x}_1; \mathbf{x}_1) \tag{101}$$

$$+ \frac{1}{2} \iint d\mathbf{x}_1\, d\mathbf{x}_2 \frac{1}{r_{12}} \rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2), \tag{102}$$

where:

$$\hat{h} = -\frac{1}{2} \nabla^2 + V \quad V = -\sum_\alpha \frac{Z_\alpha}{r_\alpha} \tag{103}$$

is the one-electron bare nuclei Hamiltonian, and V the nuclear attraction.

Equation (100) is the average kinetic energy of the electron distribution ρ_1 (it is the only term which implies the 1-electron density matrix because of the presence of the differential operator ∇_1^2 which acts on Ψ and not on Ψ^*).

Equation (101) expresses the average potential energy of the charge distribution ρ_1 in the field provided by all nuclei in the molecule.

Equation (102) expresses the average electronic repulsion of an electron pair described by the pair function ρ_2.

In this way, the molecular energy E in the Born–Oppenheimer approximation takes its simplest physically transparent form as:

$$E = E_e + E_N = E_e + \frac{1}{2}\sum_{\alpha,\beta}{}' \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \tag{104}$$

where the electronic energy E_e is evaluated in a given fixed nuclear configuration, and we added nuclear repulsion as the last term.

7.5 THE SLATER RULES

Well before density matrix techniques were introduced in molecular quantum mechanics (Löwdin, 1955a, 1955b; McWeeny, 1960; see, however, Lennard-Jones, 1931), Slater (1929) gave some simple rules for the evaluation of the matrix elements of any symmetrical sum of 1-electron and 2-electron operators between any pair of Slater dets built from *orthonormal* spin-orbitals. These rules were later extended by Löwdin (1955a) to include the case of Slater dets built from *non-orthogonal* spin-orbitals, while in the latter case Figari and Magnasco (1985) suggested convenient mathematical techniques to deal with the cofactors arising from n-substituted Slater dets. At variance with Löwdin's formulae, which go into trouble if the actual overlap matrix becomes singular, Figari and Magnasco's formulae go smoothly into the Slater formulae when overlap goes to zero.

Slater's rules are as follows. Let:

$$\Psi = \|\psi_1\,\psi_2\cdots\psi_N\| \qquad \langle\psi_i|\psi_j\rangle = \delta_{ij} \qquad \langle\Psi|\Psi\rangle = 1 \tag{105}$$

$$\Psi' = \|\psi_1'\,\psi_2'\cdots\psi_N'\| \qquad \langle\psi_i'|\psi_j'\rangle = \delta_{ij} \qquad \langle\Psi'|\Psi'\rangle = 1 \tag{106}$$

be a pair of normalized N-electron Slater dets built from orthonormal SOs. Then:

(i) 1-electron operators.

- Zero SO differences:

$$\left\langle\Psi\middle|\textstyle\sum_i \hat{O}_i\middle|\Psi\right\rangle = \sum_i \left\langle\psi_i\middle|\hat{O}_1\middle|\psi_i\right\rangle. \tag{107}$$

- One SO difference:

$$\left\langle\Psi'\middle|\textstyle\sum_i \hat{O}_i\middle|\Psi\right\rangle = \left\langle\psi_i'\middle|\hat{O}_1\middle|\psi_i\right\rangle \tag{108}$$

  if Ψ' differs from Ψ for $\psi_i' \neq \psi_i$.

- Two or more SO differences:

$$\langle \Psi' | \textstyle\sum_i \hat{O}_i | \Psi \rangle = 0. \tag{109}$$

(ii) 2-electron operators.

- Zero SO differences:

$$\langle \Psi | \textstyle\sum_{i<j} \hat{O}_{ij} | \Psi \rangle = \frac{1}{2} \sum_i \sum_j \left[\langle \psi_i \psi_j | \hat{O}_{12} | \psi_i \psi_j \rangle - \langle \psi_j \psi_i | \hat{O}_{12} | \psi_i \psi_j \rangle \right] \tag{110}$$

in the Dirac notation, or:

$$= \frac{1}{2} \sum_i \sum_j \left[(\psi_i \psi_i | \psi_j \psi_j) - (\psi_i \psi_j | \psi_j \psi_i) \right] \tag{111}$$

in the charge density notation.

- One SO difference:

$$\langle \Psi | \textstyle\sum_{i<j} \hat{O}_{ij} | \Psi \rangle = \sum_j \left[\langle \psi_i' \psi_j | \hat{O}_{12} | \psi_i \psi_j \rangle - \langle \psi_j \psi_i' | \hat{O}_{12} | \psi_i \psi_j \rangle \right] \tag{112}$$

$$= \sum_j \left[(\psi_i \psi_i' | \psi_j \psi_j) - (\psi_i \psi_j | \psi_j \psi_i') \right] \tag{113}$$

if Ψ' differs from Ψ for $\psi_i' \neq \psi_i$.

- Two SO differences:

$$\langle \Psi' | \textstyle\sum_{i<j} \hat{O}_{ij} | \Psi \rangle = \langle \psi_i' \psi_j' | \hat{O}_{12} | \psi_i \psi_j \rangle - \langle \psi_j' \psi_i' | \hat{O}_{12} | \psi_i \psi_j \rangle \tag{114}$$

$$= (\psi_i \psi_i' | \psi_j \psi_j') - (\psi_i \psi_j' | \psi_j \psi_i') \tag{115}$$

if Ψ' differs from Ψ for $\psi_i' \neq \psi_i$, $\psi_j' \neq \psi_j$.

- Three or more SO differences:

$$\langle \Psi' | \textstyle\sum_{i<j} \hat{O}_{ij} | \Psi \rangle = 0. \tag{116}$$

The Slater rules for the 2-electron operators are rederived in an independent way as Problem 7.5.

7.6 POPLE'S TWO-DIMENSIONAL CHART OF QUANTUM CHEMISTRY

During an International Symposium on Atomic and Molecular Quantum Theory at Sanibel Island, Florida, Pople (1965) presented the interesting two-dimensional chart of Quantum Chemistry illustrated below in Figure 7.1.

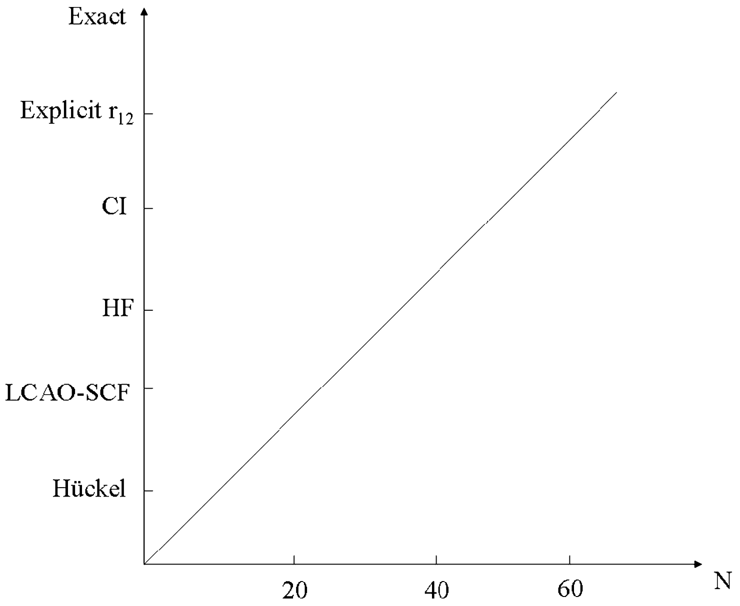

Figure 7.1 Pople's two-dimensional chart of Quantum Chemistry.

In the abscissae is the number N of electrons, in the ordinate the accuracy of quantum chemical calculations. According to Pople, the tendency at that time was a continuous divarication between scientists doing low-level calculations on electronic systems of large dimensions (moving along the abscissae axis, say Hückel-type), and those doing very accurate calculations on systems containing few electrons (moving along the ordinate axis, say James–Coolidge or Kołos–Wolniewicz calculations on H_2). He suggested that it was time for moving along the diagonal, in other words to present methods allowing for sufficient accuracy for systems having a moderately large number of electrons. This was the idea convincing Pople to present his semiempirical methods such as CNDO, INDO, etc., and the following series of GAUSSIAN programmes, where ab-initio calculations were done using STOs systematically replaced by suitable combinations of GTOs (STO-nG, 6-31G, 6-31G*, 6-31G**, etc.). These programmes are widely used today by the Chemical community.

We shall follow Pople's two-dimensional chart starting from the reference method for quantum chemical calculations on many-electron systems, the Hartree–Fock (HF) method, the best independent particle model (IPM) which is used to define exactly the *correlation energy*:

$$\begin{aligned}&\text{Correlation energy}\\&\quad=\text{exact energy of the non-relativistic Hamiltonian}\\&\qquad-\text{Hartree–Fock energy.}\end{aligned}\tag{117}$$

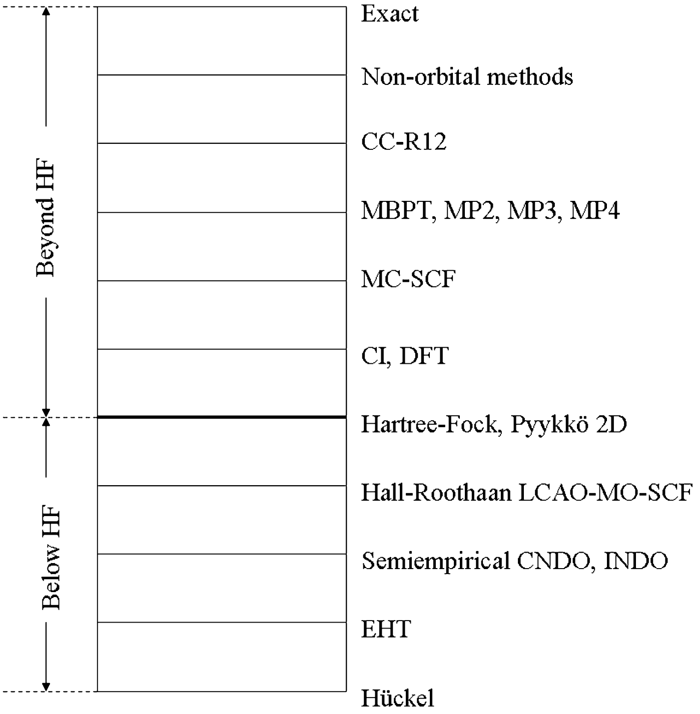

Figure 7.2 Accuracy scale of quantum chemical calculations.

The correlation energy is a not negligible quantity, amounting to about 1.1 eV per electron pair, which is very difficult to be calculated exactly. Taking HF as the best that can be done using an orbital basis without including electron correlation, following Pople's suggestion we can construct the ladder of Figure 7.2, having HF theory at its middle, Hückel theory as its bottom step, and the exact (or very accurate) results at its top.

All methods beyond HF (upper part of Figure 7.2) take into account in some way part of the electron correlation, all methods below (lower part of Figure 7.2), all belonging to the class of IPM methods, do *not* take into account electron correlation. It should be stressed at this point that, among the semiempirical post-HF methods, should be included all Kohn–Hohenberg–Sham density functional theory methods (DFT) and their variants, whose best orbitals satisfy one-electron differential equations similar to the HF ones, but take also into account some electron correlation mostly through semiempirical exchange-correlation potentials. All DFT methods based on such potentials should be considered as semiempirical methods giving more than HF.

In the following Sections, after introducing in some detail the Hartree–Fock theory for closed shells and its application to some ab-initio calculations using STO or GTO bases, we shall follow Pople's chart, first moving along the abscissae axis (Hückel theory), then moving along the diagonal (semiempirical methods), turning finally to the ordinate axis (accurate methods allowing for chemical accuracy through partial ab-initio calculation of the electron correlation).

7.7 HARTREE–FOCK THEORY FOR CLOSED SHELLS

In this Section, we shall give a rather detailed presentation of the Hartree–Fock (HF) theory for closed shells. The theory for open shells is rather more complicated, and its elements can be found in a paper by Roothaan (1960). As already said, the HF theory is the best that can be obtained within an independent particle model, and its lack of correlation follows from the fact that the HF 2-particle density matrix is simply the 2 × 2 determinant of a 1-electron quantity ρ, called the Fock–Dirac density matrix. Lennard-Jones (1931) was the first to make this derivation, which will be presented in this Chapter as Problem 7.6. As a consequence of this fact, all physical properties within the HF theory will depend on this quantity, which mathematically appears as the kernel of an integral operator having the characteristic of a projection operator. The characterization of ρ as a projector in Fock space will be given as Problem 7.7.

While most of the theory follows easily from the properties of the fundamental invariant ρ, the derivation of the HF equations characterizing the best atomic or molecular orbitals is best done in terms of the classical Roothaan work (1951a), since the orthonormality conditions which must be imposed on the orbital basis appear somewhat awkward and abstract (Löwdin, 1955b) in terms of the fundamental invariant. As a premise to such constrained optimization of the electronic energy, we shall present as Problem 7.8 a simple but general functional derivation of the method of Lagrange multipliers.

7.7.1 Basic Theory and Properties of the Fundamental Invariant ρ

Let:

$$\Psi = \|\psi_1\psi_2\cdots\psi_N\| \qquad \langle\psi_i|\psi_j\rangle = \delta_{ij} \tag{118}$$

be a normalized single determinant many-electron wavefunction of N orthonormal atomic or molecular spin-orbitals $\{\psi_i(\mathbf{x})\}$ $i = 1, 2, \cdots N$. Lennard-Jones (1931) has shown that, in this case:

$$\rho_1(\mathbf{x}_1;\mathbf{x}'_1) = \rho(\mathbf{x}_1;\mathbf{x}'_1) \tag{119}$$

$$\begin{aligned}\rho_2(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2) &= \begin{vmatrix}\rho(\mathbf{x}_1;\mathbf{x}'_1) & \rho(\mathbf{x}_1;\mathbf{x}'_2)\\ \rho(\mathbf{x}_2;\mathbf{x}'_1) & \rho(\mathbf{x}_2;\mathbf{x}'_2)\end{vmatrix}\\ &= \rho(\mathbf{x}_1;\mathbf{x}'_1)\rho(\mathbf{x}_2;\mathbf{x}'_2) - \rho(\mathbf{x}_1;\mathbf{x}'_2)\rho(\mathbf{x}_2;\mathbf{x}'_1),\end{aligned} \tag{120}$$

where:

$$\rho(\mathbf{x}_1;\mathbf{x}'_1) = \sum_{i=1}^{N}\psi_i(\mathbf{x}_1)\psi_i^*(\mathbf{x}'_1) \tag{121}$$

is the 1-electron Fock–Dirac density matrix. Equation (121) is said to offer an "orbital representation" of the density matrix. Since the 1- and 2-electron density matrices are expressed in terms of the quantity ρ, all physical properties of the many-electron system in the HF approximation will depend only on ρ, which will hence be characterized as the fundamental physical invariant of the system. It can be easily shown (Problem 7.7) that ρ has the following properties:

(i) ρ is *invariant* (namely, it does not change) against a unitary transformation among its $\{\psi_i(\mathbf{x})\}$:

$$\psi_i'(\mathbf{x}) = \sum_j \psi_j(\mathbf{x}) U_{ji} \tag{122}$$

$$\rho'(\mathbf{x}_1; \mathbf{x}_1') \equiv \rho(\mathbf{x}_1; \mathbf{x}_1'). \tag{123}$$

(ii) ρ has the properties of a projection operator (a projector) in the Fock space:

$$\int d\mathbf{x}_1\, \rho(\mathbf{x}_1; \mathbf{x}_1) = N \tag{124}$$

$$\int d\mathbf{x}_2\, \rho(\mathbf{x}_1; \mathbf{x}_2)\rho(\mathbf{x}_2; \mathbf{x}_1') = \rho(\mathbf{x}_1; \mathbf{x}_1') \tag{125}$$

or, symbolically (Löwdin, 1955b):

$$\operatorname{tr}\rho = N, \quad \rho^2 = \rho. \tag{126}$$

(iii) ρ is the kernel of an integral operator $\hat{\rho}$ whose effect on the regular function $\varphi(\mathbf{x})$ is:

$$\begin{aligned}
\hat{\rho}\varphi(\mathbf{x}) &= \int d\mathbf{x}'\rho(\mathbf{x}; \mathbf{x}')\hat{P}_{\mathbf{x}\mathbf{x}'}\varphi(\mathbf{x}) \\
&= \int d\mathbf{x}'\rho(\mathbf{x}; \mathbf{x}')\varphi(\mathbf{x}') \\
&= \sum_i \psi_i(\mathbf{x}) \int d\mathbf{x}'\psi_i^*(\mathbf{x}')\varphi(\mathbf{x}') \\
&= \sum_i |\psi_i\rangle\langle\psi_i|\varphi\rangle.
\end{aligned} \tag{127}$$

The projection of the function $\varphi(\mathbf{x})$ onto the Fock space characterized by ρ, $\{\psi_i\}$, is illustrated schematically in Figure 7.3. The arbitrary regular function $\varphi(\mathbf{x})$ is decomposed into its N Fock component vectors $|\psi_i\rangle$ with coefficients $\langle\psi_i|\varphi\rangle$.

7.7.2 Electronic Energy for the HF Wavefunction

The general expression (99) for the electronic energy:

$$E_e = \int d\mathbf{x}_1\, \hat{h}_1\rho_1(\mathbf{x}_1; \mathbf{x}_1')|_{\mathbf{x}_1'=\mathbf{x}_1} + \frac{1}{2}\iint d\mathbf{x}_1\, d\mathbf{x}_2 \frac{1}{r_{12}}\rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2)$$

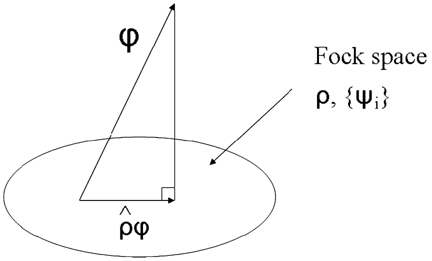

Figure 7.3 Projection of a function $\varphi(\mathbf{x})$ onto the Fock space.

becomes for the single determinant HF wavefunction (118):

$$\begin{aligned}E_e = &\int d\mathbf{x}_1\, \hat{h}_1 \rho(\mathbf{x}_1;\mathbf{x}_1')|_{\mathbf{x}_1'=\mathbf{x}_1}\\ &+\frac{1}{2}\iint d\mathbf{x}_1\, d\mathbf{x}_2 \frac{1}{r_{12}}\big[\rho(\mathbf{x}_1;\mathbf{x}_1')\rho(\mathbf{x}_2;\mathbf{x}_2')\\ &\qquad - \rho(\mathbf{x}_1;\mathbf{x}_2')\rho(\mathbf{x}_2;\mathbf{x}_1')\big]_{\mathbf{x}_1'=\mathbf{x}_1,\mathbf{x}_2'=\mathbf{x}_2}.\end{aligned} \tag{128}$$

The 2-electron part of the HF electronic energy can be written as:

$$\begin{aligned}&\iint d\mathbf{x}_1\, d\mathbf{x}_2 \frac{1}{r_{12}}\big[\rho(\mathbf{x}_1;\mathbf{x}_1')\rho(\mathbf{x}_2;\mathbf{x}_2') - \rho(\mathbf{x}_1;\mathbf{x}_2')\rho(\mathbf{x}_2;\mathbf{x}_1')\big]_{\mathbf{x}_1'=\mathbf{x}_1,\mathbf{x}_2'=\mathbf{x}_2}\\ &= \int d\mathbf{x}_1 \left[\int d\mathbf{x}_2 \frac{\rho(\mathbf{x}_2;\mathbf{x}_2)}{r_{12}}\right]\rho(\mathbf{x}_1;\mathbf{x}_1')\Big|_{\mathbf{x}_1'=\mathbf{x}_1}\\ &\quad - \int d\mathbf{x}_1 \left[\int d\mathbf{x}_2 \frac{\rho(\mathbf{x}_1;\mathbf{x}_2)}{r_{12}}\hat{P}_{\mathbf{x}_1\mathbf{x}_2}\right]\rho(\mathbf{x}_1;\mathbf{x}_1')\Big|_{\mathbf{x}_1'=\mathbf{x}_1}\\ &= \int d\mathbf{x}_1\, J(\mathbf{x}_1)\rho(\mathbf{x}_1;\mathbf{x}_1) - \int d\mathbf{x}_1\, \hat{K}(\mathbf{x}_1)\rho(\mathbf{x}_1;\mathbf{x}_1')\Big|_{\mathbf{x}_1'=\mathbf{x}_1},\end{aligned} \tag{129}$$

where we define the two potential operators linear in ρ:

$$J(\mathbf{x}_1) = \int d\mathbf{x}_2 \frac{\rho(\mathbf{x}_2;\mathbf{x}_2)}{r_{12}} \tag{130}$$

the *Coulomb* potential (a multiplicative operator) due to all electrons of density ρ;

$$\hat{K}(\mathbf{x}_1) = \int d\mathbf{x}_2 \frac{\rho(\mathbf{x}_1;\mathbf{x}_2)}{r_{12}}\hat{P}_{\mathbf{x}_1\mathbf{x}_2} \tag{131}$$

the *exchange* potential, an integral operator with kernel $\rho(\mathbf{x}_1;\mathbf{x}_2)/r_{12}$.

Hence, we get for E_e in the HF approximation the alternative, yet equivalent, expressions:

$$E_e = \int d\mathbf{x}_1\, \hat{h}_1 \rho(\mathbf{x}_1;\mathbf{x}'_1)|_{\mathbf{x}'_1=\mathbf{x}_1} + \frac{1}{2}\int d\mathbf{x}_1 (J_1 - \hat{K}_1)\rho(\mathbf{x}_1;\mathbf{x}'_1)|_{\mathbf{x}'_1=\mathbf{x}_1} \tag{132}$$

$$= \int d\mathbf{x}_1\, \hat{F}_1 \rho(\mathbf{x}_1;\mathbf{x}'_1)|_{\mathbf{x}'_1=\mathbf{x}_1} - \frac{1}{2}\int d\mathbf{x}_1 (J_1 - \hat{K}_1)\rho(\mathbf{x}_1;\mathbf{x}'_1)|_{\mathbf{x}'_1=\mathbf{x}_1}, \tag{133}$$

where:

$$\hat{F} = \hat{h} + J - \hat{K} = -\frac{1}{2}\nabla^2 + V + J - \hat{K} = -\frac{1}{2}\nabla^2 + \hat{V}_{\text{eff}} \tag{134}$$

is the 1-electron Fock operator, and

$$\hat{V}_{\text{eff}} = V + J - \hat{K} \tag{135}$$

the *effective* potential felt by all electrons of density $\rho = \rho(\mathbf{x};\mathbf{x})$. In equations (134) and (135):

$$V = -\sum_{\alpha} \frac{Z_\alpha}{r_\alpha} \tag{136}$$

is the bare-nuclei potential of attraction of the electron by all nuclei of charge $+Z_\alpha$. It must be stressed that the average electron repulsion, added in (132), must be *subtracted* in (133) to avoid counting electron repulsion twice. Following Roothaan (1951a), we shall now give a variational derivation of the HF equations for the best SOs, using the method of Lagrange[3] multipliers presented as Problem 7.8.

7.7.3 Roothaan Variational Derivation of the HF Equations

We want to minimize the functional of the HF electronic energy $E_e[\psi_1, \psi_2, \cdots \psi_N]$ with respect to infinitesimal arbitrary changes in its SOs subjected to the orthonormality constraints. The N^2 constraints expressing orthonormality among the SOs can be conveniently written as the functional:

$$\mathcal{U}[\psi_1, \psi_2, \cdots \psi_N] = \sum_i \sum_{i'} \langle \psi_i | \psi_{i'} \rangle \varepsilon_{i'i}, \tag{137}$$

where $\{\varepsilon_{i'i}\}$ is the matrix of order N of the Lagrange multipliers (Problem 7.8). Then:

$$\delta\mathcal{U} = \sum_i \sum_{i'} \{\langle \delta\psi_i | \psi_{i'} \rangle + \langle \psi_i | \delta\psi_{i'} \rangle\}\varepsilon_{i'i}$$

$$= \sum_i \sum_{i'} \{\langle \delta\psi_i | \psi_{i'} \rangle \varepsilon_{i'i} + \langle \psi_{i'} | \delta\psi_i \rangle \varepsilon_{ii'}\}, \tag{138}$$

---

[3] Lagrange Joseph-Louis 1736–1813, Italian mathematician of French origin, Professor at the École Normale and at the École Polytechnique of Paris.

because the summations over $i,\ i'$ are complete, and we can interchange indices $i,\ i'$ without altering the final result. In this way, the second term in the last braces is the complex conjugate (c.c.) of the first, and the matrix of the N^2 Lagrange multipliers is Hermitian.

We have similarly for an infinitesimal change in the functional (132) of the electronic energy:

$$\begin{aligned}\delta E_e = &\sum_i \langle \delta\psi_i|\hat{h}_1|\psi_i\rangle + \sum_i \langle \psi_i|\hat{h}_1|\delta\psi_i\rangle + \frac{1}{2}\sum_i \langle \delta\psi_i|J_1 - \hat{K}_1|\psi_i\rangle \\ &+ \frac{1}{2}\sum_i \langle \psi_i|J_1 - \hat{K}_1|\delta\psi_i\rangle + \frac{1}{2}\sum_i \langle \psi_i|\delta J_1 - \delta\hat{K}_1|\psi_i\rangle \qquad (139) \\ = &\sum_i \langle \delta\psi_i|\hat{h}_1 + J_1 - \hat{K}_1|\psi_i\rangle + \text{c.c.} = \sum_i \langle \delta\psi_i|\hat{F}_1|\psi_i\rangle + \text{c.c.}, \qquad (140)\end{aligned}$$

where the 1-electron Fock operator:

$$\hat{F}_1 = \hat{h}_1 + J_1 - \hat{K}_1 \qquad (134)$$

is *constant* during the variation of the $\{\psi_i\}$. So, the Fock operator (134) appears as an essential step in the functional optimization. The identity between equations (139) and (140) is shown as Problem 7.10 for the Coulomb operator J.

We then obtain as condition for the constrained stationarity of our functionals (Problems 7.8 and 7.9):

$$\delta E'_e = \delta E_e - \delta\mathcal{U} = \sum_i \langle \delta\psi_i|\hat{F}|\psi_i\rangle - \sum_i\sum_{i'} \langle \delta\psi_i|\psi_{i'}\rangle\varepsilon_{i'i} + \text{c.c.} = 0 \qquad (141)$$

$$\sum_i \langle \delta\psi_i|\hat{F}\psi_i - \sum_{i'} \psi_{i'}\varepsilon_{i'i}\rangle + \text{c.c.} = 0. \qquad (142)$$

For the arbitrariness of the $\langle\delta\psi_i|$ the ket should identically vanish, and we obtain:

$$\hat{F}\psi_i = \sum_{i'} \psi_{i'}\varepsilon_{i'i} \quad i,\ i' = 1,\ 2, \cdots N, \qquad (143)$$

which are the Hartree–Fock equations determining the *best* SOs $\{\psi_i\}$.

Since a unitary transformation among the SOs does not alter either $\rho(\mathbf{x}_1;\mathbf{x}'_1)$ or $\hat{F}$ (which is linear in ρ), the Hermitian matrix $\{\varepsilon_{i'i}\}$ of the Lagrange multipliers can be reduced to diagonal form, and we finally obtain the Hartree–Fock equations in the form of eigenvalue equations:

$$\hat{F}\psi_i = \varepsilon_i\psi_i \quad i = 1, 2, \cdots N, \qquad (144)$$

where $\hat{F}$ is the 1-electron integro-differential operator:

$$\hat{F}(\mathbf{x}_1) = -\frac{1}{2}\nabla_1^2 + V_1 + \sum_{i'} \int d\mathbf{x}_2 \frac{\psi_{i'}(\mathbf{x}_2)\psi_{i'}^*(\mathbf{x}_2)}{r_{12}} - \sum_{i'} \int d\mathbf{x}_2 \frac{\psi_{i'}(\mathbf{x}_1)\psi_{i'}^*(\mathbf{x}_2)}{r_{12}} \hat{P}_{\mathbf{x}_1\mathbf{x}_2} \tag{145}$$

∇_1^2 being a *differential* operator and the exchange potential $\hat{K}_1$ (the last term) an *integral* operator.

Despite their apparent simple form (144), the HF equations are difficult integro-differential equations that must be solved by *iteration* (the so called SCF method), starting from a guessed set of SOs $\{\psi_i^0\}$, and revising the form of the ψ_i until self-consistency is reached. The iteration process may present problems of convergence if the starting point is not carefully chosen.

In the applications, spin can be eliminated (Problem 7.11) giving for closed shells the spinless Fock operator $\hat{F}(\mathbf{r}_1)$, which depends on the space variable only:

$$\hat{F}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 + V_1 + 2J(\mathbf{r}_1) - \hat{K}(\mathbf{r}_1), \tag{146}$$

where:

$$J(\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{R(\mathbf{r}_2;\mathbf{r}_2)}{r_{12}}, \qquad \hat{K}(\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{R(\mathbf{r}_1;\mathbf{r}_2)}{r_{12}} \hat{P}_{\mathbf{r}_1\mathbf{r}_2} \tag{147}$$

are *spinless* Coulomb and exchange potentials, and we have introduced the density matrix R for closed shells:

$$R(\mathbf{r}_1;\mathbf{r}_2) = \rho^{\alpha}(\mathbf{r}_1;\mathbf{r}_2) = \rho^{\beta}(\mathbf{r}_1;\mathbf{r}_2) = \sum_i^{\mathrm{occ}} \phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}_2), \tag{148}$$

where $\{\phi_i(\mathbf{r})\}$ $i = 1, 2, \cdots n = N/2$ are the doubly occupied spatial MOs for closed shells. R has the properties:

$$\operatorname{tr} R = n = N/2, \qquad R^2 = R \tag{149}$$

and is therefore a projector in the space of the n occupied orbitals. The HF equations for the occupied MOs become:

$$\hat{F}(\mathbf{r}_1)\phi_i(\mathbf{r}_1) = \varepsilon_i\phi_i(\mathbf{r}_1) \quad i = 1, 2, \cdots n. \tag{150}$$

The quantity:

$$\hat{G}(\mathbf{r}_1) = 2J(\mathbf{r}_1) - \hat{K}(\mathbf{r}_1) \tag{151}$$

has been called by Roothaan the total electron interaction operator.

7.7.4 Hall–Roothaan Formulation of the LCAO-MO-SCF Equations

The LCAO-MO approximation to the HF orbitals was developed by Hall (1951) and Roothaan (1951a) using the Ritz method. Given the atomic orbital basis of m AOs:

$$\boldsymbol{\chi}(\mathbf{r}) = (\chi_1 \chi_2 \cdots \chi_m) \quad m \geq n \tag{152}$$

the i-th MO is constructed by the linear combination:

$$\phi_i(\mathbf{r}) = \boldsymbol{\chi}(\mathbf{r})\mathbf{c}_i, \tag{153}$$

giving the corresponding spin-orbitals as:

$$\psi_i(\mathbf{x}) \Longrightarrow \phi_i(\mathbf{r})\alpha(s) = \phi_i, \quad \phi_i(\mathbf{r})\beta(s) = \overline{\phi}_i. \tag{154}$$

The variational optimization of the linear coefficients $\mathbf{c}_i$ yields the pseudosecular equations:

$$\mathbf{F}\mathbf{c}_i = \varepsilon_i \mathbf{M}\mathbf{c}_i \quad i = 1, 2, \cdots n \tag{155}$$

which are known as Roothaan's LCAO-MO-SCF equations (Hall assumed $\mathbf{M} = \mathbf{1}$). We have introduced the $m \times m$ Hermitian matrices:

$$\mathbf{F} = \boldsymbol{\chi}^\dagger \hat{F} \boldsymbol{\chi} \qquad F_{\mu\nu} = \langle \chi_\mu | \hat{F} | \chi_\nu \rangle \tag{156}$$

$$\mathbf{M} = \boldsymbol{\chi}^\dagger \boldsymbol{\chi} \qquad M_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \tag{157}$$

which are, respectively, the matrix representative of the Fock spinless operator and the metric of the AO basis. The pseudosecular equation of order m:

$$|\mathbf{F} - \varepsilon \mathbf{M}| = 0 \tag{158}$$

must be solved by iteration through successive revisions of matrix $\mathbf{F}$ until self-consistency is reached between the MOs determining $\mathbf{F}$ and those obtained by solution of the secular equation. This is the iterative SCF process. The m roots:

$$\underbrace{\varepsilon_1, \varepsilon_2, \cdots \varepsilon_n,}_{\text{occ}} \underbrace{\varepsilon_{n+1}, \varepsilon_{n+2}, \cdots \varepsilon_m}_{\text{unocc}} \tag{159}$$

give the orbital energies of the n (doubly occupied) spatial orbitals and of the $(m - n)$ unoccupied (empty) orbitals, while the corresponding eigenvectors:

$$\mathbf{c}_1, \mathbf{c}_2, \cdots \mathbf{c}_n, \mathbf{c}_{n+1}, \mathbf{c}_{n+2}, \cdots \mathbf{c}_m \tag{160}$$

give the form of the best orbitals, which are the LCAO-SCF approximation to the HF orbitals. ϕ_n is called the HOMO (highest occupied MO), ϕ_{n+1} the LUMO (lowest unoccupied MO). By introducing the *rectangular* ($m \times n$) matrix $\mathbf{C}$ of the doubly occupied MOs:

$$\mathbf{C} = (\mathbf{c}_1 \mathbf{c}_2 \cdots \mathbf{c}_n) \tag{161}$$

it will be possible to write the whole set of pseudoeigenvalue equations in the matrix form:

$$\hat{F}\boldsymbol{\chi}\mathbf{C} = \boldsymbol{\chi}\mathbf{C}\boldsymbol{\varepsilon} \tag{162}$$

$$\mathbf{FC} = \mathbf{MC}\boldsymbol{\varepsilon}, \tag{163}$$

where:

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_1 & 0 & \cdots & 0 \\ 0 & \varepsilon_2 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \varepsilon_n \end{pmatrix} \tag{164}$$

is the diagonal matrix collecting the orbital energies of the n doubly occupied MOs.

It is customary at this point to introduce the matrix representative over the AO basis of the spinless density matrix R for the doubly occupied MOs:

$$\begin{aligned} R(\mathbf{r};\mathbf{r}') &= \rho^{\alpha}(\mathbf{r};\mathbf{r}') = \rho^{\beta}(\mathbf{r};\mathbf{r}') = \boldsymbol{\phi}(\mathbf{r})\boldsymbol{\phi}^{\dagger}(\mathbf{r}') \\ &= \boldsymbol{\chi}(\mathbf{r})\mathbf{C}\mathbf{C}^{\dagger}\boldsymbol{\chi}^{\dagger}(\mathbf{r}') = \boldsymbol{\chi}(\mathbf{r})\mathbf{R}\boldsymbol{\chi}^{\dagger}(\mathbf{r}') \end{aligned} \tag{165}$$

where:

$$\underset{m\times m}{\mathbf{R}} = \underset{m\times n}{\mathbf{C}}\,\underset{n\times m}{\mathbf{C}^{\dagger}} \qquad R_{\mu\nu} = \sum_i^{\text{occ}} C_{\mu i} C^*_{\nu i}. \tag{166}$$

It is worth noting (Problem 7.12) that the projector properties of the density matrix $\mathbf{R}$ over the non-orthogonal AO basis are given by:

$$\mathbf{RMR} = \mathbf{R}, \qquad \operatorname{tr}\mathbf{RM} = n, \tag{167}$$

where $\mathbf{M}$ is the metric of the AO basis.

The electronic energy in the LCAO-MO-SCF approximation takes the matrix form:

$$\begin{aligned} E_e &= 2\int d\mathbf{r}_1\, \hat{F}(\mathbf{r}_1) R(\mathbf{r}_1;\mathbf{r}'_1)|_{\mathbf{r}'_1=\mathbf{r}_1} - \int d\mathbf{r}_1\, \hat{G}(\mathbf{r}_1) R(\mathbf{r}_1;\mathbf{r}'_1)|_{\mathbf{r}'_1=\mathbf{r}_1} \\ &= 2\operatorname{tr}\mathbf{FR} - \operatorname{tr}\mathbf{GR}, \end{aligned} \tag{168}$$

where $\hat{G}(\mathbf{r}_1)$ is the total electron interaction operator. Its AO representative $\mathbf{G}(\mathbf{r}_1)$ has elements:

$$\begin{aligned}
G_{\mu\nu} &= \langle \chi_\mu | \hat{G} | \chi_\nu \rangle = \langle \chi_\mu | 2J(\mathbf{r}_1) - \hat{K}(\mathbf{r}_1) | \chi_\nu \rangle \\
&= \int d\mathbf{r}_1\, \chi_\mu^*(\mathbf{r}_1) \left[2 \int d\mathbf{r}_2 \frac{R(\mathbf{r}_2;\mathbf{r}_2)}{r_{12}} - \int d\mathbf{r}_2 \frac{R(\mathbf{r}_1;\mathbf{r}_2)}{r_{12}} \hat{P}_{\mathbf{r}_1\mathbf{r}_2} \right] \chi_\nu(\mathbf{r}_1) \\
&= \int d\mathbf{r}_1\, \chi_\mu^*(\mathbf{r}_1) \left[2 \sum_\lambda \sum_\sigma \frac{\int d\mathbf{r}_2 \chi_\lambda(\mathbf{r}_2) R_{\lambda\sigma} \chi_\sigma^*(\mathbf{r}_2)}{r_{12}} \right] \chi_\nu(\mathbf{r}_1) \\
&\quad - \int d\mathbf{r}_1\, \chi_\mu^*(\mathbf{r}_1) \left[\sum_\lambda \sum_\sigma \frac{\int d\mathbf{r}_2 \chi_\lambda(\mathbf{r}_1) R_{\lambda\sigma} \chi_\sigma^*(\mathbf{r}_2)}{r_{12}} \chi_\nu(\mathbf{r}_2) \right] \\
&= \sum_\lambda \sum_\sigma P_{\lambda\sigma} \left[(\overset{1}{\chi_\nu \chi_\mu} \mid \overset{2}{\chi_\lambda \chi_\sigma}) - \frac{1}{2} (\overset{1}{\chi_\lambda \chi_\mu} \mid \overset{2}{\chi_\nu \chi_\sigma}) \right],
\end{aligned} \tag{169}$$

where we used the charge density notation for the 2-electron integrals, and have introduced the matrix:

$$\mathbf{P} = 2\mathbf{R} \qquad P_{\lambda\sigma} = 2R_{\lambda\sigma} = 2 \sum_i^{\text{occ}} C_{\lambda i} C_{\sigma i}^*. \tag{170}$$

$\mathbf{P}$ has no longer the properties of a projection operator. $G_{\mu\nu}$, the $\mu\nu$-element of the total electron interaction operator over the AO basis, is hence formed by the combination of m^2 2-electron many-centre integrals, while E_e will depend on well m^4 of such difficult integrals! The $\mu\nu$-element of the Fock matrix $\mathbf{F}$ over the AOs is:

$$F_{\mu\nu} = \langle \chi_\mu | \hat{F} | \chi_\nu \rangle = \langle \chi_\mu | \hat{h} + \hat{G} | \chi_\nu \rangle = h_{\mu\nu} + G_{\mu\nu}, \tag{171}$$

where:

$$\hat{h} = -\frac{1}{2}\nabla^2 + V \tag{172}$$

is the one-electron bare nuclei Hamiltonian.

From these matrix expressions, with suitable approximations and simplifications, we can obtain all LCAO approximations belonging to the lower steps of the HF accuracy scale (Hückel, Extended Hückel, CNDO, INDO, etc.).

An example of LCAO-MO-SCF calculation on the $^1A_1$ ground state of the H_2O molecule (belonging to C_{2v} symmetry) is given as Problem 7.13. The calculation (Pitzer and Merrifield, 1970) is performed at the experimental geometry and is based on a minimum set of 7 STOs. The factorization of the resulting secular equation is fully discussed in Chapter 8. The projector properties (167) of the matrix $\mathbf{R}$ resulting for this calculation are checked in detail as Problem 7.14.

7.7.5 Mulliken Population Analysis

The analysis of the MO electron distribution in closed shells is commonly called Mulliken[4] population analysis (Mulliken, 1955a, 1955b, 1955c), and is a generalization of our initial considerations on the 2-electron bond of Section 7.3.2.

We saw in the preceding Section that the MO theory for closed shells ($S = 0$) gives for the 1-electron density matrix:

$$\begin{aligned}\rho_1(\mathbf{x};\mathbf{x}') = \rho(\mathbf{x};\mathbf{x}') &= \sum_{i=1}^{N} \psi_i(\mathbf{x})\psi_i^*(\mathbf{x}') \\ &= \sum_i^{\text{occ}} \phi_i(\mathbf{r})\,\phi_i^*(\mathbf{r}')\big[\alpha(s)\alpha^*(s') + \beta(s)\beta^*(s')\big],\end{aligned} \tag{173}$$

where:

$$\rho^\alpha(\mathbf{r};\mathbf{r}') = \rho^\beta(\mathbf{r};\mathbf{r}') = R(\mathbf{r};\mathbf{r}') = \sum_i^{\text{occ}} \phi_i(\mathbf{r})\phi_i^*(\mathbf{r}') \tag{174}$$

the summation being over all $n = N/2$ doubly occupied (orthonormal) MOs ϕ_i. $R(\mathbf{r};\mathbf{r}')$ is the spinless 1-electron density matrix with the well-known projector properties:

$$R^2 = R, \qquad \operatorname{tr} R = n. \tag{175}$$

In the Hall–Roothaan LCAO approximation, the i-th spatial MO $\phi_i(\mathbf{r})$ is represented by the linear combination of m basic AOs $\boldsymbol{\chi}(\mathbf{r})$:

$$\phi_i(\mathbf{r}) = \boldsymbol{\chi}(\mathbf{r})\mathbf{c}_i \tag{176}$$

giving:

$$R(\mathbf{r};\mathbf{r}') = \sum_i^{\text{occ}} \phi_i(\mathbf{r})\phi_i^*(\mathbf{r}') = \boldsymbol{\chi}(\mathbf{r})\mathbf{R}\boldsymbol{\chi}^\dagger(\mathbf{r}'), \tag{177}$$

where:

$$\underset{m\times m}{\mathbf{R}} = \underset{m\times n}{\mathbf{C}}\,\underset{n\times m}{\mathbf{C}^\dagger}, \qquad R_{\mu\nu} = \sum_i^{\text{occ}} C_{\mu i}C_{\nu i}^* \tag{178}$$

is the matrix representative of R over the AO basis $\boldsymbol{\chi}$. The projector properties of matrix $\mathbf{R}$ over the non-orthogonal basis $\boldsymbol{\chi}$ are given by equations (167).

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[4] Mulliken Robert Sanderson 1896–1986, U.S. physicist, Professor of Physics and Chemistry at the University of Chicago. 1966 Nobel Prize for Chemistry.

The matrix:

$$\mathbf{P} = 2\mathbf{R}, \qquad P_{\mu\nu} = 2R_{\mu\nu} \tag{179}$$

was called by Coulson (1939) the charge and bond-order matrix. $P_{\mu\nu}$ gives the electronic charge distributed according to the (*un-normalized*) density $\chi_\mu(\mathbf{r})\,\chi_\nu(\mathbf{r})$ contributed by all doubly occupied MOs (charge for $\nu = \mu$, bond-order for $\nu \neq \mu$).

The Mulliken population matrix has instead elements $P_{\mu\nu}M_{\mu\nu}$, giving the electronic charge distributed according to the (*normalized*) density $\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r})/M_{\mu\nu}$. Then, its diagonal element ($M_{\mu\mu} = 1$):

$$P_{\mu\mu} = \text{net orbital population on orbital } \chi_\mu(\mathbf{r}), \tag{180}$$

while the off-diagonal element:

$$P_{\mu\nu}M_{\mu\nu} = \text{overlap population between } \chi_\mu(\mathbf{r}) \text{ and } \chi_\nu(\mathbf{r}). \tag{181}$$

By adding over all elements of a row (or a column) of the population matrix we obtain the gross orbital population on orbital $\chi_\mu(\mathbf{r})$:

$$Q_\mu = P_{\mu\mu} + \sum_{\nu(\neq\mu)} P_{\mu\nu}M_{\mu\nu}. \tag{182}$$

By further adding over all orbitals of atom A we obtain the gross atomic population of atom A:

$$P_{\mathrm{A}} = \sum_{\mu}^{(\mathrm{A})} Q_\mu. \tag{183}$$

As an example, we give below (Table 7.1) the complete Mulliken population matrix for ground state H_2O resulting from the Pitzer and Merrifield (1970) MO calculation discussed in Problems 7.13 and 7.14.

The qualitative physical picture emerging from Table 7.1 is immediately clear. The overlap populations are *positive* between z and y oxygen AOs and h_1, h_2 hydrogen AOs, which means that electron density *increases* between these orbitals contributing to the chemical bonding between O and H_1, H_2. The *negative* overlap population between h_1 and h_2 means that the H atoms are non-bonded. The result of the rearrangement of the electronic charge distribution when the molecule is formed becomes apparent when the gross orbital populations onto O and H_1, H_2 in H_2O are compared with the corresponding quantities in the free atoms, as given below in Table 7.2.

The data in the second column were slightly rearranged in order to compensate for the round-off errors arising from the limited number of figures used in the calculation to obtain by adding along the column the exact value $N = 10$. The resulting gross atomic charges (last column) clearly say that about 0.3254 electrons are shifted from H to O when the

Table 7.1.

Mulliken population matrix from the Pitzer and Merrifield MO calculation on ground state H_2O

$P_{\mu\nu}M_{\mu\nu}$	k'	s'	z	x	y	h_1	h_2
k'	2.00540	0	0	0	0	−0.00213	−0.00213
s'	0	1.93650	0	0	0	−0.04079	−0.04079
z	0	0	1.25408	0	0	0.10318	0.10318
x	0	0	0	1	0	0	0
y	0	0	0	0	0.67792	0.16526	0.16526
h_1	−0.00213	−0.04079	0.10318	0	0.16526	0.73336	−0.12159
h_2	−0.00213	−0.04079	0.10318	0	0.16526	−0.12159	0.73336

Table 7.2.

Gross orbital electron populations in H_2O compared to the corresponding quantities in the free atoms

AO	Molecule	Free atoms	Gross atomic charges
k'	2.0011	2	$P_O = 8.3254$
s'	1.8549	2	
z	1.4610	1	
x	2	2	
y	1.0084	1	
h_1, h_2	0.8373	1	$P_H = 1.6746$
$\sum$	10	10	

molecule is formed. This agrees with our common expectation about the electronegativities of the O and H atoms. We further notice a slight "promotion" of about $0.1451e$ from the s orbital on oxygen to the bonding p AOs (y, z), which means that little "hybridization" has occurred. So, the concept of hybridization stems directly from the analysis of the Mulliken charge distributions. We shall see later (Chapter 10) that this concept is essential in the development of the valence bond (VB) theory of directed valency in polyatomic molecules. It is rather gratifying to see that the same concept originates from two theories, such as MO and VB, which are apparently so different in their initial steps.

At this level of calculation,[5] the x orbital on O remains unchanged when the molecule is formed.

In terms of the formal charges $\delta = \pm 0.1627\,\mathrm{e}$ on the constituent atoms, the molecule appears as a dipole with the resulting moment directed along the z symmetry axis (Figure 7.4). Unfortunately, as already said, the minimum basis set greatly underestimates the value of the calculated dipole moment, but the elementary picture remains.

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[5] This is not the case when suitable polarization functions onto O and H are admitted in extended basis sets. Problem 8.9 in Chapter 8 shows that B_1 symmetry mixes $3d$ and $4f$ polarization functions on O with $2p$ and $3d$ polarization functions on the H atoms.

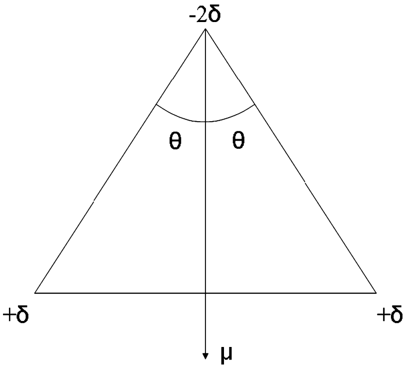

Figure 7.4 The molecular dipole in H_2O resulting from the formal charges $\pm\delta$ on the constituent atoms.

7.7.6 Atomic Bases in Quantum Chemical Calculations

We already introduced in Chapter 4 the two kinds of atomic orbitals $\chi(\mathbf{r})$ mostly used today as basis sets in quantum chemical calculations. They are orbitals having (i) an exponential decay with the radial variable r, Slater-type-orbitals or STOs, or (ii) a Gaussian decay, Gaussian-type-orbitals or GTOs. Even if the latter are still today the most widely used, recently there was an increasing interest in STOs, since STOs are definitely superior to GTOs either near the origin or in the tail of the atomic function. Furthermore, the fundamental expansion theorem of quantum mechanics (Chapter 1) tells us that truncation errors are expected when the basis set is insufficient, so that accuracy of quantum chemical calculations will depend on quality and size of the basis set. The Literature in the field is plagued by an avalanche of numbers that suffer for the lack of any sufficient accuracy being too far from the so called reference "benchmarks". In the following, we shall examine further the classification and the effect that dimension and nature of the atomic bases have on the expected accuracy of the results of quantum chemical calculations.

A *minimal* basis set is made by those AOs which are occupied in the ground state of the atoms forming the molecule: in the LCAO procedure it is not possible to construct MOs with a less number of these AOs ($m \geq n$). An *extended* basis set is made by a larger number of AOs, and may, or may not, include *polarization* functions, namely AOs which are not occupied in the ground state of the constituent atoms (empty or virtual AOs), such as, for instance, $3d$ and $4f$ functions for C, N, O, F, or $2p$ and $3d$ functions for H. Such functions, as well as AOs having even larger values of the angular quantum number l, are essential when evaluating molecular properties, such as electric multipole moments and polarizabilities (Chapter 11).

In general, we speak of single-zeta (SZ) for a minimal set, double-zeta (DZ) for a basis where each AO is described by two functions, triple-zeta (TZ) when each AO is described by three functions, and so on. If polarization functions (P) are included, we shall have DZP and TZP bases (P only on the heavy atoms) or DZPP and TZPP (when P are on the heavy atoms and on H as well). Such a nomenclature is due to Van Duijneveldt-Van de Rijdt and Van Duijneveldt (1982).

GTO-bases are usually expressed in terms of Cartesian Gaussians:

$$G_{uvw}(\mathbf{r}) = N x^u y^v z^w \exp\bigl(-cr^2\bigr) \tag{184}$$

whose number is given by the binomial coefficient $\binom{L+2}{L} = \frac{1}{2}(L+1)(L+2)$ if $L = u+v+w$. For instance, for $L=0$ we have a function of type $1s$, for $L=1$ three functions of type $2p$, for $L=2$ five functions of type $3d$ and one function $3s$, for $L=3$ seven functions $4f$ and three functions $4p$, for $L=4$ nine functions $5g$, five functions $5d$ and one function $5s$.

Since several GTOs are usually needed to represent in an adequate way a single STO, it is customary to introduce *contracted* GTO functions, where each function is the sum of a certain number of GTOs, called *primitives* (having same L but different orbital exponent c), each one multiplied by a *fixed* numerical coefficient. When such constraints are not present, we speak of uncontracted GTO bases. The most common notation can be deduced from this example on H_2O (nearly HF cartesian GTO calculation by Lazzeretti and Zanasi, 1981), which includes polarization functions on O and H:

$$\underset{\text{primitives}}{(14s\,8p\,3d\,1f|10s\,2p\,1d)} \Longrightarrow \underset{\text{contracted}}{[9s\,6p\,3d\,1f|6s\,2p\,1d]}. \tag{185}$$

The 110 primitives ($14+8\times3+3\times6+1\times10=66$ GTOs onto O, $10+2\times3+1\times6=22$ GTOs onto each H atom) give rise to 91 contracted functions ($9+6\times3+3\times6+1\times10=55$ GTOs onto O, $6+2\times3+1\times6=18$ GTOs onto each H atom). It may be noted that the polarization functions are left uncontracted. It is evident that, given the same set of primitives, it will be possible to obtain different results for different contractions. The best results will be obtained, of course, for the uncontracted basis sets.

Widely used in the different releases of GAUSSIAN programmes of Pople and coworkers (Frisch et al., 2003) are the STO-nG bases (*n* GTOs to represent a single STO), 6-31G (six GTOs for the inner-shell plus split-valence AOs described by two sets of contracted GTOs, three "inner" and one "outer"), 6-31G* (as before, but including polarization functions on the heavy atoms), 6-31G** (as before, but further including polarization functions on the H atoms as well).

To handle the numerical problem arising from the variational optimization of a large number of non-linear parameters (the orbital exponents c_i), Ruedenberg et al. (1973) introduced the so called *even-tempered* (or *geometrical*) sequences of primitive functions, where the orbital exponents c_i are restricted by a relation such as:

$$c_i = ab^i \quad i = 1, 2, \cdots m \tag{186}$$

with a, b different for functions of $s, p, d, f, \cdots$ symmetry. In such a way, it becomes necessary to optimize just *two* non-linear parameters within each symmetry type, independently of the number of primitive functions.

Examples for the ground state of the first-row H–Ne atoms are given in Table 7.3 (Clementi and Roetti, 1974), for the second-row Mg atom (^1S: $1s^2\,2s^2\,2p^6\,3s^2$) in Table 7.4

Table 7.3.

Electronic energies E_e and orbital energies ε_i (E_h) SCF/STO for the ground states of first-row atoms[a]

Atom/AO		SZ	DZ	HF
		$1s1p$	$2s2p$	$6s4p$
$H(^2S: 1s)$	E_e	−0.5		
	ε_i	−0.5		
$He(^1S: 1s^2)$	E_e	−2.847 65	−2.861 67	−2.861 68
$Li(^2S: 1s^2\,2s)$	E_e	−7.418 48	−7.432 72	−7.432 73
$1s$	ε_{1s}	−2.460	−2.478	−2.478
$2s$	ε_{2s}	−0.195	−0.196	−0.196
$Be(^1S: 1s^2\,2s^2)$	E_e	−14.556 74	−14.572 87	−14.573 02
$1s$	ε_{1s}	−4.717	−4.733	−4.733
$2s$	ε_{2s}	−0.309	−0.309	−0.309
$B(^2P: 1s^2\,2s^2\,2p)$	E_e	−24.498 37	−24.527 92	−24.529 06
$1s$	ε_{1s}	−7.678	−7.694	−7.695
$2s$	ε_{2s}	−0.484	−0.494	−0.495
$2p$	ε_{2p}	−0.300	−0.310	−0.310
$C(^3P: 1s^2\,2s^2\,2p^2)$	E_e	−37.622 39	−37.686 75	−37.688 61
$1s$	ε_{1s}	−11.302	−11.323	-11.325_5
$2s$	ε_{2s}	-0.677_5	−0.704	−0.706
$2p$	ε_{2p}	−0.402	−0.433	−0.433
$N(^4S: 1s^2\,2s^2\,2p^3)$	E_e	−54.268 90	−54.397 95	−54.400 92
$1s$	ε_{1s}	−15.593	−15.625	−15.629
$2s$	ε_{2s}	-0.892_5	−0.943	−0.945
$2p$	ε_{2p}	−0.503	−0.566	−0.568
$O(^3P: 1s^2\,2s^2\,2p^4)$	E_e	−74.540 36	−74.804 32	−74.809 37
$1s$	ε_{1s}	−20.614	−20.663	−20.669
$2s$	ε_{2s}	−1.151	−1.240	−1.244
$2p$	ε_{2p}	−0.503	−0.628	−0.632
$F(^2P: 1s^2\,2s^2\,2p^5)$	E_e	−98.942 11	−99.401 31	−99.409 30
$1s$	ε_{1s}	−26.303	−26.374	−26.383
$2s$	ε_{2s}	−1.431	−1.567	-1.572_5
$2p$	ε_{2p}	−0.526	−0.724	−0.730
$Ne(^1S: 1s^2\,2s^2\,2p^6)$	E_e	−127.812 2	−128.535 1	−128.547 05
$1s$	ε_{1s}	−32.662	−32.760	−32.772
$2s$	ε_{2s}	-1.732_5	−1.922	−1.930
$2p$	ε_{2p}	−0.562	−0.841	−0.850

[a] Clementi and Roetti (1974).

(Clementi and Roetti, 1974; Clementi and Corongiu, 1982), and for the ground state of the H_2O molecule $(^1A_1: 1a_1^2\,2a_1^2\,1b_2^2\,3a_1^2\,1b_1^2)$ in Table 7.5 (Pitzer and Merrifield, 1970; Rosenberg and Shavitt, 1975; Lazzeretti, 2004).

As a general comment on Tables 7.3 and 7.4 concerning the atomic case, we can say that the 1-term SCF approximation (SZ) is totally insufficient, giving very large errors either for electronic energy or orbital energies. For the STO bases, the SZ error in the electronic energy for the Mg atom is even larger than 1 atomic unit, while errors of several 10^{-3} E_h

Table 7.4.

Comparison between STO[a] and GTO[b] results for the ground state of the Mg atom

STO basis/AO	$3s\,1p$	$6s\,2p$	$8s\,5p$
Specification	SZ	DZ	HF
m	6	12	23
E_e	-198.8578	-199.6070	-199.6146
$\varepsilon_i/1s$	-48.9385	-49.0239	-49.0316
$2s$	-3.5979	-3.7642	-3.7676
$2p$	-2.0315	-2.2783	-2.2821
$3s$	-0.2410	-0.2523	-0.2530
GTO basis/AO	$12s\,5p$	$13s\,7p$	$16s\,8p$
Specification	Small	Medium	Large
m	27	34	40
E_e	-199.5463	-199.6009_6	-199.6119
$\varepsilon_i/1s$	-48.9787	-49.0317	-49.0315
$2s$	-3.7416	-3.7686	-3.7674
$2p$	-2.2534	-2.2835	-2.2817
$3s$	-0.2110	-0.2532	-0.2528

[a] Clementi and Roetti (1974). [b] Clementi and Corongiu (1982).

Table 7.5.

Comparison between STO and GTO results for the ground state of the H_2O molecule at the experimental geometry[a]

AO/MO	STO[b]	STO[c]	GTO[d]	
Basis set	$(2s\,1p\|1s)$	$(5s\,4p\,2d\|3s\,1p)$	$[13s\,10p\,5d\,2f\|8s\,4p\,1d]$	
Specification	1-term SCF	polarized extended	nearly HF set	
m	7	39	145	
E/E_h	-75.65560	-76.06423	-76.06687	
$\mu/e\,a_0$	0.5642	0.7849	0.7809	(0.728)[e]
$\varepsilon_i/1a_1$	-20.5046	-20.56094	-20.56354	
$2a_1$	-1.2981	-1.34986	-1.35159	
$1b_2$	-0.6386	-0.71605	-0.71655	
$3a_1$	-0.4715	-0.58343	-0.58443	
$1b_1$	-0.4251	-0.50706	-0.51008	
Valence ionization potentials/eV				
$2a_1$	35.3	36.73	36.78	(32.20)[f]
$1b_2$	17.4	19.48	19.50	(18.61)
$3a_1$	12.8	15.88	15.90	(17.74)
$1b_1$	11.6	13.80	13.88	(12.62)

[a] Herzberg (1956). [b] Pitzer and Merrifield (1970). [c] Rosenberg and Shavitt (1975). [d] Lazzeretti (2004): private communication to V. Magnasco. [e] Dyke and Muenter (1973) (Molecular Beam ERS). [f] Potts and Price (1972) (UV-PES).

are observed for the orbital energies. The 2-term SCF approximation (DZ) turns out to be sensibly better, but to reach the HF level (last column of the tables) a sensibly larger number of functions is needed.

The comparison between STO and GTO bases for the Mg atom (Table 7.4) shows how larger the number of GTOs must be in comparison with that of STO bases of roughly the same quality. The largest GTO basis ($m = 40$), containing about twice as many functions as those of HF/STO, is however still in error by about $3 \times 10^{-3}\, E_h$ in the electronic energy, the results being better for the orbital energies.

We shall now briefly comment on the molecular case of H_2O (Table 7.5). Besides molecular energy in the Born–Oppenheimer approximation (Chapter 10), $E = E_e + E_N$, electric dipole moment μ, and orbital energies ε_i, in the lower part of Table 7.5 we introduced a comparison between the ionization potentials I_i (which can be observed experimentally by UV-photoelectron spectroscopy[6]) and the negative of the calculated orbital energies:

$$I_i \approx -\varepsilon_i \tag{187}$$

a relation which is known as Koopmans' theorem. The minimum basis set calculation by Pitzer and Merrifield (1970) is definitely poor, even if STOs are used. The molecular energy is well $0.4113\, E_h$ (about $258.1\,\text{kcal mol}^{-1}$!) above the nearly HF value of the last column. The distribution of the electronic charge is largely unsatisfactory, giving an insufficient dipole moment, about 72% of the HF value and 77% of the experiment. So, the minimum basis set greatly underestimates the dipole moment, at variance with what occurs for bases of double-zeta quality, which largely overestimate the dipole moment (Magnasco et al., 1985). The polarized and extended STO basis set, the 39-term function of Rosenberg and Shavitt (1975), improves sensibly energy, which is now only $2.6 \times 10^{-3}\, E_h$ ($1.66\,\text{kcal mol}^{-1}$) above HF, and dipole moment. The calculations of the last two columns were carried out at the experimental geometry (Herzberg, 1944) O–H $= 1.811\,079\, a_0$, $2\theta = 104.45°$.

The experimental ionization potentials, given in parenthesis in the last column, show that Koopmans' theorem is hardly satisfied even by the improved values, the negative of the orbital energies in this case being 5–14% larger than the experimental ones. This shows unequivocally the importance of electron correlation effects (not included at the HF level) in the evaluation of molecular ionization potentials.

The estimated Hartree–Fock limit for the H_2O ground state is $E^{\text{HF}} = -76.0675\, E_h$, with an estimated correlation energy $E^{\text{corr}} = -0.370\, E_h$ (Rosenberg and Shavitt, 1975). From the corresponding values for $O(^3P)$, the binding energy of H_2O is calculated to be $0.3397\, E_h$ for the correlated case, which is within 91% of the experimental value of $0.3714\, E_h$. The dissociation energy of the MO wavefunction of Pitzer and Merrifield (1970) at $2\theta = 105°$, $0.1226\, E_h$, gives no more than $1/3$ of the observed experimental value.

Concluding this Section, we stress once more that the accuracy of the results obtained by LCAO-MO-SCF calculations depends (i) on the nature of the atomic basis set (STO or GTO, with or without polarization functions), and (ii) on the size of the basis (originating truncation errors).

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[6] The "fingerprints" of the molecules, said Richard N. Dixon in 1969 at Sheffield University, U.K.

Good quality (nearly HF) results were obtained by Clementi and Roetti (1974) for *atoms* (from He to Xe with $N = 54$) using STO functions, an extension of the first-row atom results given in Table 7.3.

High quality HF results, free from truncation errors, were obtained by Pekka Pyykkö and his group (Sundholm et al., 1985) for several *diatomic molecules* (H_2, LiH, BH, He_2, Li_2, Be_2, FH, N_2, CO, BeO, LiF, NaH) through direct two-dimensional integration of the Hartree–Fock equations (HF/2D). His results are the best benchmarks to date for these systems, and compare favourably with the results of the corresponding nearly complete LCAO-MO-SCF calculations with very extended (nearly saturated) basis sets containing polarization functions.

7.7.7 Localization of Molecular Orbitals

The ordinary (or canonical) MOs are one-electron functions centred at the different nuclei of the molecule, reflecting the symmetry of the point group to which the molecule belongs (Chapter 8). They are therefore *delocalized*, and bear no resemblance with the conventional chemical description of a saturated molecule in terms of inner shells, bonds and lone pairs. A transformation among the MOs is however possible, giving orbitals which are to some extent *localized*, so adhering better to chemical ideas.

As an example, let us consider the valence MOs for the ${}^1A_1$ ground state of the CH_4 molecule, which has T_d symmetry. Considering the molecule inscribed into the cube of Figure 8.22 of Chapter 8 (see also Figure 7.5), the four doubly occupied un-normalized MOs can be written as:

$$a_1 = s + \lambda h_s, \qquad t_{2x} = x + \mu h_x, \qquad t_{2y} = y + \mu h_y, \qquad t_{2z} = z + \mu h_z, \tag{188}$$

where:

$$\begin{aligned} h_s &= \frac{1}{2}(h_1 + h_2 + h_3 + h_4) \\ h_x &= \frac{1}{2}(h_1 + h_2 - h_3 - h_4) \\ h_y &= \frac{1}{2}(h_1 - h_2 + h_3 - h_4) \\ h_z &= \frac{1}{2}(h_1 - h_2 - h_3 + h_4) \end{aligned} \tag{189}$$

are symmetry combinations of the four H $1s$ AOs centred at non-contiguous vertices of the cube, transforming as s, x, y, z, respectively. They are normalized if we neglect the overlap between the $1s$ functions. The five-centre MOs (188) can be localized if we take the (un-normalized) linear combinations:

$$B_1 = a_1 + t_{2x} + t_{2y} + t_{2z}$$

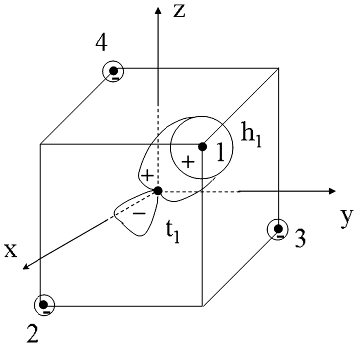

Figure 7.5 The localized bond orbital B_1 in CH_4.

$$\begin{aligned} B_2 &= a_1 + t_{2x} - t_{2y} - t_{2z} \\ B_3 &= a_1 - t_{2x} + t_{2y} - t_{2z} \\ B_4 &= a_1 - t_{2x} - t_{2y} + t_{2z}. \end{aligned} \tag{190}$$

In fact, B_1 can be written as:

$$\begin{aligned} B_1 &= s + x + y + z + \frac{\lambda}{2}(h_1 + h_2 + h_3 + h_4) \\ &\quad + \frac{\mu}{2}(h_1 + h_2 - h_3 - h_4 + h_1 - h_2 + h_3 - h_4 + h_1 - h_2 - h_3 + h_4) \\ &= \left(s + \sqrt{3}p_1\right) + \frac{\lambda + 3\mu}{2}h_1 + \frac{\lambda - \mu}{2}(h_2 + h_3 + h_4), \end{aligned} \tag{191}$$

where:

$$p_1 = \frac{x + y + z}{\sqrt{3}} \tag{192}$$

is a $2p$ orbital on C directed at the (111) vertex of the cube, where H_1 is located. So, in the transformed MO (191), the coefficient of h_1 is increased, that of $(h_2 + h_3 + h_4)$ decreased, while:

$$s + \sqrt{3}p_1 = 2t_1 \tag{193}$$

is a sp^3 hybrid on C directed towards H_1. If $\lambda \approx \mu$, the un-normalized B_1 becomes:

$$B_1 \approx t_1 + \lambda h_1, \tag{194}$$

a *localized* bond orbital (BO) describing the two-centre C–H_1 bond in CH_4 (Figure 7.5). The same is true for the remaining BOs of (190), each one describing the respective C–H bond in the molecule.

In the localized form, the CH_4 molecule is hence described in terms of four *equivalent* C–H bond orbitals.

The transformation (190) between the MOs is given by the normalized matrix:

$$\mathbf{U} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \end{pmatrix}. \tag{195}$$

Since $\mathbf{U}\mathbf{U}^\dagger = \mathbf{U}^\dagger\mathbf{U} = \mathbf{1}$, the transformation is *unitary*, which means that the physical invariant ρ of equation (121) is unchanged.

The matter was put onto a quantitative basis by Magnasco and Perico (1967, 1968), who proposed a general procedure for a non arbitrary external localization of atomic and molecular orbitals. They imposed an extremum principle on the sums of certain local orbital populations which were required to be uniformly localized in given regions of space, in particular around atoms or between pairs of atoms in the molecule. The orthogonal transformation which maximizes the localization function is obtained through an iterative sequence of 2×2 rotations between all $n(n-1)/2$ possible pairs of doubly occupied MOs. The method was exceedingly simple, the only prerequisite being the coefficients in the LCAO expansion of the MOs and the overlap integrals between the basic AOs. Localization of few Ransil's MOs (Ransil, 1960b) for the diatomic molecules LiH, BH, FH, LiF, BF, CO, Li_2, Be_2, N_2, F_2 is given in the 1967 paper, while the polyatomic molecules CH_4, NH_3, H_2O, H_2CO, HCN, C_2H_6, C_2H_4, C_2H_2 and B_2H_6 are studied in the 1968 paper. Convergence was found excellent in all cases. The results are very close to those of the energy localized orbitals obtained by Edmiston and Ruedenberg (1965) by maximizing the sum of the orbital self-repulsion energies.

7.8 HÜCKEL THEORY

Hückel theory (HT) was originally devised by Hückel (1931a, 1931b, 1932) to deal with the π electrons of planar conjugated and aromatic hydrocarbons (Coulson, 1961) having a uniform charge distribution. Recently, it was used by the author to discuss an elementary approach to a model of the chemical bond (Magnasco, 2002, 2003, 2004a).

HT amounts to a simple LCAO-MO theory of carbon π electrons, where each atom contributes an electron in its $2p\pi$ AO, assuming orthogonal AOs and with coefficients determined by the Ritz method. The elements of the Hückel secular determinant are given in terms of just two negative unspecified parameters, the diagonal α (the Coulomb integral) and the nearest neighbour off-diagonal β (the resonance or bond integral), simply introduced in a *topological* way as:

$$H_{\mu\mu} = \alpha \quad \mu = 1, 2, \cdots N$$

$$H_{\mu\nu} = \beta \quad \text{if } \nu = \mu \pm 1, \ 0 \text{ othervise} \tag{196}$$

$$S_{\mu\nu} = \delta_{\mu\nu}.$$

Therefore, Hückel theory distinguishes only between linear and closed (rings) chains.

It is useful to introduce the notation:

$$\frac{\alpha - \varepsilon}{\beta} = -x \tag{197}$$

$$\varepsilon = \alpha + x\beta, \qquad \Delta\varepsilon = \varepsilon - \alpha = x\beta, \qquad \frac{\Delta\varepsilon}{\beta} = x, \tag{198}$$

where x measures the π bond energy in units of β ($x > 0$ means bonding, $x < 0$ means antibonding). We shall denote by D_N a determinant of order N. There are two general D_N determinants of Hückel's type, that for the *linear* chain:

$$D_N = \begin{vmatrix} -x & 1 & 0 & \cdots & 0 & 0 & 0 \\ 1 & -x & 1 & \cdots & 0 & 0 & 0 \\ \multicolumn{7}{c}{\dotfill} \\ 0 & 0 & 0 & \cdots & 1 & -x & 1 \\ 0 & 0 & 0 & \cdots & 0 & 1 & -x \end{vmatrix} \tag{199}$$

and that for the *closed* chain (the ring):

$$D_N = \begin{vmatrix} -x & 1 & 0 & \cdots & 0 & 0 & 1 \\ 1 & -x & 1 & \cdots & 0 & 0 & 0 \\ \multicolumn{7}{c}{\dotfill} \\ 0 & 0 & 0 & \cdots & 1 & -x & 1 \\ 1 & 0 & 0 & \cdots & 0 & 1 & -x \end{vmatrix}. \tag{200}$$

Since elementary applications of the theory can be easily found elsewhere (among others, Murrell et al., 1965; Salem, 1966; Karplus and Porter, 1970), in the following, after introducing for the linear chain a simple recurrence relation allowing to express D_N in terms of D_{N-1} and D_{N-2}, we shall consider the general solution for the linear polyene chain and the closed polyene chain with N atoms (Coulson, 1938a, 1938b). An application to the π electron system of the allyl radical ($N = 3$) and the benzene molecule ($N = 6$) will be given next, full details being deserved to Problems 7.15 and 7.16. In Chapter 8, the benzene π MOs in real form will be obtained as well by use of group theoretical methods. The Section ends with a short elementary introduction to the band theory of solids.

7.8.1 Recurrence Relation for the Linear Chain

Coulson (1938a, 1938b) gave a recurrence relation for the linear polyene chain which allows us to obtain the expansion of D_N in terms of D_{N-1} and D_{N-2}. Expanding the determinant D_N (199) according to the elements of the first row, we obtain:

$$D_N = -xD_{N-1} - \begin{vmatrix} 1 & 1 & \cdots & 0 & 0 \\ 0 & -x & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & 1 & -x \end{vmatrix}, \tag{201}$$

where the last determinant of order $(N-1)$ can be expanded according to the elements of the first *column*, so that Coulson's recurrence formula is readily derived:

$$D_N = -xD_{N-1} - D_{N-2}, \tag{202}$$

with the starting conditions:

$$D_1 = -x \qquad D_2 = x^2 - 1. \tag{203}$$

We note that Coulson's expansion is nothing but the Cauchy expansion of D_N in terms of its first row and first column.

As an example, for $N = 3$:

$$D_3 = -xD_2 - D_1 = -x(x^2-1) + x = -x(x^2-2) \tag{204}$$

and we obtain the well known result for allyl.

For $N = 4$:

$$\begin{aligned} D_4 &= -xD_3 - D_2 = -x\big[-x(x^2-2)\big] - (x^2-1) \\ &= x^2(x^2-3) + 1 = x^4 - 3x^2 + 1 \end{aligned} \tag{205}$$

we obtain the result for linear butadiene, and so on.

7.8.2 General Solution for the Linear Chain

Coulson (1938a, 1938b) gave the general solution for the system of homogeneous linear equations for the linear polyene chain with N atoms:[7]

$$\begin{cases} -xc_1 + c_2 = 0 \\ \cdots \\ c_{m-1} - xc_m + c_{m+1} = 0. \\ \cdots \\ c_{N-1} - xc_N = 0 \end{cases} \tag{206}$$

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[7] The secular equations for linear and closed polyene chains, even with *different* βs for single and double bonds, were first solved by Lennard-Jones (1937a, 1937b). See also Hückel (1931a).

The general equation is:

$$c_{m-1} - xc_m + c_{m+1} = 0 \quad m = 1, 2, \cdots N \tag{207}$$

with the boundary conditions:

$$c_0 = c_{N+1} = 0. \tag{208}$$

The general solution is the “standing” wave:

$$c_m = A\exp(im\theta) + B\exp(-im\theta) \tag{209}$$

provided:

$$x = 2\cos\theta. \tag{210}$$

(i) From the first boundary condition it is obtained:

$$c_0 = A + B = 0 \Longrightarrow B = -A \tag{211}$$

$$c_m = A\big[\exp(im\theta) + \exp(-im\theta)\big] = 2iA\sin m\theta = C\sin m\theta \tag{212}$$

where $C = 2iA$ is a normalization factor.

The general equation gives:

$$\begin{aligned} &A\big\{\exp[i(m-1)\theta] - x\exp(im\theta) + \exp[i(m+1)\theta]\big\} \\ &\qquad + B\big\{\exp[-i(m-1)\theta] - x\exp(-im\theta) + \exp[-i(m+1)\theta]\big\} \\ &\quad = A\exp(im\theta)[\exp(-i\theta) - x + \exp(i\theta)] \\ &\qquad + B\exp(-im\theta)[\exp(-i\theta) - x + \exp(i\theta)] \\ &\quad = [A\exp(im\theta) + B\exp(-im\theta)][\exp(-i\theta) - x + \exp(i\theta)] \\ &\quad = c_m(2\cos\theta - x) = 0 \end{aligned} \tag{213}$$

so that, for $c_m \neq 0$:

$$2\cos\theta - x = 0 \Longrightarrow x = 2\cos\theta \tag{214}$$

as required.

(ii) From the second boundary condition it follows that:

$$c_{N+1} = C\sin(N+1)\theta = 0 \tag{215}$$

$$(N+1)\theta = k\pi \quad k = 1, 2, 3, \cdots N \tag{216}$$

with k a "quantum number":

$$\theta_k = \frac{k\pi}{N+1}. \tag{217}$$

Angle θ is "quantized".

Therefore, the general solution for the linear chain will be:

$$x_k = 2\cos\frac{k\pi}{N+1} \tag{218}$$

$$c_{mk} = c_k \sin m\,\frac{k\pi}{N+1}, \tag{219}$$

the first being the π bond energy of level k (in units of β), the second the coefficient of the m-th AO in the k-th MO. Problem 7.15 gives the application of the general formulae (218) and (219) to the allyl case ($N = 3$).

7.8.3 General Solution for the Closed Chain

In the same paper, Coulson (1938a, 1938b) gave also the general solution for the closed chain (ring) of N atoms:

$$\begin{cases} -xc_1 + c_2 + \cdots + c_N = 0 \\ \cdots \\ c_{m-1} - xc_m + c_{m+1} = 0 \\ \cdots \\ c_1 + \cdots + c_{N-1} - xc_N = 0. \end{cases} \tag{220}$$

The general equation for the coefficients is the *same* as that for the linear chain:

$$c_{m-1} - xc_m + c_{m+1} = 0 \quad m = 1, 2, \cdots N \tag{207}$$

but the boundary conditions are now *different*:

$$c_0 = c_N, \quad c_1 = c_{N+1} \Longrightarrow c_m = c_{m+N}, \tag{221}$$

the last being a *periodic* boundary condition.

The general solution is now the "progressive" wave:

$$c_m = A\exp(im\theta), \tag{222}$$

and the general equation (207) gives:

$$A\big\{\exp[i(m-1)\theta] - x\exp(im\theta) + \exp[i(m+1)\theta]\big\} = 0 \tag{223}$$

$$A\exp(im\theta)[\exp(-i\theta) - x + \exp(i\theta)] = c_m(2\cos\theta - x) = 0 \tag{224}$$

namely, for $c_m \neq 0$:

$$x = 2\cos\theta \tag{210}$$

as before.

From the periodic boundary condition it follows:

$$A\exp(im\theta) = A\exp[i(m+N)\theta] \tag{225}$$

$$\exp(iN\theta) = \cos N\theta + i\sin N\theta = 1 \tag{226}$$

$$N\theta = k2\pi \tag{227}$$

$$k = 0,\ \pm 1,\ \pm 2, \cdots \begin{cases} \dfrac{N}{2} & N = \text{even} \\ \pm\dfrac{N-1}{2} & N = \text{odd}, \end{cases} \tag{228}$$

where k is the "quantum number" for the ring. In this case, all energy levels are doubly degenerate except those for $k = 0$ and $k = N/2$ for $N = \text{even}$.

The general solution for the N-ring will be:

$$x_k = 2\cos\theta_k = 2\cos k\frac{2\pi}{N} \tag{229}$$

$$c_{mk} = A_k \exp\left(im\frac{2\pi k}{N}\right) \quad + \hookrightarrow \quad - \hookleftarrow. \tag{230}$$

The general MO in *complex* form will be:

$$\phi_k = A_k \sum_m \chi_m \exp\left(im\frac{2\pi k}{N}\right) \tag{231}$$

with:

$$c_{mk} = A_k \exp\left(im\frac{2\pi k}{N}\right), \qquad c^*_{mk} = A_k \exp\left(-im\frac{2\pi k}{N}\right). \tag{232}$$

The coefficients can be expressed in *real* form through the transformation:

$$\frac{c_{mk} - c^*_{mk}}{2i} = A_k \sin m\frac{2\pi k}{N} = a_{mk} \tag{233}$$

$$\frac{c_{mk} + c^*_{mk}}{2} = A_k \cos m\frac{2\pi k}{N} = b_{mk}, \tag{234}$$

giving the MOs in *real* form as:

$$\phi_k^s = \sum_m \chi_m a_{mk}, \qquad \phi_k^c = \sum_m \chi_m b_{mk}. \tag{235}$$

Problem 7.16 gives the application of the general formulae in real form to the benzene case ($N = 6$).

7.8.4 Alternant Hydrocarbons

For the allyl radical (linear chain with $N = 3$), the Hückel secular equation gives:

$$D_3 = -x(x^2 - 2) = 0 \tag{236}$$

with the ordered roots:

$$x_1 = \sqrt{2}, \qquad x_2 = 0, \qquad x_3 = -\sqrt{2}. \tag{237}$$

The corresponding MOs are (Problem 7.15):

$$\phi_1 = \frac{\chi_1 + \sqrt{2}\chi_2 + \chi_3}{2}, \qquad \phi_2 = \frac{\chi_1 - \chi_3}{\sqrt{2}}, \qquad \phi_3 = \frac{\chi_1 - \sqrt{2}\chi_2 + \chi_3}{2}. \tag{238}$$

Figure 7.6 gives the diagram of the MO levels for the allyl radical and their occupation by the electrons in the ground state, Figure 7.7 a sketch of the resulting MOs.

The electron configuration of the radical is $\phi_1^2\phi_2$, giving for the electron density:

$$P(\mathbf{r}) = P_1^\alpha + P_1^\beta = \chi_1^2 + \chi_2^2 + \chi_3^2 \tag{239}$$

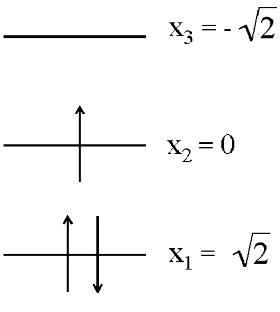

Figure 7.6 MO diagram for the allyl radical ($N = 3$).

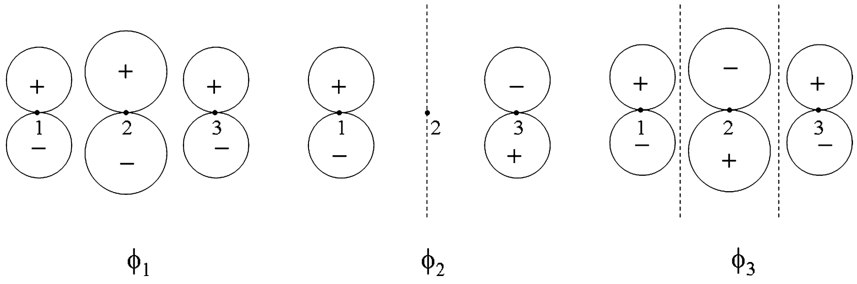

Figure 7.7 The three MOs of the allyl radical ($N = 3$).

Figure 7.8 Electron (a) and spin density (b) MO distributions in allyl radical ($N = 3$).

a *uniform* charge distribution (one electron onto each atom), and for the spin density of the doublet ($S = 1/2$) with $M_S = 1/2$:

$$Q(\mathbf{r}) = P_1^\alpha - P_1^\beta = \frac{1}{2}(\chi_1^2 + \chi_3^2). \tag{240}$$

The unpaired electron (spin α) is $1/2$ onto atom 1 and $1/2$ onto atom 3, and zero at atom 2. This MO result is however incorrect, and we shall see in Chapter 10 that the VB calculation of the spin density in $C_3H_5^\bullet$ shows that there is a *negative* spin density at the central atom, in agreement with the results from experimental ESR spectra. The error in the MO result is due to the lack of electron correlation in the wavefunction.

Figure 7.8 gives the electron and spin density MO distributions in the allyl radical.

The π bond energy (units of β) of the allyl radical is:

$$\Delta E^\pi(\text{allyl}) = 2\sqrt{2} = 2.828, \tag{241}$$

while that of an ethylenic double bond is:

$$\Delta E^\pi(\text{ethylene}) = 2. \tag{242}$$

The difference 0.828 (an attractive stabilizing energy) is called *delocalization energy* of the double bond in allyl.

For the π electron system of the benzene molecule ($N = 6$), the Hückel secular equation gives:

$$D_6 = x^6 - 6x^4 + 9x^2 - 4 = (x^2 - 4)(x^2 - 1)^2 = 0 \tag{243}$$

with the ordered roots:

$$x_1 = 2, \qquad x_2 = x_3 = 1, \qquad x_4 = x_5 = -1, \qquad x_6 = -2. \tag{244}$$

The corresponding MOs in real form are (Problems 7.16 and 8.13):

$$\begin{aligned}
\phi_1 &= \frac{1}{\sqrt{6}}(\chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 + \chi_6) \\
\phi_2 &= \frac{1}{2}(\chi_1 - \chi_3 - \chi_4 + \chi_6) \sim x \\
\phi_3 &= \frac{1}{\sqrt{12}}(\chi_1 + 2\chi_2 + \chi_3 - \chi_4 - 2\chi_5 - \chi_6) \sim y \\
\phi_4 &= \frac{1}{\sqrt{12}}(\chi_1 - 2\chi_2 + \chi_3 + \chi_4 - 2\chi_5 + \chi_6) \sim x^2 - y^2 \\
\phi_5 &= \frac{1}{2}(\chi_1 - \chi_3 + \chi_4 - \chi_6) \sim xy \\
\phi_6 &= \frac{1}{\sqrt{6}}(\chi_1 - \chi_2 + \chi_3 - \chi_4 + \chi_5 - \chi_6).
\end{aligned} \tag{245}$$

Figure 7.9 gives the diagram of the MO levels for the π electrons in benzene and their occupation by the electrons in the ground state, Figure 7.10 a sketch of the real MOs. In the drawings, we have reported only the signs of the upper lobes of the $2p_z$ AOs.

The charge distribution resulting from the ground state electron configuration $\phi_1^2\phi_2^2\phi_3^2$ is uniform (one electron onto each carbon atom):

$$P(\mathbf{r}) = P_1^\alpha + P_1^\beta = \chi_1^2 + \chi_2^2 + \chi_3^2 + \chi_4^2 + \chi_5^2 + \chi_6^2. \tag{246}$$

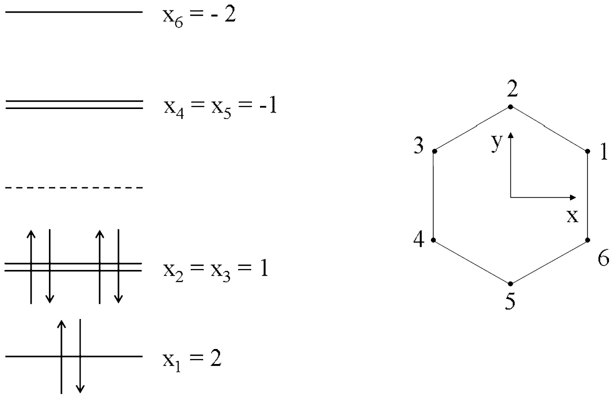

Figure 7.9 MO diagram for benzene ($N = 6$).

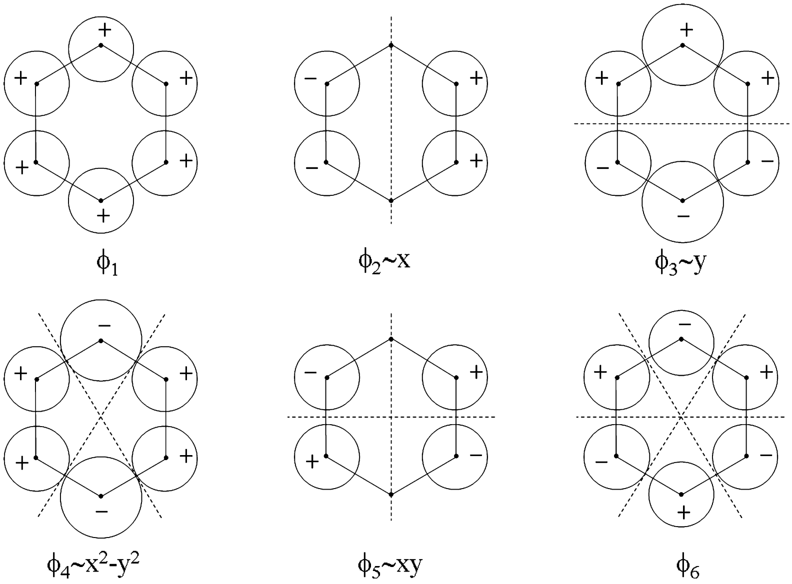

Figure 7.10 The six real MOs for the benzene ring ($N = 6$).

As far as the delocalization energy is concerned, we have for benzene:

$$\Delta E^{\pi}(\text{benzene}) = 2 \times (+2) + 4 \times (+1) = 8 \tag{247}$$

$$\Delta E^{\pi}(3\ \text{ethylenes}) = 3 \times (+2) = 6 \tag{248}$$

so that:

$$\Delta E^{\pi}(\text{benzene}) - \Delta E^{\pi}(3\ \text{ethylenes}) = 2 \tag{249}$$

is the delocalization energy (units of β) for the π system of the benzene molecule, while the stabilization energy due to the closure of the ring is (see Figure 7.11):

$$\Delta E^{\pi}(\text{benzene}) - \Delta E^{\pi}(\text{hexatriene}) = 8 - 6.988 = 1.012. \tag{250}$$

So, the closure of the chain to the ring with $N = 6$ (no tensions in the σ skeleton) is energetically favoured, while delocalization of the π bonds is the largest. This explains the great stability of the benzene ring, where the three delocalized π bonds have a completely different nature from three ethylenic double bonds.

Figure 7.11 shows the Hückel results for the MO levels resulting for $N = 4, 6, 8, 10$ in the case of the open chain and the ring. As a matter of fact, the rings for $N = 8$ and $N = 10$ are *not* planar, $N = 8$ having a "tube" conformation (the system is not aromatic), $N = 10$ being unstable in view of the strong overcrowding involving trans H-atoms inside the ring, what favours its isomerization to di-hydro-naphthalene (Figure 7.12).

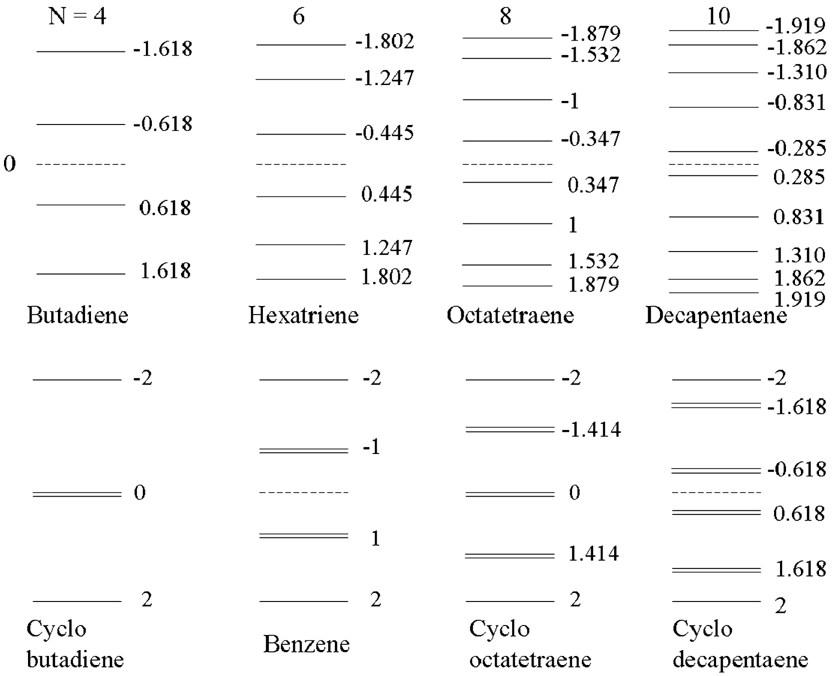

Figure 7.11 Hückel MO levels for the open chain (above) and the ring (bottom) with $N = 4, 6, 8, 10$.

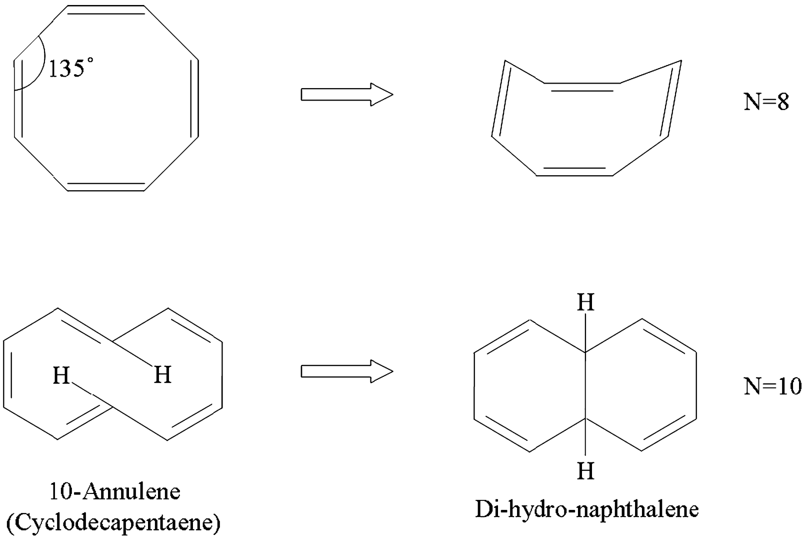

Figure 7.12 The rings with $N = 8$ and $N = 10$.

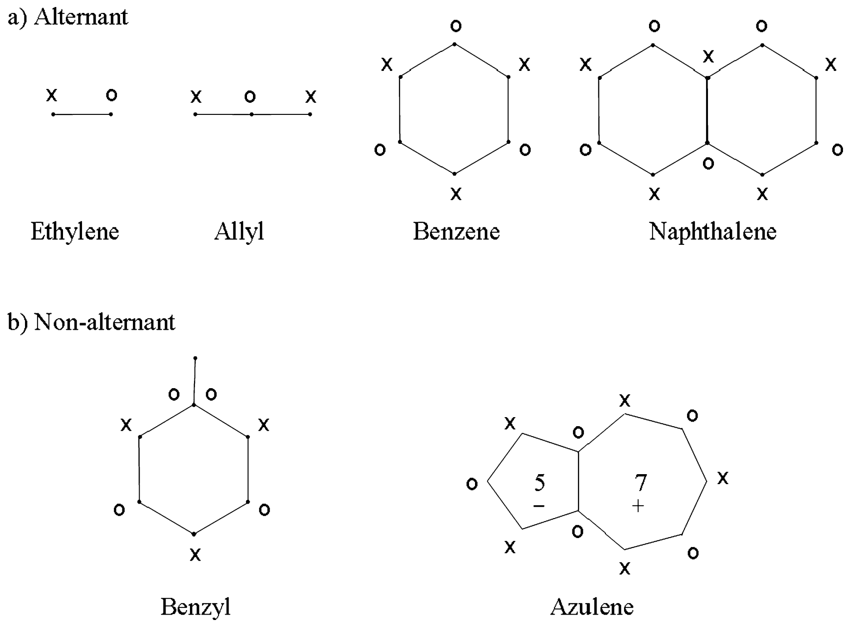

Figure 7.13 Alternant (a) and non-alternant (b) hydrocarbons.

We note from Figure 7.11 that the antibonding levels are all symmetrical about zero, and correspond to the bonding levels changed in sign. So, energy levels occur in pairs, with a π bond energy $\pm x$, and the coefficients of the paired orbitals are either the same or simply change sign. These are the properties of *alternant* hydrocarbons, which are conjugated molecules in which the carbon atoms can be divided into two sets, crossed and circled, such that no two members of the same set are bonded together (Figure 7.13a). They are characterized (as we have already seen for allyl and benzene) by a uniform charge distribution, and do not present any dipole moment in the ground state. In non-alternant hydrocarbons (Figure 7.13b), two circles (or two crosses) are close together, and these properties are lost. Ground state azulene has a dipole moment of about $0.4\,ea_0$ directed from ring 5 to 7.

7.8.5 An Introduction to Band Theory of Solids

Increasing the number of interacting AOs increases the number of resulting MOs. For the polyene chain C_NH_{N+2} the molecular orbital levels, which alvays range between $\alpha + 2\beta$ and $\alpha - 2\beta$, become closer and closer up to transforming in *bands* (a continuous succession of molecular levels) which are characteristic of solids.

Using the general formula derived by Coulson (1938a, 1938b) for the orbital energy of the k-th MO in the N-atom linear polyene chain:

$$\varepsilon_k = \alpha + 2\beta \cos \frac{\pi}{N+1} k \quad k = 1, 2, \cdots N \tag{251}$$

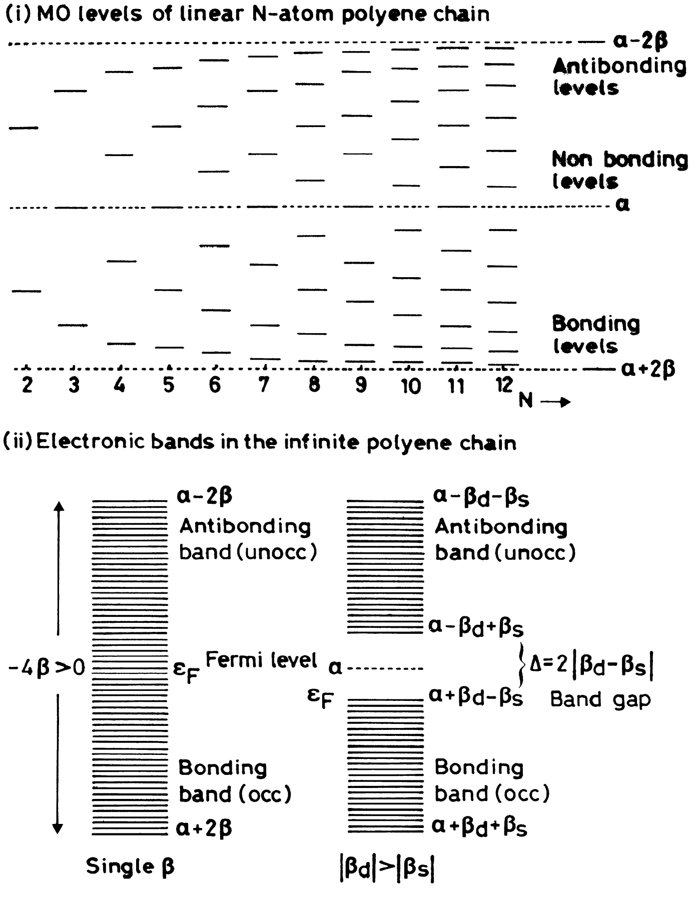

Figure 7.14 Origin of the electronic bands in solids as a limiting case of the infinite linear polyene chain.

the MO levels for $N = 2, \cdots 12$ were calculated and reported in the upper diagram of Figure 7.14. The limiting values $\alpha + 2\beta$ and $\alpha - 2\beta$ are reached asymptotically when $N \to \infty$. In this case, the energy difference between two successive levels tends to zero, and we have formation of electronic bands where the MO levels form the continuum depicted in the lower part of Figure 7.14.

These results, apparent from Figure 7.14, are easily derived from the formula above.

(i) First level ($k = 1$):

$$\varepsilon_1 = \alpha + 2\beta \cos \frac{\pi}{N+1} \qquad \lim_{N\to\infty} \varepsilon_1 = \alpha + 2\beta. \tag{252}$$

(ii) Last level ($k = N$):

$$\varepsilon_N = \alpha + 2\beta \cos \frac{\pi N}{N+1} = \alpha + 2\beta \cos \frac{\pi}{1+\dfrac{1}{N}} \qquad \lim_{N\to\infty} \varepsilon_N = \alpha - 2\beta. \tag{253}$$

(iii) Difference between two successive levels:

$$\begin{aligned}\Delta\varepsilon = \varepsilon_{k+1} - \varepsilon_k &= 2\beta\left(\cos \frac{\pi}{N+1}(k+1) - \cos \frac{\pi}{N+1}k\right)\\ &= -4\beta \sin \frac{\pi}{2}\frac{2k+1}{N+1} \sin \frac{\pi}{2}\frac{1}{N+1},\end{aligned} \tag{254}$$

where use was made of the trigonometric identity:

$$\cos\alpha - \cos\beta = -2\sin\frac{\alpha+\beta}{2}\sin\frac{\alpha-\beta}{2}. \tag{255}$$

Hence, for $N \to \infty$ $\Delta\epsilon \to 0$, and we have formation of a continuous band of molecular levels.

(iv) For $N \to \infty$, therefore, the polyene chain becomes the model for the 1-dimensional crystal. We have a bonding band with energy ranging from $\alpha + 2\beta$ to α, and an antibonding band with energy ranging from α to $\alpha - 2\beta$, which are separated by the so called Fermi level, the top of the bonding band occupied by electrons. It is important to notice that using just one β, equal for single and double bonds, there is no band gap between bonding and antibonding levels (bottom left in Figure 7.14). If we admit $|\beta_d| > |\beta_s|$, as reasonable, we have a band gap $\Delta = 2|\beta_d - \beta_s|$ (bottom right in Figure 7.14), which is of great importance in the properties of solids. Metals and covalent solids, conductors and insulators, semiconductors, all can be traced back to the model of the infinite polyene chain extended to three dimensions (McWeeny, 1979).

7.9 SEMIEMPIRICAL MO METHODS

The semiempirical MO methods are derived, at different levels of sophistication, from the LCAO-MO approach by making approximations in terms of parameters whose value is mostly determined by comparison with experimental results.

7.9.1 Extended Hückel Theory (EHT)

The extended Hückel theory (EHT) is a MO theory for hydrocarbons (even saturated) proposed by Hoffmann (1963). It makes use of an atomic basis formed by the valence s and p AOs of carbon and h AOs of the hydrogen atoms. The matrix elements include now the interactions even between atoms which are not neighbours, and are given as:

$$H_{\mu\mu} = \alpha_\mu \quad \mu = s, p, h \tag{256}$$

$$H_{\mu\nu} = \beta_{\mu\nu} = K\frac{\alpha_\mu + \alpha_\nu}{2}S_{\mu\nu}, \tag{257}$$

where $S_{\mu\nu}$ is the overlap between AOs μ and ν. The α's for the C atom are taken as the negative of the ionization potentials of the valence state of C(sp^3), namely:

$$\alpha_s = -21.4\ \text{eV}, \qquad \alpha_p = -11.4\ \text{eV}, \qquad \alpha_h = -13.6\ \text{eV}. \tag{258}$$

The expression (257) for the off-diagonal elements of H is called the Wolfsberg–Helmholtz approximation, where K is a constant whose value is assumed empirically (Hoffmann uses $K = 1.75$). At variance with Hückel's original approach, all off-diagonal terms as well as all overlaps are taken into account. As in Hückel theory, the total energy ε and the population matrix **P** are given by:

$$\varepsilon = 2\sum_i^{\text{occ}} \varepsilon_i$$

$$\mathbf{P} = 2\mathbf{R} = 2\mathbf{C}\mathbf{C}^\dagger \qquad P_{\mu\nu} = 2\sum_i^{\text{occ}} c_{\mu i}c_{\nu i}^*. \tag{259}$$

Calculations were done on many simple saturated and conjugated hydrocarbons, especially for what concerns molecular geometry, ionization energies, and torsional barriers. The method cannot be used as such for molecules containing heteroatoms.

7.9.2 CNDO Method

The CNDO (Complete Neglect of Differential Overlap) method was developed by Pople et al. (1965). It is an LCAO-MO-SCF theory limited to valence electrons and a STO minimal basis. It includes part of the electron repulsion, so that, at variance of Hückel's theory, can be used also with molecules containing heteroatoms.

In the Roothaan form of the SCF equations:

$$E_e = \sum_\mu \sum_\nu \left(F_{\mu\nu} - \frac{1}{2}G_{\mu\nu}\right)P_{\mu\nu} \tag{260}$$

$$P_{\mu\nu} = 2\sum_i^{\text{occ}} c_{\mu i}c_{\nu i}^* \tag{259}$$

$$F_{\mu\nu} = \langle\chi_\mu|\hat{F}|\chi_\nu\rangle = \langle\chi_\mu|\hat{h} + \hat{G}|\chi_\nu\rangle = h_{\mu\nu} + G_{\mu\nu} \tag{261}$$

$$h_{\mu\nu} = \langle\chi_\mu| - \frac{1}{2}\Delta^2 + V|\chi_\nu\rangle \tag{262}$$

$$G_{\mu\nu} = \langle\chi_\mu|\hat{G}|\chi_\nu\rangle = \sum_\lambda \sum_\sigma P_{\lambda\sigma}\left[(\nu\overset{1}{\,}\mu \mid \lambda\overset{2}{\,}\sigma) - \frac{1}{2}(\lambda\overset{1}{\,}\mu \mid \nu\overset{2}{\,}\sigma)\right] \tag{263}$$

the following approximations are introduced:

(i) 2-electron integrals

$$(\lambda\mu|\nu\sigma) = \gamma_{\mu\nu}\delta_{\mu\lambda}\delta_{\nu\sigma}. \tag{264}$$

It is assumed to neglect completely the differential overlap in the charge density $\chi_\lambda(\mathbf{r}_1)\chi^*_\mu(\mathbf{r}_1)$, in such a way that only the Coulomb integrals survive:

$$\gamma_{\mu\nu} = (\chi^2_\mu|\chi^2_\nu) = \begin{cases} \left(s^2_A|s^2_A\right) = \gamma_{AA} \\ \left(s^2_A|s^2_B\right) = \gamma_{AB}, \end{cases} \tag{265}$$

where the *spherical* integrals are evaluated analytically using STOs.

To obtain a theory invariant under rotation of axes onto each centre, it is assumed that the integrals γ depend only on atoms A and B.

The matrix elements of G then become:

$$\begin{aligned} G_{\mu\mu} &= \sum_\lambda \sum_\sigma P_{\lambda\sigma}\left[(\mu\mu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\mu\sigma)\right] \\ &= \sum_\lambda \sum_\sigma P_{\lambda\sigma}\left[(\underset{\text{on A}}{\mu\mu} \mid \underset{\substack{\text{on A}\\ \text{or B}}}{\lambda\sigma}) - \frac{1}{2}\gamma_{\mu\mu}\delta_{\mu\lambda}\delta_{\mu\sigma}\right] \\ &= -\frac{1}{2}P_{\mu\mu}\gamma_{AA} + \sum_\lambda \sum_\sigma P_{\lambda\sigma}(\underset{\text{on A}}{\mu\mu} \mid \underset{\substack{\text{on A}\\ \text{or B}}}{\lambda\lambda})\delta_{\lambda\sigma} \\ &= -\frac{1}{2}P_{\mu\mu}\gamma_{AA} + \sum_\lambda^{(A)} P_{\lambda\lambda}\gamma_{AA} + \sum_{B(\neq A)} \sum_\lambda^{(B)} P_{\lambda\lambda}\gamma_{AB} \\ &= -\frac{1}{2}P_{\mu\mu}\gamma_{AA} + P_{AA}\gamma_{AA} + \sum_{B(\neq A)} P_{BB}\,\gamma_{AB}, \end{aligned} \tag{266}$$

where:

$$P_{AA} = \sum_\lambda^{(A)} P_{\lambda\lambda}, \qquad P_{BB} = \sum_\lambda^{(B)} P_{\lambda\lambda} \tag{267}$$

are the total electron populations on atom A or B.

$$\begin{aligned} G_{\mu\mu'} &= \sum_\lambda \sum_\sigma P_{\lambda\sigma}\left[(\mu\mu'|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\mu'\sigma)\right] \quad \mu' \neq \mu, \text{ both on A} \\ &= -\frac{1}{2}\sum_\lambda \sum_\sigma P_{\lambda\sigma}(\mu\mu|\mu'\mu')\delta_{\mu\lambda}\delta_{\mu'\sigma} \end{aligned}$$

$$= -\frac{1}{2} P_{\mu\mu'} \gamma_{AA}. \tag{268}$$

$$G_{\mu\nu} = \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2} (\mu\lambda|\nu\sigma) \right] \quad \mu \text{ on A} \neq \nu \text{ on B}$$

$$= -\frac{1}{2} \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} \gamma_{\mu\nu} \delta_{\mu\lambda} \delta_{\nu\sigma} = -\frac{1}{2} P_{\mu\nu} \gamma_{AB}. \tag{269}$$

(ii) 1-electron integrals

$$h_{\mu\mu} = \langle \chi_\mu | -\frac{1}{2} \nabla^2 + V | \chi_\nu \rangle = \underset{\mu \text{ on A}}{U_{\mu\mu}} + \sum_{\text{B}(\neq \text{A})} V_{AB} \tag{270}$$

$$U_{\mu\mu} = -\frac{1}{2} (I_\mu + A_\mu) - \left(Z_A - \frac{1}{2} \right) \gamma_{AA}, \tag{271}$$

where:

I_μ = ionization potential (we extract an electron from χ_μ)

A_μ = electron affinity (we add an electron to χ_μ)

Z_A = "core" charge

$$V_{AB} = \left(\chi_\mu^2 | V_B \right) = -Z_B \left(\chi_\mu^2 | \chi_\nu^2 \right)$$

$$= -Z_B \left(s_A^2 | r_B^{-1} \right) \quad \text{CNDO/1} \tag{272}$$

$$= -Z_B \gamma_{AB} \quad \text{CNDO/2} \tag{273}$$

$$h_{\mu\mu'} = 0 \quad \text{if } \mu' \neq \mu \text{ both on A} \tag{274}$$

$$h_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} \quad \beta^0_{AB} = \frac{\beta^0_A + \beta^0_B}{2} \quad \mu \text{ on A}, \ \nu \text{ on B}. \tag{275}$$

CNDO/2 parameters for atoms of the first row are given in Table 7.6.

CNDO/2 turns out to be a better approximation than CNDO/1, and was next extended to the atoms of the second row (Na, Mg, Al, Si, P, S, Cl) using rather contracted $3d$ STOs (Santry and Segal, 1967).

(iii) Matrix elements.

With the previous approximations, the elements of the Fock matrix become:

$$F_{\mu\mu} = -\frac{1}{2} (I_\mu + A_\mu) + \left[(P_{AA} - Z_A) - \frac{1}{2} (P_{\mu\mu} - 1) \right] \gamma_{AA}$$

$$+ \sum_{\text{B}(\neq \text{A})} (P_{BB} - Z_B) \gamma_{AB} \quad \mu \text{ on A} \tag{276}$$

Table 7.6.

CNDO/2 parameters (eV) for first-row atoms

Atom	H	Li	Be	B	C	N	O	F
(i) STO orbital exponents/a_0^{-1}								
$1s$	1.2							
$2s$, $2p$		0.65	0.975	1.30	1.625	1.95	2.275	2.60
(ii) Ionization potentials and electron affinities/eV								
$\frac{1}{2}(I_s + A_s)$	7.18	3.11	5.95	9.59	14.05	19.32	25.39	32.37
$\frac{1}{2}(I_p + A_p)$		1.26	2.56	4.00	5.57	7.27	9.11	11.08
(iii) Atomic bond parameters/eV								
$-\beta_A^0$	9	9	13	17	21	25	31	39

$$F_{\mu\mu'} = G_{\mu\mu'} = -\frac{1}{2}P_{\mu\mu'}\gamma_{AA} \quad \mu' \neq \mu, \text{both on A} \tag{277}$$

$$F_{\mu\nu} = \beta_{AB}^0 S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{AB} \quad \mu \text{ on A}, \nu \text{ on B} \tag{278}$$

with the secular equation, assuming orthonormal AOs:

$$|\mathbf{F} - \varepsilon\mathbf{1}| = 0 \Longrightarrow \text{MO-SCF.} \tag{279}$$

CNDO/2 gives reasonable values for molecular geometries, valence angles, dipole moments and bending force constants. Torsional barriers are usually underestimated, and the method is not appropriate either for the calculation of spin densities (see INDO) or for conjugated molecules.

(iv) Molecular energy

The Born–Oppenheimer molecular energy in the CNDO/2 approximation can be written as:

$$E = E_e + E_N = \sum_A E_A + \sum_{A<B} E_{AB}, \tag{280}$$

where:

$$E_A = \sum_\mu P_{\mu\mu}U_{\mu\mu} + \frac{1}{2}\sum_\mu\sum_{\mu'}\left(P_{\mu\mu}P_{\mu'\mu'} - \frac{1}{2}P_{\mu\mu'}^2\right)\gamma_{AA} \tag{281}$$

is the energy of atom A (μ, μ' on A), and:

$$E_{AB} = \sum_\mu\sum_\nu\left[\left(2P_{\mu\nu}\beta_{AB}^0 S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}^2\gamma_{AB}\right)\right] + \left(\frac{Z_A Z_B}{R_{AB}} + P_{AA}V_{AB} + P_{BB}V_{BA} + P_{AA}P_{BB}\gamma_{AB}\right) \tag{282}$$

the interaction energy between atom A and atom B (μ on A, ν on B).

When atoms A and B are a great distance apart:

$$\gamma_{AB} = -Z_B^{-1} V_{AB} = -Z_A^{-1} V_{BA} \approx \frac{1}{R_{AB}}, \tag{283}$$

and the last term in E_{AB} gives the Coulomb interaction between atom A of effective charge $Q_A = Z_A - P_A$ and atom B of effective charge $Q_B = Z_B - P_B$, namely $Q_A Q_B / R_{AB}$. This means that CNDO/2 gives the correct electrostatic interactions at large distances between the atoms in the molecule, and is therefore appropriate to deal with molecules containing heteroatoms.

7.9.3 INDO Method

In the INDO (Intermediate Neglect of Differential Overlap) method (Pople et al., 1967), differential overlap is neglected everywhere except for *1-centre* 2-electron integrals:

$$(s^2|s^2) = (s^2|p^2) = \gamma_{AA} \tag{284}$$

which are evaluated analytically from STOs, whereas:

$$(sp|sp), \qquad (p^2|p^2), \qquad (x^2|y^2), \qquad (xy|xy) \tag{285}$$

are given semiempirical values.

This method accounts better than CNDO for the separation of levels into each atomic term, and gives reasonable values for the distribution of unpaired spins in radicals. The method is hence appropriate for the semiempirical calculations of spin densities (ESR, NMR).

7.9.4 ZINDO Method

The ZINDO (Zerner or spectroscopic INDO) method (Zerner et al., 1980) is a variant of the INDO technique suitable for calculation of quantities of spectroscopic interest. In this model, the 2-electron integrals are evaluated by calibrating at a CI-S (single) level the constant C in the Mataga–Nishimoto expression for γ_{AB}:

$$\gamma_{AB} = \left(\frac{R_{AB}}{C} + \frac{2}{\gamma_{AA} + \gamma_{BB}} \right)^{-1}. \tag{286}$$

The method allows for good precision calculation of UV and visible spectra, ionization potentials, polarizabilities and hyperpolarizabilities. Apart from rare gases, the parametrization was done for the first three rows of the periodic system and extended to the elements of the first transition series.

7.10 POST-HARTREE–FOCK METHODS

“Hartree–Fock is here, what next?” Alberte Pullman optimistically said during an international meeting on Quantum Chemistry in Paris, July 1970. We saw before that in the upper part of our scale of Figure 7.2 of Section 7.6 we placed methods going beyond Hartree–Fock, the so called Post-Hartree–Fock methods. It is now time to move along the ordinate axis of Pople’s two-dimensional chart of Quantum Chemistry. We shall not be exhaustive in treating such a large subject, rather we shall emphasize some aspects of a few methods which, mostly starting from the uncorrelated Hartree–Fock level, attempt to reach chemical accuracy (1 kcal mol^{-1} or less) in the atomization energies. We shall outline first the principles of configuration interaction (CI) and multiconfiguration SCF (MC-SCF) techniques, then turning to the classical work by James–Coolidge and Kołos–Wolniewicz, who gave accurate non-orbital treatments of the H_2 molecule, explicitly including the interelectron distance in the wavefunction. Next, we shall examine in some detail the second-order Møller–Plesset (MP2) theory, which belongs to the family of many-body perturbation theory (MBPT) techniques. Recent improvements are the MP2-R12 explicitly correlated methods by Kutzelnigg and Klopper, and the explicitly correlated coupled cluster methods (CC-R12) by Kutzelnigg, Klopper and Noga. A glance at second quantization techniques, mostly used by solid state physicists, and at the today widely used density functional theory (DFT) of Hohenberg, Sham and Kohn, concludes this Section.

7.10.1 Configuration Interaction (CI)

For a given basis of atomic or molecular spin-orbitals, we construct all possible configurations (Full-CI) in the form of many-electron Slater dets, which are then linearly combined by the Ritz method to give the CI multiconfigurational wavefunction:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N) = \sum_{\kappa} \Psi_\kappa(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N) C_\kappa. \tag{287}$$

A selection of the possible configurations can be done on symmetry grounds (molecular or spin), because only configurations belonging to the *same* symmetry and to the *same* eigenvalues S, M_S of $\hat{S}^2$ and $\hat{S}_z$ can have a non-vanishing interaction (Sections 8.6.1 and 8.6.2 of Chapter 8).

In molecules, the multideterminant functions built from the atomic spin-orbitals which are eigenstates of $\hat{S}^2$ are called valence bond (VB) structures, in so far as they describe the formation of covalent or ionic bonds between pairs of AOs (or their hybrids) of the different atoms in the molecule. This matter will be further discussed in Chapter 10. Recent advances for dealing with large-scale CI using the techniques of the unitary group can be found elsewhere (McWeeny, 1989).

The central problem of any CI approach to the correlation problem is the enormous number of configurations which are needed in the attempt to obviate to the slowness of convergence of the CI expansion, due to the difficulty of accounting for the cusp conditions for each electron pair:

$$\lim_{r_{ij}\to 0}\left(\frac{1}{\Psi_0}\frac{\partial\Psi}{\partial r_{ij}}\right)=\frac{1}{2}. \tag{288}$$

The cusp conditions on the wavefunction Ψ are needed to keep Ψ finite even in presence of the singularities in the Coulomb potentials present in $\hat{H}_e$ in the limit $r_{ij}\to 0$. Near the singular points we can write the expansion:

$$\Psi=\Psi_0\big(1+ar_{ij}+br_{ij}^2+cr_{ij}^3+\cdots\big) \tag{289}$$

for the pair of particles i and j. Then:

$$\frac{\partial\Psi}{\partial r_{ij}}=\Psi_0\left(a+2br_{ij}+3cr_{ij}^2+\cdots\right) \tag{290}$$

$$\frac{1}{\Psi_0}\frac{\partial\Psi}{\partial r_{ij}}=a+2br_{ij}+\cdots \tag{291}$$

$$\lim_{r_{ij}\to 0}\left(\frac{1}{\Psi_0}\frac{\partial\Psi}{\partial r_{ij}}\right)=a, \tag{292}$$

the *cusp condition* for the pair of particles i and j. a is a constant, given by $a=1/2$ if i, j are both electrons, $a=-Z_B$ if i is a nucleus (of charge $+Z_B$) and j an electron (Kato, 1957; Pack and Byers Brown, 1966).

In Table 7.7 we give some results (Kutzelnigg, 1985) showing the difference in convergence between the CI corrections to the hydrogen-like energy of ground state He($1s^2$) in the conventional case (upper part of Table 7.7), and in the case of a modified function satisfying the cusp condition (lower part of Table 7.7). The accurate value is $E=-2.903\,724\,377\,033\,E_h$ (Frankowski and Pekeris, 1966), improving upon the earlier result by Pekeris (1958) $E=-2.903\,724\,352\,E_h$. For the cusp-corrected function, $\Psi_0(1+\frac{1}{2}r_{12})$, the improvement in convergence is shown by the fact that the result for $l=2$ has an error 100 times less than that of the conventional expansion, while the result for $l=4$ has an error less than $1\mu E_h$ with just 156 functions, instead of about 8000.

7.10.2 Multiconfiguration SCF (MC-SCF)

MC-SCF is a multideterminant theory where the *orbitals* in the wavefunction are optimized simultaneously with the *coefficients* of the configurations (Wahl and Das, 1977). The orbitals of a few selected configurations (Optimized Valence Configurations, OVC) are usually adjusted iteratively until some kind of self-consistency is reached, together with the optimization of the linear coefficients. Even if rather complicated in its implementation, the method allows to predict a reasonable well depth in He_2 ($34.2\times 10^{-6}\,E_h$), and reasonably accurate atomization energies as Table 7.8 below shows for the ground states of a few diatomics (Wahl and Das, 1977).

Table 7.7.

Conventional and cusp-corrected CI expansions for ground state He($1s^2$)

l	Configurations	E/E_h	Error/10^{-3} E_h
(i) Conventional CI expansion			
–	Ψ_0	-2.75	153.724
0	spherical single excitations	$-2.861\,680^a$	42.044^b
0	$+s^2$	$-2.879\,027$	24.697
1	$+p^2$	$-2.900\,513$	3.211
2	$+d^2$	$-2.902\,765$	0.959
3	$+f^2$	$-2.903\,319$	0.405
4	$+g^2$	$-2.903\,517$	0.207
5	$+h^2$	$-2.903\,604$	0.120
$\sum \geq 6$		$-2.903\,723^c$	0.001
(ii) Cusp-corrected CI expansion			
–	$\Psi_0(1 + \frac{1}{2}r_{12})$	$-2.876\,582^d$	27.142
0	$+s^2$	$-2.902\,950$	0.774
1	$+p^2$	$-2.903\,678$	0.046
2	$+d^2$	$-2.903\,715$	0.009
3	$+f^2$	$-2.903\,722$	0.002
4	$+g^2$	$-2.903\,724^e$	0.000
Accurate		$-2.903\,724^f$	

[a] HF result. [b] Correlation energy. [c] 8000 interconfigurational functions. [d] Eckart-like accuracy. [e] 156 interconfigurational functions. [f] Pekeris (1958).

Table 7.8.

Atomization energies D_e (10^{-3} E_h) from optimized valence MC-SCF calculations for the ground states of some diatomics

Molecule	R_e/a_0	MC-SCF	Experiment
H_2	1.40	170.2	174.5
Li_2	5.089	36.4	37.9
O_2	2.31	125.0	186.7
F_2	–	61.4	61.7
CH	2.086	126.1	134.1
NH	–	123.9	124.9
OH	1.840	166.5	170.2
FH	1.733	227.1	225.9

Atomization energies are reproduced to better than 2 kcal mol^{-1}, near to chemical accuracy, with the exception of O_2 where the error is sensibly larger.

7.10.3 Explicitly Correlated Non-Orbital Methods

We include in this Section the classical work by James and Coolidge (1933) on the H_2 molecule, the more recent work on H_2 by Kołos and Wolniewicz (1964, 1965) on the ground state and by Kołos and Rychlewski (1990) on the excited triplet state, up to the recent extremely accurate H_2 ground state calculations by Wolniewicz (1993). An attempt to extend this approach to polyatomic molecules was made by Clementi and his group (Urdaneta et al., 1988) in terms of Cartesian Gaussians. These functions seem the appropriate basis for CI calculations including explicitly r_{12}, since in this case the many-electron integrals can be calculated efficiently in the polycentric case (Largo-Cabrerizo and Clementi, 1987; Largo-Cabrerizo et al., 1987).

(i) Inui wavefunction.

To illustrate the method it is convenient to start from the Inui (1938) work on H_2, where the un-normalized 2-electron wavefunction is expressed directly in terms of the spheroidal coordinates of the two electrons:

$$\Psi^{\pm} = \frac{1}{2\pi} \exp[-\delta(\mu_1 + \mu_2)]\big\{\exp[\gamma(\nu_1 - \nu_2)] \pm \exp[-\gamma(\nu_1 - \nu_2)]\big\}, \tag{293}$$

where δ, γ are optimizable scale factors, the $+$ sign refers to the ${}^1\Sigma_g^+$ ground state, the $-$ sign to the ${}^3\Sigma_u^+$ excited triplet state, and μ, ν the usual spheroidal coordinates:

$$\mu = \frac{r_A + r_B}{R}, \qquad \nu = \frac{r_A - r_B}{R}. \tag{294}$$

The Inui wavefunction (293) is a generalization of the well known Heitler–London wavefunction (Chapter 10) when the two basic one-centre AOs are replaced by two-centre Guillemin–Zener AOs (Problem 7.17). This function can be considered as the first (00000) term of an expansion in powers of the spheroidal coordinates of the two electrons and the interelectronic distance r_{12}, expansion which generalizes the classical wavefunction of James and Coolidge (JC) to include in the 2-electron function the dependence on $\cosh(\nu_1 - \nu_2)$ (${}^1\Sigma_g^+$ state) or $\sinh(\nu_1 - \nu_2)$ (${}^3\Sigma_u^+$ state). At variance with the original JC function, this dependence allows to describe correctly the dissociation of the ground state, and to represent in an adequate way the triplet state in the Van der Waals region.

(ii) James–Coolidge wavefunction.

The un-normalized JC function for H_2 is:

$$\Psi(1,2) = \sum_i [\Phi_i(1,2) + \Phi_i(2,1)]c_i, \tag{295}$$

where c_i are linear variational parameters, and the basis functions Φ_i are given by:

$$\Phi_i = \frac{1}{2\pi} \exp[-\delta(\mu_1 + \mu_2)]\mu_1^m \mu_2^n \nu_1^j \nu_2^k \rho^p = (mnjkp), \tag{296}$$

with an optimizable scale factor δ, $\rho = 2r_{12}/R$, $mnjkp$ positive or zero integers with $j + k =$ even for the ground state. This function includes explicitly the electron correlation in the wavefunction through the powers of r_{12}, but, even being for that time (1933) a great success for the accurate description of the bond energy in H_2 ($\Delta E = -0.173\,465\,E_h$ at $R = 1.4\,a_0$ with 13 basis functions and $\delta = 1$), cannot describe correctly the dissociation of the H_2 molecule because the cosh term is lacking, nor the excited triplet state because of the lacking of the sinh term.

(iii) Kołos–Wolniewicz wavefunction.

The basis functions Φ_i are now:

$$\begin{aligned}\Phi_i = \frac{1}{2\pi}\exp(-\delta\mu_1 - \overline{\delta}\mu_2)[&\exp(\gamma\nu_1 + \overline{\gamma}\nu_2)\\ &+ \exp(-\gamma\nu_1 - \overline{\gamma}\nu_2)]\mu_1^m\mu_2^n\nu_1^j\nu_2^k\rho^p, \end{aligned}\tag{297}$$

where δ, $\overline{\delta}$, γ, $\overline{\gamma}$ are optimizable scale factors. Putting $\overline{\delta} = \delta$, $\overline{\gamma} = -\gamma$, we obtain the exponential part of the Inui function, while for $\overline{\delta} = \delta$, $\gamma = \overline{\gamma} = 0$ we obtain the original basis of James–Coolidge. This function is the best possible for H_2 (when all parameters are variationally optimized), describes correctly the dissociation of H_2 and the excited triplet state, provided we take the – sign in the hyperbolic part and $j + k =$ odd in the powers of ν. Table 7.9 collects the results obtained during the years with this kind of wavefunctions for the ${}^1\Sigma_g^+$ ground state of H_2 at $R_e = 1.4\,a_0$, the minimum of the potential energy curve.

It should be noted that KSM (Kołos et al., 1986) used a 249-term expansion of the form (297) in the region $0.2 \le R \le 4.8\,a_0$ and a 72-term expansion containing 30 new terms in the region $4.8 \le R \le 12\,a_0$, resulting in a slight discontinuity near $R = 4.8\,a_0$. To avoid this

Table 7.9.

Improvements in the calculation of molecular energy for the H_2 (${}^1\Sigma_g^+$) ground state for James–Coolidge generalized wavefunctions

Authors	N	δ	$\overline{\delta}$	γ	$\overline{\gamma}$	E/E_h
HL/27[b]	1[a]	0.7	0.7	0.7	0.7	−1.105 47
WANG/28[c]	1[a]	0.819	0.819	0.819	0.819	−1.139 05
INUI/38[d]	1[a]	0.852	0.852	0.672	0.672	−1.149 15
JC/33[e]	13	1	1	0	0	−1.173 465
KW/64[f]	54	1	1	0	0	$-1.174\,469_9$
MSF/93[g]	118	0.852	0.852	0.672	0.672	−1.174 472
KW/65[h]	80	1.072	1.072	0	0	−1.174 474 4
BC/78[i]	249	1.117	1.117	0	0	−1.174 475 65
KSM/86[j]	249	1.311	1.135	0.670	0.033	−1.174 475 668
W/93[k]	279	1.311	1.135	0.670	0.033	−1.174 475 671

[a] Single term wavefunction, $m = n = j = k = p = 0$. [b] Heitler and London (1927). [c] Wang (1928). [d] Inui (1938). [e] James and Coolidge (1933). [f] Kołos and Wolniewicz (1964). [g] Magnasco et al. (1993). [h] Kołos and Wolniewicz (1965). [i] Bishop and Cheung (1978). [j] Kołos et al. (1986). [k] Wolniewicz (1993).

problem, Wolniewicz (1993) combined the two sets, diagonalizing the Hamiltonian for *all* internuclear distances in the space spanned by the *unique* set of $N = 279$ basis functions.

7.10.4 Second-Order Møller–Plesset (MP2) Theory

MP2 belongs to the family of the so called many-body perturbation theories (MBPT) which, starting from a HF wavefunction as a reference, take into consideration multiple excitations from the unperturbed occupied orbitals to the unoccupied (empty) ones (Szabo and Ostlund, 1989). In this way, energy corrections are obtained which directly account for some electron correlation. The theory is often expressed using second quantization and diagrammatic techniques (McWeeny, 1989) which are widely used in many-body physics. The theory can be extended to any order of perturbation theory, the low-order terms in the expansion having been first given by Møller and Plesset (1934). We shall briefly outline the second-order theory using the more familiar language of Slater dets.

MP2 is a second-order perturbative theory (Chapter 11) having $\hat{H} = \hat{H}_0 + V$, where:

(i) Unperturbed Hamiltonian

$$\hat{H}_0 = \sum_i \hat{F}_i \tag{298}$$

the sum of 1-electron Fock operators;

(ii) Unperturbed wavefunction

$$\Psi_0 = \Psi_0^{\mathrm{HF}} \tag{299}$$

the single determinant HF wavefunction;

(iii) Perturbation

$$V = \frac{1}{2}\sum_{i,j}{}' \frac{1}{r_{ij}} - \sum_i (J_i - \hat{K}_i) \tag{300}$$

the deviation of the instantaneous electron repulsion from its average value at the HF level. The energy in first order (Problem 7.18):

$$E_0 + E_1 = E_0^{\mathrm{HF}} \tag{301}$$

is nothing but the HF energy, so that the second-order correction to the energy in the MP theory, MP2, gives directly the correlation energy to this level of approximation. It can be shown (Problem 7.19) that a *singly excited* determinant has vanishing matrix element of the perturbation V with the Hartree–Fock Ψ_0:

$$\langle \Psi(\psi_i \to \psi_p)|V|\Psi_0^{\mathrm{HF}}\rangle = 0 \tag{302}$$

a relation which is known as Brillouin's theorem. In equation (302), $\Psi(\psi_i \to \psi_p)$ denotes a Slater det where the i-th occupied orbital is replaced by the p-th unoccupied one. E_2^{MP} is hence expressed in terms of *biexcitations* from Ψ_0 ($\psi_i \to \psi_p$, $\psi_j \to \psi_q$, with i, j occupied orbitals in Ψ_0, p, q unoccupied orbitals). By adding over all possible biexcitations, it is obtained:

$$
\begin{aligned}
E_2 &= \langle \Psi_1(\text{biexcitations})|V|\Psi_0^{\mathrm{HF}}\rangle \\
&= -\sum_{\kappa} \frac{|\langle \Psi_\kappa(\psi_i \to \psi_p, \psi_j \to \psi_q)|V|\Psi_0^{\mathrm{HF}}\rangle|^2}{\Delta E_\kappa} \\
&= -\frac{1}{4} \sum_{i,j}^{\mathrm{occ}} \sum_{p,q}^{\mathrm{unocc}} \frac{|\langle \psi_p \psi_q | \frac{1}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_q \psi_p | \frac{1}{r_{12}} | \psi_i \psi_j \rangle|^2}{(\varepsilon_p - \varepsilon_i) + (\varepsilon_q - \varepsilon_j)} \\
&= -\frac{1}{4} \sum_{i,j}^{\mathrm{occ}} \sum_{p,q}^{\mathrm{unocc}} \frac{|(\overset{1}{\psi_i \psi_p} \mid \overset{2}{\psi_j \psi_q}) - (\overset{1}{\psi_i \psi_q} \mid \overset{2}{\psi_j \psi_p})|^2}{(\varepsilon_p - \varepsilon_i) + (\varepsilon_q - \varepsilon_j)} < 0,
\end{aligned}
\tag{303}
$$

where $(\varepsilon_p - \varepsilon_i)$ and $(\varepsilon_q - \varepsilon_j)$ are (positive) orbital excitation energies, the first integral represents the Coulomb repulsion between the pair of transition densities $\{\psi_i(\mathbf{x}_1)\psi_p^*(\mathbf{x}_1)\}$ and $\{\psi_j(\mathbf{x}_2)\psi_q^*(\mathbf{x}_2)\}$, the second is the exchange integral. In the last row we used for the 2-electron integrals the charge density notation (Chapter 13). In expression (303) all summations are unrestricted. Table 7.10 gives some SCF and MP2 results for molecular energy and other observable properties for ground state H_2O (Bartlett et al., 1979) obtained using the $(5s\,4p\,2d|3s\,1p)$ 39-function STO basis set of Rosenberg and Shavitt (1975). The nearly HF molecular energy is seen to be $2.64 \times 10^{-3}\,E_h$ higher than the best HF calculation to date for H_2O (Lazzeretti, 2004), $E = -76.066\,87\,E_h$, obtained with the GTO $[13s\,10p\,5d\,2f|8s\,4p\,1d]$ contracted basis set, and which is very close to the estimated HF limit of $E = -76.067\,5\,E_h$. It is apparent from Table 7.10 the great improvement of MP2 results for the properties, but not for the correlation energy, which is only 76% of the es-

Table 7.10.

SCF and MP2 results[a] for molecular energy and other observables for ground state H_2O ($^1A_1$)

Property	SCF	MP2	Exact
E/E_h	−76.06423	−0.2818	−0.370
R_e/a_0	1.776	1.811	1.809
$2\theta_e/^{\circ}$	106.1	104.4	104.5
$f_{rr}/10^5$ dyne cm^{-1}	9.79	8.55	8.45
$f_{\theta\theta}$	0.88	0.78	0.76
μ/ea_0	0.785	(0.750)[b]	0.728

[a] Bartlett et al. (1979). [b] Rosenberg et al. (1976) (SD).

timated accurate value of the last column. Higher order corrections (MP3 $= -0.2850\,E_h$, MP4 $= -0.2882\,E_h$) improve little upon this result. For this reason, the MP method was improved in recent years by the Kutzelnigg group, to include explicitly the r_{12}-term in the wavefunction, as we shall see in the next Section.

7.10.5 MP2-R12 Method

For closed-shell states of atoms and molecules, Kutzelnigg and Klopper (KK, 1991) derived formulae which include linear r_{12}-dependent terms in the MP2 or MP3 (third-order MP theory) methods. Two variants of the method were proposed, (i) a standard approximation B which ensures that in the atomic case the error due to the truncation of the basis set at some angular quantum number L goes as $\propto L^{-7}$, instead of L^{-1} as in conventional calculations without r_{12} terms (see the final considerations of Section 7.10.1 and Table 7.7), and (ii) another standard approximation A which has an error as $\propto L^{-5}$, but is simpler and better balanced for basis sets of moderate size. The explicit expressions for Møller–Plesset perturbation theory of second and third order with linear r_{12} terms, MP2-R12 and MP3-R12 respectively, are given explicitly in the two standard approximations.

It must be noted that in the modified theory, in addition to traditional and new 2-electron integrals (Chapter 13), new 3-electron and 4-electron integrals arise, like:

$$\langle\varphi(1,2,3)|r_{12}g_{13}|\varphi(1,2,3)\rangle \quad g_{13}=\frac{1}{r_{13}} \tag{304}$$

$$\langle\varphi(1,2,3)|r_{12}g_{13}r_{23}|\varphi(1,2,3)\rangle \tag{305}$$

$$\langle\varphi(1,2,3,4)|r_{12}g_{23}r_{34}|\varphi(1,2,3,4)\rangle. \tag{306}$$

Closed formulae for these integrals over STOs are available for the atomic case (Fromm and Hill, 1987; Remiddi, 1991), but are exceedingly complicated and their evaluation is very time consuming. The situation is even worst for molecules, where polycentric integrals occur. To get out of these bottlenecks, KK suggested that, making the hypothesis of "completeness insertion":

$$\begin{aligned}
&\langle\varphi_1(1)\varphi_2(2)\varphi_3(3)|r_{12}g_{13}|\varphi_1(1)\varphi_2(2)\varphi_3(3)\rangle\\
&\quad=\sum_{pqr}\langle\varphi_1(1)\varphi_2(2)\varphi_3(3)|r_{12}|\varphi_p(1)\varphi_q(2)\varphi_r(3)\rangle\\
&\qquad\times\langle\varphi_p(1)\varphi_q(2)\varphi_r(3)|g_{13}|\varphi_1(1)\varphi_2(2)\varphi_3(3)\rangle\\
&\quad=\sum_{pqr}\langle\varphi_1(1)\varphi_2(2)|r_{12}|\varphi_p(1)\varphi_q(2)\rangle\delta_{3r}\\
&\qquad\times\langle\varphi_p(1)\varphi_r(3)|g_{13}|\varphi_1(1)\varphi_3(3)\rangle\delta_{2q}\\
&\quad=\sum_{p}\langle\varphi_1(1)\varphi_2(2)|r_{12}|\varphi_p(1)\varphi_2(2)\rangle\langle\varphi_p(1)\varphi_3(3)|g_{13}|\varphi_1(1)\varphi_3(3)\rangle,
\end{aligned} \tag{307}$$

Table 7.11.

SCF, MP2, MP2-R12 results $(E_h)^a$ for small molecules of the first row at the experimental geometry

Molecule	SCF	MP2	MP2-R12	Exact
H_2		−0.0334	−0.0342	−0.0408
CH_4	−40.21568	−0.23790	−0.27182	
NH_3	−56.22285	−0.28000	−0.32065	
H_2O	−76.06580	−0.3304	−0.36050	−0.370
HF	−100.07022	−0.33975	−0.37884	
Ne	−128.54696	−0.35075	−0.38855	

[a] GTO basis sets:
H_2: $(14s\,8p\,4d\,1f) \rightarrow [9s\,8p\,4d\,1f]$.
CH_4, NH_3: $(12s\,7p\,3d\,1f|7s\,2p) \rightarrow [8s\,5p\,3d\,1f|5s\,2p]$.
H_2O: $(12s\,7p\,4d\,2f|10s\,3p\,1d) \rightarrow [9s\,7p\,4d\,2f|7s\,3p\,1d]$.
HF: $[14s\,9p\,3d\,1f|10s\,3p\,1d]$.
Ne: $[16s\,10p\,7d\,3f]$.

the difficult 3-electron integral can be reduced to an infinite series of products between more tractable 2-electron integrals. However, this introduces some errors, especially for incomplete (unsaturated) basis sets. The MP2-R12 method with STO or GTO bases was applied (Termath et al., 1991) to the ground state of the atomic closed-shell systems He, Be, Ne, Mg, Ar, Ca, Cu^+, Zn^{+2}, Kr. STO bases with $l \leq 5$ give errors not greater than 1% of the estimated limits, while about the same error is obtained with GTO bases with $l \leq 3$. The MP2-R12 method with GTO bases was applied (Klopper and Kutzelnigg, 1991) to the ground state of the closed-shell molecules H_2, LiH, HF, H_2O, NH_3, CH_4, Be_2, N_2, F_2, C_2H_2 at their equilibrium geometries. In all cases, the correlation energies are now evaluated within few % of the limiting values expected for these systems. For He_2 a localized representation gives good results for the dispersion interaction at two internuclear distances. At the minimum of the potential well ($R = 5.6\,a_0$) the SCF repulsive energy ($+29.2 \times 10^{-6}\,E_h$) is corrected by MP2 to $-17.7 \times 10^{-6}\,E_h$, and to the very accurate value of $-33.9 \times 10^{-6}\,E_h$ by MP2-R12 in the standard approximation B. The potential curve of Be_2 vs R is also significantly improved by MP2-R12 as compared to conventional MP2. Table 7.11 illustrates these results for H_2 and for the ground state of the ten-electron molecules of the first row, CH_4, NH_3, H_2O, HF, and the united atom Ne. The improvement due to the introduction of the r_{12} term into MP2 is evident from Table 7.11. Where comparison with exact or accurate estimated values is possible, we see that over 97% of the correlation energy is accounted for H_2O, while for H_2 (84%) there is about a 2% improvement over MP2.

7.10.6 CC-R12 Method

The explicitly correlated coupled cluster method (CC-R12) was recently developed by Noga and Kutzelnigg (1994). It belongs to the family of the so called R12 methods we have seen in the preceding Sections and, in its most evolute form to date, the CCSD(T)-

Table 7.12.

Comparison between atomization energies D_e ($10^{-3}\ E_h$) obtained from different correlated-R12 calculations in the $(s\,p\,d\,f\,g\,h\,|\,s\,p\,d\,f)$ GTO basis and experimental results

Molecule	SCF	MP2-R12	CCSD(T)-R12	Experiment
NH_3	324.1	454.5	475.0	475.3
H_2O	255.1	378.6	371.5	371.4
HF	159.4	233.1	226.0	225.9
N_2	191.2	385.2	364.3	364.2
CO	289.7	435.6	415.1	413.9
F_2	−49.3	69.4	61.8	62.2

R12 method, gives values of the atomization energies for small molecules which are almost in perfect agreement with experiment. In CC-R12 theory, we start from the single determinant HF reference function Ψ_0^{HF} and construct the *exponential ansatz* for the variational wavefunction:

$$\Psi = \exp(\hat{S})\Psi_0^{\mathrm{HF}}. \tag{308}$$

In conventional CC theories, $\hat{S} \equiv \hat{T}$ is usually a *cluster excitation* operator which creates substituted (excited) determinants by replacing the occupied MOs by unoccupied (virtual or empty) ones. In CC-R12 theory, $\hat{S}$ not only includes $\hat{T}$, but also what we call the r_{12}-contribution to the double-excitation cluster operator, i.e. $\hat{S} = \hat{T} + \hat{R}$. The operator $\hat{R}_{ij}^{kl}$ creates unconventionally substituted determinants in which a *pair* of occ orbitals i, j is replaced by another pair of occ orbitals k, l multiplied by the interelectronic distance r_{12}. We saw in the preceding Section that, if the 1-electron basis set is *saturated* for the lower angular momenta (l), the difficult many-electron integrals, which would otherwise enter the working equations, either disappear or can be neglected. The theory is developed using diagrammatic techniques. The theory was applied (Tunega et al., 1997; Tunega and Noga, 1998) to the calculation of accurate values of static polarizabilities (second-order properties, see Chapter 11) for atomic Be(^1S) and molecular LiH($^1\Sigma^+$). Table 7.12 gives a comparison of SCF, MP2-R12 and CCSD(T)-R12 calculated values (Noga et al., 2001) with experimental results for the atomization energies of a few simple molecules of the first row. The calculations were carried at the highly accurate geometries optimized at the CCSD(T) level. The last column gives the experimental equilibrium nonrelativistic atomization energies at $T = 0°$ K. It is seen that the CCSD(T)-R12 values are in perfect agreement with experiment. All values are referred to the bottom of the potential energy surface.

The performance of the explicitly correlated coupled cluster method was examined in detail by Noga, Tunega, Klopper and Kutzelnigg (NTKK) (Noga et al., 1995) for the four electron systems Be, Li$^-$, LiH, and, more recently, by Bukowski, Jeziorski and Szalewicz (BJS) (Bukowski et al., 1999) for the two- and four-electron systems He, Li$^+$, H_2, Be, Li$^-$, LiH. Table 7.13 gives some results for the atomic Be(^1S) and the molecular

Table 7.13.

Benchmark results[a] for the correlation energies (E_h) of prototype atomic and molecular four-electron systems

	Be(^1S)	LiH($^1\Sigma^+$)
SCF	−14.573 012[b]	−7.987 346[b]
(i) Conventional		
MP2	−0.074 292	−0.071 006
MP3	−0.084 405	−0.079 234
MP4	−0.088 888	−0.081 353
CCSD	−0.092 540	−0.082 035
CCSD(T)	−0.093 190	−0.082 199
(ii) R12		
MP2	−0.076 248 (−0.076 358)[c]	−0.072 869 (−0.072 890)[c]
MP3	−0.085 292 (−0.085 225)	−0.079 989 (−0.079 990)
MP4	−0.089 998 (−0.089 801)	−0.082 307 (−0.082 232)
CCSD	−0.093 661 (−0.093 665)	−0.082 980 (−0.082 990)
CCSD(T)	−0.094 293	−0.083 143

[a] GTO basis sets:
Be: $16s\,10p\,6d\,5f\,4g$; Li: $11s\,8p\,6d\,5f$; H: $9s\,8p\,6d\,5f$.
[b] Noga et al. (1995). [c] Bukowski et al. (1999).

LiH($^1\Sigma^+$, $R = 3.015\,a_0$) cases taken from NTKK and BJS. The values by BJS (in parenthesis) are believed to be the most accurate available to date.

7.10.7 A Short Outline of Second Quantization

It seems the time for giving here a short outline of second quantization techniques, for more details the reader being referred to elsewhere (Longuet-Higgins, 1966; McWeeny, 1989).

For an independent particle model in which spin-orbitals ψ_i, ψ_j, $\cdots \psi_p$ are occupied by electrons, a many-electron wavefunction $\Psi_{ij\cdots p}(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N)$ is the Schroedinger representation of a *state vector* or *ket*, denoted by $|i\,j \cdots p\rangle$, where the labels indicate the spin-orbitals to which the electrons are assigned. The wavefunction itself is a function of the electronic variables, and there is a one-to-one correspondence between state vector and wavefunction:

$$|i\,j \cdots p\rangle \longleftrightarrow \Psi_{ij\cdots p}(\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N). \tag{309}$$

Instead of spin-orbital labels, we could alternatively give the *occupation numbers* (0, 1) of the whole ordered set of available spin-orbitals. For example, $|011010\cdots\rangle$ would stand for the 3-electron state with electrons in ψ_2, ψ_3 and ψ_5, the corresponding Schroedinger wavefunction being:

$$\Psi_{2,3,5}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \|\psi_2(\mathbf{x}_1)\, \psi_3(\mathbf{x}_2)\psi_5(\mathbf{x}_3)\|. \tag{310}$$

When a state vector is represented by a linear combination of such kets, we speak of the *occupation number representation*: the corresponding vector space, whose basis vectors comprise all possible kets, corresponding to *any* number of electrons, is called the Fock space. The Fock space, thus, focuses attention on the state vectors themselves, rather than on the wavefunctions that represent them, and extends the space to include state vectors with any number of electrons. The approach originated in field theory, where the "particles" are photons that are created or annihilated in emission or absorption processes, and is largely used in solid state theoretical physics. The use of Fock space is commonly described as the method of *second quantization*.

Further details can be found in McWeeny (1989; see also Longuet-Higgins, 1966), where expressions are given for the matrix elements of the operators $\hat{h}$ and g in terms of *creation* and *annihilation* operators, $a_\kappa^\dagger = a_\kappa^+$ and $a_\kappa = a_\kappa^-$, satisfying the anticommutation relations:

$$a_\kappa^- a_\lambda^+ + a_\lambda^- a_\kappa^+ = \delta_{\kappa\lambda}. \tag{311}$$

The expectation value of the electronic energy is:

$$E_e = \sum_{r,s} \langle a_r^+ a_s^- \rangle h_{rs} + \frac{1}{2} \sum_{r,s,t,u} \langle a_r^+ a_s^+ a_u^- a_t^- \rangle (\overset{1}{tr} \mid \overset{2}{us}) \tag{312}$$

whatever the number of electrons.

7.10.8 Density Functional Theory (DFT)

DFT is based on two theorems, proved by Hohenberg and Kohn (1964), and on a computational scheme proposed by Kohn and Sham (1965).

(i) The first theorem states that the electronic structure of the ground state of a system (Ψ_0 and all derived physical observables, among which E_0) is uniquely determined by the ground state electronic density, $\rho_0(\mathbf{r})$.

(ii) The second theorem states a variational criterion for the determination of ρ_0 and E_0 starting from an arbitrary function $\rho(\mathbf{r})$ constrained by the normalization condition:

$$\int d\mathbf{r}\, \rho(\mathbf{r}) = N \tag{313}$$

$$E[\rho] \geq E[\rho_0], \quad E[\rho_0] = E_0 \tag{314}$$

where N is the total number of the electrons of the system. E_0 can therefore be found by minimizing with the method of Lagrange multipliers the functional

$$E[\rho] = V_{en} + J + E_{kxc} + V_{nn} \tag{315}$$

with respect to arbitrary infinitesimal changes in the form of the function $\rho(\mathbf{r})$.

In this expression, the different functionals are:

$$V_{en}[\rho] = \int d\mathbf{r}\, V(\mathbf{r})\rho(\mathbf{r}) \tag{316}$$

the average potential energy of ρ in the field of the nuclei, with:

$$V(\mathbf{r}) = -\sum_{\alpha} \frac{Z_\alpha}{|\mathbf{r}-\mathbf{r}_\alpha|}; \tag{317}$$

$$J[\rho] = \frac{1}{2}\int d\mathbf{r}\, J(\mathbf{r})\rho(\mathbf{r}) = \frac{1}{2}\iint d\mathbf{r}\, d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r}) \tag{318}$$

the Coulomb interaction of the ρ with itself;

$$E_{kxc}[\rho] = \int d\mathbf{r}\, G(\mathbf{r};[\rho]) \tag{319}$$

a term which describes the kinetic (k)–exchange (x)–correlation (c) energy of the ρ in terms of $G(\mathbf{r})$, a universal functional of the ρ. The analytic form of $G(\mathbf{r})$ is *not* known, but it can be given different approximations (e.g. LDA, B-LYP, etc.);

$$V_{nn} = \frac{1}{2}\sum_{\alpha}\sum_{\beta} \frac{Z_\alpha Z_\beta}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} \tag{320}$$

the nuclear repulsion.

We note that the different potentials occurring in the previous formulae are nothing but the *functional derivatives* of the different terms making $E[\rho]$ with respect to the ρ itself:

$$\frac{\delta V_{en}[\rho]}{\delta\rho(\mathbf{r})} = V(\mathbf{r}) \tag{321}$$

$$\frac{\delta J[\rho]}{\delta\rho(\mathbf{r})} = J(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{322}$$

$$\frac{\delta T[\rho]}{\delta\rho(\mathbf{r})} = -\frac{1}{2}\nabla^2 \tag{323}$$

the kinetic energy operator. As an example, from (318):

$$\delta J[\rho] = \frac{1}{2}\int d\mathbf{r}\, J(\mathbf{r})\delta\rho(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}\, \delta J(\mathbf{r})\rho(\mathbf{r}) = \int d\mathbf{r}\, J(\mathbf{r})\delta\rho(\mathbf{r}) \tag{324}$$

since the two terms in (324) are equal (Problem 7.10). Then equation (322) follows.

The constrained variational problem for the energy is:

$$\delta E[\rho] - \lambda\delta\left[\int d\mathbf{r}\,\rho(\mathbf{r}) - N\right] = 0 \tag{325}$$

$$\delta E[\rho] - \lambda\int d\mathbf{r}\,\delta\rho(\mathbf{r}) = 0, \tag{326}$$

so that the Euler–Lagrange parameter will be:

$$\lambda = \frac{\delta E[\rho]}{\delta\rho(\mathbf{r})}. \tag{327}$$

For the infinitesimal variation of the energy functional (315) we have:

$$\begin{aligned} \delta E[\rho] &= \delta V_{en}[\rho] + \delta J[\rho] + \delta T[\rho] + \delta V_{xc}[\rho] \\ &= \int d\mathbf{r}\,V(\mathbf{r})\delta\rho(\mathbf{r}) + \int d\mathbf{r}\,J(\mathbf{r})\delta\rho(\mathbf{r}) \\ &\quad + \int d\mathbf{r}\left[-\frac{1}{2}\nabla^2\delta\rho(\mathbf{r};\mathbf{r}')\right]_{\mathbf{r}'=\mathbf{r}} + \int d\mathbf{r}\,V_{xc}(\mathbf{r})\delta\rho(\mathbf{r}), \end{aligned} \tag{328}$$

so that the functional derivative will be:

$$\frac{\delta E[\rho]}{\delta\rho(\mathbf{r})} = -\frac{1}{2}\nabla^2 + V(\mathbf{r}) + J(\mathbf{r}) + V_{xc}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r}), \tag{329}$$

where the effective potential at **r**:

$$V_{\text{eff}}(\mathbf{r}) = V(\mathbf{r}) + J(\mathbf{r}) + V_{xc}(\mathbf{r}), \tag{330}$$

is the sum of the electron-nuclear attraction potential, plus the Coulomb potential of the electrons of density ρ, plus the exchange-correlation potential for all the electrons. It is seen that the effective potential (330) differs from the usual Hartree–Fock potential by the still undetermined *correlation potential* in V_{xc}.

(iii) The Kohn–Sham method is based on the two previous theorems but allows us to calculate explicitly the most important part of the kinetic energy. It consists in solving the parallel problem for a system of N pseudo-independent electrons having the same electron density of that of the actual system:

$$\rho(\mathbf{r}) = 2\sum_i |\phi_i(\mathbf{r})|^2, \tag{331}$$

where the Kohn–Sham (KS) orbitals $\phi_i(\mathbf{r})$ satisfy the so called KS equations:

$$\hat{h}^{\text{KS}}(\mathbf{r})\,\phi_i(\mathbf{r}) = \varepsilon_i\,\phi_i(\mathbf{r}) \quad i = 1, 2, \cdots n, \tag{332}$$

where:

$$\hat{h}^{\mathrm{KS}}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V^{\mathrm{KS}}(\mathbf{r}) \tag{333}$$

is the 1-electron KS-hamiltonian, and:

$$V^{\mathrm{KS}}(\mathbf{r}) = V(\mathbf{r}) + J(\mathbf{r}) + V_{xc}(\mathbf{r}) \tag{330}$$

the KS effective potential (330). The Kohn–Sham equations are solved iteratively until self-consistency in a way similar to HF.

We can make the following considerations on the KS-DFT.

1. The KS scheme gives directly E_0 and ρ_0 exact for the ground state. The Ψ^{KS} built as the determinant of doubly occupied KS ϕ_i has no whatever relation with the true Ψ_0, except that it gives the *same* ρ_0.
2. The crucial problem in the KS scheme is the definition of the exchange-correlation potential $V_{xc}(\mathbf{r})$:

$$V_{xc}(\mathbf{r}) = -\frac{1}{2}\int d\mathbf{r}' \frac{\rho(\mathbf{r};\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\hat{P}_{\mathbf{r}\mathbf{r}'} + V_c(\mathbf{r}). \tag{334}$$

   Even if V_{xc} cannot be exactly defined, it can be given semiempirical or ab-initio evaluations. At variance with what occurs in the conventional quantum chemical methods, $E_{xc}[\rho]$ cannot be improved in a systematic way. Usually, in DFT we start from a *model* for which an exact solution exists: the uniform electron gas or local density approximation (LDA). The results are:

$$T[\rho] = C_F \int d\mathbf{r}\,\rho(\mathbf{r})^{5/3}, \quad C_F = \frac{3}{10}(3\pi^2)^{2/3} \tag{335}$$

$$E_x[\rho] = -C_x \int d\mathbf{r}\,\rho(\mathbf{r})^{4/3}, \quad C_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}. \tag{336}$$

   $E_x[\rho]$ is given by an expression due to Vosko et al. (1980), based on a two-point Padé approximant (Baker, 1975) in the RPA approximation.
3. One of the difficulties of DFT is that the integrals which arise in the KS equations cannot be evaluated by analytic means because of the fractional powers of the density. We must therefore resort to numerical quadrature techniques.
4. Given a regular density, any functional of ρ is a function of ρ and its derivatives. The LDA approximation can then be seen as the first term in a Taylor expansion involving the gradients of the exact functionals. Therefore, $V_{xc}[\rho]$ will depend on $\rho(\mathbf{r})$ and on $|\nabla\rho(\mathbf{r})|$. This allows us to go beyond the LDA approximation, as with the B-LYP (Becke–Lee–Yang–Parr) correlation potential.
5. The LDA approximation is not adequate for making predictions useful in Computational Chemistry, being not better than ordinary SCF. To go further, we must include

functionals involving $\nabla\rho(\mathbf{r})$. The average cost of a DFT calculation goes as m^4 (same as SCF), compared to m^6 of a CI-SD calculation and m^7 of a MP4 (m is the number of basis functions). With the best functionals to date it is possible to obtain bond lengths within 0.01 Å for diatomic molecules of the first-row atoms, and atomization energies within 3 kcal mol^{-1} (SCF 78, LDA 40, MP2 7, CC-R12 0.25 kcal mol^{-1}).

7.11 PROBLEMS 7

7.1. Show that the Li ground state is a doublet S.

Answer:

$$\hat{S}^2\|1s\overline{1s}2s\| = \frac{1}{2}\left(\frac{1}{2}+1\right)\|1s\overline{1s}2s\|. \quad S = M_S = \frac{1}{2}.$$

Hint:

Use Dirac's formula for $N=3$:

$$\hat{S}^2 = \frac{3}{4}\hat{I} + \hat{P}_{12} + \hat{P}_{13} + \hat{P}_{23}\,.$$

7.2. Show that the Be ground state is a singlet S.

Answer:

$$\hat{S}^2\|1s\overline{1s}2s\overline{2s}\| = 0(0+1)\|1s\overline{1s}2s\overline{2s}\| \quad S = M_S = 0.$$

Hint:

Use Dirac's formula for $N=4$:

$$\hat{S}^2 = \hat{P}_{12} + \hat{P}_{13} + \hat{P}_{14} + \hat{P}_{23} + \hat{P}_{24} + \hat{P}_{34}.$$

7.3. Find the electron density and the spin density for the ground state of the H_2 molecule described by the MO wavefunction in which the bonding $\sigma_g = \frac{a+b}{\sqrt{2+2S}}$ MO is doubly occupied by electrons with opposed spin.

Answer:

$$P(\mathbf{r}_1;\mathbf{r}_1) = 2\sigma_g(\mathbf{r}_1)\,\sigma_g^*(\mathbf{r}_1)$$

$$Q(\mathbf{r}_1;\mathbf{r}_1) = 0.$$

Hint:

Follow the definitions of Section 7.3.2.

7.4. Find the electron density and the spin densities for the triplet excited state of the H_2 molecule described by the MO wavefunction in which the bonding $\sigma_g = \frac{a+b}{\sqrt{2+2S}}$ and the antibonding $\sigma_u = \frac{b-a}{\sqrt{2-2S}}$ MOs are singly occupied by electrons with either spin.

Answer:

$$\begin{aligned}
&S = 1, \qquad M_S = 1\\
&P(\mathbf{r}_1;\mathbf{r}_1) = Q(\mathbf{r}_1;\mathbf{r}_1) = \sigma_g^2(\mathbf{r}_1) + \sigma_u^2(\mathbf{r}_1)\\
&S = 1, \qquad M_S = 0\\
&P(\mathbf{r}_1;\mathbf{r}_1) = \sigma_g^2(\mathbf{r}_1) + \sigma_u^2(\mathbf{r}_1), \qquad Q(\mathbf{r}_1;\mathbf{r}_1) = 0\\
&S = 1, \qquad M_S = -1\\
&P(\mathbf{r}_1;\mathbf{r}_1) = \sigma_g^2(\mathbf{r}_1) + \sigma_u^2(\mathbf{r}_1), \qquad Q(\mathbf{r}_1;\mathbf{r}_1) = -P(\mathbf{r}_1;\mathbf{r}_1).
\end{aligned}$$

Hint:
Same as for Problem 7.3.

7.5. Derive the Slater rules for the matrix element of the 2-electron operator.

Answer:
Equations (110)–(116) of the main text.
Hint:
Use the equivalent definition of the normalized N-electron Slater det as:

$$\|\psi_1\psi_2\cdots\psi_i\cdots\psi_j\cdots\psi_N\| = \frac{1}{\sqrt{N!}}\sum_P(-1)^p\hat{P}\psi_1\psi_2\cdots\psi_i\cdots\psi_j\cdots\psi_N,$$

where $\hat{P}$ is the permutation operator (Section 7.2.2) and p the parity of the permutation, and the fact that the spin-orbitals are assumed to be orthonormal.

7.6. Derive the 1- and 2-electron density matrices for the normalized many-electron wavefunction constructed as a single determinant of orthonormal spin-orbitals $\{\psi_i(\mathbf{x})\}$:

$$\begin{aligned}
&\Psi = \|\psi_1\psi_2\cdots\psi_N\|\\
&\langle\psi_i|\psi_j\rangle = \delta_{ij}, \quad i,j = 1,2,\cdots N.
\end{aligned}$$

Answer:
Lennard-Jones (1931) found that, in this case:

$$\rho_1(\mathbf{x}_1;\mathbf{x}_1') = \rho(\mathbf{x}_1;\mathbf{x}_1')$$

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \begin{vmatrix} \rho(\mathbf{x}_1; \mathbf{x}'_1) & \rho(\mathbf{x}_1; \mathbf{x}'_2) \\ \rho(\mathbf{x}_2; \mathbf{x}'_1) & \rho(\mathbf{x}_2; \mathbf{x}'_2) \end{vmatrix},$$

where:

$$\rho(\mathbf{x}_1; \mathbf{x}'_1) = \sum_{i=1}^{N} \psi_i(\mathbf{x}_1)\psi_i^*(\mathbf{x}'_1)$$

is the Fock–Dirac density matrix.
Hint:
Use the definitions (29) and the equivalent of (62) for the density matrices, and the Cauchy expansion of the Ψ-determinant according to its (N, N)-element.

7.7. Derive the properties of the Fock–Dirac density matrix $\rho(\mathbf{x}; \mathbf{x}') = \sum_i \psi_i(\mathbf{x})\, \psi_i^*(\mathbf{x}')$ represented by a basis of N orthonormal SOs $\{\psi_i(\mathbf{x})\}$.

Answer:

(i) Invariance of ρ against the unitary transformation $\{U_{ji}\}$ among its SOs, equations (122) and (123) of the main text.
(ii) Projection operator properties of ρ:

$$\operatorname{tr} \rho = N \quad \text{conservation}$$
$$\rho^2 = \rho \quad \text{idempotency}$$

equations (124)–(126) of the main text.

Hint:
Use definition (121), and the orthogonality and normalization properties of the SO basis.

7.8. Give an elementary derivation of the method of Lagrange multipliers for a function $f(x_1, x_2, \cdots x_N)$ of N variables subject to m constraints $\varphi_r(x_1, x_2, \cdots x_N) = 0$.

Answer:
The system of $N + m$ equations determining the extremum points of the function f and the m Lagrange multipliers λ_r is:

$$\begin{cases} \dfrac{\partial f}{\partial x_i} - \displaystyle\sum_r \lambda_r \dfrac{\partial \varphi_r}{\partial x_i} = 0 & i = 1, 2, \cdots N \\ \varphi_r(x_1, x_2, \cdots x_N) = 0 & r = 1, 2, \cdots m. \end{cases}$$

Hint:
It is convenient to subtract from the original function f the m constraints, each one multiplied by a suitable Lagrange multiplier λ, and to write then the extremum conditions for the resulting unconstrained N-variable function (Problem 7.9).

7.9. Show that the unconstrained variation of the energy functional $\varepsilon = HM^{-1}$ is fully equivalent to the result obtained by the method of Lagrange multipliers.

Answer:

$$\delta H - \varepsilon \delta M = 0.$$

Hint:

Take an infinitesimal variation of the energy functional ε taking into account the normalization condition $M = 1$.

7.10. Show the identity between equations (139) and (140) of the main text.

Answer:

Limiting ourselves to the Coulomb integral J, we have:

$$\sum_i \langle \delta\psi_i | J_1 | \psi_i \rangle + \sum_i \langle \psi_i | J_1 | \delta\psi_i \rangle = \sum_i \langle \psi_i | \delta J_1 | \psi_i \rangle.$$

Hint:

Use the definitions (121) and (130) of ρ and J, and interchange in the integrals summation indices i, i' and electron labels $1, 2$.

7.11. Eliminate spin from the Fock operator for closed shells.

Answer:

$$\hat{F}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 + V_1 + 2J(\mathbf{r}_1) - \hat{K}(\mathbf{r}_1),$$

where:

$$J(\mathbf{r}_1) = \int d\mathbf{x}_2 \frac{R(\mathbf{r}_2; \mathbf{r}_2)}{r_{12}},$$

$$\hat{K}(\mathbf{r}_1) = \int d\mathbf{x}_2 \frac{R(\mathbf{r}_1; \mathbf{r}_2)}{r_{12}} \hat{P}_{\mathbf{r}_1\mathbf{r}_2}$$

are *spinless* Coulomb and exchange potentials, and $R(\mathbf{r}_1; \mathbf{r}_2)$ the spinless density matrix for closed shells.

Hint:

Make $\hat{F}(\mathbf{x}_1) = \hat{F}(\mathbf{r}_1 s_1)$ act on the spin-orbital function $\phi_i(\mathbf{r}_1)\alpha(s_1)$, say, and integrate over the spin variable of electron 2.

7.12. Find the projector properties of the density matrix **R** over the non-orthogonal AO basis $\boldsymbol{\chi}$ with metric **M**.

Answer:

$$\mathbf{RMR} = \mathbf{R} \quad \text{idempotency}$$

$$\operatorname{tr}\mathbf{RM} = n \quad \text{conservation,}$$

where n is the number of the doubly occupied MOs.

Hint:
Use the properties of the density matrix $R(\mathbf{r};\mathbf{r}')$ over the orthogonal MOs and the LCAO expression for the latter.

7.13. Transform the Pitzer and Merrifield minimum basis STO MO coefficients for ground state H_2O to a set where $\langle k|s\rangle = 0$.

Answer:

A_1	k	s	z	h_1	h_2
$1a_1$	1.000 42	0.018 28	0.003 38	−0.004 31	−0.004 31
$2a_1$	−0.029 94	0.821 60	0.138 67	0.140 58	0.140 58
$3a_1$	−0.031 11	−0.541 20	0.779 63	0.287 41	0.287 41
$4a_1$	0.084 28	0.844 20	0.700 74	−0.745 36	−0.745 36

B_2	y	h_1	h_2
$1b_2$	0.582 21	0.514 05	−0.514 05
$2b_2$	0.991 62	−0.890 44	0.890 44

Hint:
Schmidt orthogonalize the original s' STO to the inner shell AO k'.

7.14. Check the projector properties of the density matrix **R** over the modified AO basis of Problem 7.13 for the Pitzer and Merrifield MO calculation on ground state H_2O.

Answer:

$$\mathbf{RMR} = \begin{pmatrix} 1.002\,71 & 0.010\,53 & -0.024\,99 & 0 & 0 & -0.017\,46 & -0.017\,46 \\ 0.010\,53 & 0.968\,22 & -0.307\,84 & 0 & 0 & -0.040\,07 & -0.040\,07 \\ -0.024\,98 & -0.307\,84 & 0.627\,01 & 0 & 0 & 0.243\,54 & 0.243\,54 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.338\,98 & 0.299\,33 & -0.299\,33 \\ -0.017\,46 & -0.040\,07 & 0.243\,54 & 0 & 0.299\,33 & 0.366\,69 & -0.161\,93 \\ -0.017\,46 & -0.040\,07 & 0.243\,54 & 0 & -0.299\,33 & -0.161\,92 & 0.366\,69 \end{pmatrix}$$

compared to the directly calculated **R** matrix:

$$\mathbf{R} = \begin{pmatrix} 1.002\,70 & 0.010\,53 & -0.025\,00 & 0 & 0 & -0.017\,46 & -0.017\,46 \\ 0.010\,53 & 0.968\,26 & -0.307\,90 & 0 & 0 & -0.040\,10 & -0.040\,10 \\ -0.025\,00 & -0.307\,90 & 0.627\,04 & 0 & 0 & 0.243\,54 & 0.243\,54 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.338\,96 & 0.299\,31 & -0.299\,31 \\ -0.017\,46 & -0.040\,10 & 0.243\,54 & 0 & 0.299\,31 & 0.366\,68 & -0.161\,91 \\ -0.017\,46 & -0.040\,10 & 0.243\,54 & 0 & -0.299\,31 & -0.161\,91 & 0.366\,68 \end{pmatrix}$$

$$\mathrm{tr}\,\mathbf{R} = 5.00005.$$

Hint:
Use the definitions given in the main text and matrix multiplication rules.

7.15. Find roots and coefficients of the AOs in the MOs for the allyl radical ($N = 3$) using the general formulae for the linear chain derived in Section 7.8.2.

Answer:

$$x_1 = \sqrt{2}, \qquad x_2 = 0, \qquad x_3 = -\sqrt{2}.$$

$$\phi_1 = \frac{\chi_1 + \sqrt{2}\chi_2 + \chi_3}{2}, \qquad \phi_2 = \frac{\chi_1 - \chi_3}{\sqrt{2}}, \qquad \phi_3 = \frac{\chi_1 - \sqrt{2}\chi_2 + \chi_3}{2}.$$

Hint:
Use equations (218) and (219) of Coulson's general solution for the linear chain with $N = 3$.

7.16. Find roots and coefficients of the AOs in the MOs in *real* form for the π electrons in benzene ($N = 6$) using the general formulae for the closed chain derived in Section 7.8.3.

Answer:
The results are given in equations (244) and (245).

Hint:
Use equations (229), (233), (234) and (235) of Coulson's general solution for the closed chain with $N = 6$.

7.17. Find the relation between Heitler–London and Inui wavefunctions.

Answer:

The relations between the non-linear parameters (orbital exponents and scale factors) in Heitler–London and Inui wavefunctions are:

$$\delta = \frac{R}{2}(c_A + c_B), \qquad \gamma = \frac{R}{2}(c_A - c_B)$$

$$c_A = \frac{\delta + \gamma}{R}, \qquad c_B = \frac{\delta - \gamma}{R}.$$

The Heitler–London wavefunction is obtained from the Inui wavefunction by putting $\delta = \gamma$ $(c_B = 0)$.

Hint:

Express the exponentials in spheroidal coordinates.

7.18. Show that the energy in first order of MP theory is the HF energy, expression (301).

Answer:

$$E_0 + E_1 = E_0^{\mathrm{HF}}.$$

Hint:

Use Slater's rules (107), (110) for the matrix elements of Slater dets with zero spin-orbital differences.

7.19. Find the off-diagonal matrix elements of the perturbation V with single and double excitations from the Hartree–Fock $\Psi_0 = \Psi_0^{\mathrm{HF}}$.

Answer:

Single excitation:

$$\left\langle \Psi(i \to p) \middle| V \middle| \Psi_0^{\mathrm{HF}} \right\rangle = 0 \quad \text{Brillouin's theorem}$$

Double excitations:

$$\left\langle \Psi(i \to p, j \to q) \middle| V \middle| \Psi_0^{\mathrm{HF}} \right\rangle = \langle \psi_p \psi_q | \frac{1}{r_{12}} | \psi_i \psi_j \rangle - \langle \psi_q \psi_p | \frac{1}{r_{12}} | \psi_i \psi_j \rangle.$$

Hint:

Use Slater's rules for the matrix elements of Slater dets having one and two spin-orbital differences.

7.12 SOLVED PROBLEMS

7.1. Using Dirac's formula for $N = 3$, we find for the component with $M_S = +1/2$:

$$\begin{aligned}
\hat{S}^2\|1s\overline{1s}2s\| &= \left(\frac{3}{4}\,\hat{I} + \hat{P}_{12} + \hat{P}_{13} + \hat{P}_{23}\right)\|1s\overline{1s}2s\| \\
&= \frac{3}{4}\|1s\overline{1s}2s\| + \|\overline{1s}1s2s\| + \|1s\overline{1s}2s\| + \|1s1s\overline{2s}\| \\
&= \frac{3}{4}\|1s\overline{1s}2s\| = \frac{1}{2}\left(\frac{1}{2} + 1\right)\|1s\overline{1s}2s\|,
\end{aligned}$$

where the second and third determinant cancel altogether, and the last one vanishes because of the Pauli principle.

7.2. Using Dirac's formula for $N = 4$, we find:

$$\begin{aligned}
\hat{S}^2\|1s\overline{1s}2s\overline{2s}\| &= (\hat{P}_{12} + \hat{P}_{13} + \hat{P}_{14} + \hat{P}_{23} + \hat{P}_{24} + \hat{P}_{34})\|1s\overline{1s}2s\overline{2s}\| \\
&= \|\overline{1s}1s2s\overline{2s}\| + \|1s\overline{1s}2s\overline{2s}\| + \|\overline{1s1s}2s2s\| \\
&\quad + \|1s1s\overline{2s2s}\| + \|1s\overline{1s}2s\overline{2s}\| + \|1s\overline{1s2s}2s\| \\
&= 0(0+1)\|1s\overline{1s}2s\overline{2s}\|,
\end{aligned}$$

where the first and sixth determinant are nothing but the second and fifth with minus sign, while the third and fourth are identically zero for the exclusion principle.

7.3. The MO wavefunction for ground state H_2 $({}^1\Sigma_g^+)$ is:

$$\Psi\left(\sigma_g^2, {}^1\Sigma_g^+\right) = \|\sigma_g\,\overline{\sigma}_g\| = \sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)\frac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)],$$

where we notice that the space part is symmetric and the spin part antisymmetric. Then:

$$\rho_1(\mathbf{x}_1;\mathbf{x}_1) = 2\int d\mathbf{x}_2 \begin{array}{l} \sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)\,\dfrac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)] \\ \sigma_g^*(\mathbf{r}_1)\sigma_g^*(\mathbf{r}_2)\dfrac{1}{\sqrt{2}}\left[\alpha^*(s_1)\beta^*(s_2) - \beta^*(s_1)\alpha^*(s_2)\right] \end{array}$$

$$P_1(\overset{\alpha}{\mathbf{r}_1};\overset{\alpha}{\mathbf{r}_1}) = P_1(\overset{\beta}{\mathbf{r}_1};\overset{\beta}{\mathbf{r}_1}) = R(\mathbf{r}_1;\mathbf{r}_1) = \sigma_g(\mathbf{r}_1)\sigma_g^*(\mathbf{r}_1),$$

where R is the notation usual in the MO-LCAO theory. Then:

$$P(\mathbf{r}_1;\mathbf{r}_1) = P_1^\alpha + P_1^\beta = 2\sigma_g(\mathbf{r}_1)\sigma_g^*(\mathbf{r}_1) = 2|\sigma_g(\mathbf{r}_1)|^2$$

is the electron density, and:

$$Q(\mathbf{r}_1;\mathbf{r}_1) = P_1^\alpha - P_1^\beta = 0$$

the spin density. The electron density integrates to:

$$\int d\mathbf{r}_1 P(\mathbf{r}_1;\mathbf{r}_1) = 2\int d\mathbf{r}_1 [\sigma_g(\mathbf{r}_1)]^2 = 2$$

since the bonding MO $\sigma_g = \frac{a+b}{\sqrt{2+2S}}$ is normalized to 1. The electron density distribution in the H_2 molecule can be further analyzed into its atomic and overlap contributions, equations (54)–(57):

$$\begin{aligned} P(\mathbf{r}_1;\mathbf{r}_1) &= 2\,\frac{(a+b)^2}{2+2S} = \frac{a^2(\mathbf{r}_1)+b^2(\mathbf{r}_1)+a(\mathbf{r}_1)b(\mathbf{r}_1)+b(\mathbf{r}_1)a(\mathbf{r}_1)}{1+S} \\ &= q_A a^2(\mathbf{r}_1) + q_B b^2(\mathbf{r}_1) + q_{AB}\frac{a(\mathbf{r}_1)b(\mathbf{r}_1)}{S} + q_{BA}\frac{b(\mathbf{r}_1)a(\mathbf{r}_1)}{S}, \end{aligned}$$

where:

$$q_A = q_B = \frac{1}{1+S}$$

is the fraction of electronic charge on A or B distributed with the normalized atomic densities $a^2(\mathbf{r}_1)$ or $b^2(\mathbf{r}_1)$;

$$q_{AB} = q_{BA} = \frac{S}{1+S}$$

the fraction of electronic charge distributed with the normalized overlap densities $\frac{a(\mathbf{r}_1)b(\mathbf{r}_1)}{S}$ or $\frac{b(\mathbf{r}_1)a(\mathbf{r}_1)}{S}$.

We can check that:

$$q_A + q_B + q_{AB} + q_{BA} = 2$$

the total number of electrons in the bonding MO σ_g. At the equilibrium distance $R_e = 1.4a_0$, for $1s$ AOs:

$$S \approx \frac{3}{4}: \quad q_A = q_B = \frac{4}{7} \approx 0.57, \quad q_{AB} = q_{BA} = \frac{3}{7} \approx 0.43$$

showing that in the bound H_2 molecule the charge on atoms is less than that in the free H atoms ($q_A = q_B = 1$): 0.43 electrons are shifted from each atom to the interbond region, screening internuclear repulsion. The two electrons are distributed in the molecule according to the following scheme (Figure 7.15).

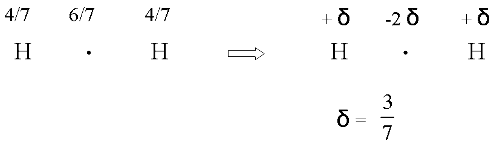

Figure 7.15 Origin of the quadrupole moment in H_2.

Such a distribution of the electronic charge (the dot means the midpoint of the bond) determines the first non-zero electric moment of the centrosymmetric H_2 molecule, its quadrupole moment.

7.4. The three MO wavefunctions of the triplet $({}^3\Sigma_u^+)$ state of H_2 are:

$$\|\sigma_g\sigma_u\| \qquad S=1,\ M_S=1$$

$$\frac{1}{\sqrt{2}}\{\|\sigma_g\overline{\sigma_u}\|+\|\overline{\sigma_g}\sigma_u\|\} \qquad 0$$

$$\|\overline{\sigma_g\sigma_u}\| \qquad -1$$

and can be written by separating space from spin part as:

$$\frac{1}{\sqrt{2}}[\sigma_g(\mathbf{r}_1)\sigma_u(\mathbf{r}_2)-\sigma_u(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)]\begin{cases}\alpha(s_1)\alpha(s_2)\\[1ex] \dfrac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2)+\beta(s_1)\alpha(s_2)]\\[1ex] \beta(s_1)\beta(s_2).\end{cases}$$

We then have for the different spin components of the wavefunction:

- $S=1,\ M_S=1$ (all electrons have spin α)

$$\rho_1(\mathbf{x}_1\,;\,\mathbf{x}_1)=\left[\sigma_g(\mathbf{r}_1)\sigma_g^*(\mathbf{r}_1)+\sigma_u(\mathbf{r}_1)\sigma_u^*(\mathbf{r}_1)\right]\alpha(s_1)\alpha^*(s_1)$$

$$P_1(\overset{\alpha}{\mathbf{r}_1}\,;\,\overset{\alpha}{\mathbf{r}_1})=\sigma_g(\mathbf{r}_1)\sigma_g^*(\mathbf{r}_1)+\sigma_u(\mathbf{r}_1)\sigma_u^*(\mathbf{r}_1)$$

$$P_1(\overset{\beta}{\mathbf{r}_1}\,;\,\overset{\beta}{\mathbf{r}_1})=0$$

$$P(\mathbf{r}_1\,;\,\mathbf{r}_1)=P_1^{\alpha}=\sigma_g^2(\mathbf{r}_1)+\sigma_u^2(\mathbf{r}_1)=Q(\mathbf{r}_1;\mathbf{r}_1).$$

In this case, the spin density coincides with the electron density.

- $S=1,\ M_S=0$

$$\rho_1(\mathbf{x}_1;\,\mathbf{x}_1)=\frac{1}{2}\left[\sigma_g(\mathbf{r}_1)\sigma_g^*(\mathbf{r}_1)+\sigma_u(\mathbf{r}_1)\sigma_u^*(\mathbf{r}_1)\right]\left[\alpha(s_1)\alpha^*(s_1)+\beta(s_1)\beta^*(s_1)\right]$$

$$P_1(\overset{\alpha}{\mathbf{r}_1}\,;\overset{\alpha}{\mathbf{r}_1}) = P_1(\overset{\beta}{\mathbf{r}_1}\,;\overset{\beta}{\mathbf{r}_1}) = \frac{1}{2}\big[\sigma_g(\mathbf{r}_1)\sigma_g^*(\mathbf{r}_1) + \sigma_u(\mathbf{r}_1)\sigma_u^*(\mathbf{r}_1)\big]$$

$$P(\mathbf{r}_1;\mathbf{r}_1) = P_1^\alpha + P_1^\beta = \sigma_g^2(\mathbf{r}_1) + \sigma_u^2(\mathbf{r}_1)$$

$$Q(\mathbf{r}_1;\mathbf{r}_1) = P_1^\alpha - P_1^\beta = 0.$$

The spin density is zero, but the electron density is the same.

- $S = 1,\ M_S = -1$ (all electrons have spin β)

$$\rho_1(\mathbf{x}_1;\mathbf{x}_1) = \big[\sigma_g(\mathbf{r}_1)\sigma_g^*(\mathbf{r}_1) + \sigma_u(\mathbf{r}_1)\sigma_u^*(\mathbf{r}_1)\big]\beta(s_1)\beta^*(s_1)$$

$$P_1(\overset{\beta}{\mathbf{r}_1}\,;\overset{\beta}{\mathbf{r}_1}) = \sigma_g(\mathbf{r}_1)\sigma_g^*(\mathbf{r}_1) + \sigma_u(\mathbf{r}_1)\sigma_u^*(\mathbf{r}_1)$$

$$P_1(\overset{\alpha}{\mathbf{r}_1}\,;\overset{\alpha}{\mathbf{r}_1}) = 0$$

$$P(\mathbf{r}_1\,;\,\mathbf{r}_1) = P_1(\overset{\beta}{\mathbf{r}_1}\,;\overset{\beta}{\mathbf{r}_1}) = \sigma_g^2(\mathbf{r}_1) + \sigma_u^2(\mathbf{r}_1)$$

$$Q(\mathbf{r}_1\,;\,\mathbf{r}_1) = -P_1^\beta = -\big[\sigma_g^2(\mathbf{r}_1) + \sigma_u^2(\mathbf{r}_1)\big].$$

The distribution of the electronic charge in the triplet state of H_2 gives:

$$q_A = q_B = \frac{1}{1-S^2} > 1, \quad q_{AB} = q_{BA} = -\frac{S^2}{1+S^2} < 0,$$

where the charge on the atoms in the molecule is now *larger* than that of the free atoms, which means that the electrons escape from the bond region ($q_{AB}, q_{BA} < 0$) giving repulsion.

In this way, a simple analysis of the electron charge distribution in the molecule reveals at once the bonding or antibonding situations occurring between the interacting atoms. A chemical bond is formed only for the singlet ground state ${}^1\Sigma_g^+$.

7.5. Elementary derivation of the Slater rules for a symmetrical sum of 2-electron operators.

- Zero SO differences

$$\langle\|\overset{1}{\psi_1}\,\overset{2}{\psi_2}\cdots\overset{i}{\psi_i}\cdots\overset{j}{\psi_j}\cdots\overset{N}{\psi_N}\,\||\sum_{i<j}\hat{O}_{ij}|\|\,\overset{1}{\psi_1}\,\overset{2}{\psi_2}\cdots\overset{i}{\psi_i}\cdots\overset{j}{\psi_j}\cdots\overset{N}{\psi_N}\,\|\rangle$$

$$= \frac{1}{N!}\bigg\langle\sum_P(-1)^p\hat{P}\,\overset{1}{\psi_1}\,\overset{2}{\psi_2}\cdots\overset{i}{\psi_i}\cdots\overset{j}{\psi_j}\cdots\overset{N}{\psi_N}\bigg|\sum_{i<j}\hat{O}_{ij}$$

$$\times\bigg|\sum_P(-1)^p\hat{P}\,\overset{1}{\psi_1}\,\overset{2}{\psi_2}\cdots\overset{i}{\psi_i}\cdots\overset{j}{\psi_j}\cdots\overset{N}{\psi_N}\bigg\rangle.$$

Bring into the first two places ψ_i and ψ_j through a number of interchanges in the bra and the ket which leaves the matrix element *unchanged* (electrons are always kept in dictionary order):

$$= \frac{1}{N!}\left\langle \sum_P (-1)^p \hat{P}\psi_i\psi_j\cdots\psi_1\cdots\psi_2\cdots\psi_N \middle| \sum_{i<j}\hat{O}_{ij}\right.$$

$$\times\left|\sum_P (-1)^p \hat{P}\psi_i\psi_j\cdots\psi_1\cdots\psi_2\cdots\psi_N\right\rangle.$$

All $N!$ terms in the ket give the same result, so that:

$$= \left\langle \sum_P (-1)^p \hat{P}\psi_i\psi_j\cdots\psi_1\cdots\psi_2\cdots\psi_N \middle| \hat{O}_{12}+\hat{O}_{13}+\cdots\right.$$

$$\times\left|\psi_i\psi_j\cdots\psi_1\cdots\psi_2\cdots\psi_N\right\rangle$$

$$= \langle\psi_i\psi_j - \psi_j\psi_i|\hat{O}_{12}|\psi_i\psi_j\rangle + \cdots$$

because, for the orthogonality of the SOs, the only terms surviving in the bra are (i) the term corresponding to the identity $\langle\psi_i\psi_j|$, and (ii) that corresponding to the single interchange $\langle\psi_j\psi_i|$. The same is true for all $\frac{N(N-1)}{2}$ distinct $\hat{O}_{ij}$, so that we obtain:

$$\langle\Psi|\sum_{i<j}\hat{O}_{ij}|\Psi\rangle = \sum_{i<j}\left[\langle\psi_i\psi_j|\hat{O}_{12}|\psi_i\psi_j\rangle - \langle\psi_j\psi_i|\hat{O}_{12}|\psi_i\psi_j\rangle\right].$$

It is possible to eliminate the restriction over j since the term $j = i$ vanishes identically because of the exchange term, but it is necessary in this case to introduce the factor $1/2$ accounting for the number of distinct pairs, so that we finally obtain:

$$\langle\Psi|\sum_{i<j}\hat{O}_{ij}|\Psi\rangle = \frac{1}{2}\sum_i\sum_j\left[\langle\psi_i\psi_j|\hat{O}_{12}|\psi_i\psi_j\rangle - \langle\psi_j\psi_i|\hat{O}_{12}|\psi_i\psi_j\rangle\right],$$

where the first integral is called the Coulomb term and the second the exchange term.

- One SO difference

$$\langle\|\overset{1}{\psi_1}\,\overset{2}{\psi_2}\cdots\overset{i}{\psi_i'}\cdots\overset{N}{\psi_N}\,\||\sum_{i<j}\hat{O}_{ij}|\|\,\overset{1}{\psi_1}\,\overset{2}{\psi_2}\cdots\overset{i}{\psi_i}\cdots\overset{N}{\psi_N}\,\|\rangle$$

$$= \frac{1}{N!}\left\langle \sum_P (-1)^p \hat{P}\,\overset{1}{\psi_1}\,\overset{2}{\psi_2}\cdots\overset{i}{\psi_i'}\cdots\overset{N}{\psi_N} \middle| \sum_{i<j}\hat{O}_{ij}\right.$$

$$\times\left|\sum_P (-1)^p \hat{P}\,\overset{1}{\psi_1}\,\overset{2}{\psi_2}\cdots\overset{i}{\psi_i}\cdots\overset{N}{\psi_N}\right\rangle$$

$$
\begin{aligned}
&= \frac{1}{N!}\Bigg\langle \sum_P (-1)^p \hat{P}\psi_i'\psi_2\cdots\psi_1\cdots\psi_N \Bigg| \sum_{i<j}\hat{O}_{ij} \\
&\quad \times \Bigg| \sum_P (-1)^p \hat{P}\psi_i\psi_2\cdots\psi_1\cdots\psi_N \Bigg\rangle \\
&= \Bigg\langle \sum_P (-1)^p \hat{P}\psi_i'\psi_2\cdots\psi_1\cdots\psi_N \Bigg| \hat{O}_{12} + \hat{O}_{13} + \cdots \Bigg| \psi_i\psi_2\cdots\psi_1\cdots\psi_N \Bigg\rangle \\
&= \langle \psi_i'\psi_2 - \psi_2\psi_i' | \hat{O}_{12} | \psi_i\psi_2\rangle + \langle \psi_i'\psi_3 - \psi_3\psi_i' | \hat{O}_{13} | \psi_i\psi_3\rangle + \cdots \\
&= \sum_{j(\neq i)} \big[\langle \psi_i'\psi_j | \hat{O}_{12} | \psi_i\psi_j\rangle - \langle \psi_j\psi_i' | \hat{O}_{12} | \psi_i\psi_j\rangle \big] \\
&= \sum_{j} \big[\langle \psi_i'\psi_j | \hat{O}_{12} | \psi_i\psi_j\rangle - \langle \psi_j\psi_i' | \hat{O}_{12} | \psi_i\psi_j\rangle \big]
\end{aligned}
$$

since the term $j = i$ cancels identically in the complete summation.

- Two SO differences

$$
\langle \| \overset{1}{\psi_1}\, \overset{2}{\psi_2} \cdots \overset{i}{\psi_i'} \cdots \overset{j}{\psi_j'} \cdots \overset{N}{\psi_N} \| | \sum_{i<j} \hat{O}_{ij} | \| \overset{1}{\psi_1}\, \overset{2}{\psi_2} \cdots \overset{i}{\psi_i} \cdots \overset{j}{\psi_j} \cdots \overset{N}{\psi_N} \| \rangle
$$

$$
\begin{aligned}
&= \frac{1}{N!}\Bigg\langle \sum_P (-1)^p \hat{P}\, \overset{1}{\psi_1}\, \overset{2}{\psi_2} \cdots \overset{i}{\psi_i'} \cdots \overset{j}{\psi_j'} \cdots \overset{N}{\psi_N} \Bigg| \sum_{i<j}\hat{O}_{ij} \\
&\quad \times \Bigg| \sum_P (-1)^p \hat{P}\, \overset{1}{\psi_1}\, \overset{2}{\psi_2} \cdots \overset{i}{\psi_i} \cdots \overset{j}{\psi_j} \cdots \overset{N}{\psi_N} \Bigg\rangle \\
&= \frac{1}{N!}\Bigg\langle \sum_P (-1)^p \hat{P}\psi_i'\psi_j'\cdots\psi_1\cdots\psi_2\cdots\psi_N \Bigg| \sum_{i<j}\hat{O}_{ij} \\
&\quad \times \Bigg| \sum_P (-1)^p \hat{P}\psi_i\psi_j\cdots\psi_1\cdots\psi_2\cdots\psi_N \Bigg\rangle \\
&= \Bigg\langle \sum_P (-1)^p \hat{P}\psi_i'\psi_j'\cdots\psi_1\cdots\psi_2\cdots\psi_N \Bigg| \hat{O}_{12} + \hat{O}_{13} + \cdots \\
&\quad \times \Bigg| \psi_i\,\psi_j\cdots\psi_1\cdots\psi_2\cdots\psi_N \Bigg\rangle \\
&= \langle \psi_i'\psi_j' - \psi_j'\psi_i' | \hat{O}_{12} | \psi_i\psi_j\rangle = \langle \psi_i'\psi_j' | \hat{O}_{12} | \psi_i\psi_j\rangle - \langle \psi_j'\psi_i' | \hat{O}_{12} | \psi_i\psi_j\rangle
\end{aligned}
$$

is the only surviving term. In this way, all formulae (110)–(115) of the main text have been rederived. Of course, for a three substituted determinant, the matrix element of $\hat{O}_{12}$ is zero.

7.6. 1- and 2-electron density matrices for the single det wavefunction.

We shall follow here the derivation given by C.A. Coulson in an after-dinner Lennard-Jones Lecture during the 1963 Oxford Summer School. Let the N-electron wavefunction be given in the form of the single Slater det of orthonormal SOs $\{\psi_i(\mathbf{x}_i)\}$ $i = 1, 2, \cdots N$:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \cdots & \psi_N(\mathbf{x}_2) \\ & \cdots & & \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix}.$$

Consider the analytic function (a determinant of order N):

$$\rho_N = N!\Psi\Psi^* = \begin{vmatrix} \rho(\mathbf{x}_1;\mathbf{x}_1) & \rho(\mathbf{x}_1;\mathbf{x}_2) & \cdots & \rho(\mathbf{x}_1;\mathbf{x}_N) \\ \rho(\mathbf{x}_2;\mathbf{x}_1) & \rho(\mathbf{x}_2;\mathbf{x}_2) & \cdots & \rho(\mathbf{x}_2;\mathbf{x}_N) \\ & \cdots & & \\ \rho(\mathbf{x}_N;\mathbf{x}_1) & \rho(\mathbf{x}_N;\mathbf{x}_2) & \cdots & \rho(\mathbf{x}_N;\mathbf{x}_N) \end{vmatrix},$$

where:

$$\rho(\mathbf{x}_1;\mathbf{x}_2) = \psi_1(\mathbf{x}_1)\psi_1^*(\mathbf{x}_2) + \cdots + \psi_N(\mathbf{x}_1)\psi_N^*(\mathbf{x}_2) = \sum_{i=1}^{N} \psi_i(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2).$$

We used in ρ_N matrix multiplication rules after interchanging in Ψ^* rows and columns.

We now do in ρ_N an integration over the infinitesimal space-spin volume element $d\mathbf{x}_N$ using (Lennard-Jones, 1931) the Cauchy expansion (Chapter 2, Section 2.2.3) of the determinant ρ_N in terms of the N-th row and N-th column:

$$\begin{aligned} \rho_N = \rho(\mathbf{x}_N;\mathbf{x}_N)\rho_{N-1} - \sum_i\sum_j \{&\rho(\mathbf{x}_i;\mathbf{x}_N)\rho(\mathbf{x}_N;\mathbf{x}_j) \\ &\times \text{cofactor of } \rho(\mathbf{x}_i;\mathbf{x}_j) \text{ in } \rho_{N-1}\}. \end{aligned}$$

Integrating over $d\mathbf{x}_N$ gives:

$$\begin{aligned} \int d\mathbf{x}_N \rho_N = \rho_{N-1} &\int d\mathbf{x}_N \rho(\mathbf{x}_N;\mathbf{x}_N) \\ &- \sum_i\sum_j \{\text{cofactor}\} \int d\mathbf{x}_N \rho(\mathbf{x}_i;\mathbf{x}_N)\rho(\mathbf{x}_N;\mathbf{x}_j) \\ &= N\rho_{N-1} - \sum_i\sum_j \rho(\mathbf{x}_i;\mathbf{x}_j)\{\text{cofactor}\}. \end{aligned}$$

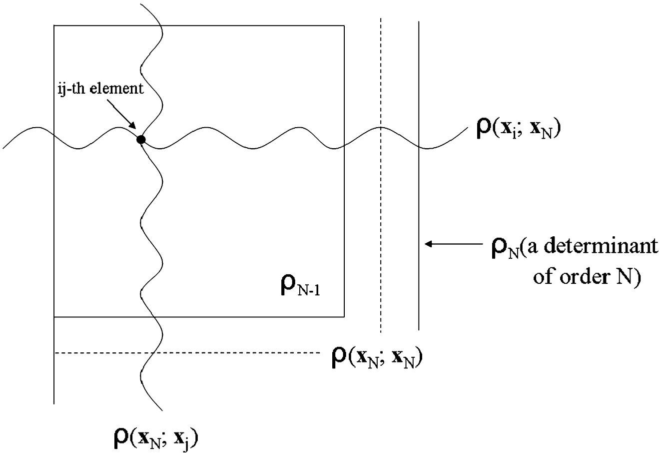

Figure 7.16 Cauchy expansion of ρ_N.

But $\sum_{j=1}^{N-1} \rho(\mathbf{x}_i; \mathbf{x}_j)$ {cofactor} is the expansion of a determinant of order $(N-1)$ according to elements of its i-th row: we add up all the columns getting ρ_{N-1}. Next, summing over i, we simply add up $(N-1)$ times ρ_{N-1}. Therefore, we obtain:

$$\int d\mathbf{x}_N \rho_N = N\rho_{N-1} - (N-1)\rho_{N-1} = \rho_{N-1}.$$

Similarly, by doing repeated integrations:

$$\int d\mathbf{x}_{N-1}\rho_{N-1} = N\rho_{N-2} - (N-2)\rho_{N-2} = 2\rho_{N-2}$$

$$\int d\mathbf{x}_{N-2}\rho_{N-2} = 3\rho_{N-3}$$

$$\dots$$

$$\int d\mathbf{x}_3\rho_3 = (N-2)\rho_2$$

$$\int d\mathbf{x}_2\rho_2 = (N-1)\rho_1$$

$$\int d\mathbf{x}_1\rho_1 = N.$$

By multiplying together all integrations above but the last two, it follows:

$$\int d\mathbf{x}_N\, d\mathbf{x}_{N-1}\, d\mathbf{x}_{N-2} \cdots d\mathbf{x}_3\, \rho_N = 1 \cdot 2 \cdot 3 \cdots (N-2)\rho_2 = (N-2)!\rho_2,$$

so that ρ_2 (a determinant of order 2) is given by:

$$\begin{aligned}
\rho_2 &= \frac{1}{(N-2)!}\int d\mathbf{x}_N\, d\mathbf{x}_{N-1}\cdots d\mathbf{x}_3\, \rho_N \\
&= \frac{N!}{(N-2)!}\int d\mathbf{x}_N\, d\mathbf{x}_{N-1}\cdots d\mathbf{x}_3 \Psi\Psi^* \\
&= N(N-1)\int d\mathbf{x}_3\cdots d\mathbf{x}_N \Psi\Psi^* = \rho_2(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1,\mathbf{x}_2),
\end{aligned}$$

which is nothing but equation (62) defining the 2-particle density function.

Hence, we have shown that, for the single determinant wavefunction of orthonormal SOs, the 2-particle density function is given by:

$$\rho_2(\mathbf{x}_1,\mathbf{x}_2\,;\,\mathbf{x}_1,\mathbf{x}_2) = \rho_2 = \begin{vmatrix} \rho(\mathbf{x}_1;\mathbf{x}_1) & \rho(\mathbf{x}_1;\mathbf{x}_2) \\ \rho(\mathbf{x}_2;\mathbf{x}_1) & \rho(\mathbf{x}_2;\mathbf{x}_2) \end{vmatrix},$$

the 2 × 2 determinant of the Fock invariant ρ, the latter coinciding with the 1-particle density matrix:

$$\rho(\mathbf{x}_1;\mathbf{x}_2) = \sum_{i=1}^{N} \psi_i(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2) = \rho_1(\mathbf{x}_1;\mathbf{x}_2).$$

7.7. Properties of the fundamental invariant.

Using matrix notation and matrix multiplication rules:

$$\begin{aligned}
&\boldsymbol{\psi}(\mathbf{x}) = (\psi_1\,\psi_2\cdots\psi_N) \quad \text{row matrix of SOs} \\
&\rho(\mathbf{x}_1;\mathbf{x}'_1) = \sum_i \psi_i(\mathbf{x}_1)\psi_i^*(\mathbf{x}'_1) = \boldsymbol{\psi}(\mathbf{x}_1)\boldsymbol{\psi}^\dagger(\mathbf{x}'_1),
\end{aligned}$$

the orthonormal properties of the SO basis $\{\psi_i(\mathbf{x})\}$ and the unitary properties of the matrix $\mathbf{U} = \{U_{ji}\}$ give:

(i) Invariance:

$$\begin{aligned}
&\boldsymbol{\psi}' = \boldsymbol{\psi}\mathbf{U} \qquad \mathbf{U}\mathbf{U}^\dagger = \mathbf{U}^\dagger\mathbf{U} = \mathbf{1} \\
&\rho'(\mathbf{x}_1;\mathbf{x}'_1) = \boldsymbol{\psi}'(\mathbf{x}_1)\boldsymbol{\psi}'^\dagger(\mathbf{x}'_1) = \boldsymbol{\psi}(\mathbf{x}_1)\mathbf{U}\mathbf{U}^\dagger\boldsymbol{\psi}^\dagger(\mathbf{x}'_1) = \boldsymbol{\psi}(\mathbf{x}_1)\boldsymbol{\psi}^\dagger(\mathbf{x}'_1) = \rho(\mathbf{x}_1;\mathbf{x}'_1).
\end{aligned}$$

(ii) Conservation:

$$\begin{aligned}
\operatorname{tr}\rho &= \int d\mathbf{x}_1 \rho(\mathbf{x}_1;\mathbf{x}'_1)|_{\mathbf{x}'_1=\mathbf{x}_1} = \int d\mathbf{x}_1 \rho(\mathbf{x}_1;\mathbf{x}_1) \\
&= \sum_i \int d\mathbf{x}_1 \psi_i(\mathbf{x}_1)\psi_i^*(\mathbf{x}_1) = \sum_i \delta_{ii} = N.
\end{aligned}$$

(iii) Idempotency:

$$\begin{aligned}
\rho^2 &= \int d\mathbf{x}_2 \rho(\mathbf{x}_1; \mathbf{x}_2)\rho(\mathbf{x}_2; \mathbf{x}'_1) \\
&= \sum_i \sum_j \int d\mathbf{x}_2 \psi_i(\mathbf{x}_1)\psi_i^*(\mathbf{x}_2)\psi_j(\mathbf{x}_2)\psi_j^*(\mathbf{x}'_1) \\
&= \sum_i \sum_j \psi_i(\mathbf{x}_1)\psi_j^*(\mathbf{x}'_1) \int d\mathbf{x}_2 \psi_i^*(\mathbf{x}_2)\psi_j(\mathbf{x}_2) \\
&= \sum_i \sum_j \psi_i(\mathbf{x}_1)\psi_j^*(\mathbf{x}'_1)\delta_{ij} \\
&= \sum_i \psi_i(\mathbf{x}_1)\psi_i^*(\mathbf{x}'_1) = \rho(\mathbf{x}_1; \mathbf{x}'_1) = \rho.
\end{aligned}$$

These results show that ρ has the properties of the projection operator of Figure 7.3, whose action on an arbitrary regular function $\varphi(\mathbf{x})$ is shown in equation (127).

7.8. The method of Lagrange multipliers for a function of N variables subject to m constraints.

Let the N-variable function:

$$f(x_1, x_2, \cdots x_N)$$

be subject to the m constraints (equations relating the *same* variables):

$$\varphi_r(x_1, x_2, \cdots x_N) = 0 \quad r = 1, 2, \cdots m.$$

We construct the N-variable function:

$$F(x_1, x_2, \cdots x_N) = f(x_1, x_2, \cdots x_N) - \sum_{r=1}^{m} \lambda_r \varphi_r(x_1, x_2, \cdots x_N),$$

where λ_r is a Lagrange multiplier, and minimize it *without* constraints obtaining as necessary condition for stationarity:

$$dF = df - \sum_r \lambda_r d\varphi_r = 0.$$

Putting equal to zero the coefficients of dx_i we obtain the N equations:

$$\begin{cases} \dfrac{\partial f}{\partial x_i} - \sum\limits_r \lambda_r \dfrac{\partial \varphi_r}{\partial x_i} = 0 & i = 1, 2, \cdots N \\ \varphi_r(x_1, x_2, \cdots x_N) = 0 & r = 1, 2, \cdots m \end{cases}$$

which, together with the equations defining the m constraints, form a system of $N+m$ equations allowing to determine the extremum points $(x_1^0, x_2^0, \cdots x_N^0)$ and the Lagrange multipliers $(\lambda_1, \lambda_2, \cdots \lambda_m)$. In our case, f and φ_r are *functionals*, and the variables x_i are the spin-orbitals $\psi_i(\mathbf{x})$.

7.9. Unconstrained variation of the energy functional:

$$\varepsilon = HM^{-1}.$$

Taking an infinitesimal arbitrary variation of ε, we have:

$$\delta\varepsilon = M^{-1}\delta H - HM^{-1-1}\delta M = M^{-1}(\delta H - \varepsilon\delta M) = 0$$

namely:

$$\delta H - \varepsilon\delta M = 0.$$

So, the unconstrained variation of the energy functional ε is fully equivalent to the separate variation of H minus the separate variation of the constraint M (here, the normalization integral) multiplied by the Lagrange multiplier ε. ε plays hence the role of the Lagrange multiplier of Problem 7.8.

7.10. According to definitions (121) and (130) we have:

$$J_1 = \int d\mathbf{x}_2 \frac{\rho(\mathbf{x}_2;\mathbf{x}_2)}{r_{12}} = \sum_{i'} \int d\mathbf{x}_2 \frac{\psi_{i'}(\mathbf{x}_2)\psi_{i'}^*(\mathbf{x}_2)}{r_{12}}$$

$$\delta J_1 = \int d\mathbf{x}_2 \frac{\delta\rho(\mathbf{x}_2;\mathbf{x}_2)}{r_{12}} = \sum_{i'} \int d\mathbf{x}_2 \frac{\psi_{i'}(\mathbf{x}_2)\delta\psi_{i'}^*(\mathbf{x}_2) + \delta\psi_{i'}(\mathbf{x}_2)\psi_{i'}^*(\mathbf{x}_2)}{r_{12}}$$

$$\begin{aligned}
&\sum_i \langle\psi_i|\delta J_1|\psi_i\rangle \\
&\quad= \sum_i \int d\mathbf{x}_1 \psi_i^*(\mathbf{x}_1)\left[\sum_{i'} \int d\mathbf{x}_2 \frac{\psi_{i'}(\mathbf{x}_2)\delta\psi_{i'}^*(\mathbf{x}_2) + \delta\psi_{i'}(\mathbf{x}_2)\psi_{i'}^*(\mathbf{x}_2)}{r_{12}}\right]\psi_i(\mathbf{x}_1) \\
&\quad= \text{interchange in the integrals summation indices } i, i' \text{ and electron labels } 1, 2 \\
&\quad= \sum_{i'} \int d\mathbf{x}_2 \psi_{i'}^*(\mathbf{x}_2)\left[\sum_i \int d\mathbf{x}_1 \frac{\psi_i(\mathbf{x}_1)\delta\psi_i^*(\mathbf{x}_1) + \delta\psi_i(\mathbf{x}_1)\psi_i^*(\mathbf{x}_1)}{r_{12}}\right]\psi_{i'}(\mathbf{x}_2) \\
&\quad= \sum_i \int d\mathbf{x}_1 \delta\psi_i^*(\mathbf{x}_1)\left[\sum_{i'} \int d\mathbf{x}_2 \frac{\psi_{i'}(\mathbf{x}_2)\psi_{i'}^*(\mathbf{x}_2)}{r_{12}}\right]\psi_i(\mathbf{x}_1) \\
&\qquad+ \sum_i \int d\mathbf{x}_1 \psi_i^*(\mathbf{x}_1)\left[\sum_{i'} \int d\mathbf{x}_2 \frac{\psi_{i'}(\mathbf{x}_2)\psi_{i'}^*(\mathbf{x}_2)}{r_{12}}\right]\delta\psi_i(\mathbf{x}_1) \\
&\quad= \sum_i \langle\delta\psi_i|J_1|\psi_i\rangle + \sum_i \langle\psi_i|J_1|\delta\psi_i\rangle
\end{aligned}$$

which is the required result. The same holds for the variation of the exchange integral $\delta \hat{K}_1$.

7.11. Elimination of spin from $\hat{F}(\mathbf{x}_1)$ for closed shells.

$$\begin{aligned}\hat{F}(\mathbf{x}_1) = \hat{F}(\mathbf{r}_1 s_1) &= -\frac{1}{2}\nabla_1^2 + V_1 \\ &+ \int d\mathbf{r}_2\, ds_2 \frac{\rho(\mathbf{r}_2 s_2; \mathbf{r}_2 s_2)}{r_{12}} - \int d\mathbf{r}_2\, ds_2 \frac{\rho(\mathbf{r}_1 s_1; \mathbf{r}_2 s_2)}{r_{12}} \hat{P}_{\mathbf{r}_1 s_1, \mathbf{r}_2 s_2}\end{aligned}$$

$$\begin{aligned}&\hat{F}(\mathbf{r}_1 s_1)\phi_i(\mathbf{r}_1)\alpha(s_1) \\ &= \left(-\frac{1}{2}\nabla_1^2 + V_1\right)\phi_i(\mathbf{r}_1)\alpha(s_1) \\ &\quad + \int d\mathbf{r}_2\, ds_2 \frac{R(\mathbf{r}_2; \mathbf{r}_2)}{r_{12}}\big[\alpha(s_2)\alpha^*(s_2) + \beta(s_2)\beta^*(s_2)\big]\phi_i(\mathbf{r}_1)\,\alpha(s_1) \\ &\quad - \int d\mathbf{r}_2\, ds_2 \frac{R(\mathbf{r}_1; \mathbf{r}_2)}{r_{12}}\big[\alpha(s_1)\alpha^*(s_2) + \beta(s_1)\beta^*(s_2)\big]\phi_i(\mathbf{r}_2)\alpha(s_2) \\ &= \left(-\frac{1}{2}\nabla_1^2 + V_1\right)\phi_i(\mathbf{r}_1)\alpha(s_1) \\ &\quad + 2\int d\mathbf{r}_2 \frac{R(\mathbf{r}_2; \mathbf{r}_2)}{r_{12}}\phi_i(\mathbf{r}_1)\alpha(s_1) \\ &\quad - \int d\mathbf{r}_2 \frac{R(\mathbf{r}_1; \mathbf{r}_2)}{r_{12}}\hat{P}_{\mathbf{r}_1\mathbf{r}_2}\phi_i(\mathbf{r}_1)\,\alpha(s_1) \\ &= \left(-\frac{1}{2}\nabla_1^2 + V_1 + 2J(\mathbf{r}_1) - \hat{K}(\mathbf{r}_1)\right)\phi_i(\mathbf{r}_1)\alpha(s_1)\end{aligned}$$

from which follows equation (146) of the main text.

7.12. We start from the definitions:

$$R(\mathbf{r}; \mathbf{r}') = \boldsymbol{\chi}(\mathbf{r})\mathbf{R}\boldsymbol{\chi}^\dagger(\mathbf{r}') = \sum_\mu \sum_\nu \chi_\mu(\mathbf{r}) R_{\mu\nu} \chi_\nu^*(\mathbf{r}')$$

$$\boldsymbol{\chi}^\dagger \boldsymbol{\chi} = \mathbf{M}.$$

Then:

(i) Idempotency:

$$\int d\mathbf{r}''\, R(\mathbf{r}; \mathbf{r}'') R(\mathbf{r}''; \mathbf{r}') = R(\mathbf{r}; \mathbf{r}')$$

$$\int d\mathbf{r}''\boldsymbol{\chi}(\mathbf{r})\mathbf{R}\boldsymbol{\chi}^{\dagger}(\mathbf{r}'')\cdot\boldsymbol{\chi}(\mathbf{r}'')\mathbf{R}\boldsymbol{\chi}^{\dagger}(\mathbf{r}')=\boldsymbol{\chi}(\mathbf{r})\mathbf{RMR}\boldsymbol{\chi}^{\dagger}(\mathbf{r}')=\boldsymbol{\chi}(\mathbf{r})\mathbf{R}\boldsymbol{\chi}^{\dagger}(\mathbf{r}'),$$

whence it follows:

$$\mathbf{RMR}=\mathbf{R}.$$

(ii) Conservation:

$$\int d\mathbf{r}R(\mathbf{r};\mathbf{r})=\sum_{\mu}\sum_{\nu}R_{\mu\nu}\int d\mathbf{r}\chi_{\nu}^{*}(\mathbf{r})\chi_{\mu}(\mathbf{r})$$
$$=\sum_{\mu}\sum_{\nu}R_{\mu\nu}M_{\nu\mu}=\operatorname{tr}\mathbf{RM}=n,$$

where $n=N/2$ is the number of doubly occupied MOs.

7.13. The H_2O molecule is chosen to lie in the yz-plane, with the oxygen atom at the origin of a right-handed cartesian system having z as C_2 symmetry axis. Among other geometries, reported by Pitzer and Merrifield (PM, 1970), we choose the experimental geometry, O–H $=1.8103\,a_0$ and $2\theta=105°$ (not the best for the MO wavefunction), which was used in the pioneering work by Ellison and Shull (1955) on H_2O. The minimum basis set of 7 STOs has orbital exponents chosen by Slater's rules: $c_k=7.7$, $c_s=c_p=2.275$, $c_h=1.0$.

The obvious short notation for the AOs is: $1s_{\mathrm{O}}=k'$, $2s_{\mathrm{O}}=s'$, $2p_{z\mathrm{O}}=z$, $2p_{x\mathrm{O}}=x$, $2p_{y\mathrm{O}}=y$, $1s_{\mathrm{H}_1}=h_1$, $1s_{\mathrm{H}_2}=h_2$. The overlap integrals for the original set given by PM are[8]: $\langle k'|s'\rangle=0.23345$, $\langle k'|h\rangle=0.06097$, $\langle s'|h\rangle=0.50884$, $\langle z|h\rangle=0.21184$, $\langle y|h_1\rangle=0.27607$, $\langle y|h_2\rangle=-0.27607$, $\langle h_1|h_2\rangle=0.37459$.

The SCF-MO coefficients and the orbital energies from PM are:

A_1	k'	s'	z	$h_s=\frac{1}{\sqrt{2}}(h_1+h_2)$	ε_i/E_h
$1a_1$	0.99603	0.01880	0.00338	−0.00609	−20.5046
$2a_1$	−0.22719	0.84496	0.13867	0.19881	−1.2981
$3a_1$	0.09883	−0.55661	0.77963	0.40646	−0.4715
$4a_1$	−0.11845	0.86816	0.70074	−1.05410	0.4013
B_1	x				
$1b_1$	1.0				−0.4251
B_2	y	$h_y=\frac{1}{\sqrt{2}}(h_1-h_2)$			
$1b_2$	0.58221	0.72698			−0.6386
$2b_2$	0.99162	−1.25927			0.5909

---

[8] PM give only the value $S_{\sigma h}=0.34798$, so that $S_{zh}=S_{\sigma h}\cos\theta$, $S_{yh}=S_{\sigma h}\sin\theta$.

Negative orbital energies denote *bonding* MOs, positive energies *antibonding* MOs, which are empty in the ground state. Within each definite symmetry type (Chapter 8), the MOs are given in order of ascending energies, so that the electron configuration of the ${}^1A_1$ ground state of the H_2O molecule ($N = 10$, $n = 5$, $m = 7$) will be:

$$\mathrm{H_2O}\,({}^1A_1):\; 1a_1^2\,2a_1^2\,1b_2^2\,3a_1^2\,1b_1^2.$$

The molecule will be stable since all its bonding MOs are doubly occupied by electrons with opposed spin, but the PM minimum basis MO results for the total molecular energy E and the dipole moment μ are disappointingly poor:

$$E(\text{MO-SCF}) = -75.655\,6\,E_h, \qquad \mu = 0.564\,2\,ea_0$$

compared to the nearly HF results (Lazzeretti, 2004) obtained with an extended polarized GTO set contracted to $[13s\,10p\,5d\,2f\,|8s\,4p\,1d]$:

$$E(\text{HF}) \approx -76.066\,87\,E_h, \qquad \mu = 0.780\,9\,ea_0.$$

We now turn to the required transformation of the coefficients of the SCF MOs after the Schmidt orthogonalization of s' against k'. Let k', s' be the non-orthogonal AOs, having $S = \langle k'|s'\rangle \neq 0$, and k, s the Schmidt-orthogonalized AOs with $\langle k|s\rangle = 0$. The transformation between normalized AOs can be written in matrix form as:

$$(k \quad s) = (k' \quad s')\begin{pmatrix} 1 & -S(1-S^2)^{-1/2} \\ 0 & (1-S^2)^{-1/2} \end{pmatrix} = (k' \quad s')\mathbf{O},$$

where $\mathbf{O}$ is the matrix doing Schmidt orthogonalization. The *inverse* transformation is then:

$$(k' \quad s') = (k \quad s)\mathbf{O}^{-1},$$

where:

$$\mathbf{O}^{-1} = (\det\mathbf{O})^{-1}\begin{pmatrix} (1-S^2)^{-1/2} & S(1-S^2)^{-1/2} \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & S \\ 0 & (1-S^2)^{1/2} \end{pmatrix}$$

is the inverse matrix.

Introducing the numerical value $S = 0.233\,45$, it is easily obtained:

$$k' = k, \qquad s' = 0.233\,45\,k + 0.972\,37\,s.$$

Therefore:

$$1a_1 = 0.996\,03\,k' + 0.018\,80\,s' + \cdots = 1.000\,42\,k + 0.018\,28\,s + \cdots$$

Proceeding in this way, we construct the table given as answer to this Problem.

7.14. From the results of the preceding Problem, the 7 × 5 rectangular matrix of the coefficients $\mathbf{C}$ in the PM basis is:

$$\begin{array}{ccc}
 & & \chi\\
\mathbf{C}= & \left(\begin{array}{ccccc}
1.00042 & -0.02934 & -0.03111 & 0 & 0\\
0.01828 & 0.8216 & -0.5412 & 0 & 0\\
0.0034 & 0.1387 & 0.7796 & 0 & 0\\
0 & 0 & 0 & 0 & 1\\
0 & 0 & 0 & 0.5822 & 0\\
-0.00431 & 0.1406 & 0.2874 & 0.5141 & 0\\
-0.00431 & 0.1406 & 0.2874 & -0.5141 & 0
\end{array}\right) & \begin{array}{c} k\\ s\\ z\\ x\\ y\\ h_1\\ h_2\end{array}\\
\boldsymbol{\phi}\ \text{occ} & \begin{array}{ccccc} 1a_1 & 2a_1 & 3a_1 & 1b_2 & 1b_1\end{array} &
\end{array}$$

with its 5 × 7 transposed matrix:

$$\mathbf{C}^{\dagger}=\left(\begin{array}{ccccccc}
1.00042 & 0.01828 & 0.0034 & 0 & 0 & -0.00431 & -0.00431\\
-0.02934 & 0.8216 & 0.1387 & 0 & 0 & 0.1406 & 0.1406\\
-0.03111 & -0.5412 & 0.7796 & 0 & 0 & 0.2874 & 0.2874\\
0 & 0 & 0 & 0 & 0.5822 & 0.5141 & -0.5141\\
0 & 0 & 0 & 1 & 0 & 0 & 0
\end{array}\right).$$

Multiplying $\mathbf{C}$ by $\mathbf{C}^{\dagger}$ gives matrix $\mathbf{R}$:

$$\mathbf{R}=\left(\begin{array}{ccccccc}
1.00270 & 0.01053 & -0.02500 & 0 & 0 & -0.01746 & -0.01746\\
0.01053 & 0.96826 & -0.30790 & 0 & 0 & -0.04010 & -0.04010\\
-0.02500 & -0.30790 & 0.62704 & 0 & 0 & 0.24354 & 0.24354\\
0 & 0 & 0 & 1 & 0 & 0 & 0\\
0 & 0 & 0 & 0 & 0.33896 & 0.29931 & -0.29931\\
-0.01746 & -0.04010 & 0.24354 & 0 & 0.29931 & 0.36668 & -0.16191\\
-0.01746 & -0.04010 & 0.24354 & 0 & -0.29931 & -0.16191 & 0.36668
\end{array}\right).$$

Using the complete metric matrix of the modified AO basis:

$$\mathbf{M} = \begin{array}{c} \left(\begin{array}{ccccccc} 1 & 0 & 0 & 0 & 0 & 0.060\,97 & 0.060\,97 \\ 0 & 1 & 0 & 0 & 0 & 0.508\,66 & 0.508\,66 \\ 0 & 0 & 1 & 0 & 0 & 0.211\,84 & 0.211\,84 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0.276\,07 & -0.276\,07 \\ 0.060\,97 & 0.508\,66 & 0.211\,84 & 0 & 0.276\,07 & 1 & 0.374\,59 \\ 0.060\,97 & 0.508\,66 & 0.211\,84 & 0 & -0.276\,07 & 0.374\,59 & 1 \end{array}\right) \begin{array}{c} k \\ s \\ z \\ x \\ y \\ h_1 \\ h_2 \end{array} \\ \begin{array}{ccccccc} k & s & z & x & y & h_1 & h_2 \end{array} \end{array}$$

matrix multiplication of **R** by **M** gives:

$$\mathbf{RM} = \begin{pmatrix} 1.000\,57 & -0.007\,23 & -0.032\,40 & 0 & 0 & 0.037\,19 & 0.037\,19 \\ 0.005\,64 & 0.927\,46 & -0.324\,89 & 0 & 0 & 0.372\,81 & 0.372\,81 \\ 0.004\,70 & -0.060\,14 & 0.730\,22 & 0 & 0 & 0.309\,46 & 0.309\,46 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.504\,22 & 0.280\,77 & -0.280\,77 \\ -0.004\,98 & 0.064\,06 & 0.286\,92 & 0 & 0.445\,24 & 0.418\,79 & -0.077\,06 \\ -0.004\,98 & 0.064\,06 & 0.286\,92 & 0 & -0.445\,24 & -0.077\,06 & 0.418\,79 \end{pmatrix}.$$

We notice that while matrices **R** and **M** are symmetric, their product is not, but it becomes symmetric after multiplication by **R**. By further matrix multiplication of **RM** by **R** idempotency is proved, while the trace of **RM** is easily seen to give 5, apart from round-off errors.

7.15. Allyl radical calculation from the general formulae for the linear chain with $N = 3$.

We recall that Hückel roots and coefficients are nothing but the eigenvalues and eigenvectors of the Hückel matrix **H**. We have:

$$N = 3 \qquad \theta_k = k\frac{\pi}{4} \quad k = 1, 2,\ 3.$$

(i) Roots:

$$x_k = 2\cos k\,\frac{\pi}{4}$$

$$x_1 = 2\cos\frac{\pi}{4} = \frac{2}{\sqrt{2}} = \sqrt{2}$$

$$x_2 = 2\cos\frac{2\pi}{4} = 0$$

$$x_3 = 2\cos\frac{3\pi}{4} = 2\cos 135^{\circ} = -\frac{2}{\sqrt{2}} = -\sqrt{2}.$$

(ii) Coefficients:

$$c_{mk} = \sin m\frac{k\pi}{4}.$$

If C is a normalization factor:

$$\begin{aligned}
\phi_1 &= C\sum_{m=1}^{3}\chi_m \sin m\frac{\pi}{4} = C\left(\chi_1 \sin\frac{\pi}{4} + \chi_2 \sin\frac{2\pi}{4} + \chi_3 \sin\frac{3\pi}{4}\right)\\
&= C\left(\chi_1\frac{1}{\sqrt{2}} + \chi_2 + \chi_3\frac{1}{\sqrt{2}}\right) = \frac{\chi_1 + \sqrt{2}\chi_2 + \chi_3}{2}\\
\phi_2 &= C\sum_{m=1}^{3}\chi_m \sin m\frac{\pi}{2} = \frac{\chi_1 - \chi_3}{\sqrt{2}}\\
\phi_3 &= C\sum_{m=1}^{3}\chi_m \sin m\,\frac{3\pi}{4} = \frac{\chi_1 - \sqrt{2}\chi_2 + \chi_3}{2}.
\end{aligned}$$

7.16. π electron benzene calculation from the general formulae (*real* form) for the closed chain with $N = 6$.

This application is of some interest since it illustrates well some arbitrariness connected to the numbering of the atoms (hence, of the AOs) along the benzene ring, and to the choice of coordinate axes in the molecular plane. Our reference is that of Figure 7.9, where atoms are numbered in an anticlockwise sense with atom 1 placed in the positive xy-plane (the same reference chosen in Problem 8.13 where benzene is treated according to C_{6v} symmetry). This choice is however arbitrary, different equivalent descriptions being connected by unitary transformations among the MOs.

We have:

$$N = 6 \qquad \theta_k = k\frac{2\pi}{6} = k\frac{\pi}{3} \qquad k = 0, \pm 1, \pm 2,\ 3$$

(i) Roots:

$$\begin{aligned}
x_k &= 2\cos k\,\frac{\pi}{3}\\
x_0 &= 2\\
x_1 &= x_{-1} = 2\cos\frac{\pi}{3} = 1
\end{aligned}$$

$$x_2 = x_{-2} = 2\cos\frac{2\pi}{3} = -1$$

$$x_3 = 2\cos\frac{3\pi}{3} = 2\cos\pi = -2.$$

(ii) *Real* coefficients:

$$a_{mk} = A\sin m\,\frac{k\pi}{3}, \qquad b_{mk} = A\cos m\,\frac{k\pi}{3},$$

where A is a normalization factor;

$$\begin{aligned}
\phi_0 = \phi_0^c &= A\sum_{m=1}^{6}\chi_m\cos 0 = \frac{1}{\sqrt{6}}(\chi_1+\chi_2+\chi_3+\chi_4+\chi_5+\chi_6)\\
\phi_1^s &= A\sum_{m=1}^{6}\chi_m\sin m\frac{\pi}{3} = \frac{1}{2}(\chi_1+\chi_2-\chi_4-\chi_5)\\
\phi_1^c &= A\sum_{m=1}^{6}\chi_m\cos m\,\frac{\pi}{3} = \frac{1}{\sqrt{12}}(\chi_1-\chi_2-2\chi_3-\chi_4+\chi_5+2\chi_6)\\
\phi_2^s &= A\sum_{m=1}^{6}\chi_m\sin m\,\frac{2\pi}{3} = \frac{1}{2}(\chi_1-\chi_2+\chi_4-\chi_5)\\
\phi_2^c &= A\sum_{m=1}^{6}\chi_m\cos m\,\frac{2\pi}{3} = \frac{1}{\sqrt{12}}(-\chi_1-\chi_2+2\chi_3-\chi_4-\chi_5+2\chi_6)\\
\phi_3 = \phi_3^c &= A\sum_{m=1}^{6}\chi_m\cos m\,\frac{3\pi}{3} = \frac{1}{\sqrt{6}}(-\chi_1+\chi_2-\chi_3+\chi_4-\chi_5+\chi_6).
\end{aligned}$$

The MOs obtained in this way differ from those of Figure 7.10 by a unitary transformation **U**. Matrix **U** is the result of a two-step transformation on the Coulson set, first (i) a rotation of 60° of the coordinate axes about z (*passive* transformation, see Chapter 8), so that atom 1 is replaced by 2, 2 by 3, and so on; second (ii) a transformation restoring the order of the basic vectors of E_1 and E_2 symmetry as defined in Chapter 8. So, the transformation between the two sets is:

$$(\phi_1\phi_2\phi_3\phi_4\phi_5\phi_6) = \left(\phi_0\phi_1^s\phi_1^c\phi_2^s\phi_2^c\phi_3\right)\mathbf{U}$$

$$\mathbf{U}=\begin{pmatrix} 1 & & & \\ & \begin{matrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{matrix} & & 0 \\ 0 & & \begin{matrix} \frac{\sqrt{3}}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{\sqrt{3}}{2} \end{matrix} & \\ & & & -1 \end{pmatrix}.$$

We check this result for the E_1 degenerate set:

$$\begin{aligned} \frac{1}{2}\phi_1^s+\frac{\sqrt{3}}{2}\phi_1^c &= \chi_1\left(\frac{1}{4}+\frac{\sqrt{3}}{2}\cdot\frac{1}{2\sqrt{3}}\right)+\chi_2\left(\frac{1}{4}-\frac{\sqrt{3}}{2}\cdot\frac{1}{2\sqrt{3}}\right) \\ &+\chi_3\left(0-\frac{\sqrt{3}}{2}\cdot\frac{2}{2\sqrt{3}}\right)+\chi_4\left(-\frac{1}{4}-\frac{\sqrt{3}}{2}\cdot\frac{1}{2\sqrt{3}}\right) \\ &+\chi_5\left(-\frac{1}{4}+\frac{\sqrt{3}}{2}\cdot\frac{1}{2\sqrt{3}}\right)+\chi_6\left(0+\frac{\sqrt{3}}{2}\cdot\frac{2}{2\sqrt{3}}\right) \\ &=\frac{1}{2}(\chi_1-\chi_3-\chi_4+\chi_6)=\phi_2\sim x \end{aligned}$$

$$\begin{aligned} \frac{\sqrt{3}}{2}\phi_1^s-\frac{1}{2}\phi_1^c &= \chi_1\left(\frac{\sqrt{3}}{2}\cdot\frac{1}{2}-\frac{1}{2}\cdot\frac{1}{2\sqrt{3}}\right)+\chi_2\left(\frac{\sqrt{3}}{2}\cdot\frac{1}{2}+\frac{1}{2}\cdot\frac{1}{2\sqrt{3}}\right) \\ &+\chi_3\left(0+\frac{1}{2}\cdot\frac{2}{2\sqrt{3}}\right)+\chi_4\left(-\frac{\sqrt{3}}{2}\cdot\frac{1}{2}+\frac{1}{2}\cdot\frac{1}{2\sqrt{3}}\right) \\ &+\chi_5\left(-\frac{\sqrt{3}}{2}\cdot\frac{1}{2}-\frac{1}{2}\cdot\frac{1}{2\sqrt{3}}\right)+\chi_6\left(0-\frac{1}{2}\cdot\frac{2}{2\sqrt{3}}\right) \\ &=\frac{\sqrt{3}}{4}\left(\frac{2}{3}\chi_1+\frac{4}{3}\chi_2+\frac{2}{3}\chi_3-\frac{2}{3}\chi_4-\frac{4}{3}\chi_5-\frac{2}{3}\chi_6\right) \\ &=\frac{1}{\sqrt{12}}(\chi_1+2\chi_2+\chi_3-\chi_4-2\chi_5-\chi_6)=\phi_3\sim y. \end{aligned}$$

7.17. Relation between Heitler–London and Inui wavefunctions.

The Heitler–London wavefunction for the ground state of the H_2 molecule is:

$$\Psi(^1\Sigma_g^+) = N(ab + ba)\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha),$$

where $a = 1s_A$ and $b = 1s_B$ are $1s$ AOs centred at A and B. If we take for a, b the 2-centre Guillemin–Zener AOs:

$$a = \exp[-(c_A r_A + c_B r_B)] \qquad b = \exp[-(c_A r_B + c_B r_A)],$$

introducing spheroidal coordinates for the two electrons:

$$r_A = \frac{R}{2}(\mu + \nu), \qquad r_B = \frac{R}{2}(\mu - \nu)$$

we have:

$$\begin{aligned}
ab + ba &= \exp(-c_A r_{A1} - c_B r_{B1}) \cdot \exp(-c_A r_{B2} - c_B r_{A2}) \\
&\quad + \exp(-c_A r_{B1} - c_B r_{A1}) \cdot \exp(-c_A r_{A2} - c_B r_{B2}) \\
&= \exp\left[-\frac{c_A R}{2}(\mu_1 + \nu_1 + \mu_2 - \nu_2)\right] \\
&\quad \times \exp\left[-\frac{c_B R}{2}(\mu_1 - \nu_1 + \mu_2 + \nu_2)\right] \\
&\quad + \exp\left[-\frac{c_A R}{2}(\mu_1 - \nu_1 + \mu_2 + \nu_2)\right] \\
&\quad \times \exp\left[-\frac{c_B R}{2}(\mu_1 + \nu_1 + \mu_2 - \nu_2)\right] \\
&= \exp\left[-\frac{c_A R}{2}(\mu_1 + \mu_2)\right] \cdot \exp\left[-\frac{c_A R}{2}(\nu_1 - \nu_2)\right] \\
&\quad \times \exp\left[-\frac{c_B R}{2}(\mu_1 + \mu_2)\right] \cdot \exp\left[\frac{c_B R}{2}(\nu_1 - \nu_2)\right] \\
&\quad + \exp\left[-\frac{c_A R}{2}(\mu_1 + \mu_2)\right] \cdot \exp\left[\frac{c_A R}{2}(\nu_1 - \nu_2)\right] \\
&\quad \times \exp\left[-\frac{c_B R}{2}(\mu_1 + \mu_2)\right] \cdot \exp\left[-\frac{c_B R}{2}(\nu_1 - \nu_2)\right].
\end{aligned}$$

Therefore:

$$\begin{aligned}ab+ba &= \exp\left[-\frac{R}{2}(c_A+c_B)(\mu_1+\mu_2)\right]\\ &\quad\times\left\{\exp\left[\frac{R}{2}(c_A-c_B)(\nu_1-\nu_2)\right]+\exp\left[-\frac{R}{2}(c_A-c_B)(\nu_1-\nu_2)\right]\right\}\\ &= \exp[-\delta(\mu_1+\mu_2)]\left\{\exp[\gamma(\nu_1-\nu_2)]+\exp[-\gamma(\nu_1-\nu_2)]\right\}\\ &= 2\exp[-\delta(\mu_1+\mu_2)]\cosh[\gamma(\nu_1-\nu_2)],\end{aligned}$$

which is the Inui wavefunction for the ground state, if we pose:

$$\delta=\frac{R}{2}(c_A+c_B), \qquad \gamma=\frac{R}{2}(c_A-c_B).$$

The inverse transformation between the non-linear parameters is:

$$c_A=\frac{\delta+\gamma}{R}, \qquad c_B=\frac{\delta-\gamma}{R}.$$

The conventional Heitler–London wavefunction in terms of 1-centre AOs can be obtained from the Inui wavefunction by posing:

$$\delta=\gamma, \qquad c_B=0.$$

Putting:

$$\delta\neq 0, \qquad \gamma=0$$

we obtain the exponentially decreasing part of the James–Coolidge wavefunction.

7.18. The energy in first order of Møller–Plesset (MP) theory.
If Ψ_0 is the single determinant HF wavefunction:

$$\Psi_0=\|\psi_1\psi_2\cdots\psi_i\cdots\psi_N\|=\Psi_0^{\mathrm{HF}},$$

the zeroth-order MP energy will be:

$$\begin{aligned}E_0 &= \left\langle\Psi_0^{\mathrm{HF}}\middle|\hat{H}_0\middle|\Psi_0^{\mathrm{HF}}\right\rangle=\langle\|\psi_1\psi_2\cdots\psi_N\|\,|\sum_i\hat{F}_i|\,\|\psi_1\psi_2\cdots\psi_N\|\rangle\\ &= \sum_i\langle\psi_i|\hat{F}_1|\psi_i\rangle=\sum_i\varepsilon_i,\end{aligned}$$

and the first-order MP energy:

$$
\begin{aligned}
E_1 &= \langle \Psi_0^{\mathrm{HF}}|V|\Psi_0^{\mathrm{HF}}\rangle \\
&= \langle \|\psi_1\psi_2\cdots\psi_N\||\frac{1}{2}\sum_{i,j}{}'\frac{1}{r_{ij}} - \sum_i (J_i - \hat{K}_i)|\|\psi_1\psi_2\cdots\psi_N\|\rangle \\
&= \frac{1}{2}\sum_i\sum_j\left[\langle\psi_i\psi_j|\frac{1}{r_{12}}|\psi_i\psi_j\rangle - \langle\psi_j\psi_i|\frac{1}{r_{12}}|\psi_i\psi_j\rangle\right] \\
&\quad - \sum_i\langle\psi_i|J_1 - \hat{K}_1|\psi_i\rangle \\
&= -\frac{1}{2}\sum_i\sum_j\left[\langle\psi_i\psi_j|\frac{1}{r_{12}}|\psi_i\psi_j\rangle - \langle\psi_j\psi_i|\frac{1}{r_{12}}|\psi_i\psi_j\rangle\right] = -V_{ee}.
\end{aligned}
$$

Hence, it follows:

$$
E_0 + E_1 = \textstyle\sum_i \varepsilon_i - V_{ee} = E_0^{\mathrm{HF}}
$$

which is the electronic energy in the HF approximation.

7.19. The Brillouin theorem for HF Ψ_0.

Using Slater's rules (108) and (112) for the matrix elements of the Slater det with *one* spin-orbital difference, we have:

$$
\begin{aligned}
&\langle\Psi(i\to p)|V|\Psi_0^{\mathrm{HF}}\rangle \\
&= \langle \|\psi_1\psi_2\cdots\psi_p\cdots\psi_N\||\frac{1}{2}\sum_{i,j}{}'\frac{1}{r_{ij}} - \sum_i (J_i - \hat{K}_i)|\|\psi_1\psi_2\cdots\psi_i\cdots\psi_N\|\rangle \\
&= \sum_j\left[\langle\overset{1}{\psi_p}\,\overset{2}{\psi_j}|\frac{1}{r_{12}}|\overset{1}{\psi_i}\,\overset{2}{\psi_j}\rangle - \langle\overset{1}{\psi_j}\,\overset{2}{\psi_p}|\frac{1}{r_{12}}|\overset{1}{\psi_i}\,\overset{2}{\psi_j}\rangle\right] - \langle\psi_p|J_1 - \hat{K}_1|\psi_i\rangle \\
&= \langle\psi_p|J_1 - \hat{K}_1|\psi_i\rangle - \langle\psi_p|J_1 - \hat{K}_1|\psi_i\rangle = 0
\end{aligned}
$$

which is Brillouin's theorem for single excitations. For the double excitations, from Slater's rules (109) and (114) for *two* spin-orbital differences, we obtain:

$$\langle \Psi(i \to p, j \to q)|V|\Psi_0^{\mathrm{HF}}\rangle$$

$$= \langle \|\psi_1\psi_2\cdots\psi_p\cdots\psi_q\cdots\psi_N\|\,|\frac{1}{2}\sum_{i,j}{}' \frac{1}{r_{ij}} - \sum_i (J_i - \hat{K}_i)|$$

$$\times \|\psi_1\psi_2\cdots\psi_i\cdots\psi_j\cdots\psi_N\|\rangle$$

$$= \langle \overset{1}{\psi_p}\,\overset{2}{\psi_q}\,|\frac{1}{r_{12}}|\,\overset{1}{\psi_i}\,\overset{2}{\psi_j}\,\rangle - \langle \overset{1}{\psi_q}\,\overset{2}{\psi_p}\,|\frac{1}{r_{12}}|\,\overset{1}{\psi_i}\,\overset{2}{\psi_j}\,\rangle$$

since the integral over the 1-electron operator vanishes for the double excitation.

– 8 –

Molecular Symmetry and Group Theoretical Methods

8.1 INTRODUCTION

Most of the following owes much to Simon Altmann's excellent Chapter on Group Theory in Vol. II of Bates "Quantum Theory" (Altmann, 1962), offered as post-Doc lectures at various Oxford Summer Schools in Theoretical Chemistry during the years 1960–1970.

We start from elementary considerations, often intuitive, of the properties of symmetry operations in Quantum Mechanics, next introducing for advanced work group theoretical methods mostly using matrix techniques. An interesting alternative approach shifting emphasis from the theory of matrix representation to the theory of algebras was given by Hall (1967), and will be occasionally followed in a few points of this work. Good presentation is also in Landau and Lifshitz (1958), while advanced applications can be found, among others, in Meijer and Bauer (1962) and Kaplan (1975).

Symmetry is a fundamental physical property which can never be violated, and which offers interesting simplifications even without doing effective quantum mechanical calculations. Even if the Schroedinger wave equation cannot be solved exactly, there are several results which depend only on the symmetry properties of the problem, and which can be obtained exactly with the aid of that branch of linear algebra known as group theory. As a part of Mathematics, abstract group theory was developed to some extent by the young mathematician Galois[1] well before its applications to Physics, due mostly to Weyl[2] (1931) and Wigner[3] (1959), and to Chemistry by Mulliken (1933) and by Rosenthal and Murphy (1936). The majority of applications contained in this Chapter will be concerned with finite molecular point groups, while a short outline of continuous and permutation groups will be given in Section 7. The Chapter ends, as usual, with a large number of problems which are completely worked out in the last Section.

8.2 SYMMETRY AND QUANTUM MECHANICS

Let R be a symmetry operation, i.e. an operation exchanging *identical* particles (electrons or nuclei). If $\hat{R}$ is the linear Hermitian operator associated with R, the Hamiltonian $\hat{H}$ will be left unchanged by any operation R so that $\hat{R}$ will commute with $\hat{H}$:

$$[\hat{H}, \hat{R}] = 0, \tag{1}$$

and the symmetry operation R will be a constant of the motion. Now, if Ψ_i is a solution of the Schroedinger equation belonging to the eigenvalue E_i:

$$\hat{H}\Psi_i = E_i\Psi_i \tag{2}$$

$$\hat{R}(\hat{H}\Psi_i) = \hat{R}(E_i\Psi_i) \tag{3}$$

$$\hat{H}(\hat{R}\Psi_i) = E_i(\hat{R}\Psi_i), \tag{4}$$

and we are left with two possibilities.

---

[1] Galois Evariste 1811–1832, French mathematician.

[2] Weyl Hermann 1885–1955, German mathematician, Professor at the Universities of Zürich, Göttingen and Princeton.

[3] Wigner Eugene Paul 1902–1995, U.S. physicist, Professor of Physics at the Palmer Physical Laboratory of the University of Princeton, New Jersey. 1963 Nobel Prize for Physics.

(i) Let E_i be a non-degenerate eigenvalue. Then it follows from equation (4) that:

$$\hat{R}\Psi_i = a\Psi_i \tag{5}$$

where, apart from a phase factor:

$$a = \pm 1 \tag{6}$$

if we require $\hat{R}\Psi_i$ to be normalized to unity. Hence, it follows that the function Ψ_i has definite symmetry properties under the transformation with the operator $\hat{R}$:

$$\hat{R}\Psi_i = +\Psi_i \quad \text{symmetric} \tag{7}$$

$$\hat{R}\Psi_i = -\Psi_i \quad \text{antisymmetric.} \tag{8}$$

In the language of group theory, the eigenvalues ±1 are called the characters of a 1-dimensional representation.

(ii) Otherwise, let E_i be a k-degenerate eigenvalue. Then, any linear combination of the k linearly independent functions $\{\Psi_{ij}\}$ $j = 1, 2, \cdots k$ with constant coefficients (subject to normalization) will be a solution of equation (4), with coefficients satisfying the matrix multiplication rule (Chapter 2), say:

$$\hat{R}\hat{S} = \hat{T}, \qquad \mathbf{D}(R)\mathbf{D}(S) = \mathbf{D}(T)^4, \qquad \mathbf{RS} = \mathbf{T}, \tag{9}$$

and where all the matrices (order k) are unitary matrices. We then say that the functions $\{\Psi_{ij}\}$ $j = 1, 2, \cdots k$ form a basis for a k-degenerate matrix representation of the group of symmetry operations. The characters are now the trace of the corresponding matrices.

Symmetry allows to simplify the study of any molecular system through (i) the construction of symmetry-adapted basis functions by use of suitable projection operators, and (ii) the selection rules which allow to decide what matrix elements are zero independently of their effective calculation. Particular importance in atomic theory has the rotation group (a continuous group with infinite elements made by all rotations leaving a sphere invariant, see Section 7) which determines the transformation properties of angular momenta.

8.3 MOLECULAR SYMMETRY

Many polyatomic molecules have a molecular symmetry due to the existence in space of identical nuclei (e.g. the H_2O molecule). The set of all h symmetry elements of a molecule defines the point symmetry group (order h) which characterizes that molecule.

---

[4] $\mathbf{D}(R) = \mathbf{R}$ is the matrix representative of the symmetry operator $\hat{R}$ in the basis $\{\Psi_{ij}\}$ (from the German word *darstellung*).

Table 8.1.

Molecular point group, symmetry operations R, symmetry-defined types (irreps) Γ^i, and order h of the group for a few important groups of finite order

Group	R	Γ^i	h
$C_{2v}(2mm)$[a]	$I, C_2, \sigma_v, \sigma_v'$	A_1, A_2, B_1, B_2	4
$C_{3v}(3m)$	$I, 2C_3, 3\sigma_v$	A_1, A_2, E	6
$C_{5v}(5m)$	$I, 2C_5, 2C_5^2, 5\sigma_v$	A_1, A_2, E_1, E_2	10
$C_{6v}(6mm)$	$I, 2C_6, 2C_3, C_2, 3\sigma_v, 3\sigma_d$	$A_1, A_2, B_1, B_2, E_1, E_2$	12
$C_{2h}(2/m)$	I, C_2, i, σ_h	A_g, A_u, B_g, B_u	4
$D_{2h}(mmm)$	I, C_2^z, C_2^x, C_2^y	$A_{1g}, B_{1g}, B_{2g}, B_{3g}$	8
	$i, \sigma_{xy}, \sigma_{yz}, \sigma_{zx}$	$A_{1u}, B_{1u}, B_{2u}, B_{3u}$	
$D_{3h}(\overline{6}mm)$	$I, 2C_3, 3C_2$	A_1', A_2', E'	12
	$\sigma_h, 2S_3, 3\sigma_v$	A_1'', A_2'', E''	
$D_{6h}(6/mmm)$	$I, 2C_6, 2C_3, C_2, 3\sigma_v, 3\sigma_d$	$A_{1g}, A_{2g}, B_{1g}, B_{2g}, E_{1g}, E_{2g}$	24
	$\sigma_h, 2S_6, 2S_3, i, 3C_3', 3C_2''$	$A_{1u}, A_{2u}, B_{1u}, B_{2u}, E_{1u}, E_{2u}$	
$D_{3d}(\overline{3}m)$	$I, 2C_3, 3C_2$	A_{1g}, A_{2g}, E_g	12
	$i, 2S_6, 3\sigma_d$	A_{1u}, A_{2u}, E_u	
$T_d(\overline{4}3m)$	$I, 8C_3, 3C_2, 6\sigma_d, 6S_4$	A_1, A_2, E, T_1, T_2	24
$O_h(m3m)$	$I, 8C_3, 6C_2, 6C_4, 3C_2$	$A_{1g}, A_{2g}, E_g, T_{1g}, T_{2g}$	48
	$i, 8S_6, 6S_4, 6\sigma_d, 3\sigma_h$	$A_{1u}, A_{2u}, E_u, T_{1u}, T_{2u}$	

[a] Crystallographic notation (Tinkham, 1964).

In the following, we shall refer some molecules to the different symmetry groups using a notation due to Schoenflies[5], usual in Theoretical Chemistry and Spectroscopy, giving the symmetry operations R, the symmetry-defined types (irreducible representations, or irreps, in the language of group theory) Γ^i, and, lastly, the order of the group h (Table 8.1). For comparison, the crystallographic notation (Tinkham, 1964) is given in parenthesis. We may notice from the outset that the number of symmetry operations R coincides with the order of the group, while the number of irreps coincides with the number of classes grouping different operations (see Section 8.5.4 on group theory).

We now list the main symmetry operations occurring in Table 8.1 either in the Schoenflies or in the crystallographic notation.

(i) Schoenflies notation.
$I =$ identity.
$C_n =$ rotation by $2\pi/n$ about an axis.
$\sigma_v =$ reflection in a plane containing the main symmetry axis.
$\sigma_h =$ reflection in a plane perpendicular to the main symmetry axis.
$\sigma_d =$ reflection in a plane containing the main symmetry axis and bisecting the angle between the binary axes perpendicular to the main symmetry axis.
$S_n =$ rotatory reflection, a rotation by $2\pi/n$ followed by a reflection in a plane perpendicular to the rotation axis.

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[5] Schoenflies Arthur 1853–1928, German mathematician, Professor of Mathematics at the University of Frankfurt.

(ii) Crystallographic notation.

$n =$ rotation by $2\pi/n$ about an axis.
$\overline{n} =$ roto-inversion, rotation by $2\pi/n$ followed by inversion.
$\overline{1} =$ inversion i.
$\overline{2} =$ binary rotation (C_2) followed by inversion $=$ reflection in a plane perpendicular to the rotation axis.
$m =$ reflection plane ("mirror").
$/m =$ horizontal reflection plane $= \sigma_h$.

We now list the symmetry-defined types (irreps) Γ_i occurring in Table 8.1.

A: 1-dimensional irrep, symmetric with respect to rotation about the main symmetry axis. If more than one: $A_1, A_2, \cdots$
B: 1-dimensional irrep, antisymmetric with respect to rotation about the main symmetry axis. If more than one: $B_1, B_2, \cdots$
E: 2-dimensional irrep. If more than one: $E_1, E_2, \cdots$ (Y_{l1} transforms like E_1, Y_{l2} transforms like $E_2, \cdots$).
T: 3-dimensional irrep. If more than one: $T_1, T_2, \cdots$
g, u: even (gerade) or odd (ungerade) with respect to the inversion i.
$'$ or $''$: even or odd with respect to the reflection σ_h.
$\Sigma, \Pi, \Delta, \Phi, \cdots$: irreps of the axial rotation group ($C_{\infty v}$). Apart from Σ, all are 2-dimensional.
$S, P, D, F, \cdots$: irreps of the full rotation group (R_3). Dimensionality: $1, 3, 5, 7, \cdots$ $(2l + 1)$.

Finally, we summarize the notation of the molecular point groups (Table 8.1) in the Schoenflies notation.

C_n: a single rotation axis C_n.
C_{nv}: C_n with n vertical symmetry planes.
C_{nh}: C_n with a horizontal symmetry plane.
D_n: n binary axes (C_2) perpendicular to C_n.
D_{nh}: D_n with a horizontal symmetry plane.
D_{nd}: D_n with n symmetry planes σ_d.
S_n: a single rotation-reflection axis.
T: the group of regular tetrahedron (I, C_2, C_3).
T_d: T with symmetry planes (T, σ_d, S_4).
T_h: T with centre of symmetry.
O: the group of regular octahedron or cube.
O_h: O with centre of symmetry.
$C_{\infty v}$: (infinite) axial rotation group.
$D_{\infty h}$: (infinite) axial rotation group with centre of symmetry.

We end this Section by giving (Table 8.2) the point group of a few simple polyatomic molecules.

Table 8.2.

Point groups of a few polyatomic molecules

$D_{\infty h}$	Homonuclear diatomics or centrosymmetric linear polyatomic molecules
	H_2, Li_2, N_2, O_2, F_2, C_2H_2, CO_2
$C_{\infty v}$	Heteronuclear diatomics or linear polyatomic molecules without centre of symmetry
	LiH, CO, NO, HX, HCN, COS
C_{2v}	Bent triatomics
	H_2O, H_2S, H_2Se, H_2Te, SO_2, cis-$C_2H_2X_2$, syn-H_2O_2, C_5H_5N (pyridine), $C_{14}H_{10}$ (phenanthrene)
C_{3v}	Pyramidal molecules
	NH_3, PH_3, AsH_3, SbH_3, CH_3X, CHX_3, PCl_3
C_{2h}	trans-$C_2H_2X_2$, anti-H_2O_2
D_{2h}	C_2H_4 (ethylene), $C_{10}H_8$ (naphthalene), $C_{14}H_{10}$ (anthracene), B_2H_6 (diborane)
D_{3d}	Staggered ethane C_2H_6
D_{3h}	Eclipsed ethane C_2H_6
D_{6h}	Benzene C_6H_6
T_d	Tetrahedral molecules
	CH_4, SiH_4, GeH_4, SnH_4, CX_4
O_h	SF_6

8.4 SYMMETRY OPERATIONS AS TRANSFORMATION OF COORDINATE AXES

8.4.1 Passive and Active Representations of Symmetry Operations

We now turn to define exactly what is meant by symmetry operation. Consider first the H_2O molecule, introducing a right-handed Cartesian system of coordinates with the molecule in the yz-plane and the x-axis perpendicular to the molecular plane and pointing in the appropriate direction (Figure 8.1). The symmetry axis is along z, the plane zx bisecting the molecule.

Because of the indistinguishability of the two H nuclei, we can pass from I to II without altering the energy of the molecule (we simply interchange the labels which would arbitrarily distinguish the two H nuclei). The result of going from I to II corresponds to a reflection of the two identical H nuclei across the zx-plane (which is a symmetry plane for H_2O): we say that we have done a *symmetry operation*, in this case a reflection σ'_v across the (vertical) plane zx. Evidently, III is identical to II, since an observer placed in O would see in both cases two physically indistinguishable situations.

We see, therefore, that we can do the symmetry operation in either of two ways:

(1) *Passive* transformation: we subject the coordinate axes to the symmetry operation leaving fixed the points (III).
(2) *Active* transformation: we subject the space points to the symmetry operation leaving fixed the reference system (II).

In general, an operation R done on the axes can be visualized as the inverse operation, R^{-1}, acting on the space point. Even if more difficult to visualize, we shall always refer in the

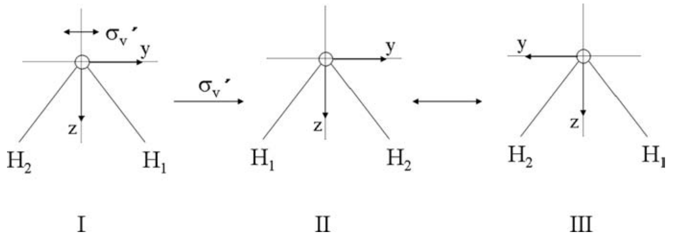
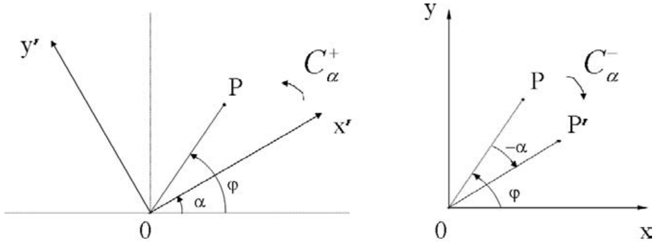


Figure 8.1 Reflection in the vertical plane σ_v' bisecting the molecular plane.



(i) Passive rotation

(ii) Active rotation

Figure 8.2 Passive (left) and active (right) transformations expressing the *same* positive rotation C_α^+.

following to a "symmetry operation as a transformation of the coordinate axes" (the passive transformation). As a second example (Figure 8.2), consider a point P on the coordinate plane xy. The positive rotation by $+\alpha$ (C_α^+) about z in the *passive* representation (left part of Figure 8.2, rotation of axes by $+\alpha$ in the anticlockwise sense), is equivalent to the rotation by $-\alpha$ (clockwise, right part of Figure 8.2) of the point in the *active* representation. Positive rotations are always anticlockwise.

Identity, rotations and inversion are *primitive* symmetry operations, all others being *compounded* symmetry operations. For instance, the reflection across a plane is always expressible as a binary rotation about an axis perpendicular to the plane followed by inversion. We can write:

$$iC_2 = \sigma, \tag{10}$$

where we write on the right the operation done first. We can compound the symmetry operations, the result of more symmetry operations still being a symmetry operation (generally, however, the commutative law does not hold, namely $RS \neq SR$). Given an operation R we can define its inverse, R^{-1}, as that operation which brings anything to the initial state:

$$RR^{-1} = R^{-1}R = I. \tag{11}$$

We then have:

$$I^{-1} = I, \qquad \left(C_n^+\right)^{-1} = C_n^-, \qquad \left(S_n^+\right)^{-1} = S_n^-, \qquad i^{-1} = i, \qquad \sigma^{-1} = \sigma. \tag{12}$$

The inverse of the product of two symmetry operations R, S is:

$$(RS)^{-1} = S^{-1}R^{-1}. \tag{13}$$

8.4.2 Symmetry Transformations in Coordinate Space

We now examine the effect of rotation and reflection of a space point P in the passive representation.

(i) Rotation of coordinate axes.

We have the geometric relations:

$$\begin{aligned} x &= \overline{OP}\cos\varphi \\ y &= \overline{OP}\sin\varphi \\ \widehat{POX'} &= \varphi - \alpha. \end{aligned} \tag{14}$$

The transformation of the coordinates of the point P under the rotation C_α^+ will be:

$$\begin{cases} x' = \overline{OP}\cos(\varphi - \alpha) = \overline{OP}(\cos\varphi\cos\alpha + \sin\varphi\sin\alpha) \\ y' = \overline{OP}\sin(\varphi - \alpha) = \overline{OP}(\sin\varphi\cos\alpha - \cos\varphi\sin\alpha) \end{cases} \tag{15}$$

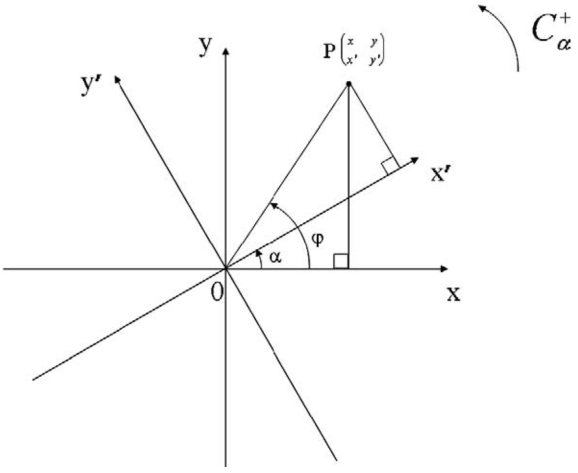


Figure 8.3 Rotation of the space point P about the z-axis.

namely:

$$\begin{cases} x' = x\cos\alpha + y\sin\alpha \\ y' = -x\sin\alpha + y\cos\alpha \end{cases} \tag{16}$$

which can be written in matrix form[6]:

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \underbrace{\begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix}}_{\mathbf{D}(C_\alpha^+)} \begin{pmatrix} x \\ y \end{pmatrix}, \tag{17}$$

where $\mathbf{D}(C_\alpha^+)$ is the matrix representative (darstellung) of the anticlockwise (positive) rotation C_α^+, with the inverse transformation:

$$\begin{pmatrix} x \\ y \end{pmatrix} = \underbrace{\begin{pmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{pmatrix}}_{\mathbf{D}(C_\alpha^-)} \begin{pmatrix} x' \\ y' \end{pmatrix} \tag{18}$$

$\mathbf{D}(C_\alpha^-)$ being the matrix describing the clockwise (negative) rotation C_α^- of the coordinate axes. The matrices describing rotations, $\mathbf{D}(C_\alpha^+)$ and $\mathbf{D}(C_\alpha^-)$, are orthogonal matrices so that:

$$\mathbf{D}(C_\alpha^+)\mathbf{D}(C_\alpha^-) = \begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix} \begin{pmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{pmatrix} = \mathbf{1}. \tag{19}$$

(ii) Reflection of coordinate axes.

We have:

$$\begin{aligned} x &= \overline{OP}\cos\varphi \\ y &= \overline{OP}\sin\varphi \\ \widehat{POX'} &= \varphi - 2\alpha. \end{aligned} \tag{20}$$

The transformation of the coordinates of the point P under the reflection σ_α will be:

$$\begin{cases} x' = \overline{OP}\cos(\varphi - 2\alpha) = \overline{OP}(\cos\varphi\cos 2\alpha + \sin\varphi\sin 2\alpha) \\ y' = -\overline{OP}\sin(\varphi - 2\alpha) = -\overline{OP}(\sin\varphi\cos 2\alpha - \cos\varphi\sin 2\alpha) \end{cases} \tag{21}$$

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[6] We shall always take coordinates as columns and basis functions as rows.

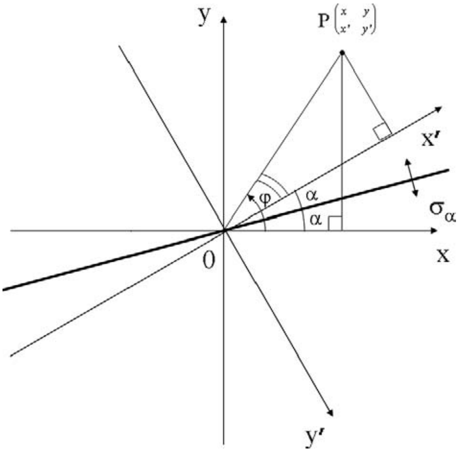


Figure 8.4 Reflection of the space point P across the plane σ_α.

namely:

$$\begin{cases} x' = x\cos 2\alpha + y\sin 2\alpha \\ y' = x\sin 2\alpha - y\cos 2\alpha \end{cases} \tag{22}$$

and, in matrix form:

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \underbrace{\begin{pmatrix} \cos 2\alpha & \sin 2\alpha \\ \sin 2\alpha & -\cos 2\alpha \end{pmatrix}}_{\mathbf{D}(\sigma_\alpha)} \begin{pmatrix} x \\ y \end{pmatrix}. \tag{23}$$

The inverse transformation is described by the *same* matrix:

$$\mathbf{D}\big(\sigma_\alpha^{-1}\big) = \mathbf{D}(\sigma_\alpha). \tag{24}$$

8.4.3 Symmetry Operators and Transformations in Function Space

Symmetry operations are described by linear operators $\hat{R}$ having as representatives in a given basis *orthogonal* matrices $\mathbf{D}(R) = \mathbf{R}$.

Now, let $\hat{R}q$ be the coordinate transformation of the space point P under the symmetry operation $\hat{R}$:

$$q' = \hat{R}q, \tag{25}$$

and:

$$f'(q) = \hat{R}f(q) \tag{26}$$

the transformation of the function $f(q)$ under $\hat{R}$. A transformation of the coordinate axes must not alter the value of the function at each point of space:

$$f'(q') = f(q) \tag{27}$$

namely:

$$\hat{R}f(\hat{R}q) = f(q). \tag{28}$$

Applying equation (28) to the point $R^{-1}q$ we obtain the fundamental relation:

$$\hat{R}f(q) = f(R^{-1}q), \tag{29}$$

namely, *the function transformed under a symmetry operation is nothing but the function calculated by subjecting its argument to the inverse transformation.*

In the following, we omit the caret on the operation R.

(i) Rotation of a function by C_α^+.

Proceeding as in Figure 8.3, we have:

$$\varphi' = C_\alpha^+\varphi = \varphi - \alpha \quad C_\alpha^-\varphi = \varphi + \alpha. \tag{30}$$

1. Transformation of p-functions ($l = 1$):

$$p_x \propto \sin\theta\cos\varphi \qquad p_y \propto \sin\theta\sin\varphi \tag{31}$$

$$\begin{aligned} C_\alpha^+ p_x(\varphi) &= p_x(C_\alpha^-\varphi) = p_x(\varphi+\alpha) = \sin\theta\cos(\varphi+\alpha) \\ &= \sin\theta(\cos\varphi\cos\alpha - \sin\varphi\sin\alpha) = p_x\cos\alpha - p_y\sin\alpha \end{aligned} \tag{32}$$

$$C_\alpha^+ p_y(\varphi) = p_y(C_\alpha^-\varphi) = p_x\sin\alpha + p_y\cos\alpha \tag{33}$$

giving the matrix transformation (footnote 6):

$$C_\alpha^+(p_x p_y) = \underbrace{\left(C_\alpha^+ p_x C_\alpha^+ p_y\right)}_{\text{rotated basis}} = \underbrace{(p_x p_y)}_{\text{old basis}} \underbrace{\begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix}}_{\mathbf{D}(C_\alpha^+)} \tag{34}$$

with the character:

$$\chi\left(C_\alpha^+\right) = \mathrm{tr}\mathbf{D}_p\left(C_\alpha^+\right) = 2\cos\alpha \quad (p\text{-basis}). \tag{35}$$

2. Transformation of d-functions ($l = 2$):

$$d_{x^2-y^2} \propto \sin^2\theta\cos 2\varphi \qquad d_{xy} \propto \sin^2\theta\sin 2\varphi \tag{36}$$

$$\begin{aligned} C_\alpha^+ d_{x^2-y^2} &= d_{x^2-y^2}\left(C_\alpha^- \varphi\right) = \sin^2\theta\cos(2\varphi+2\alpha) \\ &= \sin^2\theta(\cos 2\varphi\cos 2\alpha - \sin 2\varphi \sin 2\alpha) \\ &= d_{x^2-y^2}\cos 2\alpha - d_{xy}\sin 2\alpha \end{aligned} \tag{37}$$

$$\begin{aligned} C_\alpha^+ d_{xy} &= d_{xy}\left(C_\alpha^- \varphi\right) = \sin^2\theta\sin(2\varphi+2\alpha) \\ &= d_{x^2-y^2}\sin 2\alpha + d_{xy}\cos 2\alpha \end{aligned} \tag{38}$$

giving the matrix transformation:

$$\begin{aligned} C_\alpha^+\left(d_{x^2-y^2}\, d_{xy}\right) &= \left(C_\alpha^+ d_{x^2-y^2}\; C_\alpha^+ d_{xy}\right) \\ &= \left(d_{x^2-y^2}\, d_{xy}\right) \underbrace{\begin{pmatrix} \cos 2\alpha & \sin 2\alpha \\ -\sin 2\alpha & \cos 2\alpha \end{pmatrix}}_{\mathbf{D}\left(C_\alpha^+\right)} \end{aligned} \tag{39}$$

$$\chi\left(C_\alpha^+\right) = \operatorname{tr}\mathbf{D}_d\left(C_\alpha^+\right) = 2\cos 2\alpha \quad (d\text{-basis}). \tag{40}$$

The matrix representative of the *same* operation C_α^+ is *different* in the basis $(d_{x^2-y^2}\, d_{xy})$. Hence, it is always necessary to specify the *basis* to which the representative is referred.

(ii) Reflection of a function across the plane σ_α.
Taking into account Figure 8.4, we have:

$$\varphi' = \sigma_\alpha^{-1}\varphi = \sigma_\alpha\varphi = \varphi + 2(\alpha - \varphi) = 2\alpha - \varphi. \tag{41}$$

Proceeding as in (i) we have the following results.

1. Transformation of p-functions ($l = 1$):

$$\sigma_\alpha p_x(\varphi) = p_x\left(\sigma_\alpha^{-1}\varphi\right) = p_x(\sigma_\alpha\varphi) = p_x\cos 2\alpha + p_y \sin 2\alpha \tag{42}$$

$$\sigma_\alpha p_y(\varphi) = p_y\left(\sigma_\alpha^{-1}\varphi\right) = p_y(\sigma_\alpha\varphi) = p_x\sin 2\alpha - p_y \cos 2\alpha \tag{43}$$

$$\sigma_\alpha(p_x p_y) = (\sigma_\alpha p_x \sigma_\alpha p_y) = (p_x p_y) \underbrace{\begin{pmatrix} \cos 2\alpha & \sin 2\alpha \\ \sin 2\alpha & -\cos 2\alpha \end{pmatrix}}_{\mathbf{D}_p(\sigma_\alpha)} \tag{44}$$

$$\chi(\sigma_\alpha) = \operatorname{tr}\mathbf{D}_p(\sigma_\alpha) = 0 \quad (p\text{-basis}). \tag{45}$$

2. Transformation of d-functions ($l = 2$):

$$\sigma_\alpha\left(d_{x^2-y^2}\, d_{xy}\right) = \left(d_{x^2-y^2}\, d_{xy}\right) \underset{\mathbf{D}_d(\sigma_\alpha)}{\begin{pmatrix} \cos 4\alpha & \sin 4\alpha \\ \sin 4\alpha & -\cos 4\alpha \end{pmatrix}} \tag{46}$$

$$\chi(\sigma_\alpha) = \operatorname{tr} \mathbf{D}_d(\sigma_\alpha) = 0 \quad (d\text{-basis}). \tag{47}$$

Examples

1. $C^{+}_{\pi/2} p_x = -p_y \qquad C^{+}_{\pi/2} p_y = p_x.$
2. $C^{+}_{\pi/4} d_{x^2-y^2} = -d_{xy} \qquad C^{+}_{\pi/4} d_{xy} = d_{x^2-y^2}.$
3. Symmetry plane $\sigma(zx) \qquad \alpha = 0°.$
   $\sigma(\alpha = 0°)\, p_y = -p_y.$

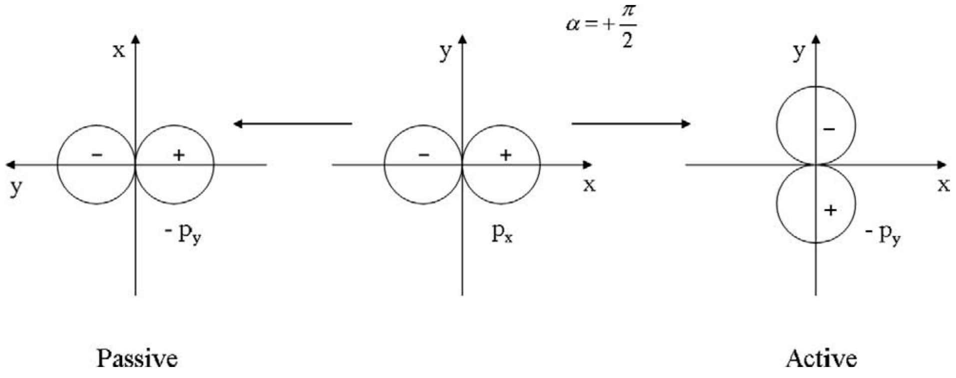


Figure 8.5 Rotation of p_x by $\alpha = \pi/2$.

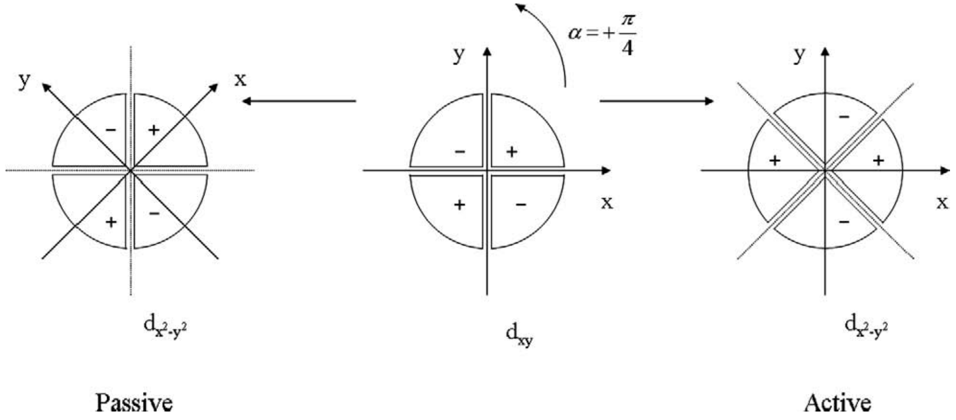


Figure 8.6 Rotation of d_{xy} by $\alpha = \pi/4$.

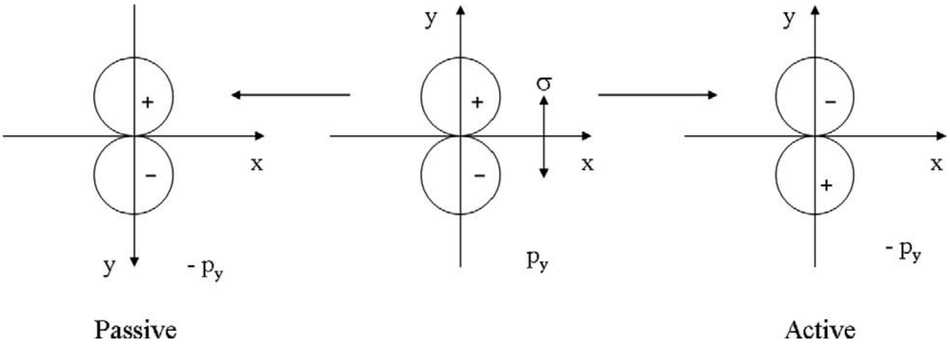


Figure 8.7 Reflection of p_y across $\sigma(zx)$.

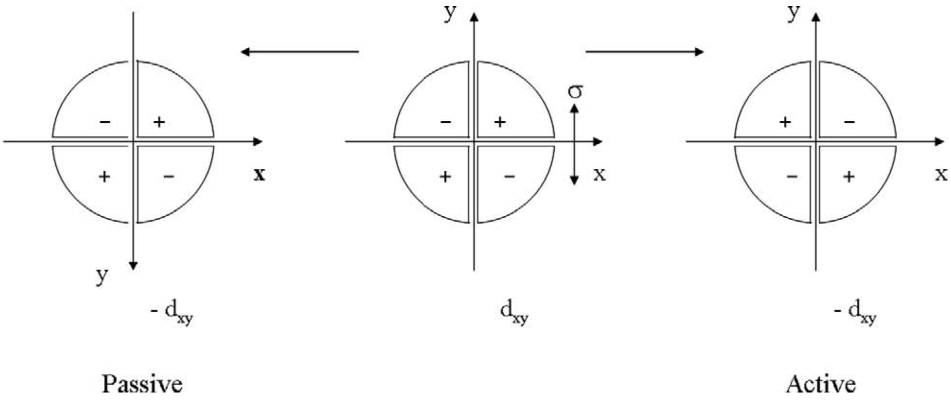


Figure 8.8 Reflection of d_{xy} across $\sigma(zx)$.

4. $\sigma(\alpha = 0°) d_{xy} = -d_{xy}$.

8.4.4 Matrix Representatives of Symmetry Operators

We give below three theorems on the matrix representatives of symmetry operators.

Theorem 1. *Given a* complete *set of orthonormal basis functions* χ_k $(k = 1, 2, \cdots N)$, *the* $D(R)_{ij}$*-element of the matrix representative of the operator* $\hat{R}$ *in the basis* $\boldsymbol{\chi}$ *is given by*:

$$D(R)_{ij} = \int d\mathbf{r}\, \chi_i^*(\mathbf{r}) \hat{R} \chi_j(\mathbf{r}) = \langle \chi_i | \hat{R} | \chi_j \rangle \tag{48}$$

and, in matrix form:

$$\hat{R}\boldsymbol{\chi} = \boldsymbol{\chi}\mathbf{D}_\chi(R) \tag{49}$$

$$\boldsymbol{\chi}^\dagger \hat{R} \boldsymbol{\chi} = (\boldsymbol{\chi}^\dagger \boldsymbol{\chi})\mathbf{D}_\chi(R) = \mathbf{D}_\chi(R). \tag{50}$$

Theorem 2. *If $RS = T$ in coordinate space, then $\hat{R}\hat{S} = \hat{T}$ in function space.* In fact:

$$\begin{aligned}\hat{R}\hat{S}f(q) &= \hat{R}f'(q) = f'(R^{-1}q) = \hat{S}f(R^{-1}q) = f(S^{-1}R^{-1}q) = f(T^{-1}q)\\ &= \hat{T}f(q).\end{aligned} \tag{51}$$

Theorem 3. *There is a one-to-one correspondence between the product of two operators $\hat{R}$, $\hat{S}$ and the product $\mathbf{D}(R)\mathbf{D}(S)$ of their representatives.* Namely, if:

$$\hat{R}\hat{S} = \hat{T} \Longrightarrow \mathbf{D}(R)\mathbf{D}(S) = \mathbf{D}(T). \tag{52}$$

Proof.

$$\hat{S}\boldsymbol{\chi} = \boldsymbol{\chi}\mathbf{D}(S) \qquad \hat{R}\boldsymbol{\chi} = \boldsymbol{\chi}\mathbf{D}(R) \tag{53}$$

$$\hat{T}\boldsymbol{\chi} = \hat{R}\hat{S}\boldsymbol{\chi} = \hat{R}\boldsymbol{\chi}\mathbf{D}(S) = \boldsymbol{\chi}\mathbf{D}(R)\mathbf{D}(S) = \boldsymbol{\chi}\mathbf{D}(T) \tag{54}$$

so that:

$$\mathbf{D}(R)\mathbf{D}(S) = \mathbf{D}(T). \quad \text{Q.E.D.} \tag{52}$$

8.4.5 Similarity Transformations

We give in this Section three further theorems concerning the transformation properties of the matrix representatives $\mathbf{D}(R)$ of a symmetry operator $\hat{R}$.

Theorem 1. *If basis $\boldsymbol{\chi}$ is changed into basis $\boldsymbol{\chi}'$ by the transformation $\mathbf{U}$, then the representative $\mathbf{D}_{\chi'}(R)$ of $\hat{R}$ in the new basis is related to the representative $\mathbf{D}_{\chi}(R)$ in the old basis by the* similarity transformation (*55*):

$$\boldsymbol{\chi}' = \boldsymbol{\chi}\mathbf{U} \Longrightarrow \mathbf{D}_{\chi'}(R) = \mathbf{U}^{-1}\mathbf{D}_{\chi}(R)\mathbf{U}. \tag{55}$$

Proof.

$$\hat{R}\boldsymbol{\chi} = \boldsymbol{\chi}\mathbf{D}_{\chi}(R) = \boldsymbol{\chi}'\mathbf{U}^{-1}\mathbf{D}_{\chi}(R) \tag{56}$$

$$\hat{R}\boldsymbol{\chi}\mathbf{U} = \boldsymbol{\chi}'\mathbf{U}^{-1}\mathbf{D}_{\chi}(R)\mathbf{U} \tag{57}$$

namely:

$$\hat{R}\boldsymbol{\chi}' = \boldsymbol{\chi}'\mathbf{D}_{\chi'}(R). \quad \text{Q.E.D.} \tag{58}$$

A similarity transformation is hence a change in the representative of an operator $\hat{R}$ induced by a change in the basis.

Theorem 2. *Representatives of an operator $\hat{R}$ related by a similarity transformation have the same trace* (*sum of the diagonal matrix elements*). *This means that the trace of a matrix representative is* invariant *under a similarity transformation.*

Similarity transformations bear a particular importance, since it is always possible to do a change in the basis (namely, to choose matrix $\mathbf{U}$) in a way such that the new basis be reduced to block ("sausage") form and the corresponding matrix representatives to block-diagonal form.

Theorem 3. *If we obtain a representative of an operator $\hat{R}$ in a block-diagonal form*, *its basis separates into two* (*or more*) *independent sub-bases* (*the "sausage"*), *and each block of the matrix representative is by itself a* (*reduced*) *representative of the operator.*

For finding a basis which shows a characteristic behaviour under all symmetry operations $\hat{R}$ of the group, whose matrix representatives cannot be further simplified by similarity transformations (which are, in other words, *irreducible*), we must resort to more formal group theoretical methods, as we go to discuss in the next Section.

8.5 GROUP THEORETICAL METHODS

8.5.1 Axioms of Group Theory

Def. An (abstract) group $G\{G_1, G_2, \cdots, G_h\}$ of order h is given by a *closed* set of h elements satisfying the following properties:

(i) There is a *composition* law (usually, but not necessarily, the multiplication law) such that $G_r G_s = G_t$ still belongs to G (we say that a group is *closed* with respect to the symbolic multiplication).

(ii) The law of composition is *associative*:

$$(G_r G_s) G_t = G_r (G_s G_t). \tag{59}$$

(iii) There is the *identity* or unity (or neutral) element G_μ, such that:

$$G_r G_\mu = G_\mu G_r = G_r. \tag{60}$$

(iv) Each element has an *inverse* G_r^{-1}, such that:

$$G_r G_r^{-1} = G_r^{-1} G_r = G_\mu. \tag{61}$$

(v) In general, the commutative law does not hold, i.e.:

$$G_r G_s \neq G_s G_r. \tag{62}$$

If:

$$G_r G_s = G_s G_r \tag{63}$$

the group is said to be Abelian[7] (commutative group).

8.5.2 Examples of Groups

1. The set of integers (positive and negative) $\{a\}$ forms an infinite Abelian group with respect to addition:

$$\begin{array}{ccc} a+b=c & (a+b)+c=a+(b+c) & a+0=0+a=a \\ \text{addition} & \text{associative} & 0 \text{ is the neutral element} \\ a-a=0 & a+b=b+a. & \\ -a \text{ is the inverse} & \text{commutative} & \end{array} \tag{64}$$

2. The set of numbers $\{1, i, -1(i^2), -i\,(i^3)\}$ forms an Abelian group of order 4 with respect to multiplication[8]. We have the multiplication table:

Multiplication table	1	i	-1	$-i$
1	1	i	-1	$-i$
i	i	-1	$-i$	1
-1	-1	$-i$	1	i
$-i$	$-i$	1	i	-1

Each element of the group occurs only once along each row and each column. The identity element is 1.

The inverse of:	1	i	-1	$-i$
is:	1	$-i$	-1	i

3. The set of symmetry operations transforming the equilateral triangle into itself forms a finite group of order 6 (the point group C_{3v}). The elements are the 6 symmetry operations: I, C_3^+, C_3^-, σ_1, σ_2, σ_3 (Figure 8.9), having the multiplication table:

Multiplication table	I	C_3^+	C_3^-	σ_1	σ_2	σ_3
I	I	C_3^+	C_3^-	σ_1	σ_2	σ_3
C_3^+	C_3^+	C_3^-	I	σ_2	σ_3	σ_1
C_3^-	C_3^-	I	C_3^+	σ_3	σ_1	σ_2
σ_1	σ_1	σ_3	σ_2	I	C_3^-	C_3^+
σ_2	σ_2	σ_1	σ_3	C_3^+	I	C_3^-
σ_3	σ_3	σ_2	σ_1	C_3^-	C_3^+	I

---

[7] Abel Niels Henrik 1802–1828, Norwegian mathematician.

[8] i is the imaginary unit ($i^2 = -1$).

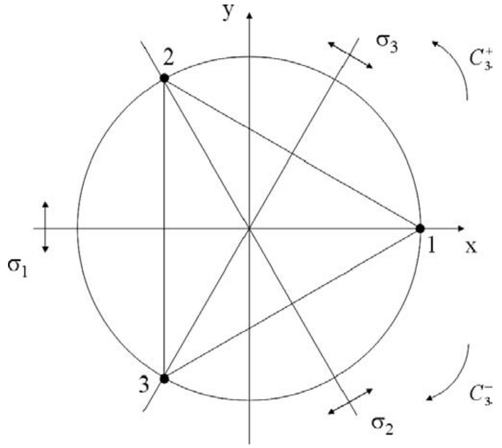


Figure 8.9 Symmetry elements of the equilateral triangle.

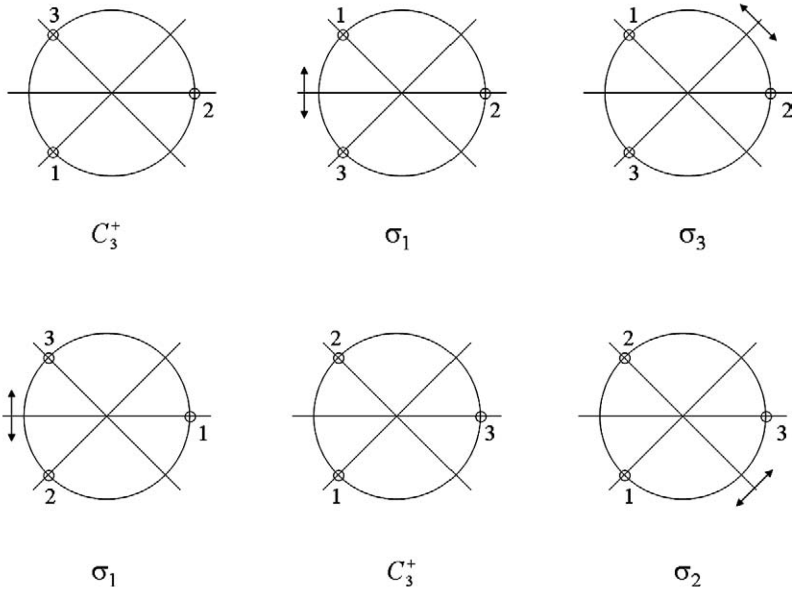


Figure 8.10 The product of two symmetry operations of the group C_{3v} is not commutative (active representation).

Taking Figure 8.9 as reference, Figure 8.10 shows the non-commutation of the product of the two operations σ_1 and C_3^+ of the group C_{3v} (the operation on the right being done first):

$$\sigma_1 C_3^+ = \sigma_3 \qquad C_3^+ \sigma_1 = \sigma_2. \tag{65}$$

Starting from the 3-term basis functions:

$$\boldsymbol{\chi} = (|1\rangle \ |2\rangle \ |3\rangle) \tag{66}$$

we further show how to construct the matrix representatives $\mathbf{D}(C_3^+)$ and $\mathbf{D}(C_3^-)$. We have:

$$C_3^+|1\rangle = |3\rangle \qquad C_3^+|2\rangle = |1\rangle \qquad C_3^+|3\rangle = |2\rangle \tag{67}$$

$$C_3^+\boldsymbol{\chi} = (C_3^+|1\rangle \ C_3^+|2\rangle \ C_3^+|3\rangle) = (|1\rangle \ |2\rangle \ |3\rangle) \underbrace{\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}}_{\mathbf{D}(C_3^+)} \tag{68}$$

$$C_3^-|1\rangle = |2\rangle \qquad C_3^-|2\rangle = |3\rangle \qquad C_3^-|3\rangle = |1\rangle \tag{69}$$

$$C_3^-\boldsymbol{\chi} = (|1\rangle \ |2\rangle \ |3\rangle) \underbrace{\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}}_{\mathbf{D}(C_3^-)}. \tag{70}$$

Matrix multiplication then shows:

$$\mathbf{D}(C_3^+)\mathbf{D}(C_3^-) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} = \mathbf{1} \tag{71}$$

in agreement with the result of the multiplication table.

4. The set of the six functions:

$$I(x) = x \qquad A(x) = (1-x)^{-1} \qquad B(x) = 1 - x^{-1} \tag{72}$$

$$C(x) = x^{-1} \qquad D(x) = 1 - x \qquad E(x) = x(1-x)^{-1} \tag{73}$$

forms a group of order 6 with respect to the *substitution* of one function into the other as a function of a function[9] (Hall, 1967). The group is not Abelian. The substitution table is given below, the details being in Problem 8.5.

Substitution table	I	A	B	C	D	E
I	I	A	B	C	D	E
A	A	B	I	E	C	D
B	B	I	A	D	E	C
C	C	D	E	I	A	B
D	D	E	C	B	I	A
E	E	C	D	A	B	I

8.5.3 Isomorphism

Let G and G' be two finite groups of the same order h:

$$G\{G_1, G_2, \cdots, G_h\} \tag{74}$$

$$G'\{G'_1, G'_2, \cdots, G'_h\}. \tag{75}$$

The two groups G and G' are *isomorphic* if:

1. There is a one-to-one correspondence between each element G_r of G and G'_r of G':

$$G'_1 \leftrightarrow G_1, \quad G'_2 \leftrightarrow G_2, \quad \cdots, \quad G'_h \leftrightarrow G_h \tag{76}$$

2. The symbolic multiplication rule is preserved:

$$G_r G_s = G_t \text{ in } G \quad \leftrightarrow \quad G'_r G'_s = G'_t \text{ in } G'. \tag{77}$$

If only property 1 is valid, the two groups are called homomorphic. As an example, are isomorphic the three groups of order 4:

(a) The numbers	1	i	-1	$-i$
(b) The matrices	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$
(c) The cyclic group C_4	I	$C_4^1 = C_4^+$	$C_4^2 = C_2$	$C_4^3 = C_4^-$

when as composition rule is assumed the ordinary multiplication rule for (a) and (c), and the matrix multiplication rule for (b). The easy proof is left to the reader.
As a further example, are isomorphic the three groups of order 6:

---

[9] This substitutional group is a particular *finite* subgroup of the continuous group of conformal transformations.

(d) The group C_{3v} of the symmetry operations of the equilateral triangle.
(e) The group of the 3×3 representative matrices of C_{3v} in the basis of the three $1s$ functions $(h_1 h_2 h_3)$.
(f) The group of the 2×2 matrices (E symmetry) representative of C_{3v} in the symmetry-adapted basis $(h_x h_y)$.

We have:

(d) $C_{3v}\{I, C_3^+, C_3^-, \sigma_1, \sigma_2, \sigma_3\}$

$$\begin{array}{lcccccc}
\text{(e)} & \mathbf{D}_\chi(I) & \mathbf{D}_\chi(C_3^+) & \mathbf{D}_\chi(C_3^-) & \mathbf{D}_\chi(\sigma_1) & \mathbf{D}_\chi(\sigma_2) & \mathbf{D}_\chi(\sigma_3) \\
\begin{array}{l}\boldsymbol{\chi}\text{ basis}\\(h_1h_2h_3)\end{array} &
\begin{pmatrix}1&\cdot&\cdot\\\cdot&1&\cdot\\\cdot&\cdot&1\end{pmatrix} &
\begin{pmatrix}\cdot&1&\cdot\\\cdot&\cdot&1\\1&\cdot&\cdot\end{pmatrix} &
\begin{pmatrix}\cdot&\cdot&1\\1&\cdot&\cdot\\\cdot&1&\cdot\end{pmatrix} &
\begin{pmatrix}1&\cdot&\cdot\\\cdot&\cdot&1\\\cdot&1&\cdot\end{pmatrix} &
\begin{pmatrix}\cdot&\cdot&1\\\cdot&1&\cdot\\1&\cdot&\cdot\end{pmatrix} &
\begin{pmatrix}\cdot&1&\cdot\\1&\cdot&\cdot\\\cdot&\cdot&1\end{pmatrix}
\end{array}$$

$$\begin{array}{lcccccc}
\text{(f)} & \mathbf{D}_{\chi'}(I) & \mathbf{D}_{\chi'}(C_3^+) & \mathbf{D}_{\chi'}(C_3^-) & \mathbf{D}_{\chi'}(\sigma_1) & \mathbf{D}_{\chi'}(\sigma_2) & \mathbf{D}_{\chi'}(\sigma_3) \\
\begin{array}{l}\boldsymbol{\chi}'\text{ basis}\\(h_xh_y)\end{array} &
\begin{pmatrix}1&\cdot\\\cdot&1\end{pmatrix} &
\begin{pmatrix}\bar{c}&s\\\bar{s}&\bar{c}\end{pmatrix} &
\begin{pmatrix}\bar{c}&\bar{s}\\s&\bar{c}\end{pmatrix} &
\begin{pmatrix}1&\cdot\\\cdot&\bar{1}\end{pmatrix} &
\begin{pmatrix}\bar{c}&\bar{s}\\\bar{s}&c\end{pmatrix} &
\begin{pmatrix}\bar{c}&s\\s&c\end{pmatrix}
\end{array}$$

In fact:

$$\mathbf{D}_\chi(\sigma_1)\mathbf{D}_\chi(C_3^+) = \begin{pmatrix}1&\cdot&\cdot\\\cdot&\cdot&1\\\cdot&1&\cdot\end{pmatrix}\begin{pmatrix}\cdot&1&\cdot\\\cdot&\cdot&1\\1&\cdot&\cdot\end{pmatrix} = \begin{pmatrix}\cdot&1&\cdot\\1&\cdot&\cdot\\\cdot&\cdot&1\end{pmatrix} = \mathbf{D}_\chi(\sigma_3)$$

$$\mathbf{D}_{\chi'}(\sigma_1)\mathbf{D}_{\chi'}(C_3^+) = \begin{pmatrix}1&\cdot\\\cdot&\bar{1}\end{pmatrix}\begin{pmatrix}\bar{c}&s\\\bar{s}&\bar{c}\end{pmatrix} = \begin{pmatrix}\bar{c}&s\\s&c\end{pmatrix} = \mathbf{D}_{\chi'}(\sigma_3)$$

as $\sigma_1 C_3^+ = \sigma_3$ in C_{3v}, and so on. In the above matrices we posed: $c = \frac{1}{2}$, $\bar{c} = -\frac{1}{2}$, $s = \frac{\sqrt{3}}{2}$, $\bar{s} = -\frac{\sqrt{3}}{2}$.

8.5.4 Conjugation and Classes

Any two elements A and B of a group G are said *conjugate* if they are related by a similarity transformation with all other elements X of the group:

$$A = X^{-1} B X. \tag{78}$$

The set of all conjugate elements defines a *class*. Conjugate operations are always of the same nature (rotations with rotations, reflections with reflections, never rotations with reflections). We can give a geometric interpretation to conjugation, by saying that A represents the same operation as B when the reference axes are subjected to the transformation X. From the multiplication table of the group C_{3v}, we have for instance:

$$\begin{array}{ll}
I^{-1}C_3^+I = C_3^+ & I^{-1}C_3^-I = C_3^- \\
C_3^-C_3^+C_3^+ = C_3^+ & C_3^-C_3^-C_3^+ = C_3^- \\
C_3^+C_3^+C_3^- = C_3^+ & C_3^+C_3^-C_3^- = C_3^- \\
\sigma_1^{-1}C_3^+\sigma_1 = C_3^- & \sigma_1^{-1}C_3^-\sigma_1 = C_3^+ \\
\sigma_2^{-1}C_3^+\sigma_2 = C_3^- & \sigma_2^{-1}C_3^-\sigma_2 = C_3^+ \\
\sigma_3^{-1}C_3^+\sigma_3 = C_3^- & \sigma_3^{-1}C_3^-\sigma_3 = C_3^+
\end{array} \tag{79}$$

so that we can conclude that C_3^+, C_3^- form a class $(2C_3)$. In the same way, we can show that $\sigma_1, \sigma_2, \sigma_3$ form a class (3σ).

The point group C_{3v} has therefore three classes:

$$\begin{array}{ll}
I & \text{identity} \\
2C_3 & \text{ternary rotations} \\
3\sigma & \text{reflections.}
\end{array} \tag{80}$$

The number of classes is equal to the number of the irreducible representations (irreps) of the symmetry group, while in a commutative (Abelian) group the number of classes is equal to the order of the group.

8.5.5 Representations and Characters

(i) Representations.

Let $G\{G_1, G_2, \cdots, G_h\}$ be a group of h elements, and $\{\mathbf{D}(G_1), \mathbf{D}(G_2), \cdots, \mathbf{D}(G_h)\}$ a group of matrices isomorphic to G. We then say that the group of matrices gives a *representation* (darstellung) of the group G. If we have a representation of a group in the form of a group of matrices, we also have an infinite number of representations. In fact, we can apply a similarity transformation to all matrices of a given representation, thereby obtaining a *new* representation of the group, and so on:

$$\mathbf{D}(G_r) \to \mathbf{U}^{-1}\mathbf{D}(G_r)\mathbf{U} \tag{81}$$

$$\begin{aligned}
\mathbf{D}(G_r)\mathbf{D}(G_s) = \mathbf{D}(G_t) \Longrightarrow & \big(\mathbf{U}^{-1}\mathbf{D}(G_r)\mathbf{U}\big)\big(\mathbf{U}^{-1}\mathbf{D}(G_s)\mathbf{U}\big) \\
&= \mathbf{U}^{-1}\mathbf{D}(G_r)\mathbf{D}(G_s)\mathbf{U} = \mathbf{U}^{-1}\mathbf{D}(G_t)\mathbf{U}
\end{aligned} \tag{82}$$

namely, the multiplication rule is maintained during the similarity transformation.

If, by applying a similarity transformation with a unitary matrix $\mathbf{U}$ to a representation of a group G in the form of a group of matrices, we obtain a new representation whose

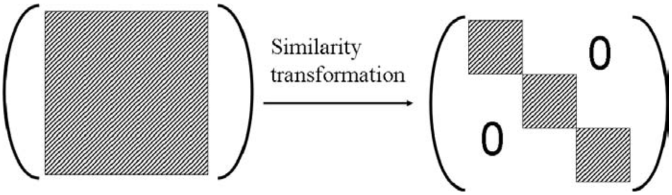


Figure 8.11 A similarity transformation can reduce a matrix representative (left) to block-diagonal form (right).

matrices have a block-diagonal form, we say that the representation has been *reduced* (Figure 8.11).

The set of functions which are needed to find a (generally *reducible*) representation Γ of a symmetry group forms a basis for the representation. The functions forming a basis for the *irreducible representations* (irreps) of a symmetry group are said to be *symmetry-adapted* functions: these functions transform in the simplest and characteristic way under the symmetry operations of the group.

(ii) Characters.

In group theory, the *trace* of the representative in matrix form of a symmetry operator $\hat{R}$ is called the *character* of the operation corresponding to $\hat{R}$, and is denoted by $\chi(R)$. Almost all books on group theory contain extensive Tables of Characters for the main point groups (among others, see: Eyring et al., 1944; Tinkham, 1964). In the following, we shall show for some selected groups (C_{3v} and C_{6v}) how to construct the complete matrices for all symmetry operations corresponding to degenerate irreducible representations, which are essential for constructing symmetry-adapted functions using the powerful projection operator methods of Section 7.

The characters have the following properties:

1. The condition that two representations be equivalent is that they have the same characters.
2. The characters are invariant under any transformation of the basis.
3. The characters are the same for all symmetry operations belonging to the same class.

As an example, consider three $1s$ AOs ($h_1h_2h_3$) at the vertices of an equilateral triangle (Figure 8.12).

We now construct the transformation table of the three functions under C_{3v} symmetry, find the representatives of all operations $\hat{R}$ and their corresponding characters, finally comparing these results with those obtained by a basis of three $1s$ AOs transforming according to the three coordinate axes ($h_xh_yh_z$). We shall see that the two bases are related by a unitary transformation which reduces the former basis and matrix representatives to a block-diagonal form.

$\boldsymbol{\chi}$ basis:

$$\boldsymbol{\chi} = (h_1h_2h_3) \qquad \hat{R}\boldsymbol{\chi} = \boldsymbol{\chi}\mathbf{D}_\chi(R) \tag{83}$$

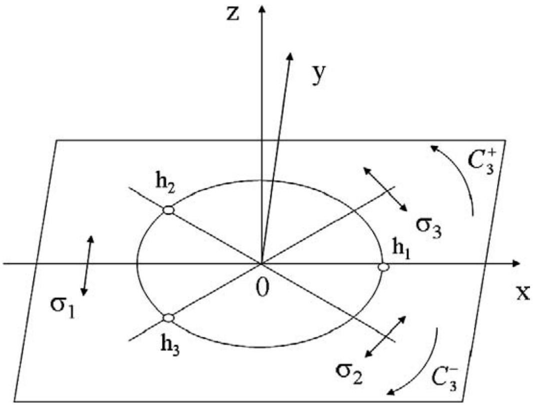


Figure 8.12 Three H 1*s* AOs at the vertices of an equilateral triangle (symmetry C_{3v}).

$\boldsymbol{\chi}'$ basis:

$$\boldsymbol{\chi}' = (h_x h_y h_z) \qquad \hat{R}\boldsymbol{\chi}' = \boldsymbol{\chi}'\mathbf{D}_{\chi'}(R) \tag{84}$$

$$\mathbf{D}_{\chi'}(R) = \mathbf{U}^{\dagger}\mathbf{D}_{\chi}(R)\mathbf{U}. \tag{85}$$

(i) Transformation table under C_{3v}:

$\hat{R}\chi$	I	C_3^+	C_3^-	σ_1	σ_2	σ_3
h_1	h_1	h_3	h_2	h_1	h_3	h_2
h_2	h_2	h_1	h_3	h_3	h_2	h_1
h_3	h_3	h_2	h_1	h_2	h_1	h_3

The basis $\boldsymbol{\chi}'$ transforming according to the three coordinate axes can be immediately found by simple inspection of Figure 8.12. We find:

$$h_x \propto 2h_1 - h_2 - h_3, \qquad h_y \propto h_2 - h_3, \qquad h_z \propto h_1 + h_2 + h_3 \tag{86}$$

giving the normalized functions[10]:

$$h_x = \frac{2h_1 - h_2 - h_3}{\sqrt{6}}, \qquad h_y = \frac{h_2 - h_3}{\sqrt{2}}, \qquad h_z = \frac{h_1 + h_2 + h_3}{\sqrt{3}}. \tag{87}$$

Therefore, the transformation from the old to the new (symmetry-adapted) basis will be:

$$\boldsymbol{\chi}' = \boldsymbol{\chi}\mathbf{U}$$

---

[10] We neglect the overlap between 1*s* AOs.

$$(h_x h_y h_z) = (h_1 h_2 h_3) \underset{\mathbf{U}}{\begin{pmatrix} \frac{2}{\sqrt{6}} & 0 & \frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{3}} \end{pmatrix}}. \tag{88}$$

It is easily verified by direct matrix multiplication that matrix $\mathbf{U}$ is *unitary*:

$$\mathbf{U}\mathbf{U}^{\dagger} = \mathbf{U}^{\dagger}\mathbf{U} = \mathbf{1}. \tag{89}$$

We now construct the matrix representatives of the operations $\hat{R}$ in the two bases.

$$\begin{array}{ccccccc}
\boldsymbol{\chi}\text{-basis} & \mathbf{D}_{\chi}(I) & \mathbf{D}_{\chi}(C_3^{+}) & \mathbf{D}_{\chi}(C_3^{-}) & \mathbf{D}_{\chi}(\sigma_1) & \mathbf{D}_{\chi}(\sigma_2) & \mathbf{D}_{\chi}(\sigma_3) \\
(h_1 h_2 h_3) & \begin{pmatrix} 1 & \cdot & \cdot \\ \cdot & 1 & \cdot \\ \cdot & \cdot & 1 \end{pmatrix} & \begin{pmatrix} \cdot & 1 & \cdot \\ \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \end{pmatrix} & \begin{pmatrix} \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \\ \cdot & 1 & \cdot \end{pmatrix} & \begin{pmatrix} 1 & \cdot & \cdot \\ \cdot & \cdot & 1 \\ \cdot & 1 & \cdot \end{pmatrix} & \begin{pmatrix} \cdot & \cdot & 1 \\ \cdot & 1 & \cdot \\ 1 & \cdot & \cdot \end{pmatrix} & \begin{pmatrix} \cdot & 1 & \cdot \\ 1 & \cdot & \cdot \\ \cdot & \cdot & 1 \end{pmatrix} \\
\chi(\Gamma) & 3 & 0 & 0 & 1 & 1 & 1
\end{array}$$

$$\boldsymbol{\chi}' = \boldsymbol{\chi}\mathbf{U} \tag{90}$$

$$\begin{array}{ccccccc}
\boldsymbol{\chi}'\text{-basis} & \mathbf{D}_{\chi'}(I) & \mathbf{D}_{\chi'}(C_3^{+}) & \mathbf{D}_{\chi'}(C_3^{-}) & \mathbf{D}_{\chi'}(\sigma_1) & \mathbf{D}_{\chi'}(\sigma_2) & \mathbf{D}_{\chi'}(\sigma_3) \\
\begin{array}{cc} (h_x h_y \mid & h_z) \\ E & A_1 \\ 2\times 2 & 1\times 1 \end{array} & \left(\begin{array}{cc|c} 1 & \cdot & \\ \cdot & 1 & 0 \\ \hline \multicolumn{2}{c|}{0} & 1 \end{array}\right) & \left(\begin{array}{cc|c} \bar{c} & s & \\ \bar{s} & \bar{c} & 0 \\ \hline \multicolumn{2}{c|}{0} & 1 \end{array}\right) & \left(\begin{array}{cc|c} \bar{c} & \bar{s} & \\ s & \bar{c} & 0 \\ \hline \multicolumn{2}{c|}{0} & 1 \end{array}\right) & \left(\begin{array}{cc|c} 1 & \cdot & \\ \cdot & \bar{1} & 0 \\ \hline \multicolumn{2}{c|}{0} & 1 \end{array}\right) & \left(\begin{array}{cc|c} \bar{c} & \bar{s} & \\ \bar{s} & c & 0 \\ \hline \multicolumn{2}{c|}{0} & 1 \end{array}\right) & \left(\begin{array}{cc|c} \bar{c} & s & \\ s & c & 0 \\ \hline \multicolumn{2}{c|}{0} & 1 \end{array}\right) \\
\chi(\Gamma') & 3 & 0 & 0 & 1 & 1 & 1
\end{array}$$

Γ' splits into the two irreps: $\Gamma' = E + A_1$.

The new basis has the following transformation table.

$\hat{R}\chi'$	I	C_3^{+}	C_3^{-}	σ_1	σ_2	σ_3
h_x	h_x	$-\frac{1}{2}h_x - \frac{\sqrt{3}}{2}h_y$	$-\frac{1}{2}h_x + \frac{\sqrt{3}}{2}h_y$	h_x	$-\frac{1}{2}h_x - \frac{\sqrt{3}}{2}h_y$	$-\frac{1}{2}h_x + \frac{\sqrt{3}}{2}h_y$
h_y	h_y	$\frac{\sqrt{3}}{2}h_x - \frac{1}{2}h_y$	$-\frac{\sqrt{3}}{2}h_x - \frac{1}{2}h_y$	$-h_y$	$-\frac{\sqrt{3}}{2}h_x + \frac{1}{2}h_y$	$\frac{\sqrt{3}}{2}h_x + \frac{1}{2}h_y$
h_z	h_z	h_z	h_z	h_z	h_z	h_z

8.5.6 Irreducible Representations

We now give without proof five theorems on irreducible representations.

Theorem 1. *The number of irreducible representations is equal to the number of classes.*

Theorem 2. *The necessary and sufficient condition that a representation* Γ *be irreducible is that the sum* (*over all the operations* $\hat{R}$ *of the group*) *of the squares of the moduli of the characters be equal to the order h of the group*:

$$\sum_R \chi^*(R)\chi(R) = \sum_R |\chi(R)|^2 = h. \tag{91}$$

Theorem 3. The preceding theorem is a particular case of the following one. *Given any two irreducible representations* Γ^i *and* Γ^j *of a group*:

$$\sum_R \chi^i(R)^* \chi^j(R) = h\delta_{ij} \tag{92}$$

which is known as the orthogonality relation *for the characters*. We can also say that *the characters of non-equivalent irreps form a system of orthogonal vectors.*

Theorem 4. Theorem 3 is a particular case of the more general *orthogonality theorem* for the components (in the form of matrices) of the h elements of the group:

$$\sum_R \mathbf{D}^i(R)^*_{mn} \mathbf{D}^j(R)_{m'n'} = \frac{h}{l_i}\delta_{ij}\delta_{mm'}\delta_{nn'}, \tag{93}$$

where h is the order of the group, *and* l_i *the dimensionality of the i-th irrep*. In other words: *the components* (*in the form of matrices*) *of the h elements of the group can be considered as the components of an h-dimensional vector, orthogonal to other vectors obtained by a different choice of the indices m, n, and to any other vector obtained from a different irreducible representation.*

Theorem 5. *Functions that belong to different irreducible representations or to different columns of the same are* orthogonal.

From the orthogonality theorems it follows immediately that the number of times (a_j) a given irrep Γ^j occurs in the reducible representation Γ can be determined as:

$$\underset{\text{reducible}}{\mathbf{D}^\Gamma(R)} = \sum_i a_i \underset{\text{irreducible}}{\mathbf{D}^i(R)} \quad \text{matrices} \tag{94}$$

$$\chi^\Gamma(R) = \sum_i a_i \chi^i(R) \quad \text{characters.} \tag{95}$$

Multiplying both sides of the last equation by $\chi^j(R)^*$ and adding over all operations $\hat{R}$ of the group, we find immediately:

$$\sum_R \chi^j(R)^* \chi^\Gamma(R) = \sum_i a_i \Big(\sum_R \chi^j(R)^* \chi^i(R) \Big) = \sum_i a_i h \delta_{ij} = h a_j, \tag{96}$$

giving:

$$a_j = \frac{1}{h} \sum_R \chi^j(R)^* \chi^\Gamma(R) \tag{97}$$

as the number of times that the j-th irrep occurs in the reducible representation Γ.

As a further example, we shall verify all previous theorems using the example of the three $1s$ AOs $(h_1 h_2 h_3)$ belonging to C_{3v} symmetry. The character table and the symmetry-adapted functions transforming as (x, y, z) are:

C_{3v}	I	$2C_3$	3σ	Symmetry-adapted functions
A_1	1	1	1	$h_z = \frac{1}{\sqrt{3}}(h_1 + h_2 + h_3)$
A_2	1	1	-1	
E	2	-1	0	$h_x = \frac{1}{\sqrt{6}}(2h_1 - h_2 - h_3), h_y = \frac{1}{\sqrt{2}}(h_2 - h_3)$
Γ reducible	3	0	1	original basis $(h_1 h_2 h_3)$

Then:

$$\sum_R |\chi^\Gamma(R)|^2 = 9 + 1 + 1 + 1 = 12. \tag{98}$$

Γ is a *reducible* representation. Using equation (97):

$$A_1\colon \quad a_{A_1} = \frac{1}{6}(3 + 0 + 3) = 1$$

$$A_2\colon \quad a_{A_2} = \frac{1}{6}(3 + 0 - 3) = 0$$

$$E\colon \quad a_E = \frac{1}{6}(6 + 0 + 0) = 1.$$

Hence, Γ splits into:

$$\Gamma = A_1 + E. \tag{99}$$

8.5.7 Construction of Symmetry-Adapted Functions

An important consequence of the orthogonality theorems is the possibility of constructing projection operators (projectors) $\hat{P}^i$ which, acting on a function without any symmetry, project out the component having the definite symmetry i and transforming as the irrep Γ^i. For l_i-dimensional irreps, the projector for the component λ will be:

$$\hat{P}^i_{\lambda\lambda} = \frac{l_i}{h} \sum_R \mathbf{D}^i(R)^*_{\lambda\lambda} \hat{R}. \tag{100}$$

This powerful projector requires the complete knowledge of the matrices $\mathbf{D}^i(R)$ and not only of the characters. If this is not possible, we can use the simpler, but weaker, projector:

$$\hat{P}^i = \frac{l_i}{h} \sum_R \chi^i(R)^* \hat{R} \tag{101}$$

which is based on the characters only. We must note, however, that whereas projector (101) works well with 1-dimensional irreps, in the case of multi-dimensional irreps it gives symmetry-adapted functions that are not linearly independent. Subsequent Schmidt-orthogonalization is then necessary to get the full set of linearly independent symmetry-adapted functions. We now verify the projector properties of the operator (101) in the case of the isosceles lamina of symmetry C_{2v} (Figure 8.13).

The set of symmetry operations transforming the isosceles lamina into itself makes a group of order 4 (called the C_{2v} group). The group is commutative (Abelian), which means

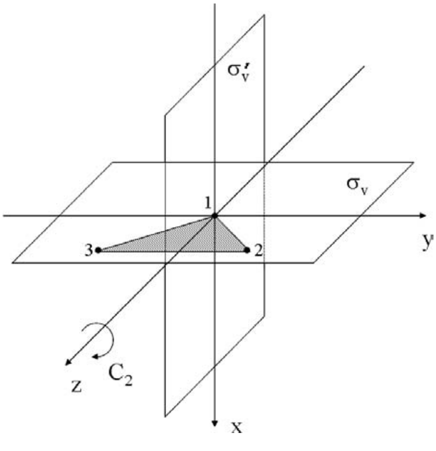


Figure 8.13 Symmetry elements transforming the isosceles lamina into itself under the symmetry C_{2v}.

that the number of symmetry operations is equal to the number of classes and to the number of irreps. Transformation table and character table are (Problem 8.1):

C_{2v}	I	C_2	σ_v	σ_v'
I	I	C_2	σ_v	σ_v'
C_2	C_2	I	σ_v'	σ_v
σ_v	σ_v	σ_v'	I	C_2
σ_v'	σ_v'	σ_v	C_2	I

C_{2v}	I	C_2	σ_v	σ_v'
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	−1	1
B_2	1	−1	1	−1

The properties characterizing (101) as a projection operator are:

$$\hat{P}^i \hat{P}^j = \hat{P}^i \delta_{ij} \quad \text{idempotency (mutual exclusivity)} \tag{102}$$

$$\sum_i \hat{P}^i = \hat{I} \quad \text{completeness (resolution of the identity).} \tag{103}$$

Omitting the caret for short, we have for our isosceles lamina:

$$\begin{aligned}
A_1\colon \quad & P^{A_1} = \frac{1}{4}\sum_R \chi^{A_1}(R)R = \frac{1}{4}(I + C_2 + \sigma_v + \sigma_v') \\
A_2\colon \quad & P^{A_2} = \frac{1}{4}\sum_R \chi^{A_2}(R)R = \frac{1}{4}(I + C_2 - \sigma_v - \sigma_v') \\
B_1\colon \quad & P^{B_1} = \frac{1}{4}\sum_R \chi^{B_1}(R)R = \frac{1}{4}(I - C_2 - \sigma_v + \sigma_v') \\
B_2\colon \quad & P^{B_2} = \frac{1}{4}\sum_R \chi^{B_2}(R)R = \frac{1}{4}(I - C_2 + \sigma_v - \sigma_v').
\end{aligned} \tag{104}$$

Using the transformation table we immediately find:

(i)
$$\begin{aligned}
P^{A_2}P^{A_2} &= \frac{1}{16}(I + C_2 - \sigma_v - \sigma_v')(I + C_2 - \sigma_v - \sigma_v') \\
&= \frac{1}{16}(4I + 4C_2 - 4\sigma_v - 4\sigma_v') = \frac{1}{4}(I + C_2 - \sigma_v - \sigma_v') \\
&= P^{A_2} \quad \text{idempotency}
\end{aligned} \tag{105}$$

(ii)
$$\begin{aligned}
P^{A_1}P^{A_2} &= \frac{1}{16}(I + C_2 + \sigma_v + \sigma_v')(I + C_2 - \sigma_v - \sigma_v') \\
&= \frac{1}{16}[(I + C_2 + \sigma_v + \sigma_v') + (C_2 + I + \sigma_v' + \sigma_v) \\
&\quad - (\sigma_v + \sigma_v' + I + C_2) - (\sigma_v' + \sigma_v + C_2 + I)] \\
&= 0 \quad \text{mutual exclusivity}
\end{aligned} \tag{106}$$

$$\text{(iii)}\qquad \sum_i P^i = P^{A_1} + P^{A_2} + P^{B_1} + P^{B_2}$$

$$= \frac{1}{4}[(I + C_2 + \sigma_v + \sigma_v') + (I + C_2 - \sigma_v - \sigma_v')$$

$$+ (I - C_2 - \sigma_v + \sigma_v') + (I - C_2 + \sigma_v - \sigma_v')]$$

$$= \frac{1}{4}(4I) = I \quad \text{completeness.} \tag{107}$$

Many other applications on the construction of symmetry-adapted functions for H_2O, NH_3, CH_4 and C_6H_6 are given as Problems in Section 8.

8.5.8 The Wigner Method

Once symmetry-adapted functions are obtained from a given basis using the projector methods described in the previous Subsection, the matrix $\mathbf{U}$ which reduces a reducible representation Γ can be easily constructed. Wigner (1959) gave however an alternative way of finding matrix $\mathbf{U}$, which is based upon diagonalization of the *Galois sum* of all representative matrices belonging to a given class.

For a class of two operations A, B we have:

$$X^{-1}AX = B \qquad X^{-1}BX = A \tag{108}$$

$$X^{-1}AX + X^{-1}BX = B + A$$

$$X^{-1}(A + B)X = A + B.$$

Multiplying both members on the left by X:

$$(A + B)X = X(A + B), \tag{109}$$

so that $A + B$ (the Galois sum of all operations belonging to the given class) commutes with all symmetry operations X. According to Wigner, the matrix $\mathbf{U}$ that reduces the reducible representation Γ is given by the matrix built from the eigenvectors arising from the diagonalization of $A + B$. We shall take as an example the class of ternary rotations of C_{3v}. We have (Section 8.5.5):

$$\begin{array}{ccccccc} \mathbf{D}_\chi(C_3^+) & & \mathbf{D}_\chi(C_3^-) & & & & \\ \begin{pmatrix} \cdot & 1 & \cdot \\ \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \end{pmatrix} & + & \begin{pmatrix} \cdot & \cdot & 1 \\ 1 & \cdot & \cdot \\ \cdot & 1 & \cdot \end{pmatrix} & = & \begin{pmatrix} \cdot & 1 & 1 \\ 1 & \cdot & 1 \\ 1 & 1 & \cdot \end{pmatrix} & \Longrightarrow & \begin{vmatrix} -\lambda & 1 & 1 \\ 1 & -\lambda & 1 \\ 1 & 1 & -\lambda \end{vmatrix} = 0. \\ & & & & \text{Galois sum} & & \text{Secular equation} \end{array} \tag{110}$$

Expanding the secular determinant we find the cubic equation:

$$\lambda^3 - 3\lambda - 2 = (\lambda + 1)(\lambda^2 - \lambda - 2) = (\lambda + 1)^2(\lambda - 2) = 0 \tag{111}$$

giving the roots:

$$\underbrace{\lambda_1 = \lambda_2 = -1,}_{\text{twice}} \qquad \lambda_3 = 2. \tag{112}$$

The eigenvectors are calculated in the usual way by substituting each eigenvalue in turn in the homogeneous system taking into account normalization (Chapter 2). The results are:

$$\text{(i)} \qquad \lambda_1 = -1 \qquad \mathbf{c}_1 = \begin{pmatrix} \frac{2}{\sqrt{6}} \\ -\frac{1}{\sqrt{6}} \\ -\frac{1}{\sqrt{6}} \end{pmatrix} \tag{113}$$

$$\text{(ii)} \qquad \lambda_2 = -1 \qquad \mathbf{c}_2 = \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix} \tag{114}$$

$$\text{(iii)} \qquad \lambda_3 = 2 \qquad \mathbf{c}_3 = \begin{pmatrix} \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \end{pmatrix} \tag{115}$$

We therefore obtain matrix **U** as:

$$\mathbf{U} = (\mathbf{c}_1\ \mathbf{c}_2\ \mathbf{c}_3) = \begin{pmatrix} \frac{2}{\sqrt{6}} & 0 & \frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{3}} \end{pmatrix} \tag{116}$$

which is seen to coincide with the result found previously.

In the same way, it can be shown that the same matrix **U** can be obtained from the Galois sum of the reflections $\mathbf{D}_\chi(\sigma_1) + \mathbf{D}_\chi(\sigma_2) + \mathbf{D}_\chi(\sigma_3)$.

8.5.9 Subgroups and Direct-Product Groups

A subgroup is a set of elements of a group which is a group in itself: for instance, C_{3v} is a subgroup of D_{3h}. If two groups, G (order h) and G' (order h'), have (i) as common element only the identity I, and (ii) commuting elements, then the group:

$$G'' = G \times G' \quad (\text{order } hh') \tag{117}$$

is said the *direct-product group* of G by G'. G and G' are said to be *subgroups* of G''. The representations (and the characters) of the direct-product group G'' can be expressed through the product of those of the subgroups G and G'.

As an example, given the two groups C_{3v} (order 6) and C_s (order 2):

C_{3v}	I	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

C_s	I	σ_h
A'	1	1
A''	1	−1

the direct-product group is:

$$D_{3h} = C_{3v} \times C_s \quad (\text{order } 6 \times 2 = 12) \tag{118}$$

D_{3h}	I	$2C_3$	$3\sigma_v$	σ_h	$2S_3$	$3C'_2$
A'_1	1	1	1	1	1	1
A'_2	1	1	−1	1	1	−1
A''_1	1	1	−1	−1	−1	1
A''_2	1	1	1	−1	−1	−1
E'	2	−1	0	2	−1	0
E''	2	−1	0	−2	1	0

As a second example of direct-product group, we can take the symmetry point group of the benzene (C_6H_6) molecule, $D_{6h} = C_{6v} \times C_s = D_6 \times C_i$. Most properties of the π-electron MOs of benzene can be derived in the simplest way in terms of its subgroup C_{6v} (Problem 13).

We observe at this point that in the D_{nh} groups the centre of symmetry is lacking for $n =$ odd, and we can take $D_{nh} = C_{nv} \times C_s$. For $n =$ even, D_{nh} has a centre of symmetry, and it is customary to take $D_{nh} = D_n \times C_i$, where D_n is the dihedral group (n symmetry planes intersecting at angles $2\pi/n$) and C_i the inversion group, having as elements the identity I and the inversion operation i. This is because, as we have already said, i is a *primitive* symmetry operation (like rotations) whereas reflections are not. So, for $n =$ even, the irreducible representations of D_{nh} bear the characteristic suffixes g and u (even or odd under inversion, from the German "gerade" and "ungerade").

8.6 APPLICATIONS

We now introduce the fundamental theorem of symmetry, upon which are based all applications of group theory to physical problems.

8.6.1 The Fundamental Theorem of Symmetry

The most important applications of group theoretical methods in Quantum Chemistry are based on Theorem 5 of Section 8.5.6 concerning the orthogonality of functions belonging to different irreducible representations or to different columns of the same (Altmann, 1962), and on the fact that the full Hamiltonian $\hat{H}$ or other model Hamiltonians such as $\hat{F}$ (the Fock operator) or H (the Hückel Hamiltonian) are totally symmetric operators. Then, from:

$$\langle \psi_a^{(i)} | \psi_b^{(j)} \rangle = 0 \quad j \neq i,\ b \neq a \tag{119}$$

it follows that for $\hat{O} = \hat{H}, \hat{F}, H$:

$$\langle \psi_a^{(i)} | \hat{O} | \psi_b^{(j)} \rangle = 0 \tag{120}$$

which is known as fundamental theorem of symmetry. In other words, all matrix elements of the totally symmetric operator $\hat{O}$ between symmetry-adapted functions belonging to different symmetries are zero, independently of any effective calculation. This result is of great importance for the factorization of secular determinants and for the very existence of selection rules.

8.6.2 Selection Rules

An alternative way at looking at the same problem is the statement that the necessary and sufficient condition for an integral such as (120) to be different from zero is that the representation to which its integrand belongs contains the totally symmetric representation (Altmann, 1962). Consider the general matrix element of the operator $\hat{O}$:

$$I = \langle \psi_a(\Gamma^i) | \hat{O}(\Gamma^j) | \psi_b(\Gamma^k) \rangle, \tag{121}$$

where the functions ψ_a and ψ_b belong to the irreps Γ^i and Γ^k, and the operator $\hat{O}$ to the irrep Γ^j. The matrix element I will be different from zero if and only if the direct product $\Gamma^i \times \Gamma^k$ contains the irrep Γ^j, or, alternatively, if $\Gamma^i \times \Gamma^j \times \Gamma^k$ contains the totalsymmetric irrep (A_1 for C_{3v}). As an example, under C_{3v}:

$$\langle \psi_a(A_2) | x(E) | \psi_b(E) \rangle \neq 0 \tag{122}$$

because:

$$A_2 \times E = E \quad \text{and } x \sim E. \tag{123}$$

$$\langle\psi_a(E)|z(A_1)|\psi_b(E)\rangle \neq 0 \tag{124}$$

because it is reducible and splits into:

$$E \times E = A_1 + A_2 + E \quad \text{and } z \sim A_1. \tag{125}$$

$$\langle\psi_a(A_2)|z(A_1)|\psi_b(E)\rangle = 0 \tag{126}$$

because:

$$A_2 \times A_1 \times E = E \tag{127}$$

and it does not contain the irrep A_1.

8.6.3 Ground State Electron Configuration of Polyatomic Molecules

Group theoretical notation is always used in the spectroscopic classification of the electronic states described by MO wavefunctions. We give below the electron configuration of the ground state ${}^{2S+1}X$ of a few polyatomic molecules.

(i) Ground state of homonuclear diatomics ($D_{\infty h}$)

$$\mathrm{H}_2^+\big({}^2\Sigma_g^+\colon\ 1\sigma_g\big) \qquad \mathrm{H}_2\big({}^1\Sigma_g^+\colon\ 1\sigma_g^2\big)$$

$$\mathrm{He}_2^+\big({}^2\Sigma_u^+\colon\ 1\sigma_g^2 1\sigma_u\big) \qquad \big[\mathrm{He}_2\big({}^1\Sigma_g^+\colon\ 1\sigma_g^2 1\sigma_u^2\big)\big] \quad \text{Van der Waals molecule}$$

$$\mathrm{Li}_2\big({}^1\Sigma_g^+\colon\ 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2\big) \qquad \big[\mathrm{Be}_2\big({}^1\Sigma_g^+\colon\ 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2\big)\big]$$

$$\mathrm{N}_2\big({}^1\Sigma_g^+\colon\ 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2\big) = [\mathrm{Be}_2]\,\underset{\text{triple bond}}{1\pi_u^4 3\sigma_g^2}$$

$$\mathrm{O}_2\big({}^3\Sigma_g^-\colon\ 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2\big) \quad \text{paramagnetic molecule}$$

$$\mathrm{F}_2\big({}^1\Sigma_g^+\colon\ [\mathrm{Be}_2] 1\pi_u^4 3\sigma_g^2 1\pi_g^4\big).$$

(ii) Ground state (${}^1\Sigma_g^+$) of centrosymmetric linear polyatomics ($D_{\infty h}$)

$$\mathrm{C}_2\mathrm{H}_2\colon\ 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 \underset{\text{triple bond}}{3\sigma_g^2 1\pi_u^4} \quad N = 14$$

$$\mathrm{CO}_2\colon\ \underbrace{1\sigma_g^2 1\sigma_u^2 2\sigma_g^2}_{\text{core}}\,\underbrace{3\sigma_g^2 2\sigma_u^2 4\sigma_g^2 3\sigma_u^2 1\pi_u^4 1\pi_g^4}_{\text{valence}} \quad N = 22.$$

(iii) Heteronuclear diatomics ($C_{\infty v}$)

$$\mathrm{HX}\left({}^1\Sigma^+\right) \quad \text{with } X = \text{halogen}$$

$$\text{HF: } 1\sigma^2|2\sigma^2 3\sigma^2 1\pi^4 \quad N = 10$$

$$\text{HCl: } 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4|4\sigma^2 5\sigma^2 2\pi^4 \quad N = 18$$

$$\text{HBr: } \underbrace{\underset{K(2)}{1\sigma^2} \mid \underset{L(8)}{2\sigma^2 3\sigma^2 1\pi^4} \mid \underset{M(18)}{4\sigma^2 5\sigma^2 2\pi^4 6\sigma^2 3\pi^4 1\delta^4}}_{\text{core}} \mid \underbrace{7\sigma^2 8\sigma^2 4\pi^4}_{\text{valence}} \quad N = 36.$$

(iv) Ground state (${}^1A_1$) of bent $\mathrm{XH_2}$ molecules (C_{2v})

$$\mathrm{H_2O}\text{: } 1a_1^2|2a_1^2 1b_2^2 3a_1^2 1b_1^2 \quad N = 10$$

$$\mathrm{H_2S}\text{: } \underbrace{1a_1^2|2a_1^2 1b_2^2 3a_1^2 1b_1^2}_{\text{core}} | \underbrace{4a_1^2 2b_2^2 5a_1^2 2b_1^2}_{\text{valence}} \quad N = 18.$$

(v) Ground state (${}^1A_1$) of pyramidal $\mathrm{XH_3}$ molecules (C_{3v})

$$\mathrm{NH_3}\text{: } 1a_1^2|2a_1^2 1e^4 3a_1^2 \quad N = 10$$

$$\mathrm{PH_3}\text{: } \underbrace{\underset{\sim 1s^2}{1a_1^2} \mid \underset{2s^2}{2a_1^2} \; \underset{2p^6}{1e^4 3a_1^2}}_{\text{core}} \mid \underbrace{4a_1^2 2e^4 5a_1^2}_{\text{valence}} \quad N = 18.$$

(vi) Ground state (${}^1A_1$) of tetrahedral $\mathrm{XH_4}$ molecules (T_d)

$$\mathrm{CH_4}\text{: } 1a_1^2|2a_1^2 1t_2^6 \quad N = 10$$

$$\mathrm{SiH_4}\text{: } \underbrace{1a_1^2|2a_1^2 1t_2^6}_{\text{core}} | \underbrace{3a_1^2 2t_2^6}_{\text{valence}} \quad N = 18.$$

(vii) π-electron system of benzene (D_{6h})

$$\mathrm{C_6H_6}\text{: } a_{1u}^2 e_{1g}^4 \quad N_\pi = 6.$$

(viii) π-electron system of naphthalene (D_{2h}) (Murrell, 1963)

$$\mathrm{C_{10}H_8}\text{: } 1b_{1u}^2 1b_{3g}^2 1b_{2g}^2 2b_{1u}^2 1a_{1u}^2 \quad N_\pi = 10.$$

8.7 AN OUTLINE OF CONTINUOUS AND PERMUTATION GROUPS

8.7.1 Continuous Groups

(i) Group elements are *infinite* in number.
(ii) Group elements form a *continuum*, i.e. the individual elements can be specified by giving the values of one or more parameters α (for instance, the three Eulerian angles which specify an arbitrary rotation of a rigid body) which can vary in a continuous way.
(iii) For a one-parameter group with elements $A(\alpha)$, the multiplication table $A(\gamma) = A(\beta)A(\alpha)$ becomes a *functional relation* determining γ from α and β, say $\gamma = f(\beta,\alpha)$. The continuity requirement means that $f(\beta,\alpha)$ must be a *continuous function* of both variables. If f can be differentiated any number of times with respect to α and β (f is then said to be *analytic*), then we have the Lie[11] groups.

Example. The group consisting of all matrices of the form:

$$A(\alpha) = \begin{pmatrix} 1 & \alpha \\ 0 & 1 \end{pmatrix}. \tag{128}$$

For $\alpha = 0$, $A(0) = \mathbf{1}$; $[A(\alpha)]^{-1} = A(-\alpha)$; multiplication table: $\gamma = \alpha + \beta$, that can be differentiated any number of times:

$$A(\beta)A(\alpha) = \begin{pmatrix} 1 & \beta \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 1 & \alpha \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & \alpha+\beta \\ 0 & 1 \end{pmatrix} = A(\alpha+\beta) = A(\gamma) \tag{129}$$

with $\gamma = \alpha + \beta$.

8.7.2 Continuous Lie Groups

- $GL(m)$ = General Linear group in m-dimensions is the infinite set of all real non-singular $m \times m$ matrices $\{\mathbf{A}\}$.
- $SL(m)$ = Special Linear (or unimodular) group is the subgroup of $GL(m)$ consisting of all $m \times m$ matrices $\{\mathbf{A}\}$ whose determinant is unity.
- $O(m)$ = Orthogonal group in m-dimensions is the infinite set of all *real* $m \times m$ matrices $\mathbf{A}$ satisfying $\mathbf{A}\tilde{\mathbf{A}} = \tilde{\mathbf{A}}\mathbf{A} = \mathbf{1}$, whence $\mathbf{A}^{-1} = \tilde{\mathbf{A}}$.
- $U(m)$ = Unitary group in m-dimensions is the infinite set of all $m \times m$ matrices $\mathbf{U}$ with *complex* elements satisfying $\mathbf{U}\mathbf{U}^\dagger = \mathbf{U}^\dagger\mathbf{U} = \mathbf{1}$, whence $\mathbf{U}^{-1} = \mathbf{U}^\dagger$.
- $SU(m)$ = Special Unitary group in m-dimensions is the subgroup of $U(m)$ consisting of all $m \times m$ matrices $\mathbf{U}$ whose determinant is unity.

---

[11] Lie Sophus 1842–1899, Norwegian mathematician, Professor of Mathematics at the Universities of Christiania and Leipzig.

In the unitary group approach to large-scale CI (McWeeny, 1989), $U(2m) = U(m) \times SU(2)$ is the Kronecker product of $U(m)$ for the m-dimensional space of basis functions $\{\phi_i\}$ by the special unitary group $SU(2)$ in 2-dimensions concerning spin functions. All transformations of the spin-orbital set $\phi_1\alpha, \phi_1\beta, \phi_2\alpha, \cdots, \phi_m\alpha, \phi_m\beta$ will form the $U(2m)$ group.

8.7.3 Transformation Properties of Spherical Harmonics

The spherical harmonics (SHs) $Y_{lm}(\theta, \varphi)$ form a basis to represent rotations. They transform under a rotation C_α according to:

$$\hat{C}_\alpha Y_{lm}(\theta, \varphi) = \sum_{m'=-l}^{l} Y_{lm'}(\theta, \varphi) D(C_\alpha)_{m'm}, \tag{130}$$

where the coefficients $D(R)_{m'm}$ form a matrix representative of the rotation C_α of dimension $(2l+1)$. The corresponding representation is, in general, reducible, and the number of times that each irrep is contained in the reducible one is obtained as usual. To obtain the characters for the reducible representation, consider a rotation $\hat{C}_\alpha^+$ by α about the polar axis z of the SH. Since, apart from a normalization factor:

$$Y_{lm}(\theta, \varphi) \propto P_l^m(\cos\theta)\exp(im\varphi) \quad \text{complex form} \tag{131}$$

we shall have:

$$\hat{C}_\alpha^+ Y_{lm'}(\theta, \varphi) = Y_{lm'}(\theta, \varphi+\alpha) = P_l^{m'}(\cos\theta)\exp[im'(\varphi+\alpha)] = \exp(im'\alpha)Y_{lm'}(\theta, \varphi). \tag{132}$$

Using this result for all values $m' = -l, \cdots l$, we obtain:

$$\mathbf{D}\big(C_\alpha^+\big) = \begin{pmatrix} e^{-il\alpha} & & & \\ & e^{-i(l-1)\alpha} & & \\ & & \ddots & \\ & & & e^{il\alpha} \end{pmatrix} \tag{133}$$

$$\begin{aligned} \chi^l\big(C_\alpha^+\big) &= \sum_{m=-l}^{l} e^{im\alpha} = \frac{\sin(l+\frac{1}{2})\alpha}{\sin\frac{\alpha}{2}} \quad \text{for } \alpha \neq 0 \\ \chi^l\big(C_\alpha^+\big) &= 2l+1 \quad \text{for } \alpha = 0. \end{aligned} \tag{134}$$

In fact, the summation over m is a geometric progression, giving:

$$\begin{array}{cccccccccc} & 1 & 2 & & l & l+1 & & 2l-1 & 2l & \\ -l & -l+1 & -l+2 & \cdots & 0 & 1 & \cdots & l-1 & l & x = \exp(i\alpha) \end{array}$$

$$
\begin{aligned}
\sum_{m=-l}^{l}(e^{i\alpha})^m &= \sum_m x^m \\
&= x^{-l} + x^{-l+1} + x^{-l+2} + \cdots + x^{-l+l} + x^{-l+(l+1)} + \cdots + x^{-l+2l} \\
&= x^{-l}\underbrace{(1 + x + x^2 + \cdots + x^{2l})}_{\text{geometric progression}} \\
&= x^{-l}\frac{1-x^{2l+1}}{1-x} = \frac{x^{l+1}-x^{-l}}{x-1}\cdot\frac{x^{-1/2}}{x^{-1/2}} \\
&= \frac{x^{l+\frac{1}{2}} - x^{-(l+\frac{1}{2})}}{x^{1/2}-x^{-1/2}} = \frac{e^{i(l+\frac{1}{2})\alpha} - e^{-i(l+\frac{1}{2})\alpha}}{e^{i\frac{1}{2}\alpha} - e^{-i\frac{1}{2}\alpha}} = \frac{\sin(l+\frac{1}{2})\alpha}{\sin\frac{\alpha}{2}}
\end{aligned} \tag{135}
$$

$$
\lim_{\alpha\to 0}\frac{\sin(l+\frac{1}{2})\alpha}{\sin\frac{\alpha}{2}} = \frac{l+\frac{1}{2}}{\frac{1}{2}}\lim_{\alpha\to 0}\frac{\cos(l+\frac{1}{2})\alpha}{\cos\frac{\alpha}{2}} = 2l+1. \tag{136}
$$

Hence, we have two cases.

(i) $l = \text{integer}$ e.g. $l = 1$ $\chi(C_\alpha^+) = \frac{\sin\frac{3}{2}\alpha}{\sin\frac{\alpha}{2}}$ (137)

$$
C_{3v} \qquad \alpha = \frac{2\pi}{3} \qquad \chi(C_3^+) = \frac{\sin\frac{3}{2}\cdot\frac{2\pi}{3}}{\sin\frac{1}{2}\cdot\frac{2\pi}{3}} = \frac{\sin\pi}{\sin\frac{\pi}{3}} = 0 \tag{138}
$$

as it must be for p-functions.

(ii) $l = \text{semi-integer}$ e.g. $l = \frac{1}{2}$ (spin) $\chi(C_\alpha^+) = \frac{\sin\alpha}{\sin\frac{\alpha}{2}}$ (139)

$$
\chi(C_{\alpha+2\pi}^+) = \frac{\sin(\alpha+2\pi)}{\sin(\frac{\alpha}{2}+\pi)} = -\frac{\sin\alpha}{\sin\frac{\alpha}{2}} = -\chi(C_\alpha^+) = \chi(\tilde{I}) \quad \text{\textit{not} the identity operation} \tag{140}
$$

$$
\chi(C_{\alpha+4\pi}^+) = \frac{\sin(\alpha+4\pi)}{\sin(\frac{\alpha}{2}+2\pi)} = \frac{\sin\alpha}{\sin\frac{\alpha}{2}} = \chi(C_\alpha^+) = \chi(I) \quad \text{the \textit{true} identity operation.} \tag{141}
$$

So, the *true* identity operation is a *rotation* by 4π and not by 2π. Hence, we have *double-valued* representations $\Longrightarrow$ *double groups* (Möbius ring).

8.7.4 Rotation Groups

The group of point operations in a three-dimensional space which leaves a sphere invariant is isomorphic with the orthogonal group $O(3)$. The group requires three continuous parameters, which in terms of Euler angles are (i) the angles θ, φ specifying the direction of the rotation axis, an (ii) the angle ψ which is the angle of rotation about this axis. An index ±

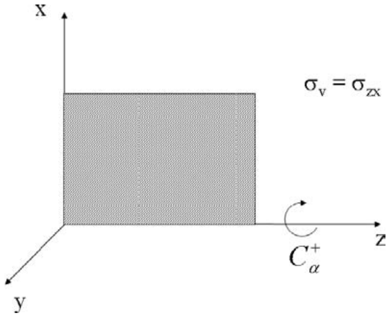


Figure 8.14 Symmetry operations of $C_{\infty v}$.

is needed to specify whether the rotation is *proper* (determinant of $\mathbf{A} = +1$) or *improper* (determinant of $\mathbf{A} = -1$).

As introductory to the three-dimensional rotation group we consider the following three groups.

(i) Axial group, consisting of all rotations C_α about a fixed axis (usually taken as the z axis). The character table is:

C_∞	I	C_α
$\Gamma(0)$	1	1
$\Gamma(m)$	1	$e^{im\alpha}$

(ii) $C_{\infty v}$ group, which contains in addition a symmetry plane σ_v through the x and z axes. It is important to note that σ_v *reverses* the direction of rotation. The character table for complex functions is:

$C_{\infty v}$	I	C_α	σ_v
$\Gamma(0^+)$	1	1	1
$\Gamma(0^-)$	1	1	-1
$\Gamma(m)$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} e^{im\alpha} & 0 \\ 0 & e^{-im\alpha} \end{pmatrix}$	$\begin{pmatrix} 0 & (-1)^m \\ (-1)^m & 0 \end{pmatrix}$

$\Gamma(0^+)$ is usually denoted by Σ^+, $\Gamma(0^-)$ by Σ^-, while the irreps $\Gamma(m)$ are all 2-fold degenerate, and are usually denoted by $\Gamma(1) = \Pi$, $\Gamma(2) = \Delta$, $\Gamma(3) = \Phi$, $\cdots$

For *complex* p-functions p_+, p_- with Condon–Shortley phase:

$$p_+ = -\frac{e^{i\varphi}}{\sqrt{2\pi}} \qquad p_- = \frac{e^{-i\varphi}}{\sqrt{2\pi}} \tag{142}$$

it is important to note that, under $\hat{\sigma_v}$:

$$\hat{\sigma_v} p_+ = -\frac{e^{-i\varphi}}{\sqrt{2\pi}} = -p_- \qquad \hat{\sigma_v} p_- = \frac{e^{i\varphi}}{\sqrt{2\pi}} = -p_+ \tag{143}$$

so that:

$$\hat{\sigma_v}(p_+ p_-) = (p_+ p_-)\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \qquad \underset{\text{complex}}{\mathbf{D}_p(\sigma_v)} = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \tag{144}$$

Since, for *real* p-functions: $\hat{\sigma_v} x = x$, $\hat{\sigma_v} y = -y$

$$\hat{\sigma_v}(xy) = (xy)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \underset{\text{real}}{\mathbf{D}_p(\sigma_v)} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{145}$$

the matrices representing the *same* operation $\hat{\sigma_v}$ are entirely different for complex or real functions.

(iii) $D_{\infty h}$ group, which contains in addition to $C_{\infty v}$ the inversion $\hat{\imath}$ (with respect to a centre of symmetry, e.g. homonuclear diatomics), so that:

$$D_{\infty h} = C_{\infty v} \times C_i. \tag{146}$$

The character table for *complex* functions is:

$D_{\infty h}$	I	$2C_\alpha$	σ_v	i	$2iC_\alpha$	$i\sigma_v$
$\Gamma_g(0^+)$	1	1	1	1	1	1
$\Gamma_u(0^+)$	1	1	1	−1	−1	−1
$\Gamma_g(0^-)$	1	1	−1	1	1	−1
$\Gamma_u(0^-)$	1	1	−1	−1	−1	1
$\Gamma_g(m)$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} e^{im\alpha} & 0 \\ 0 & e^{-im\alpha} \end{pmatrix}$	$\begin{pmatrix} 0 & (-1)^m \\ (-1)^m & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} e^{im\alpha} & 0 \\ 0 & e^{-im\alpha} \end{pmatrix}$	$\begin{pmatrix} 0 & (-1)^m \\ (-1)^m & 0 \end{pmatrix}$
$\Gamma_u(m)$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} e^{im\alpha} & 0 \\ 0 & e^{-im\alpha} \end{pmatrix}$	$\begin{pmatrix} 0 & (-1)^m \\ (-1)^m & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -e^{im\alpha} & 0 \\ 0 & -e^{-im\alpha} \end{pmatrix}$	$\begin{pmatrix} 0 & (-1)^{m+1} \\ (-1)^{m+1} & 0 \end{pmatrix}$

$$\chi(C_\alpha) = e^{im\alpha} + e^{-im\alpha} = 2\cos m\alpha \tag{147}$$

$$\begin{array}{ll} m = & 1,\ 2,\ 3,\ 4,\ 5,\ \cdots \\ & \Pi,\ \Delta,\ \Phi,\ Y,\ H,\ \cdots \end{array}$$

8.7.5 Permutation Group

It is also called the S_N symmetric group of $N!$ permutations. Since the spin operators $\hat{S}^2$ and $\hat{S}_z$ are *symmetrical* in the $N!$ permutations of the particle labels, if η_{SM_S} is an eigenfunction belonging to the eigenvalues $S(S+1)$ and M_S of the spin operators, there will also be $N!$ spin functions belonging to the *same* value of SM_S. This means that any spin eigenfunction η_{SM_S} remains a spin eigenfunction with the same eigenvalue after permutation of the spin variables. Thus, if there are (Wigner):

$$f_S^N = \frac{(2S+1)N!}{(\frac{N}{2}-S)!(\frac{N}{2}+S+1)!} \tag{148}$$

linearly independent functions of given SM_S, we can then say that, for any permutation $\hat{P}$ of the spin variables:

$$\begin{aligned}
&\hat{P}\eta_{SM_S}(s_1, s_2, \cdots s_i, \cdots s_j, \cdots s_N) \\
&\quad = \eta_{SM_S}(s_1, s_2, \cdots s_j, \cdots s_i, \cdots s_N) \\
&\quad = \sum_{i=1}^{f_S^N} \eta_{SM_S}(s_1, s_2, \cdots s_i, \cdots s_j, \cdots s_N) P_{ij}
\end{aligned} \tag{149}$$

the result must necessarily be some linear combination of the full $\{\eta_{SM_S}\}$ set. In this way, the set $\{\eta_{SM_S}\}$ provides a basis for a f_S^N-irreducible representation of the symmetric group S_N of $N!$ permutations of the spin variables. We can write, in the usual notation:

$$\hat{P}\boldsymbol{\eta}_{SM_S} = \boldsymbol{\eta}_{SM_S}\mathbf{D}(P) \qquad \mathbf{D}(P)_{ij} = P_{ij}, \tag{150}$$

where the $f_S^N \times f_S^N$ matrix representative $\mathbf{D}(P)$ has as ij-element the expansion coefficient P_{ij}.

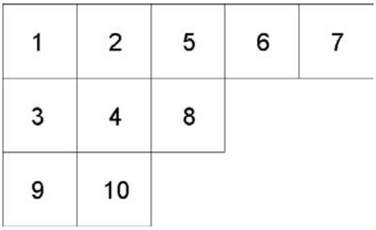
In the theory of the symmetric group S_N (Rutherford, 1948; Kaplan, 1975; McWeeny, 1989; Paldus and Wormer, 1989; Gallup, 2002), irreps are specified by Young Tableaux $[\lambda]$, where $[\lambda]$ denotes a partition (or shape or diagram or pattern) of the given set of labels. For instance, a possible tableau for $N = 10$ is given in Figure 8.15.

$$\begin{aligned}
&[\lambda] = [\lambda_1, \lambda_2, \lambda_3] \\
&\lambda_1 = 5, \qquad \lambda_2 = 3, \qquad \lambda_3 = 2.
\end{aligned} \tag{151}$$

In a "standard representation", reading along rows and down columns, the numbers must always appear in ascending order.

From every set of standard tableaux it is possible to set up Young–Yamanouchi–Wigner projection operators (compare equation 100):

$$\hat{Y}_{ij}^{[\lambda]} = \frac{f_\lambda}{N!}\sum_P \mathbf{D}^{[\lambda]}(P)_{ij}\hat{P} \quad \text{un-normalized Wigner projector} \tag{152}$$



1	2	5	6	7
3	4	8		
9	10			

Figure 8.15 A Young tableau.

that, acting on an arbitrary function of numbered variables, will generate a set of basis functions carrying the [λ] irrep (symmetry-adapted functions).

Similar considerations apply to the spatial wavefunctions (either exact or approximate) which are eigenfunctions of a Hamiltonian operator which is *invariant* under all permutations of the *spatial* variables, so that a g-fold degenerate set of spinless wavefunctions should likewise carry an irrep of S_N. Wigner (1959) has suggested how to construct many-electron wavefunctions satisfying the Pauli principle, starting from orbital products, by taking suitable "dual" or "associated" irreps of separate spatial and spin functions (for details, see McWeeny, 1989). With a spinless Hamiltonian, it is hence possible to obtain the usual energy expectation value using either (i) a linear combination of Slater determinants, or (ii) a linear combination of purely spatial functions of appropriate symmetry, "dual" to the required irreps for spin, which can therefore be not considered explicitly (this is at the origin of the so called Spin-Free Quantum Chemistry: Matsen, 1964, 1970). Modern valence bond (VB) theory was also reformulated using these techniques (Goddard III, 1967a, 1967b; Gerratt, 1971; Gallup, 1973, 2002; Cooper et al., 1987; McWeeny, 1990).

8.8 PROBLEMS 8

8.1. Construct the multiplication table of the group C_{2v}.

Answer:

C_{2v}	I	C_2	σ_v	σ_v'
I	I	C_2	σ_v	σ_v'
C_2	C_2	I	σ_v'	σ_v
σ_v	σ_v	σ_v'	I	C_2
σ_v'	σ_v'	σ_v	C_2	I

Hint:
Use Figure 8.13 recalling that the operation on the right must be done first.

8.2. Construct the multiplication table of the group C_{3v}.

Answer:

C_{3v}	I	C_3^+	C_3^-	σ_1	σ_2	σ_3
I	I	C_3^+	C_3^-	σ_1	σ_2	σ_3
C_3^+	C_3^+	C_3^-	I	σ_2	σ_3	σ_1
C_3^-	C_3^-	I	C_3^+	σ_3	σ_1	σ_2
σ_1	σ_1	σ_3	σ_2	I	C_3^-	C_3^+
σ_2	σ_2	σ_1	σ_3	C_3^+	I	C_3^-
σ_3	σ_3	σ_2	σ_1	C_3^-	C_3^+	I

Hint:
Proceed in the same way as in Problem 8.1.

8.3. Construct the multiplication table of the cyclic group of order 4 (C_4).

Answer:

C_4	I	C_4^+	C_4^{+2}	C_4^{+3}
I	I	C_4^+	C_4^{+2}	C_4^{+3}
C_4^+	C_4^+	C_4^{+2}	C_4^{+3}	I
C_4^{+2}	C_4^{+2}	C_4^{+3}	I	C_4^{+2}
C_4^{+3}	C_4^{+3}	I	C_4^+	C_4^{+3}

Hint:
Follow the suggestions of the previous Problems.

8.4. Find the classes of the point group C_{5v}.

Answer:
The four classes are:

$$I = C_5^{+5}$$
$$C_5, C_5^4 = C_5^+, C_5^-$$
$$C_5^2, C_5^3 = C_5^{+2}, C_5^{-2}$$
$$\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5.$$

Hint:
Acting on the set of five functions ($|1\rangle, |2\rangle, |3\rangle, |4\rangle, |5\rangle$) with the rotations C_5, C_5^2, C_5^3, C_5^4 show that $C_5^+, C_5^{+4} = C_5^-$ and $C_5^{+2}, C_5^{+3} = C_5^{-2}$ belong to two different classes.

8.5. Construct the *substitution* table of the six functions group of example 4 in Section 8.5.1.

Answer:

Transformation table	*I*	*A*	*B*	*C*	*D*	*E*
I	*I*	*A*	*B*	*C*	*D*	*E*
A	*A*	*B*	*I*	*E*	*C*	*D*
B	*B*	*I*	*A*	*D*	*E*	*C*
C	*C*	*D*	*E*	*I*	*A*	*B*
D	*D*	*E*	*C*	*B*	*I*	*A*
E	*E*	*C*	*D*	*A*	*B*	*I*

Hint:
Substitute each function in turn into the other.

8.6. Construct the (reducible) representatives of the symmetry operations of the group C_{2v} for H_2O in the minimum basis set ($m = 7$).

Answer:

$$\mathbf{D}(I) = \begin{pmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{pmatrix} \qquad \mathbf{D}(C_2) = \begin{pmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \bar{1} & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \bar{1} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \end{pmatrix}$$

$$\mathbf{D}(\sigma_v) = \begin{pmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \bar{1} & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{pmatrix} \qquad \mathbf{D}(\sigma_v') = \begin{pmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \bar{1} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \end{pmatrix}.$$

Hint:
Use $\hat{R}\chi = \chi \mathbf{D}_\chi(R)$ and the transformation table of the basis χ under the symmetry operations of C_{2v}.

8.7. Construct the C_{2v} symmetry-adapted basis for H_2O in the minimum basis set ($m = 7$).

Answer:

$$\begin{aligned}
A_1&:\quad k, s, z, h_z = \frac{1}{\sqrt{2}}(h_1 + h_2)\\
A_2&:\quad \text{no function with this symmetry}\\
B_1&:\quad x\\
B_2&:\quad y, h_y = \frac{1}{\sqrt{2}}(h_1 + h_2).
\end{aligned}$$

Hint:
The symmetry-adapted functions for H_2O can be obtained in this simple case either (i) by direct inspection, or (ii) in a more systematic way, by use of the simplest projector $\hat{P}^i = \frac{l_i}{h}\sum_R \chi^i(R)^*\hat{R}$, and of the transformation and character tables of the point group C_{2v}.

8.8. Construct the C_{2v} symmetry-adapted basis for H_2O in the extended basis set ($m = 12$) including polarization functions onto the oxygen atom.

Answer:

$$\begin{aligned}
A_1&:\quad k, s, z, \frac{3z^2 - r^2}{2}, x^2 - y^2, h_z = \frac{1}{\sqrt{2}}(h_1 - h_2)\\
A_2&:\quad xy\\
B_1&:\quad x, zx\\
B_2&:\quad y, yz, h_y = \frac{1}{\sqrt{2}}(h_1 - h_2).
\end{aligned}$$

Hint:
Use the direct product of the transformation properties of x, y, z under C_{2v}.

8.9. Construct the C_{2v} symmetry-adapted basis for H_2O in the large basis set ($m = 35$) including polarization functions onto the oxygen and the hydrogen atoms.

Answer:

$$\begin{aligned}
A_1&:\quad k, s, z, \frac{3z^2 - r^2}{2}, x^2 - y^2, \frac{5z^3 - 3zr^2}{2}, (x^2 - y^2)z\\
&\quad\ h_z = \frac{1}{\sqrt{2}}(h_1 + h_2)
\end{aligned}$$

$$\frac{1}{\sqrt{2}}(z_1+z_2),\ \frac{1}{\sqrt{2}}(y_1-y_2)$$

$$\frac{1}{\sqrt{2}}\left(z_1^2+z_2^2\right),\ \frac{1}{\sqrt{2}}\left(x_1^2-y_1^2+x_2^2-y_2^2\right),\ \frac{1}{\sqrt{2}}(y_1z_1-y_2z_2) \qquad 13$$

A_2: xy, xyz

$$\frac{1}{\sqrt{2}}(x_1-x_2)$$

$$\frac{1}{\sqrt{2}}\left(x_1^2-y_1^2-x_2^2+y_2^2\right),\ \frac{1}{\sqrt{2}}(x_1y_1-x_2y_2),\ \frac{1}{\sqrt{2}}(z_1x_1-z_2x_2) \qquad 6$$

B_1: $x, zx, x(x^2-3y^2), x(5z^2-r^2)$

$$\frac{1}{\sqrt{2}}(x_1+x_2)$$

$$\frac{1}{\sqrt{2}}(x_1y_1+x_2y_2),\ \frac{1}{\sqrt{2}}(z_1x_1+z_2x_2) \qquad 7$$

B_2: $y, yz, y(3x^2-y^2), y(5z^2-r^2)$

$$h_y=\frac{1}{\sqrt{2}}(h_1-h_2)$$

$$\frac{1}{\sqrt{2}}(z_1-z_2),\ \frac{1}{\sqrt{2}}(y_1+y_2)$$

$$\frac{1}{\sqrt{2}}\left(z_1^2-z_2^2\right),\ \frac{1}{\sqrt{2}}(y_1z_1+y_2z_2) \qquad 9$$

Hint:
Use the same techniques of Problem 8.8.

8.10. Construct the (reducible) matrix representatives of the symmetry operations of the group C_{3v} for NH_3 in the minimum basis set ($m=8$).

Answer:

$$\mathbf{D}(I)=\begin{pmatrix}
1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1
\end{pmatrix}
\qquad
\mathbf{D}(C_3^+)=\begin{pmatrix}
1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \bar{c} & s & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \bar{s} & \bar{c} & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\
\cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot
\end{pmatrix}$$

$$\mathbf{D}(C_3^-) = \begin{pmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \bar{c} & \bar{s} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & s & \bar{c} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \end{pmatrix} \qquad \mathbf{D}(\sigma_1) = \begin{pmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \bar{1} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \end{pmatrix}$$

$$\mathbf{D}(\sigma_2) = \begin{pmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \bar{c} & \bar{s} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \bar{s} & c & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \end{pmatrix} \qquad \mathbf{D}(\sigma_3) = \begin{pmatrix} 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \bar{c} & s & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & s & c & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{pmatrix}.$$

Hint:
Use the suggestions of Problem 8.6.

8.11. Construct the C_{3v} symmetry-adapted basis for NH_3 in the minimum basis set ($m = 8$).

Answer:

$$A_1\colon \quad k, s, z, h_z = \frac{1}{\sqrt{3}}(h_1 + h_2 + h_3)$$

$$A_2\colon \quad \text{no function with this symmetry}$$

$$\begin{aligned} E\colon \quad & x, h_x = \frac{1}{\sqrt{6}}(2h_1 - h_2 - h_3) \\ & y, h_y = \frac{1}{\sqrt{2}}(h_2 - h_3). \end{aligned}$$

Hint:
Same as in Problem 8.7.

8.12. Construct the T_d symmetry-adapted basis for CH_4 in the minimum basis set ($m = 9$).

Answer:

$$A_1\colon\quad k, s, z$$

A_2: no function with this symmetry

$$\begin{aligned}
T\colon\quad & x, h_x = \frac{1}{2}(h_1 + h_2 - h_3 - h_4)\\
& y, h_y = \frac{1}{2}(h_1 - h_2 + h_3 - h_4)\\
& z, h_z = \frac{1}{2}(h_1 - h_2 - h_3 + h_4).
\end{aligned}$$

Hint:
Because of the high symmetry of the CH_4 molecule, symmetry arguments can be used to write at once the correct symmetry combinations of the four 1*s* AOs onto the H atoms transforming as s, x, y, z.

8.13. Construct the C_{6v} symmetry-adapted basis for the π-electron system of benzene C_6H_6 in the minimum basis set ($m = 6$).

Answer:

$$A_1\colon\quad a_1 = \frac{1}{\sqrt{6}}(\chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 + \chi_6)$$

A_2: no function with this symmetry

$$B_1\colon\quad b_1 = \frac{1}{\sqrt{6}}(\chi_1 - \chi_2 + \chi_3 - \chi_4 + \chi_5 - \chi_6)$$

B_2: no function with this symmetry

$$\begin{aligned}
E_1\colon\quad & e_{1x} = \frac{1}{2}(\chi_1 - \chi_3 - \chi_4 + \chi_6) \sim x\\
& e_{1y} = \frac{1}{\sqrt{12}}(\chi_1 + 2\chi_2 + \chi_3 - \chi_4 - 2\chi_5 - \chi_6) \sim y
\end{aligned}$$

$$\begin{aligned}
E_2\colon\quad & e_{2,x^2-y^2} = \frac{1}{\sqrt{12}}(\chi_1 - 2\chi_2 + \chi_3 + \chi_4 - 2\chi_5 + \chi_6) \sim x^2 - y^2\\
& e_{2,xy} = \frac{1}{2}(\chi_1 - \chi_3 + \chi_4 - \chi_6) \sim xy.
\end{aligned}$$

Hint:
Same as in Problem 8.7.

8.14. Find the electronic states resulting from the MO configuration π_g^2.

Answer:
The physically accessible 2-electron states resulting from the MO configuration π_g^2 are:

$$^3\Sigma_g^-, {}^1\Sigma_g^+, {}^1\Delta_g.$$

Hint:
Write all possible 2-electron Slater determinants, and use the operators $\hat{L}_z$, $\hat{\sigma}$, $\hat{\imath}$, $\hat{S}^2$ to do the classification of the resulting electronic states.

8.15. Find the classification of the MO ground state of the O_2 molecule.

Answer:

$$\Psi\left(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2\right) = \Psi\left({}^3\Sigma_g^-\right).$$

Hint:
Use the transformation table of real $2p\pi$ AOs onto atoms A and B, and of the resulting real MOs, under the operations $\hat{L}_z$, $\hat{\sigma}$, $\hat{\imath}$, $\hat{S}^2$, and the elementary properties of determinants.

8.16. Write the VB wavefunction for ground state O_2 and classify its electronic state.

Answer:
It will be shown in Chapter 10 that, in the ultrashort notation, the three components of the triplet VB wavefunction for ground state O_2 are:

$$\begin{aligned}
\Psi_1 &= \frac{1}{\sqrt{2}}[(x_A y_B) + (x_B y_A)] && S = 1, M_S = 1 \\
\Psi_2 &= \frac{1}{2}[(x_A \overline{y}_B) + (\overline{x}_A y_B) + (x_B \overline{y}_A) + (\overline{x}_B y_A)] && 0 \\
\Psi_3 &= \frac{1}{\sqrt{2}}[(\overline{x}_A \overline{y}_B) + (\overline{x}_B \overline{y}_A)]. && -1
\end{aligned}$$

Hint:
Write the covalent VB wavefunction for ground state O_2 in the ultrashort notation specifying only the two unpaired π-electrons, and verify its symmetry properties using the transformation table of Problem 8.15.

8.17. Verify that under C_{3v} the state resulting from the e^4 electron configuration belongs to the symmetry A_1.

Answer:

$$\hat{R}\|e_x\overline{e}_x e_y\overline{e}_y\| = \|e_x\overline{e}_x e_y\overline{e}_y\| \quad \text{for any } \hat{R}.$$

Hint:
Act with the linear symmetry operators $\hat{R}$ of the point group C_{3v} on the Slater determinant $\|e_x\bar{e}_x e_y\bar{e}_y\|$, using the C_{3v} transformation table for the functions e_x, e_y, and the elementary properties of determinants.

8.18. Find the symmetry of the first few real spherical tensors under $C_{\infty v}$ and $D_{\infty h}$ symmetry.

Answer:
The results are collected in Table 8.4.

Hint:
The first few real spherical tensors are (see Chapter 11):

$$m = 0$$

$$R_{10} = z,\ R_{30} = \frac{5z^3 - 3zr^2}{2} = \frac{z}{2}(2z^2 - 3x^2 - 3y^2) \qquad l = \text{odd}$$

$$R_{50} = \frac{z}{2}(8z^4 + 15x^4 + 15y^4 - 40z^2x^2 - 40z^2y^2 + 30x^2y^2)$$

$$R_{20} = \frac{3z^2 - r^2}{2} = \frac{1}{2}(2z^2 - x^2 - y^2) \qquad l = \text{even}$$

$$R_{40} = \frac{1}{8}(8z^4 + 3x^4 + 3y^4 - 24z^2x^2 - 24z^2y^2 + 6x^2y^2)$$

$$m \neq 0$$

$$\begin{array}{ll} (x, y) & l = 1, m = 1, -1 \\ (zx, yz) & l = 2, m = 1, -1 \\ (x^2 - y^2, xy) & l = 2, m = 2, -2 \end{array}$$

$$\left(\frac{\sqrt{6}}{4}x(4z^2 - x^2 - y^2), \frac{\sqrt{6}}{4}y(4z^2 - x^2 - y^2)\right) \qquad l = 3, m = 1, -1$$

$$\left(\frac{\sqrt{15}}{2}(x^2 - y^2)z, \sqrt{15}xyz\right) \qquad l = 3, m = 2, -2$$

$$\left(\frac{\sqrt{10}}{4}(x^2 - 3y^2)x, \frac{\sqrt{10}}{4}(3x^2 - y^2)y\right) \qquad l = 3, m = 3, -3.$$

Their symmetry properties can then be found in terms of the transformation properties of Cartesian coordinates and their products.

8.9 SOLVED PROBLEMS

8.1. In constructing a (symbolic) multiplication table, we must recall first that $R_k = R_i R_j$ is the result of the intersection of the column headed by R_i and the row headed by R_j, and that the operation on the right must be done first. Then, with reference to Figure 8.13, we easily find:

$$\begin{array}{llll}
II = I & C_2 I = C_2 & \sigma_v I = \sigma_v & \sigma'_v I = \sigma'_v \\
I C_2 = C_2 & C_2 C_2 = I & \sigma_v C_2 = \sigma'_v & \sigma'_v C_2 = \sigma_v \\
I \sigma_v = \sigma_v & C_2 \sigma_v = \sigma'_v & \sigma_v \sigma_v = I & \sigma'_v \sigma_v = C_2 \\
I \sigma'_v = \sigma'_v & C_2 \sigma'_v = \sigma_v & \sigma_v \sigma'_v = C_2 & \sigma'_v \sigma'_v = I.
\end{array}$$

8.2. Proceeding as in Problem 8.1, and taking as an example the results of equation (65) and Figure 8.10, we obtain the table wanted.

8.3. Make reference to Figure 8.16, and proceed as in Problems 8.1 and 8.2, noting that, if C_4^+ is the anticlockwise rotation of $2\pi/4 = 90^\circ$ (Figure 8.17):

$$C_4^{+2} = C_2, C_4^{+3} = C_4^-, C_4^{+4} = I.$$

8.4. Classes of the point group C_{5v}.

With reference to Figure 8.18, acting on the set of the five functions

$$(|1\rangle, |2\rangle, |3\rangle, |4\rangle, |5\rangle)$$

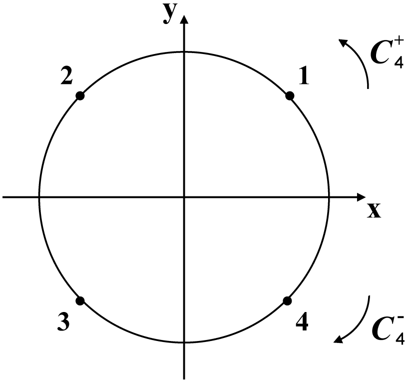
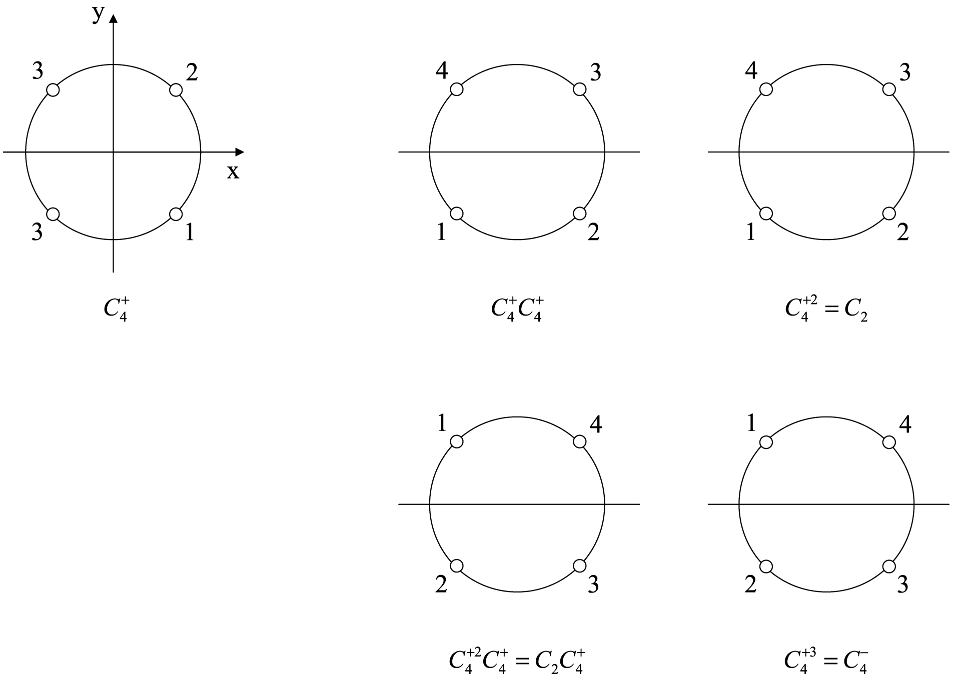


Figure 8.16 Reference system for the cyclic group C_4.



C_4^+ $\quad C_4^+C_4^+$ $\quad C_4^{+2} = C_2$

$C_4^{+2}C_4^+ = C_2C_4^+$ $\quad C_4^{+3} = C_4^-$

Figure 8.17 Successive rotations in the cyclic group C_4.

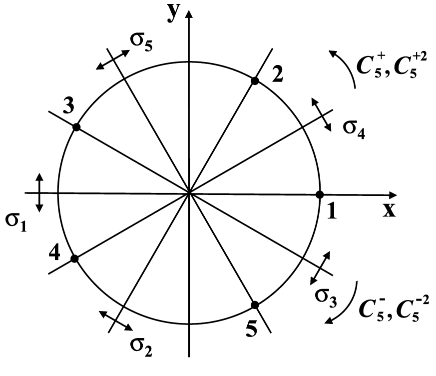


Figure 8.18 Symmetry elements of the point group C_{5v}.

we have:

$$C_5^+|1\rangle = |5\rangle, \quad C_5^+|2\rangle = |1\rangle, \quad C_5^+|3\rangle = |2\rangle, \quad C_5^+|4\rangle = |3\rangle, \quad C_5^+|5\rangle = |4\rangle$$

$$C_5^{+2}|1\rangle = |4\rangle, \quad C_5^{+2}|2\rangle = |5\rangle, \quad C_5^{+2}|3\rangle = |1\rangle, \quad C_5^{+2}|4\rangle = |2\rangle, \quad C_5^{+2}|5\rangle = |3\rangle$$

$$C_5^{+3}|1\rangle = |3\rangle, \quad C_5^{+3}|2\rangle = |4\rangle, \quad C_5^{+3}|3\rangle = |5\rangle, \quad C_5^{+3}|4\rangle = |1\rangle, \quad C_5^{+3}|5\rangle = |2\rangle$$

$$\begin{array}{lllll}
C_5^{+4}|1\rangle = |2\rangle, & C_5^{+4}|2\rangle = |3\rangle, & C_5^{+4}|3\rangle = |4\rangle, & C_5^{+4}|4\rangle = |5\rangle, & C_5^{+4}|5\rangle = |1\rangle \\
C_5^{-}|1\rangle = |2\rangle, & C_5^{-}|2\rangle = |3\rangle, & C_5^{-}|3\rangle = |4\rangle, & C_5^{-}|4\rangle = |5\rangle, & C_5^{-}|5\rangle = |1\rangle \\
C_5^{-2}|1\rangle = |3\rangle, & C_5^{-2}|2\rangle = |4\rangle, & C_5^{-2}|3\rangle = |5\rangle, & C_5^{-2}|4\rangle = |1\rangle, & C_5^{-2}|5\rangle = |2\rangle \\
C_5^{-3}|1\rangle = |4\rangle, & C_5^{-3}|2\rangle = |5\rangle, & C_5^{-3}|3\rangle = |1\rangle, & C_5^{-3}|4\rangle = |2\rangle, & C_5^{-3}|5\rangle = |3\rangle \\
C_5^{-4}|1\rangle = |5\rangle, & C_5^{-4}|2\rangle = |1\rangle, & C_5^{-4}|3\rangle = |2\rangle, & C_5^{-4}|4\rangle = |3\rangle, & C_5^{-4}|5\rangle = |4\rangle.
\end{array}$$

Since C_n^+ and C_n^- belong to the same class, we see that the rotations $C_5^+, C_5^{+4} = C_5^-$ and $C_5^{+2}, C_5^{+3} = C_5^{-2}$ form two different classes, which, added to the class of reflections, make a total of four classes (10 symmetry operations).

8.5. The group of the six functions:

$$\begin{array}{lll}
I(x) = x & A(x) = (1-x)^{-1} & B(x) = 1 - x^{-1} \\
C(x) = x^{-1} & D(x) = 1 - x & E(x) = x(1-x)^{-1}
\end{array}$$

is a finite subgroup of order 6 of the continuous group of conformal transformations, a fractional linear group in one variable (Hall, 1967). The set of functions forms a group with respect to the *substitution* of one function into the other, as illustrated below:

$$\begin{aligned}
AA &= A[(1-x)^{-1}] = \left(1 - \frac{1}{1-x}\right)^{-1} = \left(\frac{x}{x-1}\right)^{-1} = 1 - x^{-1} = B \\
AB &= A(1-x^{-1}) = [1-(1-x^{-1})]^{-1} = (x^{-1})^{-1} = x = I \\
AC &= A(x^{-1}) = (1-x^{-1})^{-1} = \left(\frac{x-1}{x}\right)^{-1} = x(x-1)^{-1} = E \\
AD &= A(1-x) = [1-(1-x)]^{-1} = x^{-1} = C \\
AE &= A\left(\frac{x}{x-1}\right) = \left(1 - \frac{x}{x-1}\right)^{-1} = \left(\frac{1}{1-x}\right)^{-1} = 1 - x = D
\end{aligned}$$

$$\begin{aligned}
BA &= B(1-x)^{-1} = 1 - [(1-x)^{-1}]^{-1} = 1 - (1-x) = x = I \\
BB &= B(1-x^{-1}) = 1 - (1-x^{-1})^{-1} = \frac{x-1-x}{x-1} = (1-x)^{-1} = A \\
BC &= Bx^{-1} = 1 - (x^{-1})^{-1} = 1 - x = D \\
BD &= B(1-x) = 1 - (1-x)^{-1} = x(x-1)^{-1} = E \\
BE &= Bx(x-1)^{-1} = 1 - \left(\frac{x}{x-1}\right)^{-1} = 1 - \frac{x-1}{x} = \frac{x-x+1}{x} = x^{-1} = C
\end{aligned}$$

$$CA = C(1-x)^{-1} = [(1-x)^{-1}]^{-1} = 1-x = D$$

$$CB = C(1-x^{-1}) = (1-x^{-1})^{-1} = \left(\frac{x-1}{x}\right)^{-1} = x(x-1)^{-1} = E$$

$$CC = Cx^{-1} = (x^{-1})^{-1} = x = I$$

$$CD = C(1-x) = (1-x)^{-1} = A$$

$$CE = Cx(x-1)^{-1} = x^{-1}(x-1) = 1-x^{-1} = B$$

$$DA = D(1-x)^{-1} = 1-(1-x)^{-1} = \frac{1-x-1}{1-x} = x(x-1)^{-1} = E$$

$$DB = D(1-x^{-1}) = 1-\left(1-\frac{1}{x}\right) = x^{-1} = C$$

$$DC = Dx^{-1} = 1-x^{-1} = B$$

$$DD = D(1-x) = 1-(1-x) = x = I$$

$$DE = Dx(x-1)^{-1} = 1-\frac{x}{x-1} = (1-x)^{-1} = A$$

$$EA = E(1-x)^{-1} = \frac{(1-x)^{-1}}{(1-x)^{-1}-1} = \frac{1}{1-x}\,\frac{1-x}{1-(1-x)} = x^{-1} = C$$

$$EB = E(1-x^{-1}) = \frac{1-x^{-1}}{1-x^{-1}-1} = -(x-1) = 1-x = D$$

$$EC = Ex^{-1} = \frac{x^{-1}}{x^{-1}-1} = \frac{x^{-1}x}{1-x} = (1-x)^{-1} = A$$

$$ED = E(1-x) = \frac{1-x}{(1-x)-1} = \frac{x-1}{x} = 1-x^{-1} = B$$

$$EE = Ex(x-1)^{-1} = \frac{\frac{x}{x-1}}{\frac{x}{x-1}-1} = \frac{x}{x-1}\,\frac{x-1}{x-x+1} = x = I.$$

8.6. The molecule lies in the yz-plane, z being the symmetry axis, and the zx-plane bisecting the molecule (Figure 8.19).

We use the short notation for the AOs:

$$k = 1s_O, \qquad s = 2s_O, \qquad x = 2p_{xO}, \qquad y = 2p_{yO}, \qquad z = 2p_{zO},$$
$$h_1 = 1s_{H_1}, \qquad h_2 = 1s_{H_2}.$$

The transformation table of the basis $\boldsymbol{\chi} = (ksxyzh_1h_2)$ under the symmetry operations of the point group C_{2v} is:

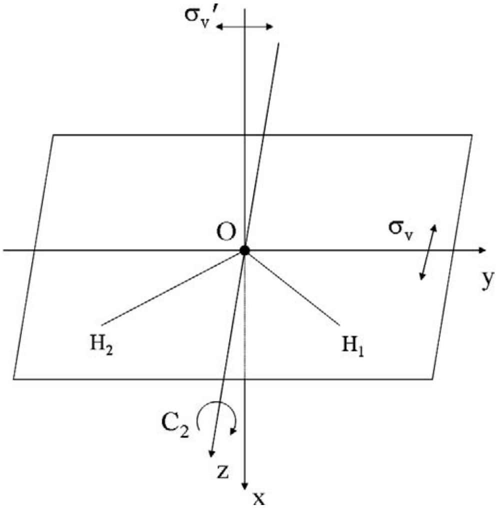


Figure 8.19 The symmetry elements of the H_2O molecule under C_{2v}.

$\hat{R}\chi$	I	C_2	σ_v	σ_v'
k	k	k	k	k
s	s	s	s	s
x	x	$-x$	$-x$	x
y	y	$-y$	y	$-y$
z	z	z	z	z
h_1	h_1	h_2	h_1	h_2
h_2	h_2	h_1	h_2	h_1

The representative matrices $\mathbf{D}_\chi(R)$ are then readily constructed using $\hat{R}\boldsymbol{\chi} = \boldsymbol{\chi}\mathbf{D}_\chi(R)$.

8.7. We use Figure 8.19 and the transformation table of Problem 8.6. The character table of C_{2v} (all irreps are 1-dimensional) is:

C_{2v}	I	C_2	σ_v	σ_v'	Symmetry basis
A_1	1	1	1	1	$k, s, z, h_z = \frac{1}{\sqrt{2}}(h_1 + h_2)$
A_2	1	1	-1	-1	
B_1	1	-1	-1	1	x
B_2	1	-1	1	-1	$y, h_y = \frac{1}{\sqrt{2}}(h_1 - h_2)$
Γ reducible	7	1	5	3	

In this simple case it is possible to write the characters of each operation $\hat{R}$, without constructing the complete 7×7 matrices of Problem 8.6, simply by noticing that $\chi(R)$ is nothing but the number of functions left *unchanged* by the operation $\hat{R}$, minus the number of functions which change sign under $\hat{R}$. It is also immediately obvious that since C_2 and σ'_v transform h_1 into h_2, and vice versa, the only possible symmetry combinations that are eigenfunctions of $\hat{C}_2$ and $\hat{\sigma}'_v$ are $h_z = \frac{1}{\sqrt{2}}(h_1 + h_2)$ (eigenvalue $+1$) and $h_y = \frac{1}{\sqrt{2}}(h_1 - h_2)$ (eigenvalue -1). The symmetry properties of the oxygen functions are also immediately evident, so that the symmetry-adapted functions for H_2O are obtained by direct inspection.

Turning to the more systematic way which makes use of group theoretical techniques, we first observe that the representation Γ of the symmetry operations of C_{2v} in the basis $\boldsymbol{\chi}$ is *reducible*, since:

$$\sum_R |\chi^\Gamma(R)|^2 = 49 + 1 + 25 + 9 = 84 \neq 4,$$

where the characters are the traces of the representative matrices of Problem 8.6.

From relation (97):

$$a_i = \frac{1}{h} \sum_R \chi^i(R) \chi^\Gamma(R)$$

we find:

$$A_1\colon \quad a_{A_1} = \frac{1}{4}(7 + 1 + 5 + 3) = 4$$

$$A_2\colon \quad a_{A_2} = \frac{1}{4}(7 + 1 - 5 - 3) = 0$$

$$B_1\colon \quad a_{B_1} = \frac{1}{4}(7 - 1 - 5 + 3) = 1$$

$$B_2\colon \quad a_{B_2} = \frac{1}{4}(7 - 1 + 5 - 3) = 2$$

so that the reducible representation Γ can be decomposed into:

$$\Gamma = 4A_1 + B_1 + 2B_2.$$

Using the soft projector $\hat{P}^i \propto \sum_R \chi^i(R)\hat{R}$, which is sufficient since all irreps are 1-dimensional, we obtain:

$$A_1\colon \quad \hat{P}^{A_1} k = k + k + k + k \propto k$$

$$\hat{P}^{A_1} s = s + s + s + s \propto s$$

$$\hat{P}^{A_1} z = z + z + z + z \propto z$$

$$\hat{P}^{A_1}h_1 = h_1 + h_2 + h_1 + h_2 \propto h_1 + h_2 \Rightarrow \frac{1}{\sqrt{2}}(h_1 + h_2)$$

after normalization (neglecting the overlap between h_1 and h_2).

A_2: $\hat{P}^{A_2}k = k + k - k - k = 0$

with the same result for all other functions.

B_1: $\hat{P}^{B_1}x = x + x + x + x \propto x$

all others being zero.

B_2: $\hat{P}^{B_2}y = y + y + y + y \propto y$

$$\hat{P}^{B_2}h_1 = h_1 - h_2 + h_1 - h_2 \propto h_1 - h_2 \Rightarrow \frac{1}{\sqrt{2}}(h_1 - h_2)$$

after normalization. All remaining functions vanish under $\hat{P}^{B_2}$.

Therefore, the symmetry-adapted basis derived by group theoretical methods is that given at the beginning of this Problem.

8.8. Even in this case, we can proceed either with the intuitive method or with the aid of group theoretical techniques. As an alternative easy way of obtaining the symmetry-adapted functions onto the oxygen atom, we can make use of the direct product of the transformation properties of x, y, z and their products. The results are those given as answer to Problem 8.8.

8.9. This problem is an extension of Problem 8.8. The 35×35 secular equation in the original basis is factorized into 13×13 (A_1), 6×6 (A_2), 7×7 (B_1), 9×9 (B_2) blocks having the symmetry of the different irreps of the point group C_{2v}, as shown in Figure 8.20.

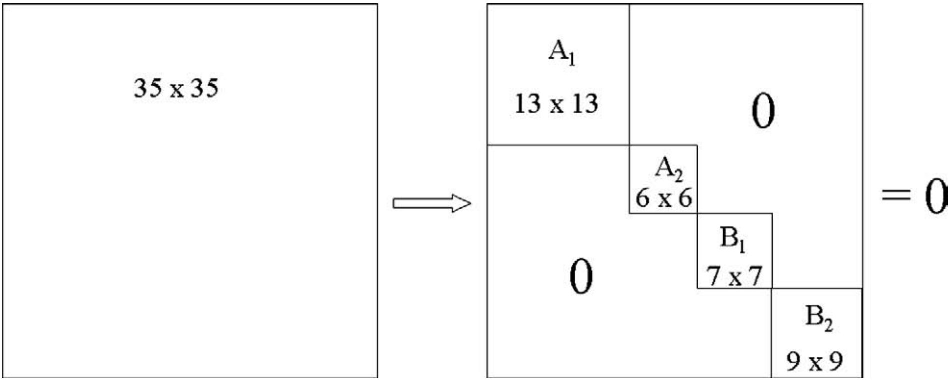


Figure 8.20 Symmetry factorization under C_{2v} of the secular equation in the large basis set for H_2O.

8.10. The three hydrogens are in the xy-plane, z being the symmetry axis.

The transformation table of the basis $\boldsymbol{\chi} = (kszxyh_1h_2h_3)$ under the symmetry operations of the point group C_{3v} is (using equations (32), (33) for rotations, and equations (42), (43) for reflections):

$\hat{R}\chi$	I	C_3^+	C_3^-	σ_1	σ_2	σ_3
k	k	k	k	k	k	k
s	s	s	s	s	s	s
z	z	z	z	z	z	z
x	x	$\bar{c}x+\bar{s}y$	$\bar{c}x+sy$	x	$\bar{c}x+\bar{s}y$	$\bar{c}x+sy$
y	y	$sx+\bar{c}y$	$\bar{s}x+\bar{c}y$	$-y$	$\bar{s}x+cy$	$sx+cy$
h_1	h_1	h_3	h_2	h_1	h_3	h_2
h_2	h_2	h_1	h_3	h_3	h_2	h_1
h_3	h_3	h_2	h_1	h_2	h_1	h_3

Then easily follow the matrices given as answer to Problem 8.10.

8.11. We use Figure 8.21 and the transformation table of Problem 8.10. The character table of C_{3v} (E is a 2-dimensional irrep whose vectors transform like x, y) is:

C_{3v}	I	C_3^+	C_3^-	σ_1	σ_2	σ_3	Symmetry basis
A_1	1	1	1	1	1	1	$k, s, z, h_z = \frac{1}{\sqrt{3}}(h_1+h_2+h_3)$
A_2	1	1	1	-1	-1	-1	
E (xy)	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \bar{c} & s \\ \bar{s} & \bar{c} \end{pmatrix}$	$\begin{pmatrix} \bar{c} & \bar{s} \\ s & c \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} \bar{c} & \bar{s} \\ \bar{s} & c \end{pmatrix}$	$\begin{pmatrix} \bar{c} & s \\ s & c \end{pmatrix}$	$x, h_x = \frac{1}{\sqrt{6}}(2h_1-h_2-h_3)$ $y, h_y = \frac{1}{\sqrt{2}}(h_2-h_3)$
Γ reducible	8	2	2	4	4	4	

The representation Γ is reducible. To construct the symmetry-adapted basis functions it will be convenient to use the powerful projector (100):

$$\hat{P}^i_{\lambda\lambda} = \frac{l_i}{h}\sum_R \mathbf{D}^i(R)^*_{\lambda\lambda}\hat{R}$$

using the complete table of characters given above and the transformation table of Problem 8.10. We obtain:

$$A_1: \quad \hat{P}^{A_1}k = k \qquad \hat{P}^{A_1}s = s \qquad \hat{P}^{A_1}z = z$$

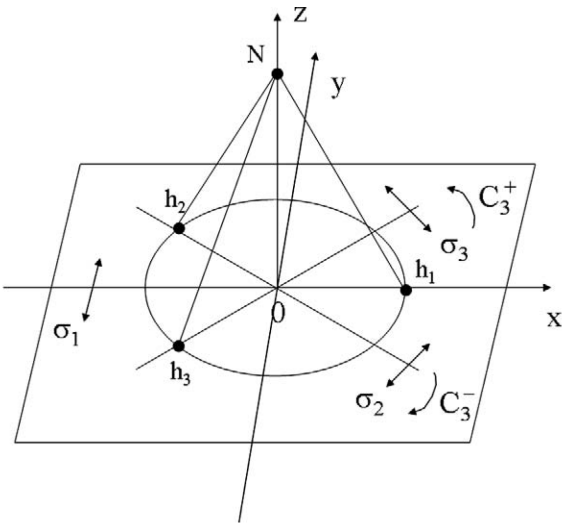


Figure 8.21 The symmetry elements of the NH$_3$ molecule under C_{3v}.

$$\hat{P}^{A_1}x = \frac{1}{6}\left(x - \frac{1}{2}x - \frac{\sqrt{3}}{2}y - \frac{1}{2}x + \frac{\sqrt{3}}{2}y + x - \frac{1}{2}x - \frac{\sqrt{3}}{2}y - \frac{1}{2}x + \frac{\sqrt{3}}{2}y\right) = 0$$

$$\hat{P}^{A_1}y = \frac{1}{6}\left(y + \frac{\sqrt{3}}{2}x - \frac{1}{2}y - \frac{\sqrt{3}}{2}x - \frac{1}{2}y - y - \frac{\sqrt{3}}{2}x + \frac{1}{2}y + \frac{\sqrt{3}}{2}x + \frac{1}{2}y\right) = 0$$

$$\hat{P}^{A_1}h_1 = \frac{1}{6}(2h_1 + 2h_2 + 2h_3) \propto h_1 + h_2 + h_3 \Rightarrow \frac{1}{\sqrt{3}}(h_1 + h_2 + h_3)$$

after normalization.

A_2: $\hat{P}^{A_2}k = \frac{1}{6}(k + k + k - k - k - k) = 0 \qquad \hat{P}^{A_2}s = \hat{P}^{A_2}z = 0$

$$\hat{P}^{A_2}x = \frac{1}{6}\left(x - \frac{1}{2}x - \frac{\sqrt{3}}{2}y - \frac{1}{2}x + \frac{\sqrt{3}}{2}y - x + \frac{1}{2}x + \frac{\sqrt{3}}{2}y + \frac{1}{2}x - \frac{\sqrt{3}}{2}y\right) = 0$$

$$\hat{P}^{A_2}y = \frac{1}{6}\left(y + \frac{\sqrt{3}}{2}x - \frac{1}{2}y - \frac{\sqrt{3}}{2}x - \frac{1}{2}y + y + \frac{\sqrt{3}}{2}x - \frac{1}{2}y - \frac{\sqrt{3}}{2}x - \frac{1}{2}y\right) = 0$$

$$\hat{P}^{A_2}h_1 = \frac{1}{6}(h_1 + h_3 + h_2 - h_1 - h_3 - h_2) = 0$$

$$E\colon \quad \hat{P}^{E}_{xx}k = \frac{2}{6}\left(k - \frac{1}{2}k - \frac{1}{2}k + k - \frac{1}{2}k - \frac{1}{2}k\right) = 0 \qquad \hat{P}^{E}_{xx}s = \hat{P}^{E}_{xx}z = 0$$

$$\begin{aligned}\hat{P}^{E}_{xx}x &= \frac{2}{6}\left\{x - \frac{1}{2}\left(-\frac{1}{2}x - \frac{\sqrt{3}}{2}y\right) - \frac{1}{2}\left(-\frac{1}{2}x + \frac{\sqrt{3}}{2}y\right) + x \right.\\ &\qquad \left. - \frac{1}{2}\left(-\frac{1}{2}x - \frac{\sqrt{3}}{2}y\right) - \frac{1}{2}\left(-\frac{1}{2}x + \frac{\sqrt{3}}{2}y\right)\right\}\\ &= \frac{1}{3}\left(2x + \frac{1}{4}x + \frac{1}{4}x + \frac{1}{4}x + \frac{1}{4}x\right) = x\end{aligned}$$

$$\begin{aligned}\hat{P}^{E}_{xx}y &= \frac{2}{6}\left\{y - \frac{1}{2}\left(\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right) - \frac{1}{2}\left(-\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right) - y \right.\\ &\qquad \left. - \frac{1}{2}\left(-\frac{\sqrt{3}}{2}x + \frac{1}{2}y\right) - \frac{1}{2}\left(\frac{\sqrt{3}}{2}x + \frac{1}{2}y\right)\right\} = 0\end{aligned}$$

$$\begin{aligned}\hat{P}^{E}_{xx}h_1 &= \frac{2}{6}\left(h_1 - \frac{1}{2}h_3 - \frac{1}{2}h_2 + h_1 - \frac{1}{2}h_3 - \frac{1}{2}h_2\right) = \frac{1}{3}(2h_1 - h_2 - h_3)\\ &\Rightarrow \frac{1}{\sqrt{6}}(2h_1 - h_2 - h_3)\end{aligned}$$

$$\hat{P}^{E}_{yy}k = \frac{2}{6}\left(k - \frac{1}{2}k - \frac{1}{2}k - k + \frac{1}{2}k + \frac{1}{2}k\right) = 0 \qquad \hat{P}^{E}_{yy}s = \hat{P}^{E}_{yy}z = 0$$

$$\begin{aligned}\hat{P}^{E}_{yy}x &= \frac{2}{6}\left\{x - \frac{1}{2}\left(-\frac{1}{2}x - \frac{\sqrt{3}}{2}y\right) - \frac{1}{2}\left(-\frac{1}{2}x + \frac{\sqrt{3}}{2}y\right) - x \right.\\ &\qquad \left. + \frac{1}{2}\left(-\frac{1}{2}x - \frac{\sqrt{3}}{2}y\right) + \frac{1}{2}\left(-\frac{1}{2}x + \frac{\sqrt{3}}{2}y\right)\right\} = 0\end{aligned}$$

$$\begin{aligned}\hat{P}^{E}_{yy}y &= \frac{2}{6}\left\{y - \frac{1}{2}\left(\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right) - \frac{1}{2}\left(-\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right) + y + \frac{1}{2}\left(-\frac{\sqrt{3}}{2}x + \frac{1}{2}y\right) \right.\\ &\qquad \left. + \frac{1}{2}\left(\frac{\sqrt{3}}{2}x + \frac{1}{2}y\right)\right\} = \frac{1}{3}\left(2y + \frac{1}{4}y + \frac{1}{4}y + \frac{1}{4}y + \frac{1}{4}y\right) = y\end{aligned}$$

$$\hat{P}^E_{yy}h_1 = \frac{2}{6}\left(h_1 - \frac{1}{2}h_3 - \frac{1}{2}h_2 - h_1 + \frac{1}{2}h_3 + \frac{1}{2}h_2\right) = 0$$

$$\hat{P}^E_{yy}h_2 = \frac{2}{6}\left(h_2 - \frac{1}{2}h_1 - \frac{1}{2}h_3 - h_3 + \frac{1}{2}h_2 + \frac{1}{2}h_1\right) = \frac{1}{3}\left(\frac{3}{2}h_2 - \frac{3}{2}h_3\right)$$

$$\Rightarrow \frac{1}{\sqrt{2}}(h_2 - h_3).$$

Hence, we obtain for the symmetry basis in the minimum set for NH_3 under C_{3v}:

$$A_1\colon \quad k, s, z, h_z = \frac{1}{\sqrt{3}}(h_1 + h_2 + h_3)$$

$$E\colon \quad x, h_x = \frac{1}{\sqrt{6}}(2h_1 - h_2 - h_3)$$

$$y, h_y = \frac{1}{\sqrt{2}}(h_2 - h_3)$$

so that the reducible representation Γ can be decomposed into:

$$\Gamma = 4A_1 + 2E.$$

8.12. We inscribe the CH_4 molecule in a cube having the C atom at its centre and the four H atoms at non-contiguous vertices of the cube (Figure 8.22).

Molecular symmetry does suggest immediately the correct symmetry combinations of the four 1*s* AOs onto the H atoms transforming as s, x, y, z:

$$h_s = \frac{1}{2}(h_1 + h_2 + h_3 + h_4)$$

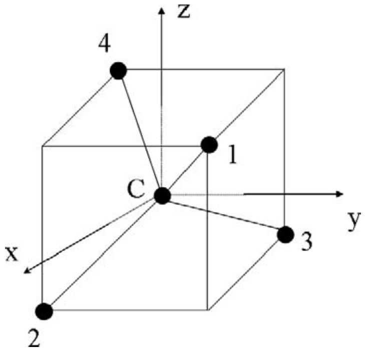


Figure 8.22 The cube circumscribing the CH_4 molecule.

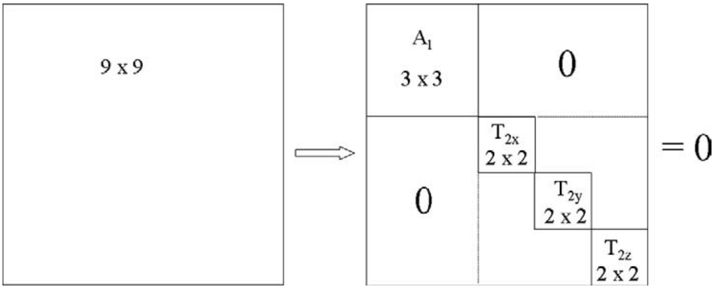


Figure 8.23 Symmetry factorization under T_d of the secular equation in the minimum basis set for CH_4.

$$h_x = \frac{1}{2}(h_1 + h_2 - h_3 - h_4)$$

$$h_y = \frac{1}{2}(h_1 - h_2 + h_3 - h_4)$$

$$h_z = \frac{1}{2}(h_1 - h_2 - h_3 + h_4)$$

so that the symmetry basis under T_d will be:

A_1: k, s, h_s

T_2: $(x, h_x), (y, h_y), (z, h_z)$.

The reducible representation Γ will be decomposed into:

$$\Gamma = 3A_1 + 2T_2.$$

The 9×9 secular equation over the original basis will be factorized into a 3×3 block (A_1) and three 2×2 blocks (T_2) transforming as (x, y, z) (Figure 8.23).

8.13. The π-electron system in benzene C_6H_6.

For our purposes, it will be sufficient to consider the point group C_{6v} ($h = 12$), a subgroup of the full D_{6h} group ($h = 24$) to which the benzene molecule C_6H_6 belongs. The principal symmetry axis will be the z-axis, perpendicular to the xy-plane of the σ-skeleton of the molecule, which is a further σ_h symmetry plane. The $2p\pi$ AOs are therefore $2p_z$, and can be sketched schematically in the drawing as $1s$ AOs with + sign above the molecular plane, and − sign below it.

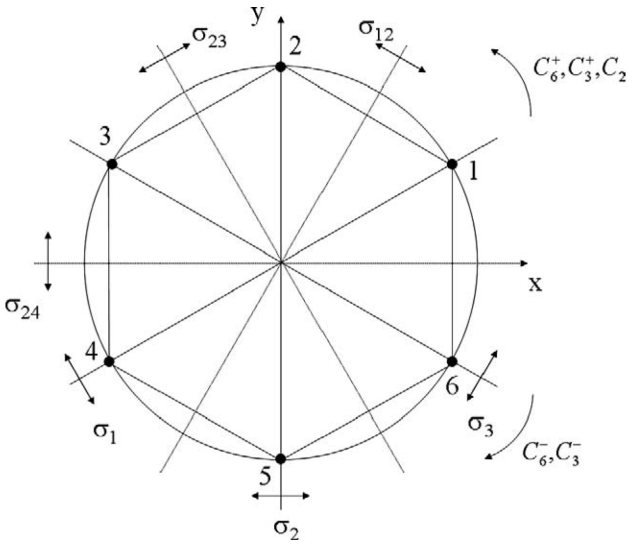


Figure 8.24 The symmetry elements of the benzene molecule C_6H_6 under C_{6v}.

The transformation table of the six $2p\pi$ AOs:

$$\chi = (\chi_1 \chi_2 \chi_3 \chi_4 \chi_5 \chi_6)$$

centred at the different C atoms in the planar hexagonal skeleton of the molecule, under the 12 symmetry operations of the point group C_{6v} (Figure 8.24), can be constructed using equations (32), (33) ($l = 1$), (37), (38) ($l = 2$) for rotations, and equations (42), (43) ($l = 1$), (46) ($l = 2$) for reflections, and is given below together with the complete character table of the point group C_{6v}.

C_{6v}	I	C_6^+	C_6^-	C_3^+	C_3^-	C_2
A_1	1	1	1	1	1	1
A_2	1	1	1	1	1	1
B_1	1	−1	−1	1	1	−1
B_2	1	−1	−1	1	1	−1
E_1 (x, y)	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} c & s \\ \bar{s} & c \end{pmatrix}$	$\begin{pmatrix} c & \bar{s} \\ s & c \end{pmatrix}$	$\begin{pmatrix} \bar{c} & s \\ \bar{s} & \bar{c} \end{pmatrix}$	$\begin{pmatrix} \bar{c} & \bar{s} \\ s & \bar{c} \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 \\ 0 & \bar{1} \end{pmatrix}$
E_2 $(x^2 - y^2, xy)$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \bar{c} & s \\ \bar{s} & \bar{c} \end{pmatrix}$	$\begin{pmatrix} \bar{c} & \bar{s} \\ s & \bar{c} \end{pmatrix}$	$\begin{pmatrix} \bar{c} & \bar{s} \\ s & \bar{c} \end{pmatrix}$	$\begin{pmatrix} \bar{c} & s \\ \bar{s} & \bar{c} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$\hat{R}\|1\rangle$	$\|1\rangle$	$\|6\rangle$	$\|2\rangle$	$\|5\rangle$	$\|3\rangle$	$\|4\rangle$

C_{6v}	σ_1	σ_2	σ_3	σ_{12}	σ_{23}	σ_{34}
A_1	1	1	1	1	1	1
A_2	−1	−1	−1	−1	−1	−1
B_1	1	1	1	−1	−1	−1
B_2	−1	−1	−1	1	1	1
E_1 (x, y)	$\begin{pmatrix} c & s \\ s & \bar{c} \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} c & \bar{s} \\ \bar{s} & \bar{c} \end{pmatrix}$	$\begin{pmatrix} \bar{c} & s \\ s & c \end{pmatrix}$	$\begin{pmatrix} \bar{c} & \bar{s} \\ \bar{s} & c \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & \bar{1} \end{pmatrix}$
E_2 $(x^2 - y^2, xy)$	$\begin{pmatrix} \bar{c} & s \\ s & c \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} \bar{c} & \bar{s} \\ \bar{s} & c \end{pmatrix}$	$\begin{pmatrix} \bar{c} & \bar{s} \\ \bar{s} & c \end{pmatrix}$	$\begin{pmatrix} \bar{c} & s \\ s & c \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & \bar{1} \end{pmatrix}$
$\hat{R}\lvert 1\rangle$	$\lvert 1\rangle$	$\lvert 3\rangle$	$\lvert 5\rangle$	$\lvert 2\rangle$	$\lvert 4\rangle$	$\lvert 6\rangle$

Using the full projector (100) we find:

$$
\begin{aligned}
A_1\colon\quad &\frac{1}{12}(\chi_1+\chi_6+\chi_2+\chi_5+\chi_3+\chi_4+\chi_1+\chi_3+\chi_5+\chi_2+\chi_4+\chi_6)\\
&=\frac{1}{6}(\chi_1+\chi_2+\chi_3+\chi_4+\chi_5+\chi_6) \Rightarrow a_1\\
&=\frac{1}{\sqrt{6}}(\chi_1+\chi_2+\chi_3+\chi_4+\chi_5+\chi_6)
\end{aligned}
$$

$$
A_2\colon\quad \frac{1}{12}(\chi_1+\chi_6+\chi_2+\chi_5+\chi_3+\chi_4-\chi_1-\chi_3-\chi_5-\chi_2-\chi_4-\chi_6)=0
$$

$$
\begin{aligned}
B_1\colon\quad &\frac{1}{12}(\chi_1-\chi_6-\chi_2+\chi_5+\chi_3-\chi_4+\chi_1+\chi_3+\chi_5-\chi_2-\chi_4-\chi_6)\\
&=\frac{1}{6}(\chi_1-\chi_2+\chi_3-\chi_4+\chi_5-\chi_6) \Rightarrow b_1\\
&=\frac{1}{\sqrt{6}}(\chi_1-\chi_2+\chi_3-\chi_4+\chi_5-\chi_6)
\end{aligned}
$$

$$
B_2\colon\quad \frac{1}{12}(\chi_1-\chi_6-\chi_2+\chi_5+\chi_3-\chi_4-\chi_1-\chi_3-\chi_5+\chi_2+\chi_4+\chi_6)=0
$$

$$
\begin{aligned}
E_{1x}\colon\quad &\frac{2}{12}\left\{\left(1+\frac{1}{2}\right)\chi_1+\left(\frac{1}{2}-\frac{1}{2}\right)\chi_2+\left(-\frac{1}{2}-1\right)\chi_3\right.\\
&\qquad\left.+\left(-1-\frac{1}{2}\right)\chi_4+\left(-\frac{1}{2}+\frac{1}{2}\right)\chi_5+\left(\frac{1}{2}+1\right)\chi_6\right\}\\
&=\frac{1}{4}(\chi_1-\chi_3-\chi_4+\chi_6) \Rightarrow e_{1x}=\frac{1}{2}(\chi_1-\chi_3-\chi_4+\chi_6)\sim x
\end{aligned}
$$

$$\begin{aligned}
E_{1y}\colon\quad & \frac{2}{12}\left\{\left(1-\frac{1}{2}\right)\chi_1+\left(\frac{1}{2}+\frac{1}{2}\right)\chi_2+\left(-\frac{1}{2}+1\right)\chi_3\right.\\
&\left.\quad+\left(-1+\frac{1}{2}\right)\chi_4+\left(-\frac{1}{2}-\frac{1}{2}\right)\chi_5+\left(\frac{1}{2}-1\right)\chi_6\right\}\\
&=\frac{1}{12}(\chi_1+2\chi_2+\chi_3-\chi_4-2\chi_5-\chi_6)\\
&\Rightarrow e_{1y}=\frac{1}{\sqrt{12}}(\chi_1+2\chi_2+\chi_3-\chi_4-2\chi_5-\chi_6)\sim y
\end{aligned}$$

$$\begin{aligned}
E_{2,x^2-y^2}\colon\quad & \frac{2}{12}\left\{\left(1-\frac{1}{2}\right)\chi_1+\left(-\frac{1}{2}-\frac{1}{2}\right)\chi_2+\left(-\frac{1}{2}+1\right)\chi_3\right.\\
&\left.\quad+\left(1-\frac{1}{2}\right)\chi_4+\left(-\frac{1}{2}-\frac{1}{2}\right)\chi_5+\left(-\frac{1}{2}-1\right)\chi_6\right\}\\
&=\frac{1}{12}(\chi_1-2\chi_2+\chi_3+\chi_4-2\chi_5+\chi_6)\\
&\Rightarrow e_{2,x^2-y^2}=\frac{1}{\sqrt{12}}(\chi_1-2\chi_2+\chi_3+\chi_4-2\chi_5+\chi_6)\sim x^2-y^2
\end{aligned}$$

$$\begin{aligned}
E_{2,xy}\colon\quad & \frac{2}{12}\left\{\left(1+\frac{1}{2}\right)\chi_1+\left(-\frac{1}{2}+\frac{1}{2}\right)\chi_2+\left(-1-\frac{1}{2}\right)\chi_3\right.\\
&\left.\quad+\left(1+\frac{1}{2}\right)\chi_4+\left(-\frac{1}{2}+\frac{1}{2}\right)\chi_5+\left(-\frac{1}{2}-1\right)\chi_6\right\}\\
&=\frac{1}{4}(\chi_1-\chi_3+\chi_4-\chi_6)\Rightarrow e_{2,xy}=\frac{1}{2}(\chi_1-\chi_3+\chi_4-\chi_6)\sim xy.
\end{aligned}$$

The reducible representation Γ splits into:

$$\Gamma = A_1 + B_1 + E_1 + E_2.$$

The 6×6 secular equation over the original π-electron basis will factorize into six 1×1 blocks (Figure 8.25).

The molecular symmetry is so high that the secular equation is completely factorized into six one-dimensional equations, which corresponds to full diagonalization of the original Hamiltonian matrix: symmetry AOs are already π MOs, the coefficients of the linear combination being completely determined by symmetry. The ground state configuration of the 6π-electrons in benzene will be:

$$^1A_1 : a_{1u}^2 e_{1g}^4,$$

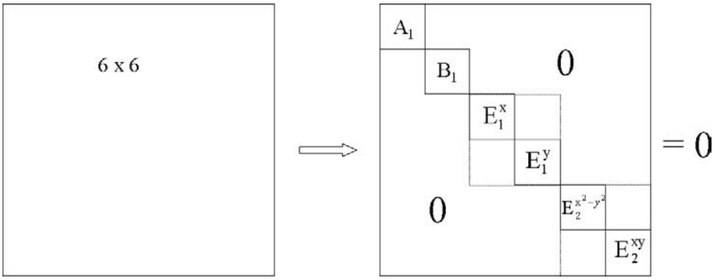


Figure 8.25 Symmetry factorization under C_{6v} of the secular equation of the π-electron basis for benzene.

where the MOs are classified even with respect to their symmetry properties with respect to inversion.

8.14. It is convenient to use MOs in *complex* form:

$$\pi_{g+} = \frac{-p_{A+} + p_{B+}}{\sqrt{2}} \propto e^{i\varphi}, \qquad \pi_{g-} = \frac{p_{A-} - p_{B-}}{\sqrt{2}} \propto e^{-i\varphi},$$

where p_+, p_- are complex AOs with Condon–Shortley phase:

$$p_+ \propto -\frac{e^{i\varphi}}{\sqrt{2\pi}}, \qquad p_- \propto \frac{e^{-i\varphi}}{\sqrt{2\pi}}.$$

The $\binom{4}{2} = 6$ 2-electron states result from all possible occupations with two electrons of the four spin-orbitals $\pi_{g+}\alpha$, $\pi_{g+}\beta$, $\pi_{g-}\alpha$, $\pi_{g-}\beta$.

The operators needed for a complete classification of the resulting electronic states are:

$$\hat{L}_z = \sum_k -i\frac{\partial}{\partial\varphi_k} = \hat{L}_{z1} + \hat{L}_{z2} \quad (i^2 = -1 \text{ is the imaginary unit})$$

$$\hat{L}_z\psi = \Lambda\psi \quad \Lambda = 0, \pm1, \pm2, \pm3, \cdots$$

$$\text{States } \Sigma, \Pi, \Delta, \Phi, \cdots$$

$$\hat{\sigma}_\alpha\varphi = 2\alpha - \varphi \qquad \hat{\sigma}_\alpha(-\varphi) = \varphi - 2\alpha$$

$$\hat{\imath}\psi = \pm\psi \qquad + = \text{gerade (even)} \quad - = \text{ungerade (odd)}.$$

We then have:

$$\hat{L}_z\pi_{g+} = \pi_{g+} \qquad \hat{L}_z\pi_{g-} = -\pi_{g-},$$

Table 8.3.

Symmetry of (normalized) Slater determinants arising from the MO electron configuration π_g^2

Slater determinant	$\pi_{g+}\alpha$	$\pi_{g-}\alpha$	$\pi_{g+}\beta$	$\pi_{g-}\beta$	Λ	M_S	Resulting states
$\psi_1 = \Vert\pi_{g+}\pi_{g-}\Vert$	1	1	0	0	0	1	$^3\Sigma^-$
$\psi_2 = \Vert\pi_{g+}\overline{\pi}_{g+}\Vert$	1	0	1	0	2	0	$^1\Delta$
$\psi_3 = \Vert\pi_{g+}\overline{\pi}_{g-}\Vert$	1	0	0	1	0	0	$^3\Sigma, {}^1\Sigma$
$\psi_4 = \Vert\pi_{g-}\overline{\pi}_{g+}\Vert$	0	1	1	0	0	0	
$\psi_5 = \Vert\pi_{g-}\overline{\pi}_{g-}\Vert$	0	1	0	1	-2	0	$^1\Delta$
$\psi_6 = \Vert\overline{\pi}_{g+}\overline{\pi}_{g-}\Vert$	0	0	1	1	0	-1	$^3\Sigma^-$

and, for the Slater determinants:

$$\hat{L}_z\Vert\pi_{g+}\pi_{g-}\Vert = \Vert\pi_{g+}\pi_{g-}\Vert + \Vert\pi_{g+} - \pi_{g-}\Vert = 0\Vert\pi_{g+}\pi_{g-}\Vert \quad \text{State } \Sigma$$

$$\hat{L}_z\Vert\pi_{g+}\overline{\pi}_{g+}\Vert = \Vert\pi_{g+}\overline{\pi}_{g+}\Vert + \Vert\pi_{g+}\overline{\pi}_{g+}\Vert = 2\Vert\pi_{g+}\overline{\pi}_{g+}\Vert \quad \text{State } \Delta.$$

For the reflection $\hat{\sigma}_\alpha$:

$$\hat{\sigma}_\alpha\pi_{g+} = e^{i2\alpha}\pi_{g-} \qquad \hat{\sigma}_\alpha\pi_{g-} = e^{-i2\alpha}\pi_{g+}$$

$$\hat{\sigma}_\alpha\Vert\pi_{g+}\pi_{g-}\Vert = \Vert e^{i2\alpha}\pi_{g-}e^{-i2\alpha}\pi_{g+}\Vert = \Vert\pi_{g-}\pi_{g+}\Vert = -\Vert\pi_{g+}\pi_{g-}\Vert$$

$$\hat{\sigma}_\alpha\Vert\pi_{g+}\overline{\pi}_{g-}\Vert = \Vert\pi_{g-}\overline{\pi}_{g+}\Vert \qquad \hat{\sigma}_\alpha\Vert\pi_{g-}\overline{\pi}_{g+}\Vert = \Vert\pi_{g+}\overline{\pi}_{g-}\Vert.$$

We obtain Table 8.3.

The complete transformation table of the six Slater determinants under the symmetry operations is then:

$\hat{O}$	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6
$\hat{L}_z$	0	$2\psi_2$	0	0	$-2\psi_5$	0
$\hat{\sigma}$	$-\psi_1$	ψ_5	ψ_4	ψ_3	ψ_2	$-\psi_6$
$\hat{\imath}$	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6
$\hat{S}^2$	$2\psi_1$	0	$\psi_3 - \psi_4$	$-(\psi_3 - \psi_4)$	0	$2\psi_6$

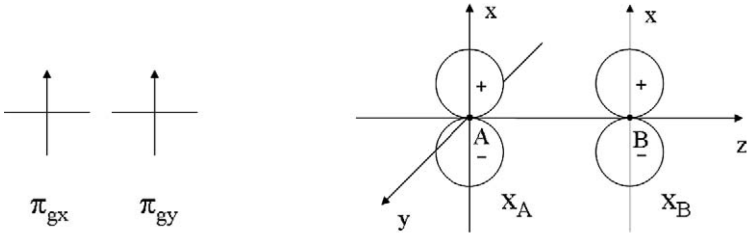


Figure 8.26 Electron configuration of ground state O_2 (left) and the $2p\pi_x$ AOs onto each O atom (right).

so that the six electronic states with definite symmetry are:

$$
\begin{array}{llll}
\hline
{}^3\Sigma_g^-: & \psi_1, & \frac{1}{\sqrt{2}}(\psi_3-\psi_4), & \psi_6 \\
 & M_S=1 & 0 & -1 \\
{}^1\Sigma_g^+: & & \frac{1}{\sqrt{2}}(\psi_3+\psi_4) & \\
{}^1\Delta_g: & \multicolumn{3}{c}{\frac{1}{\sqrt{2}}(\psi_2+\psi_5),\ \frac{1}{\sqrt{2}}(\psi_2-\psi_5).} \\
\hline
\end{array}
$$

These results can be easily checked by acting with the appropriate operators[12].

Since ${}^1\Delta$ has MOs which are doubly occupied by two electrons with opposite spin, Hund's rule will ensure that the ground state arising from the π_g^2 configuration will be the triplet ${}^3\Sigma_g^-$ (compare with the electronic ground state of the O_2 molecule).

8.15. The symmetry of the electronic MO ground state of the O_2 molecule is determined by the symmetry of its π_g electrons, which, according to Hund's rule, occupy this doubly degenerate level with parallel spin. The state is hence a triplet. All remaining 14 electrons completely fill the σ_g, σ_u and π_u MOs with paired spin, and so do not contribute to the total spin, belonging to the totally symmetric representation Σ of the point group $D_{\infty h}$. We use the MOs in *real* form (Figure 8.26).

$$\pi_{gx}=\frac{x_A-x_B}{\sqrt{2}} \qquad \pi_{gy}=\frac{y_A-y_B}{\sqrt{2}}.$$

Figure 8.27 shows the symmetry plane $\sigma(\alpha=0^{\circ})$ passing along the internuclear axis z.

(i) We recall the relation between real and complex AOs:

$$p_+\propto-\frac{e^{i\varphi}}{\sqrt{2\pi}} \qquad p_-\propto\frac{e^{-i\varphi}}{\sqrt{2\pi}} \quad \text{complex AOs}$$

---

[12] The ± specification is usually omitted for states having $\Lambda\neq0$ (Herzberg, 1957, p. 217).

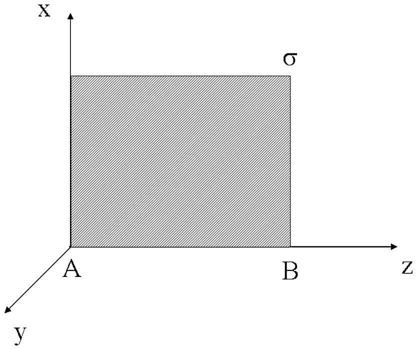


Figure 8.27 The symmetry plane $\sigma(\alpha = 0°)$ in the O_2 molecule.

$$\langle p_+|p_+\rangle = \langle p_-|p_-\rangle = 1 \qquad \langle p_+|p_-\rangle = \langle p_-|p_+\rangle = 0$$

$$x = \frac{-p_+ + p_-}{\sqrt{2}} = \frac{\cos\varphi}{\sqrt{\pi}} \qquad y = i\,\frac{p_+ + p_-}{\sqrt{2}} = \frac{\sin\varphi}{\sqrt{\pi}} \quad \text{real AOs}$$

(ii) Transformation under $\hat{L}_z = -i\,\frac{\partial}{\partial\varphi}$:

$$\hat{L}_z p_+ = p_+$$

$$\hat{L}_z p_- = -p_-$$

so that p_+, p_- are eigenfunctions of $\hat{L}_z$ with eigenvalues ±1.

$$\hat{L}_z x = \frac{-p_+ - p_-}{\sqrt{2}} = i\left(i\,\frac{p_+ + p_-}{\sqrt{2}}\right) = iy$$

$$\hat{L}_z y = i\,\frac{p_+ - p_-}{\sqrt{2}} = -i\left(\frac{-p_+ + p_-}{\sqrt{2}}\right) = -ix$$

so that x, y are *not* eigenfunctions of $\hat{L}_z$.

(iii) Transformation under $\hat{\sigma} = \hat{\sigma}_{zx}$:

$$\hat{\sigma}x = x$$

$$\hat{\sigma}y = -y$$

as it is easily seen from Figure 8.27.

(iv) Transformation under the inversion $\hat{\imath}$:

$$\hat{\imath}x = -x \qquad \hat{\imath}y = -y \qquad (\text{also } A \leftrightarrow B).$$

(v) The transformation table for *real* AOs and MOs is then:

$\hat{O}$	x_A	x_B	y_A	y_B	π_{gx}	π_{gy}
$\hat{L}_z$	iy_A	iy_B	$-ix_A$	$-ix_B$	$i\pi_{gy}$	$-i\pi_{gx}$
$\hat{\sigma}$	x_A	x_B	$-y_A$	$-y_B$	π_{gx}	$-\pi_{gy}$
$\hat{\imath}$	$-x_B$	$-x_A$	$-y_B$	$-y_A$	π_{gx}	π_{gy}

(vi) Classification of the effective 2-electron MO wavefunction:

$$\Psi(\text{MO}) = (\pi_{gx}\pi_{gy}) \qquad (\cdots) = \|1\sigma_g 1\bar{\sigma}_g \cdots 1\pi_{uy} 1\bar{\pi}_{uy} 1\pi_{gx} 1\pi_{gy}\|$$

$$\hat{L}_z\Psi = \Lambda\Psi \quad \Lambda = 0, 1, 2, 3, \cdots$$

$$\text{States } \Sigma, \Pi, \Delta, \Phi, \cdots$$

- $$\begin{aligned}\hat{L}_z\Psi &= (\hat{L}_{z1} + \hat{L}_{z2})\Psi = (\hat{L}_{z1}\pi_{gx}\pi_{gy}) + (\pi_{gx}\hat{L}_{z2}\pi_{gy}) \\ &= (i\pi_{gy}\pi_{gy}) + (\pi_{gx} - i\pi_{gx}) = i[(\pi_{gy}\pi_{gy}) - (\pi_{gx}\pi_{gx})] = 0 \cdot \Psi\end{aligned}$$

  as the two Slater determinants vanish by the exclusion principle. Thus, Ψ belongs to Σ (the z-component of the axial angular momentum operator is zero).

- $$\hat{\sigma}\Psi = (\hat{\sigma}\pi_{gx}\hat{\sigma}\pi_{gy}) = (\pi_{gx} - \pi_{gy}) = -\Psi$$

  giving the result that Ψ is a Σ^- state (Ψ changes sign under reflection in a plane containing the internuclear axis).

- $$\hat{\imath}\Psi = (\hat{\imath}\pi_{gx}\hat{\imath}\pi_{gy}) = (\pi_{gx}\pi_{gy}) = \Psi$$

  with the result that Ψ is a Σ_g^- state (even → gerade).

Taking into account spin, we can conclude that the many-electron MO wavefunction describing the two unpaired electrons in the π_g^2 configuration of ground state O_2 is a ${}^3\Sigma_g^-$ state.

8.16. It will be shown in Chapter 10 that the $M_S = 1$ component of the covalent triplet VB wavefunction describing the two 3-electron π-bonds in ground state O_2 can be written, using the same short notation of Problem 8.15, as:

$$\Psi_1 = \frac{1}{\sqrt{2}}[(x_A y_A \bar{y}_A y_B x_B \bar{x}_B) + (x_B y_B \bar{y}_B y_A x_A \bar{x}_A)],$$

which can be further contracted into the *ultrashort* notation specifying only the two unpaired π-electrons:

$$\Psi_1 = \frac{1}{\sqrt{2}}[(x_A y_B) + (x_B y_A)].$$

Using the transformation table for *real* AOs of Problem 8.15, under the different symmetry operations of $D_{\infty h}$ we obtain the following results:

- $$\begin{aligned}\hat{L}_z \Psi_1 &= \frac{1}{\sqrt{2}}\big[(\hat{L}_{z1} x_A y_B) + (\hat{L}_{z1} x_B y_A) + (x_A \hat{L}_{z2} y_B) + (x_B \hat{L}_{z2} y_A)\big] \\ &= \frac{1}{\sqrt{2}}[i(y_A y_B) + i(y_B y_A) - i(x_A x_B) - i(x_B x_A)] \\ &= \frac{1}{\sqrt{2}}[i(y_A y_B) - i(y_A y_B) - i(x_A x_B) + i(x_A x_B)] = 0 \cdot \Psi_1\end{aligned}$$

  (Σ state)

- $$\begin{aligned}\hat{\sigma} \Psi_1 &= \frac{1}{\sqrt{2}}[(\hat{\sigma} x_A \hat{\sigma} y_B) + (\hat{\sigma} x_B \hat{\sigma} y_A)] \\ &= \frac{1}{\sqrt{2}}[(x_A - y_B) + (x_B - y_A)] \\ &= \frac{1}{\sqrt{2}}[-(x_A y_B) - (x_B y_A)] = -\Psi_1\end{aligned}$$

  (Σ^- state)

- $$\begin{aligned}\hat{i} \Psi_1 &= \frac{1}{\sqrt{2}}[(\hat{i} x_A \hat{i} y_B) + (\hat{i} x_B \hat{i} y_A)] \\ &= \frac{1}{\sqrt{2}}[(-x_B - y_A) + (-x_A - y_B)] \\ &= \frac{1}{\sqrt{2}}[(x_B y_A) + (x_A y_B)] = \Psi_1\end{aligned}$$

  (Σ_g^- state).

Taking into account spin, we see that Ψ_1 properly describes the $M_S = 1$ component of the triplet ${}^3\Sigma_g^-$ characteristic of the ground state of the O_2 molecule. Similarly we can proceed with the remaining triplet components Ψ_2 ($M_S = 0$) and Ψ_3 ($M_S = -1$) of the covalent VB wavefunction of O_2.

Lastly, we shall show the equivalence, with respect to the symmetry operations of $D_{\infty h}$, of the simple *2-electron* VB wavefunction in the *ultrashort notation* with the full *6-electron* VB wavefunction describing in the *short notation* the two 3-electron π-bonds in O_2. We have:

- $$\begin{aligned} \hat{L}_z\Psi_1 &= \sum_{k=1}^{6}\hat{L}_{zk}\left\{\frac{1}{\sqrt{2}}\left[(\overset{1}{x_A}\ \overset{2}{y_A}\ \overset{3}{\bar{y}_A}\ \overset{4}{y_B}\ \overset{5}{x_B}\ \overset{6}{\bar{x}_B}) + (x_B y_B \bar{y}_B y_A x_A \bar{x}_A)\right]\right\} \\ &= \frac{1}{\sqrt{2}}\big[i(\underbrace{y_A y_A}\cdots) + i(\underbrace{y_B y_B}\cdots) && k=1 \\ &\quad - i(\underbrace{x_A x_A}\cdots) - i(\underbrace{x_B x_B}\cdots) && 2 \\ &\quad - i(x_A y_A \bar{x}_A y_B x_B \bar{x}_B) - i(x_B y_B \bar{x}_B y_A x_A \bar{x}_A) && 3 \\ &\quad - i(x_A y_A \bar{y}_A \underbrace{x_B x_B}\bar{x}_B) - i(x_B y_B \bar{y}_B \underbrace{x_A x_A}\bar{x}_A) && 4 \\ &\quad + i(x_A y_A \bar{y}_A \underbrace{y_B y_B}\bar{x}_B) + i(x_B y_B \bar{y}_B \underbrace{y_A y_A}\bar{x}_A) && 5 \\ &\quad + i(x_A y_A \bar{y}_A y_B x_B \bar{y}_B) + i(x_B y_B \bar{y}_B y_A x_A \bar{y}_A)\big] = 0\cdot\Psi_1. && 6 \end{aligned}$$

Out of the 12 terms resulting by the action of the one-electron operator $\hat{L}_z$ on Ψ_1, terms 1, 2, 3, 4, 7, 8, 9, 10 vanish because of the exclusion principle (determinants with two rows or columns equal), the 6-th and the 12-th term being reduced, after 3 interchanges, to the 5-th and 11-th term with opposite sign, so that the whole expression in square brackets vanishes as it must be. In fact:

$$\begin{aligned} &(x_B y_B \bar{x}_B y_A x_A \bar{x}_A) \to (x_A y_B \bar{x}_B y_A x_B \bar{x}_A) \\ &\quad \to (x_A y_A \bar{x}_B y_B x_B \bar{x}_A) \to (x_A y_A \bar{x}_A y_B x_B \bar{x}_B) \quad \text{3-interchanges} \end{aligned}$$

$$\begin{aligned} &(x_B y_B \bar{y}_B y_A x_A \bar{y}_A) \to (x_A y_B \bar{y}_B y_A x_B \bar{y}_A) \\ &\quad \to (x_A y_A \bar{y}_B y_B x_B \bar{y}_A) \to (x_A y_A \bar{y}_A y_B x_B \bar{y}_B) \quad \text{3-interchanges} \end{aligned}$$

- $$\begin{aligned} \hat{\sigma}\Psi_1 &= \frac{1}{\sqrt{2}}[(x_A - y_A - \bar{y}_A - y_B x_B \bar{x}_B) + (x_B - y_B - \bar{y}_B - y_A x_A \bar{x}_A)] \\ &= -\frac{1}{\sqrt{2}}[(x_A y_A \bar{y}_A y_B x_B \bar{x}_B) + (x_B y_B \bar{y}_B y_A x_A \bar{x}_A)] = -\Psi_1 \end{aligned}$$

since $(-1)^3$ can be factored out from each determinant.

- $$\begin{aligned} \hat{i}\Psi_1 &= \frac{1}{\sqrt{2}}[(-x_B - y_B - \bar{y}_B - y_A - x_A - \bar{x}_A) \\ &\qquad + (-x_A - y_A - \bar{y}_A - y_B - x_B - \bar{x}_B)] \\ &= \frac{1}{\sqrt{2}}[(x_B y_B \bar{y}_B y_A x_A \bar{x}_A) + (x_A y_A \bar{y}_A y_B x_B \bar{x}_B)] = \Psi_1 \end{aligned}$$

since $(-1)^6$ can now be factored out from each determinant. Hence, we see that manipulation of the full 6-electron VB wavefunction brings to the same results as the much simpler, and much easily tractable, 2-electron VB wavefunction. All doubly occupied AOs (or MOs) have no effect on the symmetry operations of the point group.

8.17. We recall that in the C_{3v} symmetry:

$$e_x \sim x \qquad e_y \sim y$$

giving the transformation table ($c = \frac{1}{2}, s = \frac{\sqrt{3}}{2}$):

$\hat{R}\chi$	I	C_3^+	C_3^-	σ_1	σ_2	σ_3
e_x	e_x	$-ce_x - se_y$	$-ce_x + se_y$	e_x	$-ce_x - se_y$	$-ce_x + se_y$
e_y	e_y	$se_x - ce_y$	$-se_x - ce_y$	$-e_y$	$-se_x + ce_y$	$se_x + ce_y$

We then obtain:

$$\begin{aligned}
\hat{C}_3^+\|e_x\bar{e}_x e_y\bar{e}_y\| &= \|\hat{C}_3^+ e_x \hat{C}_3^+ \bar{e}_x \hat{C}_3^+ e_y \hat{C}_3^+ \bar{e}_y\| \\
&= \|-ce_x - se_y \quad -c\bar{e}_x - s\bar{e}_y \quad se_x - ce_y \quad s\bar{e}_x - c\bar{e}_y\|
\end{aligned}$$

which can be expanded into $2^4 = 16$ determinants using determinant rules.

$$\begin{aligned}
&\hat{C}_3^+\|e_x\bar{e}_x e_y\bar{e}_y\| \\
&= \frac{3}{16}\underset{\text{Pauli}}{\|e_x\bar{e}_x e_x\bar{e}_x\|} - \frac{\sqrt{3}}{16}\underset{\text{Pauli}}{\|e_x\bar{e}_x e_x\bar{e}_y\|} - \frac{\sqrt{3}}{16}\underset{\text{Pauli}}{\|e_x\bar{e}_x e_y\bar{e}_x\|} \\
&\quad + \frac{1}{16}\|e_x\bar{e}_x e_y\bar{e}_y\| + \frac{3\sqrt{3}}{16}\underset{\text{Pauli}}{\|e_x\bar{e}_y e_x\bar{e}_x\|} - \frac{3}{16}\underset{\text{Pauli}}{\|e_x\bar{e}_y e_x\bar{e}_y\|} \\
&\quad - \frac{3}{16}\underset{\text{1-interchange}}{\|e_x\bar{e}_y e_y\bar{e}_x\|} + \frac{\sqrt{3}}{16}\underset{\text{Pauli}}{\|e_x\bar{e}_y e_y\bar{e}_y\|} + \frac{3\sqrt{3}}{16}\underset{\text{Pauli}}{\|e_y\bar{e}_x e_x\bar{e}_x\|} \\
&\quad - \frac{3}{16}\underset{\text{1-interchange}}{\|e_y\bar{e}_x e_x\bar{e}_y\|} - \frac{3}{16}\underset{\text{Pauli}}{\|e_y\bar{e}_x e_y\bar{e}_x\|} + \frac{\sqrt{3}}{16}\underset{\text{Pauli}}{\|e_y\bar{e}_x e_y\bar{e}_y\|} \\
&\quad + \frac{9}{16}\underset{\text{2-interchanges}}{\|e_y\bar{e}_y e_x\bar{e}_x\|} - \frac{3\sqrt{3}}{16}\underset{\text{Pauli}}{\|e_y\bar{e}_y e_x\bar{e}_y\|} - \frac{3\sqrt{3}}{16}\underset{\text{Pauli}}{\|e_y\bar{e}_y e_y\bar{e}_x\|} \\
&\quad + \frac{3}{16}\underset{\text{Pauli}}{\|e_y\bar{e}_y e_y\bar{e}_y\|} \\
&= \left(\frac{1}{16} + \frac{3}{16} + \frac{3}{16} + \frac{9}{16}\right)\|e_x\bar{e}_x e_y\bar{e}_y\| = \|e_x\bar{e}_x e_y\bar{e}_y\|,
\end{aligned}$$

where 12 Slater determinants vanish because of the exclusion principle, and the coefficients of the remaining 4 sum to unity after suitable interchanges of their rows and columns.

$$\begin{aligned}\hat{\sigma}_1\|e_x\bar{e}_x e_y\bar{e}_y\| &= \|\hat{\sigma}_1 e_x\hat{\sigma}_1\bar{e}_x\hat{\sigma}_1 e_y\hat{\sigma}_1\bar{e}_y\| \\ &= \|e_x\bar{e}_x - e_y - \bar{e}_y\| = (-1)^2\|e_x\bar{e}_x e_y\bar{e}_y\| = \|e_x\bar{e}_x e_y\bar{e}_y\|.\end{aligned}$$

We can do the same for the remaining symmetry operations, so that we can conclude that the determinant $\|e_x\bar{e}_x e_y\bar{e}_y\|$ describing the electron configuration e^4 belongs to the irreducible representation A_1 of C_{3v}.

8.18. Symmetry of the first few real spherical tensors under $C_{\infty v}$ and $D_{\infty h}$ symmetry.

We must construct the matrix representatives of the different symmetry operations for all irreps, particularly for the doubly degenerate ones (Π, Δ, Φ, $\cdots$), integrating in this way the character tables given in all textbooks. Using direct-product group techniques (Section 8.5.9), the symmetry operations which are of concern to us are (Tinkham, 1964) C_α^+, C_α^-, C_2', i, iC_α^+, iC_α^-, iC_2', where:

$C_\alpha^+ =$ anticlockwise (positive) rotation of angle α about the internuclear z-axis.

$C_\alpha^- =$ clockwise (negative) rotation.

$C_2' =$ rotation of π about the x-axis, perpendicular to the internuclear z-axis.

$i =$ inversion about the centre of symmetry (only for $D_{\infty h}$).

If R_{lm} and $R_{l\bar{m}}$ are a pair of *real* spherical tensors (see Chapter 11), having the form:

$$R_{lm}(\mathbf{r}) = f(r,\theta)\cos m\varphi \quad m > 0$$

$$R_{l\bar{m}}(\mathbf{r}) = f(r,\theta)\sin m\varphi$$

according to the equations of Section 8.4.3 we have, taking into account only the dependence on φ:

$$C_\alpha^+ R_{lm}(\varphi) = R_{lm}(C_\alpha^-\varphi) = f(r,\theta)\cos m(\varphi+\alpha) = R_{lm}\cos m\alpha - R_{l\bar{m}}\sin m\alpha$$

$$C_\alpha^+ R_{l\bar{m}}(\varphi) = R_{l\bar{m}}(C_\alpha^-\varphi) = f(r,\theta)\sin m(\varphi+\alpha) = R_{lm}\sin m\alpha + R_{l\bar{m}}\cos m\alpha.$$

Therefore, the 2 × 2 matrix (darstellung) describing the *rotated* basis will be:

$$\mathbf{D}_{lm}(C_\alpha^+) = \begin{pmatrix}\cos m\alpha & \sin m\alpha \\ -\sin m\alpha & \cos m\alpha\end{pmatrix} = \begin{pmatrix} c_m & s_m \\ \bar{s}_m & c_m\end{pmatrix}$$

having the character:

$$\chi_{lm}(C_\alpha^+) = \operatorname{tr}\mathbf{D}_{lm}(C_\alpha^+) = 2c_m.$$

Table 8.4.

Symmetry of the real spherical tensors under $D_{\infty h}{}^{1,2}$

$D_{\infty h}$	I	C_α^+	C_α^-	C_2'
Σ_g^+	1	1	1	1
Σ_g^-	1	1	1	−1
$E_{mg}{}^3$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} c_m & s_m \\ \bar{s}_m & c_m \end{pmatrix}$	$\begin{pmatrix} c_m & \bar{s}_m \\ s_m & c_m \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 \\ 0 & 1 \end{pmatrix}$
$E_{mg}{}^4$	$\begin{pmatrix} & \\ & \end{pmatrix}$	$\begin{pmatrix} & \\ & \end{pmatrix}$	$\begin{pmatrix} & \\ & \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & \bar{1} \end{pmatrix}$
Σ_u^+	1	1	1	1
Σ_u^-	1	1	1	−1
$E_{mu}{}^3$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} c_m & s_m \\ \bar{s}_m & c_m \end{pmatrix}$	$\begin{pmatrix} c_m & \bar{s}_m \\ s_m & c_m \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & \bar{1} \end{pmatrix}$
$E_{mu}{}^4$	$\begin{pmatrix} & \\ & \end{pmatrix}$	$\begin{pmatrix} & \\ & \end{pmatrix}$	$\begin{pmatrix} & \\ & \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 \\ 0 & 1 \end{pmatrix}$

$D_{\infty h}$	i	iC_α^+	iC_α^-	iC_2'	
Σ_g^+	1	1	1	1	$R_{(2l)0}$
Σ_g^-	1	1	1	−1	
$E_{mg}{}^3$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} c_m & s_m \\ \bar{s}_m & c_m \end{pmatrix}$	$\begin{pmatrix} c_m & \bar{s}_m \\ s_m & c_m \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 \\ 0 & 1 \end{pmatrix}$	$R_{(2l)m}, R_{(2l)\overline{m}}$ $m =$ odd
$E_{mg}{}^4$	$\begin{pmatrix} & \\ & \end{pmatrix}$	$\begin{pmatrix} & \\ & \end{pmatrix}$	$\begin{pmatrix} & \\ & \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & \bar{1} \end{pmatrix}$	$R_{(2l)m}, R_{(2l)\overline{m}}$ $m =$ even
Σ_u^+	−1	−1	−1	−1	
Σ_u^-	−1	−1	−1	1	$R_{(2l+1)0}$
$E_{mu}{}^3$	$\begin{pmatrix} \bar{1} & 0 \\ 0 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} \bar{c}_m & \bar{s}_m \\ s_m & \bar{c}_m \end{pmatrix}$	$\begin{pmatrix} \bar{c}_m & s_m \\ \bar{s}_m & \bar{c}_m \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 \\ 0 & 1 \end{pmatrix}$	$R_{(2l+1)m}, R_{(2l+1)\overline{m}}$ $m =$ odd
$E_{mg}{}^4$	$\begin{pmatrix} & \\ & \end{pmatrix}$	$\begin{pmatrix} & \\ & \end{pmatrix}$	$\begin{pmatrix} & \\ & \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & \bar{1} \end{pmatrix}$	$R_{(2l+1)m}, R_{(2l+1)\overline{m}}$ $m =$ even

[1] $c_m = \cos m\alpha$, $s_m = \sin m\alpha$ $m = 1, 2, 3, \cdots$, $\bar{a} = -a$.

[2] Matrices not given are identical with those above them.

[3] $m = 1\Pi$, $m = 3\Phi$, $m = 5H$.

[4] $m = 2\Delta$, $m = 4Y$.

Similarly:

$$\mathbf{D}_{lm}(C_\alpha^-) = \begin{pmatrix} \cos m\alpha & -\sin m\alpha \\ \sin m\alpha & \cos m\alpha \end{pmatrix} = \begin{pmatrix} c_m & \bar{s}_m \\ s_m & c_m \end{pmatrix}$$

with the same character as before.

Under C_2', we have the simple transformation of the Cartesian coordinates:

$$x' = x, \qquad y' = -y, \qquad z' = -z$$

so that:

$$C_2'(R_{lm} R_{l\bar{m}}) = (R_{lm} R_{l\bar{m}}) \begin{pmatrix} 1 & 0 \\ 0 & \bar{1} \end{pmatrix}$$

for l, m both odd or even, while:

$$C_2'(R_{lm} R_{l\bar{m}}) = (R_{lm} R_{l\bar{m}}) \begin{pmatrix} \bar{1} & 0 \\ 0 & 1 \end{pmatrix}$$

for $l =$ even, $m =$ odd, or $l =$ odd, $m =$ even.

The tensors R_{l0} ($m = 0$) have 1-dimensional irreps of type Σ, belonging to the eigenvalue $+1$ with respect to C_2' for $l =$ even, and eigenvalue -1 for $l =$ odd.

For $D_{\infty h}$ (centre of symmetry), completing these operations with the inversion i, under which:

$$x' = -x, \qquad y' = -y, \qquad z' = -z,$$

we can classify the spherical tensors as g (= even under inversion) or u (= odd under inversion).

In this way we can construct Table 8.4 for $D_{\infty h}$ (for $C_{\infty v}$, we simply suppress the index g or u). The multipole moments μ_l and polarizabilities $\alpha_{lm,l'm'}$ (Chapter 11, Section 5) are proportional to the corresponding spherical tensors and their products, respectively. Their non-vanishing components can then be found by using the selection rules of Section 8.6.2.

– 9 –

Angular Momentum Methods for Atoms

9.1 INTRODUCTION

In Chapter 1 we introduced the angular momentum $\boldsymbol{l}$ of a single particle and the corresponding quantum mechanical vector operator $\hat{\boldsymbol{l}}$[1]. We gave the expressions for the components $\hat{l}_x$, $\hat{l}_y$, $\hat{l}_z$ and the square of angular momentum operator $\hat{l^2}$, and their commutation properties in Cartesian and spherical coordinates. We introduced the ladder (shift) operators $\hat{l}_+$ (step-up) and $\hat{l}_-$ (step-down), which step-up (or step-down) the eigenfunctions Y_{lm} of the ladder specified by the quantum number l, changing $m \to m+1$ (up) or $m \to m-1$ (down). Similar operators were studied for spin in Chapter 6, where half-integer values are possible for the quantum number S ($N =$ odd). In the following, we shall introduce first the vector model for the elementary coupling of angular momenta, followed by elements of the spin–orbit coupling for light atoms to explain the origin of atomic multiplets (Condon and Shortley, 1963; Herzberg, 1944; Eyring et al., 1944). Then, we shall be concerned with many-electron atomic systems and on how we can construct angular momentum eigenfunctions starting from those of the individual electrons. This will allow us to build the correct linear combinations of the many-electron functions of given M which are eigenfunctions of $\hat{L}^2$, and therefore describe electronic states of definite L ($L = 0, 1, 2, 3, \cdots$, states S, P, D, F, $\cdots$). Besides the theory of atomic structure, this is of some importance in CI calculations on atoms. An outline of advanced methods for coupling angular momenta (Brink and

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[1] Usually, lower case $\boldsymbol{l}$, $\hat{\boldsymbol{l}}$ are deserved for angular momentum vector and vector operator for the single particle. Instead, we used $\boldsymbol{L}$, $\hat{\boldsymbol{L}}$ for the same quantities.

Satchler, 1993) will be given next, problems and solved problems concluding the Chapter, as usual.

9.2 THE VECTOR MODEL

The interpretation of atomic spectra (Herzberg, 1944) rests on the determination of the electronic configurations of atoms, which follow the ordering of the energy levels and the restrictions imposed by the Pauli principle. The coupling of the angular momenta of the single electrons gives rise to *atomic term values*, which correspond to a given electron configuration. We saw in Chapter 5 in the case of the excited $1s2s$ and $1s2p$ electron configurations of He, how electron repulsion splits degenerate levels into different terms whose fine structure is further determined by the coupling between orbital angular momentum and spin. The presence of a magnetic field (Zeeman effect) removes any further degeneracy in the energy levels, allowing for the experimental detection of all physically accessible states arising from a given electron configuration of the atoms or ions.

9.2.1 Coupling of Angular Momenta

The essence of the vector model is in the following. In a many-electron atom, each electron is assumed to have a defined orbital angular momentum specified by the quantum number l_κ, where $\boldsymbol{l}_\kappa$ is a vector of magnitude $0, 1, 2, 3, \cdots$, $(s, p, d, f, \cdots)$ in units of $\hbar$. We then add *vectorially* the single angular momenta obtaining a resultant momentum which will depend on the number, magnitude and orientation of the single vectors, orientation being restricted by quantum mechanics to certain discrete values in space. For two electrons of given l_1 and l_2, the possible resultant values of L are positive integers given by:

$$L = l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, \cdots, |l_1 - l_2| \tag{1}$$

namely:

$$|l_1 - l_2| \le L \le l_1 + l_2 \tag{2}$$

in steps of unity.

As an example, the possible values for two electrons having $l_1 = l_2 = 1$ (hence belonging to the configuration p^2) are $L = 2, 1, 0$, resulting from the vector addition of Figure 9.1.

It should be noted that, because of the strong electron interaction, the direction of each individual angular momentum is no longer constant in time, but *precesses* in such a way that the resultant angular momentum L remains constant in modulus and direction (Figure 9.2). L is therefore the only "good" quantum number in the case of the many-electron system.

The possible orientations of the resulting vector with $L = 2$ with respect to an external field directed along z are illustrated in Figure 9.3, where it is seen that the vector of modulus $|\boldsymbol{L}| = \sqrt{L(L+1)} = \sqrt{6}$ can never be oriented along the axis, its projections onto z being $M_L = 2, 1, 0, -1, -2$. In the following, we shall simply replace M_L by M.

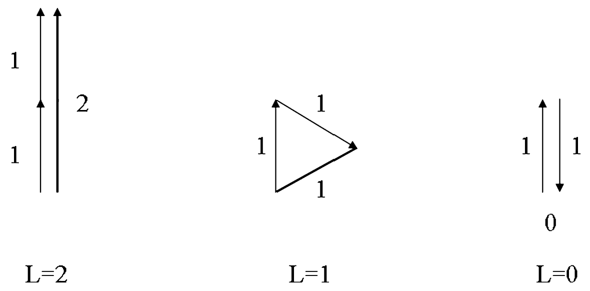


Figure 9.1 Vector coupling of two p electrons.

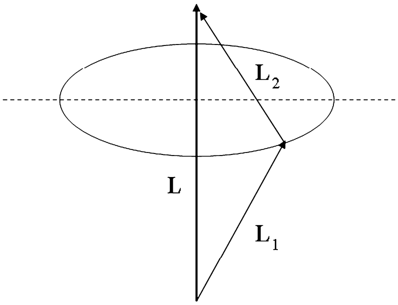


Figure 9.2 Precession of $\boldsymbol{l}_1$ and $\boldsymbol{l}_2$ around the resultant $\boldsymbol{L}$.

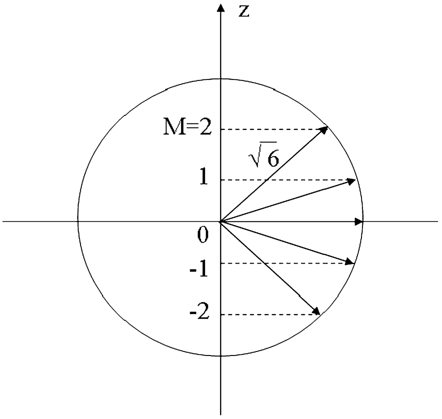


Figure 9.3 The five possible orientations of the angular momentum vector with $L = 2$.

When there are three electrons having $\boldsymbol{l}_\kappa \neq 0$, the vector addition can be made by first adding $\boldsymbol{l}_1$ to $\boldsymbol{l}_2$, then combining each of the resultant values of $\boldsymbol{L}$ with the $\boldsymbol{l}_3$ value of the remaining electron, and so on.

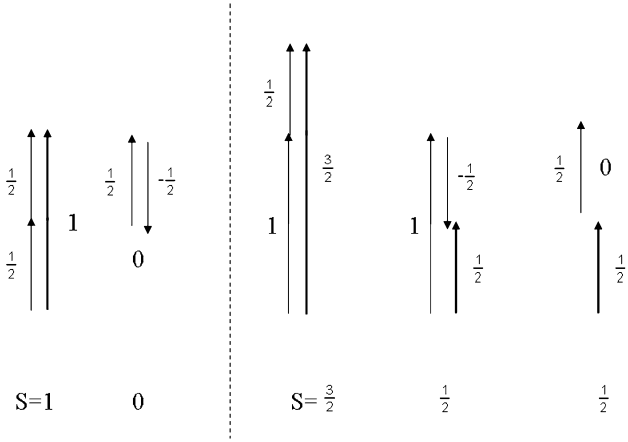


Figure 9.4 Vector coupling of three spin $1/2$.

In the language of spectroscopists, the states of the many-electron atom having definite L values are said to be the *atomic terms* corresponding to a given electron configuration. So, the p^2 configuration gives rise to the atomic terms D, P, S.

The same is true for spin angular momentum, except for possible half-integer values of the total spin quantum number S. Figure 9.4 illustrates the example of coupling three electron spin having $s_1 = s_2 = s_3 = 1/2$. In this case, we first couple 1 with 2, getting as possible S values $S = 1$ and $S = 0$. Next, we couple each resultant value of S with 3, getting $S = 3/2$ and *two* distinct $S = 1/2$. So, the vector model is seen to give the same result of Kotani's branching diagram or Wigner's formula of Chapter 6.

Figure 9.5 gives the two possible orientations with respect to the z axis of the total spin $S = 1/2$ (doublet). It is worth noting that the angle the vector $S = 1/2$ makes with the z axis in the two cases is, respectively, $\theta = 54.7°(\cos\theta = 1/\sqrt{3})$ and $\theta = 125.3°(\cos\theta = -1/\sqrt{3})$, with $\cos\theta = M_S/\sqrt{S(S+1)}$.

The quantum mechanical counterpart of the vector model is to find a regular function ψ such that, for uncoupled $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$, it satisfies the following equations:

$$\hat{L}^2\psi = L(L+1)\psi, \qquad \hat{L}_z\psi = M\psi \tag{3}$$

$$\hat{S}^2\psi = S(S+1)\psi, \qquad \hat{S}_z\psi = M_S\psi. \tag{4}$$

In other words, in absence of LS coupling, all operators above commute with the Hamiltonian $\hat{H}$ (are constants of the motion) and among themselves, so that L, M, S, M_S are "good" quantum numbers for the specification of the state of the system. The situation is quite different when $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$ are coupled, as we shall see below.

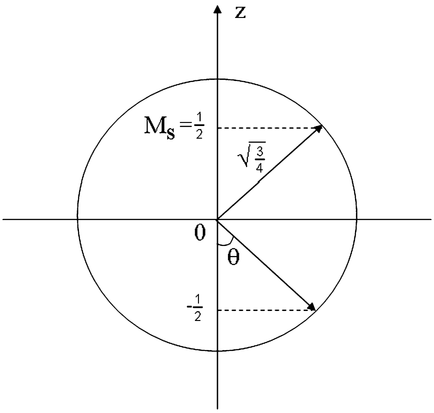


Figure 9.5 The two possible orientations of the spin vector with $S = 1/2$.

9.2.2 LS Coupling and Multiplet Structure

We saw in Chapter 6 that an electron moving in a circular orbit has associated orbital and spin magnetic momenta:

$$\hat{\boldsymbol{\mu}}_L = -\beta_e \hat{\boldsymbol{L}} \tag{5}$$

$$\hat{\boldsymbol{\mu}}_S = -g_e \beta_e \hat{\boldsymbol{S}}, \tag{6}$$

where:

$$\beta_e = \frac{e\hbar}{2mc} = 9.274015 \times 10^{-24}\ \mathrm{J\,Tesla}^{-1} \tag{7}$$

is the Bohr magneton, the unit of magnetic moment, and $g_e \approx 2$ for the single electron.

We now examine the possibility of the coupling of spin and orbital angular momentum in the case of *light* atoms, the so called LS or Russell–Saunders coupling.

With reference to Figure 9.6, the nucleus at the origin creates an electric field $\mathbf{F}$ which acts on the electron at $\mathbf{r}$:

$$\mathbf{F} = \frac{Z|e|}{r^3}\mathbf{r}, \tag{8}$$

which in turn for the electron moving with velocity $\mathbf{v}$ originates an *intrinsic* magnetic field $\mathbf{H}$ given by:

$$\mathbf{H} = \frac{\mathbf{F} \times \mathbf{v}}{c} = \frac{Z|e|}{cr^3}\mathbf{r} \times \mathbf{v} = \frac{Z|e|}{mcr^3}\boldsymbol{L} = \frac{2}{\hbar}\beta_e \frac{Z}{r^3}\hat{\boldsymbol{L}}. \tag{9}$$

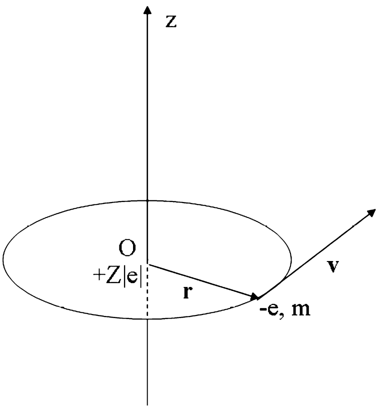


Figure 9.6 Origin of the spin–orbit coupling.

The energy of the spin magnetic dipole (6) in this magnetic field **H** will be:

$$\hat{H}^{\mathrm{SO}} = -\hat{\boldsymbol{\mu}}_S \cdot \mathbf{H} = \frac{2}{\hbar} g_e \beta_e^2 \frac{Z}{r^3} \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}. \tag{10}$$

A more accurate analysis, which takes into account relativistic effects, shows that the correct expression for $\hat{H}^{\mathrm{SO}}$ is just *half* of the expression above, so that the operator describing the LS coupling will be ($\hbar = 1$):

$$\hat{H}^{\mathrm{SO}} = g_e \beta_e^2 \frac{Z}{r^3} \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} = \xi(r)(\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}) \tag{11}$$

and, for a many-electron atom:

$$\hat{H}^{\mathrm{SO}} = \sum_i g_e \beta_e^2 \left(\frac{1}{r_i} \frac{\partial V}{\partial r_i} \right) (\hat{\boldsymbol{L}}_i \cdot \hat{\boldsymbol{S}}_i). \tag{12}$$

Now, in presence of LS coupling we must add vectorially $\boldsymbol{L}$ and $\boldsymbol{S}$ getting the resultant momentum $\boldsymbol{J}$ (Figure 9.7), about which $\boldsymbol{L}$ and $\boldsymbol{S}$ precess as in the case of Figure 9.2. J is now the "good" quantum number.

So, the vector model gives for the LS coupling the results of Figure 9.8.

The allowed values of J are:

$$|L - S| \leq J \leq L + S \tag{13}$$

if $L \geq S$, or:

$$|S - L| \leq J \leq S + L \tag{14}$$

if $S \geq L$, in steps of 1.

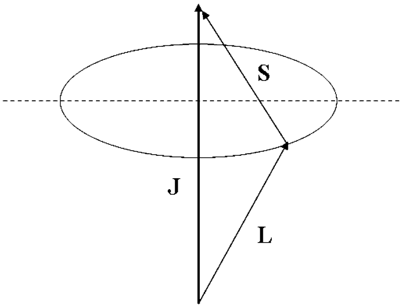


Figure 9.7 Precession of $\boldsymbol{L}$ and $\boldsymbol{S}$ around the resultant $\boldsymbol{J}$.

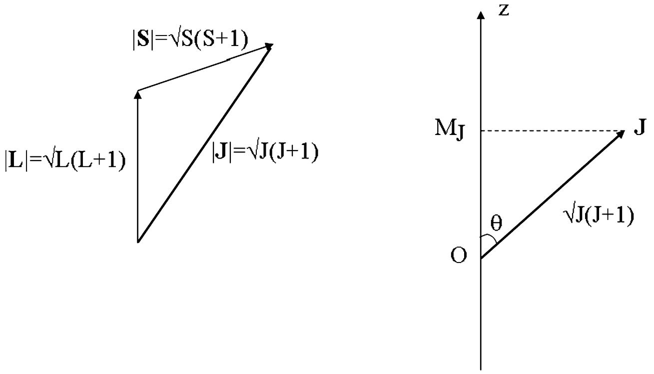


Figure 9.8 Vector addition of $\boldsymbol{L}$ and $\boldsymbol{S}$ in the Russell–Saunders scheme, and possible orientations of the resulting vector $\boldsymbol{J}$.

For the component of J along z, the $(2J+1)$ allowed values of M_J are:

$$M_J = -J, -(J-1), -(J-2), \cdots, (J-1), J. \tag{15}$$

Turning to equation (11), we see that:

$$\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}} = \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2) \tag{16}$$

so that, taking the expectation value of $\hat{H}^{\mathrm{SO}}$ over the ground state wavefunction (first-order RS perturbation theory), the relative energy of levels of given J is:

$$E_J = \frac{1}{2}A[J(J+1) - L(L+1) - S(S+1)], \tag{17}$$

where A is a constant characteristic of the atom or ion.

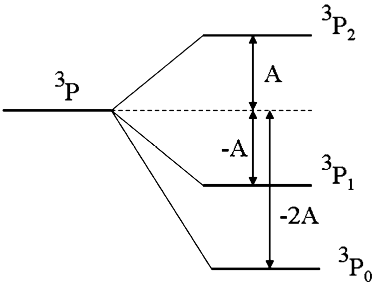


Figure 9.9 Splitting of ^3P under LS coupling.

As an example, for the ^3P term of the $1s2p$ electron configuration of He, we have:

$$L = S = 1 \qquad J = 2, 1, 0 \tag{18}$$

with the relative energies for the LS coupled states:

$$\begin{aligned} J &= 2 \qquad E_2 = \frac{1}{2}A(2\cdot 3 - 4) = A \\ J &= 1 \qquad E_1 = \frac{1}{2}A(1\cdot 2 - 4) = -A \\ J &= 0 \qquad E_0 = \frac{1}{2}A(0\cdot 1 - 4) = -2A. \end{aligned} \tag{19}$$

The splitting of the ^3P term under LS coupling is shown in Figure 9.9.

The $^3P_2$ term is 5-fold degenerate, the $^3P_1$ 3-fold degenerate, the $^3P_0$ is non-degenerate. To remove these degeneracies, we must introduce a magnetic field directed along z (Zeeman effect).

The magnetic moment operator corresponding to the quantum number J resulting from the LS coupling is:

$$\hat{\boldsymbol{\mu}}_J = -g_J \beta_e \hat{\boldsymbol{J}}, \tag{20}$$

where:

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \tag{21}$$

is called Landé g-factor. The derivation of g_J is given as Problem 9.1. Then, the potential energy of the magnetic dipole in the *uniform* magnetic field $\boldsymbol{H} = \boldsymbol{k}H$ will be:

$$V = -\hat{\boldsymbol{\mu}}_J \cdot \boldsymbol{H} = g_J \beta_e H \hat{J}_z, \tag{22}$$

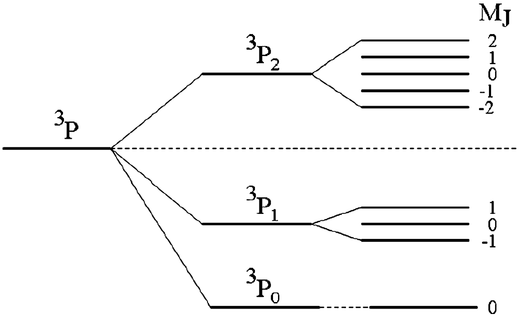


Figure 9.10 Zeeman resolution of the ^3P_J multiplet structure for He$(1s2p)$ (not in scale).

so that the energy of the $(2J+1)$ sublevels in presence of the field H will be:

$$E_{M_J} = g_J \beta_e H M_J \qquad -J \le M_J \le J \tag{23}$$

which is the formula for the linear Zeeman effect. The splitting of the Zeeman levels:

$$\Delta E_{M_J} = g_J \beta_e H [M_J - (M_J - 1)] = g_J \beta_e H \tag{24}$$

is *linear* in the strength of the external field H. Figure 9.10 gives the Zeeman splitting of the ^3P_J term, where all 9 physically accessible states have now different energies.

Interesting magnetic effects are associated to the multiplet width $\Delta = h\nu$ with respect to the temperature T. There are two extreme cases.

(i) $\Delta \ll kT$.

In this case of *narrow* multiplets, the magnetic moment is due to pure spin:

$$\frac{\mu_{\text{eff}}}{\beta_e} = [4S(S+1)]^{1/2}. \tag{25}$$

This is the case of the ions of metals of the first transition series and O_2, which follow Curie's law.

(ii) $\Delta \gg kT$.

In this case of *wide* multiplets, almost all particles are in the state of lowest energy, and the magnetic moments arise from LS coupling:

$$\frac{\mu_{\text{eff}}}{\beta_e} = g_J [J(J+1)]^{1/2}, \tag{26}$$

where g_J is the Landé g-factor. This is the case of rare earth ions, with the exception of Sm^{+3} and Eu^{+3}.

(iii) The intermediate case where $\Delta \approx kT$ is the most difficult to treat, and is exemplified by NO at room temperature, where the Curie law is not followed. This case, as well as those of Sm^{+3} and Eu^{+3}, was fully discussed by Van Vleck (1932).

9.3 CONSTRUCTION OF STATES OF DEFINITE ANGULAR MOMENTUM

9.3.1 The Matrix Method

For N electrons, we have for the angular momentum vector operator $\hat{\boldsymbol{L}}$ and its component $\hat{L}_z$:

$$\hat{\boldsymbol{L}} = \mathbf{i}\hat{L}_x + \mathbf{j}\hat{L}_y + \mathbf{k}\hat{L}_z = \sum_{\kappa=1}^{N} (\mathbf{i}\hat{L}_{x\kappa} + \mathbf{j}\hat{L}_{y\kappa} + \mathbf{k}\hat{L}_{z\kappa}) \tag{27}$$

$$\hat{L}_z = \sum_{\kappa=1}^{N} \hat{L}_{z\kappa}. \tag{28}$$

Then, the square of the angular momentum operator will be:

$$\begin{aligned}\hat{L}^2 = \hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{L}} &= \sum_{\kappa} \sum_{\lambda} \big(\hat{L}_{x\kappa}\hat{L}_{x\lambda} + \hat{L}_{y\kappa}\hat{L}_{y\lambda} + \hat{L}_{z\kappa}\hat{L}_{z\lambda}\big) \\ &= \sum_{\kappa} \big(\hat{L}_{x\kappa}^2 + \hat{L}_{y\kappa}^2 + \hat{L}_{z\kappa}^2\big) + 2\sum_{\kappa<\lambda} \big(\hat{L}_{x\kappa}\hat{L}_{x\lambda} + \hat{L}_{y\kappa}\hat{L}_{y\lambda} + \hat{L}_{z\kappa}\hat{L}_{z\lambda}\big).\end{aligned} \tag{29}$$

Introducing the complex ladder operators:

$$\hat{L}_{+\kappa} = \hat{L}_{x\kappa} + i\hat{L}_{y\kappa}, \qquad \hat{L}_{-\kappa} = \hat{L}_{x\kappa} - i\hat{L}_{y\kappa}, \tag{30}$$

it follows that:

$$\begin{aligned}&\hat{L}_{+\kappa}\hat{L}_{-\lambda} + \hat{L}_{-\kappa}\hat{L}_{+\lambda} \\ &\quad = \big(\hat{L}_{x\kappa} + i\hat{L}_{y\kappa}\big)\big(\hat{L}_{x\lambda} - i\hat{L}_{y\lambda}\big) + \big(\hat{L}_{x\kappa} - i\hat{L}_{y\kappa}\big)\big(\hat{L}_{x\lambda} + i\hat{L}_{y\lambda}\big) \\ &\quad = 2\big(\hat{L}_{x\kappa}\hat{L}_{x\lambda} + \hat{L}_{y\kappa}\hat{L}_{y\lambda}\big).\end{aligned} \tag{31}$$

Therefore:

$$\hat{L}^2 = \sum_{\kappa} \hat{L}_{\kappa}^2 + 2\sum_{\kappa<\lambda} \hat{L}_{z\kappa}\hat{L}_{z\lambda} + \sum_{\kappa<\lambda} \big(\hat{L}_{+\kappa}\hat{L}_{-\lambda} + \hat{L}_{-\kappa}\hat{L}_{+\lambda}\big). \tag{32}$$

Along the same lines seen for spin operators in Chapter 6, we have:

$$\hat{L}_{+}(lm) = [l(l+1) - m(m+1)]^{1/2}(lm+1) \tag{33}$$

$$\hat{L}_{-}(lm) = [l(l+1) - m(m-1)]^{1/2}(lm-1), \tag{34}$$

where $\hat{L}_+$ *steps up* from the (normalized) eigenfunction (lm) to the (normalized) eigenfunction $(lm+1)$, $\hat{L}_-$ *steps down* from (lm) to the (normalized) eigenfunction $(lm-1)$.

Acting on the N-electron Slater determinant $\hat{L}^2$ will give:

$$\begin{aligned}
&\hat{L}^2||\cdots(n_\kappa l_\kappa m_\kappa s_\kappa)\cdots(n_\lambda l_\lambda m_\lambda s_\lambda)\cdots|| \\
&\quad=\left[\sum_{\kappa=1}^{N} l_\kappa(l_\kappa+1)+2\sum_{\kappa<\lambda} m_\kappa m_\lambda\right]||\cdots|| \\
&\quad+\sum_{\kappa\neq\lambda}[l_\kappa(l_\kappa+1)-m_\kappa(m_\kappa+1)]^{1/2}[l_\lambda(l_\lambda+1)-m_\lambda(m_\lambda+1)]^{1/2} \\
&\quad\cdot||\cdots(n_\kappa l_\kappa m_{\kappa+1} s_\kappa)\cdots(n_\lambda l_\lambda m_{\lambda-1} s_\lambda)\cdots||, \qquad (35)
\end{aligned}$$

which is the basic formula for $\hat{L}^2$ in the case of the many-electron system.

(i) Equivalent electrons.

As an example, let us construct the states arising out of the configuration p^2 of two *equivalent* electrons with $l_1 = l_2 = 1$. Figure 9.1 says that the possible states are S, P, D corresponding to $L = 0, 1, 2$. The six spin-orbitals in complex form are:

$$p_0\alpha,\ p_0\beta,\ p_{+1}\alpha,\ p_{+1}\beta,\ p_{-1}\alpha,\ p_{-1}\beta, \qquad (36)$$

from which we can construct $\binom{6}{2} = 15$ states having the same principal quantum number n. Since ${}^1P$, ${}^3S$, ${}^3D$ are forbidden by the Pauli exclusion principle, we are left with the 15 Pauli allowed states:

$${}^1S, {}^3P, {}^1D. \qquad (37)$$

Among these 15 states arising from the p^2 configuration, there are 3 states having $M = M_S = 0$:

$$\begin{aligned}
\psi_1 &= \left\|\left(n\,1\,0\,\frac{1}{2}\right)\left(n\,1\,0\,\frac{\bar{1}}{2}\right)\right\| = ||p_0\overline{p}_0|| \\
\psi_2 &= \left\|\left(n\,1\,1\,\frac{1}{2}\right)\left(n\,1\,\bar{1}\,\frac{\bar{1}}{2}\right)\right\| = ||p_{+1}\overline{p}_{-1}|| \qquad (38) \\
\psi_3 &= \left\|\left(n\,1\,\bar{1}\,\frac{1}{2}\right)\left(n\,1\,1\,\frac{\bar{1}}{2}\right)\right\| = ||p_{-1}\overline{p}_{+1}||.
\end{aligned}$$

Acting with $\hat{L}^2$ upon each function ψ, it is obtained (Problem 9.2):

$$\begin{aligned}
\hat{L}^2\psi_1 &= 4\psi_1 + 2\psi_2 + 2\psi_3 \\
\hat{L}^2\psi_2 &= 2\psi_1 + 2\psi_2 \qquad (39) \\
\hat{L}^2\psi_2 &= 2\psi_1 + 2\psi_3.
\end{aligned}$$

Taking into account orthonormality, the matrix representative of $\hat{L}^2$ over the three basis functions will be:

$$\boldsymbol{L}^2 = \begin{pmatrix} 4 & 2 & 2 \\ 2 & 2 & 0 \\ 2 & 0 & 2 \end{pmatrix} \tag{40}$$

giving the secular equation:

$$\begin{vmatrix} 4-\lambda & 2 & 2 \\ 2 & 2-\lambda & 0 \\ 2 & 0 & 2-\lambda \end{vmatrix} = 0 \qquad \lambda = L(L+1) \tag{41}$$

which has the roots $\lambda = 0, 2, 6$ or $L = 0, 1, 2$ as it must be.

The corresponding eigenvectors are found by solving the system of homogeneous linear equations giving (41). The results are (Problem 9.3):

$$\begin{aligned} \psi(^1S) &= \frac{1}{\sqrt{3}}(\psi_1 - \psi_2 - \psi_3) \\ \psi(^3P) &= \frac{1}{\sqrt{2}}(\psi_2 - \psi_3) \\ \psi(^1D) &= \frac{1}{\sqrt{6}}(2\psi_1 + \psi_2 + \psi_3). \end{aligned} \tag{42}$$

We can easily check (Problem 9.4) that:

$$\begin{aligned} \hat{L}^2\psi(^1S) &= 0(0+1)\psi(^1S), & \hat{S}^2\psi(^1S) &= 0(0+1)\psi(^1S), \\ \hat{L}^2\psi(^3P) &= 1(1+1)\psi(^3P), & \hat{S}^2\psi(^3P) &= 1(1+1)\psi(^3P), \\ \hat{L}^2\psi(^1D) &= 2(2+1)\psi(^1D), & \hat{S}^2\psi(^1D) &= 0(0+1)\psi(^1D) \end{aligned} \tag{43}$$

so that the problem has been fully solved.

We show in Problem 9.5 that the singlet S function, $\psi(^1S)$, can be expressed in either of the alternative forms:

(i) Complex form:

$$\psi(^1S) = \frac{1}{\sqrt{3}}\left\{||p_0\overline{p}_0|| - ||p_{+1}\overline{p}_{-1}|| - ||p_{-1}\overline{p}_{+1}||\right\} \tag{44}$$

(ii) Real form:

$$\psi(^1S) = \frac{1}{\sqrt{3}}\left\{||p_x\overline{p}_x|| + ||p_y\overline{p}_y|| + ||p_z\overline{p}_z||\right\}. \tag{45}$$

Further examples for the configuration np^3 of three *equivalent* electrons are given in Problems 9.6 and 9.7.

(ii) Non-equivalent electrons.

As an example for *non-equivalent* electrons, we choose to build the singlet ^1P state out of the $2p3d$ configuration.

From the vector model we know that the possible states resulting from the coupling of the angular momenta of the single electrons ($l_1 = 1, l_2 = 2$) are P, D, F ($L = 1, 2, 3$). Taking into account spin, the Pauli allowed states are either singlets ($S = 0$) ^1P, ^1D, ^1F, or triplets ($S = 1$) ^3P, ^3D, ^3F, for a total of $(3 + 5 + 7 + 9 + 15 + 21)$ 60 states.

For the ^1P we have the following 6 Slater determinants having $M = M_S = 0$:

$$\begin{aligned}
&\left\|\left(2\,1\,1\,\frac{1}{2}\right)\left(3\,2\,\overline{1}\,\frac{\overline{1}}{2}\right)\right\| = ||p_{+1}\overline{d}_{-1}||\\
&\left\|\left(2\,1\,1\,\frac{\overline{1}}{2}\right)\left(3\,2\,\overline{1}\,\frac{1}{2}\right)\right\| = ||\overline{p}_{+1}d_{-1}||\\
&\left\|\left(2\,1\,0\,\frac{1}{2}\right)\left(3\,2\,0\,\frac{\overline{1}}{2}\right)\right\| = ||p_0\overline{d}_0||\\
&\left\|\left(2\,1\,0\,\frac{\overline{1}}{2}\right)\left(3\,2\,0\,\frac{1}{2}\right)\right\| = ||\overline{p}_0 d_0||\\
&\left\|\left(2\,1\,\overline{1}\,\frac{1}{2}\right)\left(3\,2\,1\,\frac{\overline{1}}{2}\right)\right\| = ||p_{-1}\overline{d}_{+1}||\\
&\left\|\left(2\,1\,\overline{1}\,\frac{\overline{1}}{2}\right)\left(3\,2\,1\,\frac{1}{2}\right)\right\| = ||\overline{p}_{-1}d_{+1}||,
\end{aligned} \tag{46}$$

that can be grouped into the 3 singlets ($S = 0$):

$$\begin{aligned}
\psi_1 &= \frac{1}{\sqrt{2}}\left\{||p_{+1}\overline{d}_{-1}|| + ||d_{-1}\overline{p}_{+1}||\right\}\\
\psi_2 &= \frac{1}{\sqrt{2}}\left\{||p_0\overline{d}_0|| + ||d_0\overline{p}_0||\right\}\\
\psi_3 &= \frac{1}{\sqrt{2}}\left\{||p_{-1}\overline{d}_{+1}|| + ||d_{+1}\overline{p}_{-1}||\right\}.
\end{aligned} \tag{47}$$

Acting with $\hat{L}^2$ on the first determinant of ψ_1:

$$\hat{L}^2||p_{+1}\overline{d}_{-1}|| = 6||p_{+1}\overline{d}_{-1}|| + \sqrt{12}||p_0\overline{d}_0||. \tag{48}$$

Similarly, for the second determinant of ψ_1:

$$\hat{L}^2||d_{-1}\overline{p}_{+1}|| = 6||d_{-1}\overline{p}_{+1}|| + \sqrt{12}||d_0\overline{p}_0||, \tag{49}$$

so that we shall have:

$$\begin{aligned}\hat{L}^2\psi_1 &= 6\psi_1 + \sqrt{12}\psi_2\\ \hat{L}^2\psi_2 &= 8\psi_2 + \sqrt{12}(\psi_1 + \psi_3)\\ \hat{L}^2\psi_3 &= 6\psi_3 + \sqrt{12}\psi_2.\end{aligned} \tag{50}$$

Therefore:

$$\boldsymbol{L}^2 = \begin{pmatrix} 6 & \sqrt{12} & 0\\ \sqrt{12} & 8 & \sqrt{12}\\ 0 & \sqrt{12} & 6\end{pmatrix} \tag{51}$$

giving the secular equation:

$$\begin{vmatrix} 6-\lambda & \sqrt{12} & 0\\ \sqrt{12} & 8-\lambda & \sqrt{12}\\ 0 & \sqrt{12} & 6-\lambda\end{vmatrix} = 0 \qquad \lambda = L(L+1). \tag{52}$$

Expanding the determinant, we obtain the factorized secular equation:

$$\begin{aligned}(6-\lambda)[(8-\lambda)(6-\lambda)-12] - 12(6-\lambda) &= (6-\lambda)(\lambda^2 - 14\lambda + 24)\\ &= 0,\end{aligned} \tag{53}$$

having the roots:

$$\begin{aligned}&\lambda - 6 = 0 \quad \lambda = 6 \quad L = 2 \quad \text{State } D\\ &\lambda^2 - 14\lambda + 24 = 0 \quad \lambda = 2, 12 \quad L = 1, 3 \quad \text{States } P, F.\end{aligned}$$

The eigenvectors are then formed in the usual elementary way by solving the homogeneous system:

$$\begin{cases}(6-\lambda)c_1 + \sqrt{12}c_2 = 0\\ \sqrt{12}c_1 + (8-\lambda)c_2 + \sqrt{12}c_3 = 0\\ \sqrt{12}c_2 + (6-\lambda)c_3 = 0\end{cases} \tag{54}$$

with the additional normalization condition:

$$c_1^2 + c_2^2 + c_3^2 = 1. \tag{55}$$

For the eigenvector we are interested in, $\lambda = 2$, corresponding to $L = 1$, we have:

$$c_2 = -\frac{2}{\sqrt{3}}c_1, \qquad c_3 = -\frac{\sqrt{3}}{2}c_2 = c_1, \qquad c_1 = \sqrt{\frac{3}{10}}, \tag{56}$$

so that the required singlet ^1P function will be:

$$\psi(^1P) = \sqrt{\frac{3}{10}}(\psi_1 + \psi_3) - \sqrt{\frac{2}{5}}\psi_2. \tag{57}$$

Using (50) and the Dirac formula for $N = 2$, we can easily check that:

$$\begin{aligned} \hat{L}^2\psi(^1P) &= 1(1+1)\psi(^1P) \\ \hat{S}^2\psi(^1P) &= 0(0+1)\psi(^1P) \end{aligned} \tag{58}$$

as it must be.

We then have for the ^1P state arising from the $2p3d$ configuration of two non-equivalent electrons the two alternative expressions:

(i) Complex form:

$$\begin{aligned} \psi(^1P) &= \sqrt{\frac{3}{10}}(\psi_1 + \psi_3) - \sqrt{\frac{2}{5}}\psi_2 \\ &= \sqrt{\frac{3}{20}}\left\{||p_{+1}\overline{d}_{-1}|| + ||d_{-1}\overline{p}_{+1}|| + ||p_{-1}\overline{d}_{+1}|| + ||d_{+1}\overline{p}_{-1}||\right\} \\ &\quad - \frac{1}{\sqrt{5}}\left\{||p_0\overline{d}_0|| + ||d_0\overline{p}_0||\right\} \end{aligned} \tag{59}$$

(ii) Real form:

$$\begin{aligned} \psi(^1P) &= \sqrt{\frac{3}{20}}\left\{||2p_x3\overline{d}_{zx}|| + ||3d_{zx}2\overline{p}_x|| + ||2p_y3\overline{d}_{yz}|| + ||3d_{yz}2\overline{p}_y||\right\} \\ &\quad + \frac{1}{\sqrt{5}}\left\{||2p_z3\overline{d}_{z^2}|| + ||3d_{z^2}2\overline{p}_z||\right\} \\ &= \left\{\sqrt{\frac{3}{20}}[(\overset{\mathbf{r}_1}{2p_x}\overset{\mathbf{r}_2}{3d_{zx}} + \overset{\mathbf{r}_1}{3d_{zx}}\overset{\mathbf{r}_2}{2p_x}) + (2p_y3d_{yz} + 3d_{yz}2p_y)] \right. \\ &\quad \left. + \frac{1}{\sqrt{5}}(2p_z3d_{z^2} + 3d_{z^2}2p_z)\right\}\frac{1}{\sqrt{2}}(\overset{s_1}{\alpha}\overset{s_2}{\beta} - \overset{s_1}{\beta}\overset{s_2}{\alpha}) \end{aligned} \tag{60}$$

after space-spin separation.

States such as $\psi(^1P)$ were used in CI studies of alkaline earth metals for calculating static dipole polarizabilities taking partial account of correlation effects in the valence shell (Magnasco and Amelio, 1978), and for accurate CI studies of static dipole, quadrupole and octupole polarizabilities for the ground states of H, He, Li, Be, Na, Mg (Figari et al., 1983). Correlation in the ground states of Be and Mg was introduced by allowing the ns^2 configuration to interact with the nearly degenerate np^2 configuration in a way determined by the variation theorem. Correlation in the excited states was introduced by allowing the $^1L(sl)$ configuration to interact in an optimum way with the $^1L(pl+1)$ configuration and by varying the non-spherical orbitals independently in the two configurations. The singlet excited configuration $npn'(l+1)$ is described by the many-determinant wavefunction:

$$\begin{aligned}\psi(^1L) &= \left(\frac{l+1}{4l+6}\right)^{1/2}\left\{(np_0\overline{n'(l+1)_0}) + (n'(l+1)_0\overline{np_0})\right\} \\ &\quad + \left(\frac{l+2}{8l+12}\right)^{1/2}\left\{(np_c\overline{n'(l+1)_c}) + (n'(l+1)_c\overline{np_c})\right. \\ &\quad \left.+ (np_s\overline{n'(l+1)_s}) + (n'(l+1)_s\overline{np_s})\right\}, \end{aligned} \tag{61}$$

where $(\cdots)$ denotes a normalized Slater determinant in *real* form with the doubly occupied core orbitals omitted for short, the bar refers as usual to β spin, and the orbitals subscripts to cosine (c), sine (s) or no (0) dependence on angle φ. For $n=2, n'=3, l=1, l'=2$, the general expression (61) reduces to the expression (60) derived before.

9.3.2 The Projection Operator Method

The projection operator method due to Löwdin (see Chapter 6 on spin) can be used to construct atomic states belonging to a definite value of L.

The operator projecting out of a function the state with $L=k$ is:

$$\hat{O}_k = \prod_{L(\neq k)} \frac{\hat{L}^2 - L(L+1)}{k(k+1) - L(L+1)}, \tag{62}$$

where the product includes all Ls except the particular one k we want to construct. This operator acting on the general expansion of the function in terms of L-eigenstates will annihilate all terms except that for which $L=k$, which remains unchanged. Simple applications can be found in Problems 9.8 and 9.9.

The projection operator formula for the *total* angular momentum J in the LS coupling was given by Slater (1960).

9.4 AN OUTLINE OF ADVANCED METHODS FOR COUPLING ANGULAR MOMENTA

In this last Section, we shall simply introduce some explanation for a few symbols that are frequently met in the Literature when treating angular momentum problems, such as Clebsch–Gordan coefficients, Wigner 3-j and 9-j symbols, Gaunt coefficients, and coupling rules. Details can be found in excellent books (Rose, 1957; Brink and Satchler, 1993).

9.4.1 Clebsch–Gordan Coefficients and Wigner 3-j and 9-j Symbols

Two angular momentum vectors, $|l_1m_1\rangle$ and $|l_2m_2\rangle$, can be coupled to a resultant $|LM\rangle$ by the relation:

$$|LM\rangle = \sum_{m_1m_2} |l_1m_1\rangle|l_2m_2\rangle\langle l_1m_1l_2m_2|LM\rangle, \tag{63}$$

where $\langle l_1m_1l_2m_2|LM\rangle$ is a real number called vector coupling or Clebsch–Gordan coefficient, and we used Dirac notation. The transformation (63) is *unitary*, the inverse being:

$$|l_1m_1\rangle|l_2m_2\rangle = \sum_{LM} |LM\rangle\langle LM|l_1m_1l_2m_2\rangle, \tag{64}$$

where the coefficient $\langle LM|l_1m_1l_2m_2\rangle$ is the complex conjugate of the corresponding coefficient $\langle l_1m_1l_2m_2|LM\rangle$.

In recent Literature, the Clebsch–Gordan coefficient is usually expressed in terms of the more symmetric Wigner 3-j symbol through the relation (Brink and Satchler, 1993):

$$\underset{\text{Clebsch–Gordan}}{\langle l_1m_1l_2m_2|LM\rangle} = (-1)^{l_1-l_2+M}\sqrt{2L+1}\underset{3\text{-}j}{\begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix}}. \tag{65}$$

The Wigner 3-j symbol $\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ is non-zero provided:

$$\begin{aligned} &m_1 + m_2 + m_3 = 0 \\ &|l_\mu - l_\nu| \le l_\gamma \le (l_\mu + l_\nu), \end{aligned} \tag{66}$$

and has the following general expression (Rose, 1957; Brink and Satchler, 1993):

$$\begin{aligned} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} &= \delta_{m_1+m_2+m_3,0} \times (-1)^{l_1+m_2-m_3} \\ &\times \sqrt{\frac{(l_1+l_2-l_3)!(l_1-l_2+l_3)!(-l_1+l_2+l_3)!(l_3+m_3)!(l_3-m_3)!}{(l_1+l_2+l_3+1)!(l_1+m_1)!(l_1-m_1)!(l_2+m_2)!(l_2-m_2)!}} \\ &\times \sum_\lambda (-1)^\lambda \frac{(l_1-m_1+\lambda)!(l_2+l_3+m_1-\lambda)!}{\lambda!(-l_1+l_2+l_3-\lambda)!(l_1-l_2+m_3+\lambda)!(l_3-m_3-\lambda)!}, \end{aligned} \tag{67}$$

where:

$$\max(0, l_2 - l_1 - m_3) \le \lambda \le \min(l_3 - m_3, l_2 - l_1 + l_3). \tag{68}$$

The summation over λ is limited to all integers giving non-negative factorials. The Wigner 3-j symbols are today available as standards on the Mathematica software (Wolfram, 1996), where they are evaluated in a sophisticated way in terms of hypergeometric functions (Abramowitz and Stegun, 1965) for integer or half-integer (spin) values of (l, m).

The vector coupling of three and four angular momenta implies use of Wigner 6-j or Wigner 9-j symbols, respectively.

A Wigner 9-j symbol is given as:

$$\begin{Bmatrix} l_1 & l_2 & L \\ l'_1 & l'_2 & L' \\ L_1 & L_2 & \lambda \end{Bmatrix}. \tag{69}$$

It is invariant under interchange of rows and columns, and enjoys the property:

$$\begin{aligned}
&\begin{pmatrix} \lambda & L & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} \lambda & L & L' \\ L_1 & l_1 & l'_1 \\ L_2 & l_2 & l'_2 \end{Bmatrix} \\
&= \sum_{M_1 M_2} \begin{pmatrix} L_1 & L_2 & L \\ M_1 & M_2 & 0 \end{pmatrix} \\
&\quad \times \sum_{m_1 m_2} \sum_{m'_1 m'_2} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & 0 \end{pmatrix} \begin{pmatrix} l'_1 & l'_2 & L' \\ m'_1 & m'_2 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l'_1 & L_1 \\ m_1 & m'_1 & M_1 \end{pmatrix} \\
&\quad \times \begin{pmatrix} l_2 & l'_2 & L_2 \\ m_2 & m'_2 & M_2 \end{pmatrix},
\end{aligned} \tag{70}$$

that reduces to summations over Wigner 3-j symbols, more easily calculable on Mathematica. Used backwards, relation (70) is said to express the *contraction* of summations of 3-j symbols to 9-j (Brink and Satchler, 1993). Expression (70) is met in the spherical tensor expansion of the product $\frac{1}{r_{12}} \cdot \frac{1}{r_{1'2'}}$, which occurs in the second-order theory of long-range intermolecular forces (Ottonelli, 1998; Magnasco and Ottonelli, 1999).

9.4.2 Gaunt Coefficients and Coupling Rules

The Gaunt coefficient arises from the integration of three complex spherical harmonics (with Condon–Shortley phase) of the *same* argument $\Omega = \theta, \varphi$:

$$\begin{aligned}
&\int d\Omega Y^*_{LM}(\Omega) Y_{l_1 m_1}(\Omega) Y_{l_2 m_2}(\Omega) \\
&= G\begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \quad \text{Gaunt coefficient}
\end{aligned}$$

$$= (-1)^M \sqrt{\frac{(2l_1+1)(2l_2+1)(2L+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}, \tag{71}$$

where:

$$M = m_1 + m_2. \tag{72}$$

All these results take their most simple form in terms of *modified* spherical harmonics, defined as (Brink and Satchler, 1993):

$$C_{lm}(\Omega) = \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\Omega), \tag{73}$$

having the ortho-normality properties:

$$\int d\Omega C^*_{lm}(\Omega) C_{l'm'}(\Omega) = \frac{4\pi}{2l+1} \delta_{ll'} \delta_{mm'}. \tag{74}$$

In terms of the Cs we can write:

(i) Coupling rule

$$C_{l_1m_1}(\Omega)C_{l_2m_2}(\Omega) = 2\sum_L C_{LM}(\Omega)(-1)^M(2L+1) \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}, \tag{75}$$

where: $M = m_1 + m_2$, and the finite summation is in steps of 2.

(ii) Gaunt coefficient

$$G\begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} = \int d\Omega C^*_{LM}(\Omega) C_{l_1m_1}(\Omega) C_{l_2m_2}(\Omega) = 4\pi(-1)^M \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}. \tag{76}$$

For $m_1 = m_2 = M = 0$, $l_1 + l_2 + L = 2g$ (even), it is obtained:

$$\int_0^{2\pi} d\varphi \int_{-1}^{1} dx P_{l_1}(x) P_{l_2}(x) P_L(x) = 4\pi \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}^2, \quad x = \cos\theta \tag{77}$$

which is nothing but the symmetrical Racah's formula:

$$\int_{-1}^{1} dx\, P_a(x)P_b(x)P_c(x) = 2\begin{pmatrix} a & b & c \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$= 2\left[(-1)^g \frac{g!}{(g-a)!(g-b)!(g-c)!}\sqrt{\frac{(2g-2a)!(2g-2b)!(2g-2c)!}{(2g+1)!}}\right]^2, \tag{78}$$

where a, b, c are non-negative integers and $a+b+c=2g$ even.

9.5 PROBLEMS 9

9.1. Derive the Landé g-factor for LS coupling in the vector model (Herzberg, 1944)

Answer:

$$g_J = \frac{3}{2} + \frac{S(S+1)-L(L+1)}{2J(J+1)}.$$

Hint:
Use the triangle of Figure 9.8 and the Carnot theorem.

9.2. Find the effect of $\hat{L}^2$ on the three basis functions (38) having $M = M_S = 0$.

Answer:
The result is given as equation (39).
Hint:
Make use of the equation (35) of the main text.

9.3. Find the eigenvectors of matrix (40) corresponding to $\lambda = 0, 2, 6$.

Answer:

$$\lambda = 0 \qquad \psi(^1S) = \frac{1}{\sqrt{3}}(\psi_1 - \psi_2 - \psi_3)$$

$$\lambda = 2 \qquad \psi(^3P) = \frac{1}{\sqrt{2}}(\psi_2 - \psi_3)$$

$$\lambda = 6 \qquad \psi(^1D) = \frac{1}{\sqrt{6}}(2\psi_1 + \psi_2 + \psi_3).$$

Hint:

Insert each eigenvalue in turn into the system of linear homogeneous equations determining the secular equation (41).

9.4. Check equations (43).

Hint:
Use equations (39) for $\hat{L}^2$ and the Dirac formula $\hat{S}^2 = \hat{I} + \hat{P}_{12}$ for spin.

9.5. Transform $\psi(^1S)$ from complex to real form.

Answer:
The result is expression (45).
Hint:
Use the unitary transformation connecting complex to real functions and the elementary properties of determinants.

9.6. Write all microstates arising from the np^3 configuration of three *equivalent* electrons with $l_1 = l_2 = l_3 = 1$, and construct the S quartet with $M_S = 1/2$.

Answer:
The 20 Pauli allowed microstates are:

		M	M_S
1.	$\left\|\left(n\,1\,1\,\frac{1}{2}\right)\left(n\,1\,0\,\frac{1}{2}\right)\left(n\,1\,1\,\frac{\bar{1}}{2}\right)\right\| = \|\|p_+ p_0 \bar{p}_+\|\|$	2	$\frac{1}{2}$
2.	$\left\|\left(n\,1\,1\,\frac{\bar{1}}{2}\right)\left(n\,1\,0\,\frac{\bar{1}}{2}\right)\left(n\,1\,1\,\frac{1}{2}\right)\right\| = \|\|\bar{p}_+ \bar{p}_0 p_+\|\|$	2	$-\frac{1}{2}$
3.	$\left\|\left(n\,1\,1\,\frac{1}{2}\right)\left(n\,1\,\bar{1}\,\frac{1}{2}\right)\left(n\,1\,1\,\frac{\bar{1}}{2}\right)\right\| = \|\|p_+ p_- \bar{p}_+\|\|$	1	$\frac{1}{2}$
4.	$\left\|\left(n\,1\,1\,\frac{\bar{1}}{2}\right)\left(n\,1\,\bar{1}\,\frac{\bar{1}}{2}\right)\left(n\,1\,1\,\frac{1}{2}\right)\right\| = \|\|\bar{p}_+ \bar{p}_- p_+\|\|$	1	$-\frac{1}{2}$
5.	$\left\|\left(n\,1\,1\,\frac{1}{2}\right)\left(n\,1\,0\,\frac{1}{2}\right)\left(n\,1\,0\,\frac{\bar{1}}{2}\right)\right\| = \|\|p_+ p_0 \bar{p}_0\|\|$	1	$\frac{1}{2}$
6.	$\left\|\left(n\,1\,1\,\frac{\bar{1}}{2}\right)\left(n\,1\,0\,\frac{\bar{1}}{2}\right)\left(n\,1\,0\,\frac{1}{2}\right)\right\| = \|\|\bar{p}_+ \bar{p}_0 p_0\|\|$	1	$-\frac{1}{2}$
7.	$\left\|\left(n\,1\,1\,\frac{1}{2}\right)\left(n\,1\,\bar{1}\,\frac{1}{2}\right)\left(n\,1\,0\,\frac{1}{2}\right)\right\| = \|\|p_+ p_- p_0\|\|$	0	$\frac{3}{2}$
8.	$\left\|\left(n\,1\,1\,\frac{1}{2}\right)\left(n\,1\,\bar{1}\,\frac{1}{2}\right)\left(n\,1\,0\,\frac{\bar{1}}{2}\right)\right\| = \|\|p_+ p_- \bar{p}_0\|\|$	0	$\frac{1}{2}$

9.	$\left\Vert \left(n\,1\,1\,\frac{1}{2}\right)\left(n\,1\,\bar{1}\,\frac{\overline{1}}{2}\right)\left(n\,1\,0\,\frac{1}{2}\right)\right\Vert = \lVert p_{+}\overline{p}_{-}p_{0}\rVert$	0	$\frac{1}{2}$
10.	$\left\Vert \left(n\,1\,1\,\frac{\overline{1}}{2}\right)\left(n\,1\,\bar{1}\,\frac{1}{2}\right)\left(n\,1\,0\,\frac{1}{2}\right)\right\Vert = \lVert \overline{p}_{+}p_{-}p_{0}\rVert$	0	$\frac{1}{2}$
11.	$\left\Vert \left(n\,1\,1\,\frac{\overline{1}}{2}\right)\left(n\,1\,\bar{1}\,\frac{\overline{1}}{2}\right)\left(n\,1\,0\,\frac{1}{2}\right)\right\Vert = \lVert \overline{p}_{+}\overline{p}_{-}p_{0}\rVert$	0	$-\frac{1}{2}$
12.	$\left\Vert \left(n\,1\,1\,\frac{\overline{1}}{2}\right)\left(n\,1\,\bar{1}\,\frac{1}{2}\right)\left(n\,1\,0\,\frac{\overline{1}}{2}\right)\right\Vert = \lVert \overline{p}_{+}p_{-}\overline{p}_{0}\rVert$	0	$-\frac{1}{2}$
13.	$\left\Vert \left(n\,1\,1\,\frac{1}{2}\right)\left(n\,1\,\bar{1}\,\frac{\overline{1}}{2}\right)\left(n\,1\,0\,\frac{\overline{1}}{2}\right)\right\Vert = \lVert p_{+}\overline{p}_{-}\overline{p}_{0}\rVert$	0	$-\frac{1}{2}$
14.	$\left\Vert \left(n\,1\,1\,\frac{\overline{1}}{2}\right)\left(n\,1\,\bar{1}\,\frac{\overline{1}}{2}\right)\left(n\,1\,0\,\frac{\overline{1}}{2}\right)\right\Vert = \lVert \overline{p}_{+}\overline{p}_{-}\overline{p}_{0}\rVert$	0	$-\frac{3}{2}$
15.	$\left\Vert \left(n\,1\,\bar{1}\,\frac{\overline{1}}{2}\right)\left(n\,1\,0\,\frac{\overline{1}}{2}\right)\left(n\,1\,0\,\frac{1}{2}\right)\right\Vert = \lVert \overline{p}_{-}\overline{p}_{0}p_{0}\rVert$	-1	$-\frac{1}{2}$
16.	$\left\Vert \left(n\,1\,\bar{1}\,\frac{1}{2}\right)\left(n\,1\,0\,\frac{1}{2}\right)\left(n\,1\,0\,\frac{\overline{1}}{2}\right)\right\Vert = \lVert p_{-}p_{0}\overline{p}_{0}\rVert$	-1	$\frac{1}{2}$
17.	$\left\Vert \left(n\,1\,\bar{1}\,\frac{\overline{1}}{2}\right)\left(n\,1\,1\,\frac{\overline{1}}{2}\right)\left(n\,1\,\bar{1}\,\frac{1}{2}\right)\right\Vert = \lVert \overline{p}_{-}\overline{p}_{+}p_{-}\rVert$	-1	$-\frac{1}{2}$
18.	$\left\Vert \left(n\,1\,\bar{1}\,\frac{1}{2}\right)\left(n\,1\,1\,\frac{1}{2}\right)\left(n\,1\,\bar{1}\,\frac{\overline{1}}{2}\right)\right\Vert = \lVert p_{-}p_{+}\overline{p}_{-}\rVert$	-1	$\frac{1}{2}$
19.	$\left\Vert \left(n\,1\,\bar{1}\,\frac{\overline{1}}{2}\right)\left(n\,1\,0\,\frac{\overline{1}}{2}\right)\left(n\,1\,\bar{1}\,\frac{1}{2}\right)\right\Vert = \lVert \overline{p}_{-}\overline{p}_{0}p_{-}\rVert$	-2	$-\frac{1}{2}$
20.	$\left\Vert \left(n\,1\,\bar{1}\,\frac{1}{2}\right)\left(n\,1\,0\,\frac{1}{2}\right)\left(n\,1\,\bar{1}\,\frac{\overline{1}}{2}\right)\right\Vert = \lVert p_{-}p_{0}\overline{p}_{-}\rVert$	-2	$\frac{1}{2}$

The S quartet with $M_S = 1/2$ is:

$$\psi(^4S) = \frac{1}{\sqrt{3}}(\psi_8 + \psi_9 + \psi_{10}).$$

Hint:
Use the techniques of the previous Problems.

9.7. Construct the four ^4S functions out of the np^3 configuration of three equivalent electrons (e.g. the ground state configuration of the N atom).

Answer:
The four ${}^4S$ functions ($M = 0$) are:

	M_S
$\Psi_1({}^4S) = \psi_7$	$\frac{3}{2}$
$\Psi_2({}^4S) = \frac{1}{\sqrt{3}}(\psi_8 + \psi_9 + \psi_{10})$	$\frac{1}{2}$
$\Psi_3({}^4S) = \frac{1}{\sqrt{3}}(\psi_{11} + \psi_{12} + \psi_{13})$	$-\frac{1}{2}$
$\Psi_4({}^4S) = \psi_{14}$	$-\frac{3}{2}$

Hint:
Use the techniques of the previous Problems.

9.8. Construct the allowed L-states ($L = 0, 1, 2$) out of the p^2 configuration of two equivalent electrons by the projection method.

Answer:

$$\psi({}^1S) = \frac{1}{\sqrt{3}}(\psi_1 - \psi_2 - \psi_3)$$

$$\psi({}^3P) = \frac{1}{\sqrt{2}}(\psi_2 - \psi_3)$$

$$\psi({}^1D) = \frac{1}{\sqrt{6}}(2\psi_1 + \psi_2 + \psi_3).$$

Hint:
Act on ψ_1 or ψ_2 with the projector given by equation (62).

9.9. Construct the ${}^1P$ state out of the $2p3d$ configuration of two non-equivalent electrons by the projection method.

Answer:

$$\psi({}^1P) = \sqrt{\frac{3}{10}}(\psi_1 + \psi_3) - \sqrt{\frac{2}{5}}\psi_2.$$

Hint:
Act on ψ_1 with the projector given by equation (62) which annihilates the components with $L = 2$ and 3.

9.6 SOLVED PROBLEMS

9.1. The Landé g-factor by the vector model.
With reference to the left part of Figure 9.8, we first notice that $\boldsymbol{\mu}_L$, $\boldsymbol{\mu}_S$, $\boldsymbol{\mu}_J$ are in a direction opposite to **L**, **S**, **J** with magnitude:

$$\mu_L = -\beta_e\sqrt{L(L+1)}$$

$$\mu_S = -2\beta_e\sqrt{S(S+1)}$$

$$\mu_J = -g_J\beta_e\sqrt{J(J+1)},$$

where g_J is the Landé g-factor we want to calculate. From the Carnot theorem for the triangle of sides $\sqrt{L(L+1)}$, $\sqrt{S(S+1)}$, $\sqrt{J(J+1)}$ it follows:

$$\begin{aligned} S(S+1) &= J(J+1) + L(L+1) - 2\sqrt{J(J+1)}\sqrt{L(L+1)}\cos(L, J) \\ L(L+1) &= J(J+1) + S(S+1) - 2\sqrt{J(J+1)}\sqrt{S(S+1)}\cos(S, J). \end{aligned}$$

Then, the component of μ_J in the J-direction is:

$$\mu_J = \mu_L\cos(L, J) + \mu_S\cos(S, J)$$

$$g_J\sqrt{J(J+1)} = \sqrt{L(L+1)}\cos(L, J) + 2\sqrt{S(S+1)}\cos(S, J),$$

where we have divided both members by β_e. Then it follows:

$$\begin{aligned} g_J &= \frac{\sqrt{L(L+1)}}{\sqrt{J(J+1)}}\frac{J(J+1)+L(L+1)-S(S+1)}{2\sqrt{J(J+1)}\sqrt{L(L+1)}} \\ &\quad +2\frac{\sqrt{S(S+1)}}{\sqrt{J(J+1)}}\frac{J(J+1)+S(S+1)-L(L+1)}{2\sqrt{J(J+1)}\sqrt{S(S+1)}} \\ &= \frac{J(J+1)+L(L+1)-S(S+1)+2J(J+1)+2S(S+1)-2L(L+1)}{2J(J+1)} \\ &= 1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \\ &= \frac{3}{2}+\frac{S(S+1)-L(L+1)}{2J(J+1)} \end{aligned}$$

which is the Landé g-factor for the LS coupling. For a single s-electron, $L = 0$, $S = 1/2$, $J = S$, and therefore $g_J = 2$. This spectroscopic value should not be confused with the intrinsic g-value of the electron.

9.2. We apply equation (35) in turn to ψ_1, ψ_2, ψ_3.

$$
\begin{aligned}
\hat{L}^2\psi_1 &= \hat{L}^2||p_0\overline{p}_0|| \\
&= [1(1+1)+1(1+1)+2\cdot 0\cdot 0]||p_0\overline{p}_0|| + \overset{\kappa\lambda}{12} + 21 \\
&= 4||p_0\overline{p}_0|| + [1(1+1)-0(0+1)]^{1/2} \\
&\quad \times[1(1+1)-0(0-1)]^{1/2}||p_{+1}\overline{p}_{-1}|| \\
&\quad + [1(1+1)-0(0-1)]^{1/2}[1(1+1)-0(0+1)]^{1/2}||p_{-1}\overline{p}_{+1}|| \\
&= 4\psi_1 + 2\psi_2 + 2\psi_3.
\end{aligned}
$$

$$
\begin{aligned}
\hat{L}^2\psi_2 &= \hat{L}^2||p_{+1}\overline{p}_{-1}|| \\
&= [1(1+1)+1(1+1)+2(+1)(-1)]||p_{+1}\overline{p}_{-1}|| + \overset{\kappa\ \lambda}{1\ 2} + 21 \\
&= 2||p_{+1}\overline{p}_{-1}|| + [1(1+1)-(-1)(-1+1)]^{1/2} \\
&\quad \times[1(1+1)-1(1-1)]^{1/2}||p_0\overline{p}_0|| \\
&= 2\psi_2 + 2\psi_1,
\end{aligned}
$$

since 12 is zero because we cannot exceed the top or the bottom of the ladder with $l = 1$.

$$
\begin{aligned}
\hat{L}^2\psi_3 &= \hat{L}^2||p_{-1}\overline{p}_{+1}|| \\
&= [1(1+1)+1(1+1)+2(-1)(+1)]||p_{-1}\overline{p}_{+1}|| + \overset{\kappa\ \lambda}{1\ 2} + 2\,1 \\
&= 2||p_{-1}\overline{p}_{+1}|| + [1(1+1)-(-1)(-1+1)]^{1/2} \\
&\quad \times[1(1+1)-1(1-1)]^{1/2}||p_0\overline{p}_0|| \\
&= 2\psi_3 + 2\psi_1,
\end{aligned}
$$

and we obtain equations (39) of the main text.

9.3. Eigenvectors of matrix (40) corresponding to $\lambda = 0, 2, 6$.
The homogeneous system to be solved is:

$$
\begin{cases}
(4-\lambda)c_1 + 2c_2 + 2c_3 = 0 \\
2c_1 + (2-\lambda)c_2 = 0 \\
2c_1 + (2-\lambda)c_3 = 0
\end{cases}
$$

with the normalization condition:

$$c_1^2 + c_2^2 + c_3^2 = 1.$$

(i) $\lambda = 0$
From 2. and 3. it follows immediately:

$$c_2 = c_3 = -c_1 \qquad 3c_1^2 = 1$$
$$c_1 = \frac{1}{\sqrt{3}}, \qquad c_2 = c_3 = -\frac{1}{\sqrt{3}},$$

(ii) $\lambda = 2$

$$c_1 = 0 \qquad c_3 = -c_2 \qquad 2c_2^2 = 1$$
$$c_2 = \frac{1}{\sqrt{2}}, \qquad c_3 = -\frac{1}{\sqrt{2}}.$$

(iii) $\lambda = 6$

$$c_2 = c_3 = \frac{1}{2}c_1 \qquad c_1 = \frac{2}{\sqrt{6}}$$
$$c_1 = \frac{2}{\sqrt{6}}, \qquad c_2 = c_3 = \frac{1}{\sqrt{6}}.$$

9.4. Check equations (43).
Making use of equations (39), it is obtained:

$$\hat{L}^2\psi(^1S) = \frac{1}{\sqrt{3}}(4\psi_1 + 2\psi_2 + 2\psi_3 - 2\psi_2 - 2\psi_1 - 2\psi_3 - 2\psi_1) \tag{79}$$
$$= 0(0+1)\psi(^1S) \tag{80}$$

$$\hat{L}^2\psi(^3P) = \frac{1}{\sqrt{2}}(2\psi_2 + 2\psi_1 - 2\psi_3 - 2\psi_1) = 1(1+1)\psi(^3P)$$

$$\hat{L}^2\psi(^1D) = \frac{1}{\sqrt{6}}(8\psi_1 + 4\psi_2 + 4\psi_3 + 2\psi_2 + 2\psi_1 + 2\psi_3 + 2\psi_1)$$
$$= \frac{1}{\sqrt{6}}(12\psi_1 + 6\psi_2 + 6\psi_3) = 2(2+1)\psi(^1D),$$

so that functions (42) are the correct eigenfunctions of $\hat{L}^2$ belonging to the eigenvalues $L = 0, 1, 2$, respectively. Using Dirac $\hat{S}^2 = \hat{I} + \hat{P}_{12}$, it is obtained for $\hat{S}^2$:

$$\hat{S}^2\psi(^1S) = \frac{1}{\sqrt{3}}\{||p_0\overline{p}_0|| - ||p_{+1}\overline{p}_{-1}|| - ||p_{-1}\overline{p}_{+1}||$$
$$+ ||\overline{p}_0 p_0|| - ||\overline{p}_{+1}p_{-1}|| - ||\overline{p}_{-1}p_{+1}||\} = 0(0+1)\psi(^1S)$$

$$
\begin{aligned}
\hat{S}^2\psi(^3P) &= \frac{1}{\sqrt{2}}\left\{\|p_{+1}\overline{p}_{-1}\| - \|p_{-1}\overline{p}_{+1}\| + \|\overline{p}_{+1}p_{-1}\| - \|\overline{p}_{-1}p_{+1}\|\right\} \\
&= 2\frac{1}{\sqrt{2}}\left\{\|p_{+1}\overline{p}_{-1}\| - \|p_{-1}\overline{p}_{+1}\|\right\} = 1(1+1)\psi(^3P)
\end{aligned}
$$

$$
\begin{aligned}
\hat{S}^2\psi(^1D) &= \frac{1}{\sqrt{6}}\left\{2\|p_0\overline{p}_0\| + \|p_{+1}\overline{p}_{-1}\| + \|p_{-1}\overline{p}_{+1}\|\right. \\
&\quad \left. + 2\|\overline{p}_0 p_0\| + \|\overline{p}_{+1}p_{-1}\| + \|\overline{p}_{-1}p_{+1}\|\right\} = 0(0+1)\psi(^1D),
\end{aligned}
$$

as it must be.

9.5. Transform $\psi(^1S)$ from complex to real form.
In order to transform to real functions, we must take into account the Condon–Shortley phase for the complex spherical harmonics with $m > 0$:

$$
\begin{aligned}
Y_{lm} &= (-1)^m P_l^m(\cos\theta)\exp(im\varphi) \\
Y_{l\overline{m}} &= P_l^m(\cos\theta)\exp(-im\varphi).
\end{aligned}
$$

The phase factors are chosen so as to satisfy step-up and step-down equations and the phase of Y_{l0} be real and positive (Condon and Shortley, 1963). Then:

$$
p_+ = -\frac{p_x + ip_y}{\sqrt{2}}, \qquad p_- = \frac{p_x - ip_y}{\sqrt{2}}
$$

and, introducing into the complex determinants of equation (44), for the properties of determinants we obtain:

$$
\begin{aligned}
&-\|p_+\overline{p}_-\| - \|p_-\overline{p}_+\| \\
&= -\left\|\frac{-p_x - ip_y}{\sqrt{2}} \quad \frac{\overline{p}_x - i\overline{p}_y}{\sqrt{2}}\right\| - \left\|\frac{p_x - ip_y}{\sqrt{2}} \quad \frac{-\overline{p}_x - i\overline{p}_y}{\sqrt{2}}\right\| \\
&= \frac{1}{2}\left\{\|p_x + ip_y\overline{p}_x - i\overline{p}_y\| + \|p_x - ip_y\overline{p}_x + i\overline{p}_y\|\right\} \\
&= \frac{1}{2}\left\{\|p_x\overline{p}_x - i\overline{p}_y\| + i\|p_y\overline{p}_x - i\overline{p}_y\|\right. \\
&\quad \left. + \|p_x\overline{p}_x + i\overline{p}_y\| - i\|p_y\overline{p}_x + i\overline{p}_y\|\right\} \\
&= \frac{1}{2}\left\{\|p_x\overline{p}_x\| - i\|p_x\overline{p}_y\| + i\|p_y\overline{p}_x\| + \|p_y\overline{p}_y\|\right. \\
&\quad \left. + \|p_x\overline{p}_x\| + i\|p_x\overline{p}_y\| - i\|p_y\overline{p}_x\| + \|p_y\overline{p}_y\|\right\} \\
&= \|p_x\overline{p}_x\| + \|p_y\overline{p}_y\|.
\end{aligned}
$$

Hence, we obtain:

$$\begin{aligned}\psi(^1S) &= \frac{1}{\sqrt{3}}\{||p_0\overline{p}_0|| - ||p_+\overline{p}_-|| - ||p_-\overline{p}_+||\} \quad \text{complex}\\ &= \frac{1}{\sqrt{3}}\{||p_x\overline{p}_x|| + ||p_y\overline{p}_y|| + ||p_z\overline{p}_z||\}. \quad \text{real}\end{aligned}$$

9.6. According to the vector model three equivalent p electrons with $l_1 = l_2 = l_3 = 1$ can have $L = 0, 1, 2, 3$. The state with $L = 3$ is however not allowed by the Pauli exclusion principle. The Pauli allowed states are then $\binom{6}{3} = 20$ with $L = 0, 1, 2$. The states are (Herzberg, 1944):

$$^4S: \qquad M = 0 \qquad M_S = \pm\frac{3}{2},\ \pm\frac{1}{2} \qquad \text{4 states}$$

$$^2P: \qquad M = \begin{cases} 1 & M_S = \pm\frac{1}{2} \\ 0 & \ \pm\frac{1}{2} \\ -1 & \ \pm\frac{1}{2} \end{cases} \qquad \text{6 states}$$

$$^2D: \qquad M = \begin{cases} 2 & M_S = \pm\frac{1}{2} \\ 1 & \ \pm\frac{1}{2} \\ 0 & \ \pm\frac{1}{2} \\ -1 & \ \pm\frac{1}{2} \\ -2 & \ \pm\frac{1}{2} \end{cases} \qquad \text{10 states}$$

The 20 states are given as Slater determinants numbered from 1 to 20. The S quartet with $M_S = 1/2$ must be a linear combination of functions 8, 9, 10, the remaining two being the components of the doublets ^2P and ^2D.

Proceeding as we did in the previous Problems, we see that:

$$\begin{aligned}\hat{L}^2\psi_8 &= 4\psi_8 - 2\psi_9 - 2\psi_{10}\\ \hat{L}^2\psi_9 &= 4\psi_9 - 2\psi_8 - 2\psi_9 = -2\psi_8 + 2\psi_9\\ \hat{L}^2\psi_{10} &= 4\psi_{10} - 2\psi_{10} - 2\psi_8 = -2\psi_8 + 2\psi_{10}.\end{aligned}$$

The matrix representative of $\hat{L}^2$ over these basis functions will be:

$$\boldsymbol{L}^2 = \begin{pmatrix} 4 & -2 & -2 \\ -2 & 2 & 0 \\ -2 & 0 & 2 \end{pmatrix}$$

giving the secular equation:

$$\begin{vmatrix} 4-\lambda & -2 & -2 \\ -2 & 2-\lambda & 0 \\ -2 & 0 & 2-\lambda \end{vmatrix} = 0$$

with the roots:

$$\lambda = 0, 2, 6 \Rightarrow L = 0, 1, 2$$

as it must be. The eigenvectors are:

$$\begin{aligned}
\psi(^4S) &= \frac{1}{\sqrt{3}}(\psi_8 + \psi_9 + \psi_{10}) \\
\psi(^2P) &= \frac{1}{\sqrt{2}}(\psi_9 - \psi_{10}) \\
\psi(^2D) &= \frac{1}{\sqrt{6}}(2\psi_8 - \psi_9 - \psi_{10}).
\end{aligned}$$

These results can be easily checked so that:

$$\begin{aligned}
\hat{L}^2\psi(^4S) &= 0(0+1)\psi(^4S), & \hat{S}^2\psi(^4S) &= \frac{3}{2}\left(\frac{3}{2}+1\right)\psi(^4S) \\
\hat{L}^2\psi(^2P) &= 1(1+1)\psi(^2P), & \hat{S}^2\psi(^2P) &= \frac{1}{2}\left(\frac{1}{2}+1\right)\psi(^2P) \\
\hat{L}^2\psi(^2D) &= 2(2+1)\psi(^2D), & \hat{S}^2\psi(^2D) &= \frac{1}{2}\left(\frac{1}{2}+1\right)\psi(^2D).
\end{aligned}$$

9.7. The four ^4S functions out of the np^3 configuration of three equivalent electrons. One of these functions, having $L = 0$, $M_S = 1/2$, was already found in Problem 9.6. It is:

$$\Psi_2(^4S) = \frac{1}{\sqrt{3}}(\psi_8 + \psi_9 + \psi_{10}).$$

The third function, having $L = 0$, $M_S = -1/2$, is given immediately as:

$$\Psi_3(^4S) = \frac{1}{\sqrt{3}}(\psi_{11} + \psi_{12} + \psi_{13}),$$

after spin was systematically changed in the Slater determinants having $M_S = 1/2$. For the remaining two, we start from the state of maximum spin multiplicity:

$$\psi_7 = ||p_+ p_- p_0||$$

having $S = M_S = 3/2$. Acting with $\hat{L}^2$ we find:

$$\begin{aligned}
\hat{L}^2\psi_7 &= \hat{L}^2||p_+ p_- p_0|| \\
&= 4||p_+ p_- p_0|| + 2||p_+ p_0 p_-|| + 2||p_0 p_- p_+|| \\
&= 4||p_+ p_- p_0|| - 2||p_+ p_- p_0|| - 2||p_+ p_- p_0|| \\
&= 0(0+1)\psi_7,
\end{aligned}$$

so that:

$$\Psi_1(^4S) = \psi_7$$

is the first function wanted. The like is true for ψ_{14}, which differs from ψ_7 for having all spins $-1/2$. Hence:

$$\Psi_4(^4S) = \psi_{14}$$

is the last function of the ^4S state. We can note the one-to-one correspondence between the four ^4S functions written as Slater determinants of spin-orbitals and the pure spin states arising from the $N = 3$ problem in Chapter 6:

	M_S	
$\alpha\alpha\alpha$	$\frac{3}{2}$	$S = \frac{3}{2}$
$\frac{1}{\sqrt{3}}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)$	$\frac{1}{2}$	
$\frac{1}{\sqrt{3}}(\beta\beta\alpha + \beta\alpha\beta + \alpha\beta\beta)$	$-\frac{1}{2}$	
$\beta\beta\beta$	$-\frac{3}{2}$	

9.8. Construction of the allowed L-states ($L = 0, 1, 2$) out of the p^2 configuration of two equivalent electrons by the projection method.
We saw in Section 9.3.1 that the Pauli allowed states for the p^2 configuration of two equivalent electrons are:

$$\begin{array}{cccc}
 & {}^1S, & {}^3P, & {}^1D \\
L = & 0, & 1, & 2
\end{array}$$

We saw that there are three states with $M_L = M_S = 0$:

$$\psi_1 = ||p_0\overline{p}_0|| \qquad \psi_2 = ||p_+\overline{p}_-|| \qquad \psi_3 = ||p_-\overline{p}_+||.$$

In Problem 9.2 we found that:

$$\begin{aligned}
\hat{L}^2\psi_1 &= 4\psi_1 + 2\psi_2 + 2\psi_3 \\
\hat{L}^2\psi_2 &= 2\psi_1 + 2\psi_2 \\
\hat{L}^2\psi_3 &= 2\psi_1 + 2\psi_3.
\end{aligned}$$

Wanting the S-state ($L = 0$), we must annihilate the components having $L = 1$ and $L = 2$. The corresponding projector will be:

$$\begin{aligned}
\hat{O}_0 &= \prod_{L(\neq 0)} \frac{\hat{L}^2 - L(L+1)}{-L(L+1)} = \frac{\hat{L}^2 - 1(1+1)}{-1(1+1)} \cdot \frac{\hat{L}^2 - 2(2+1)}{-2(2+1)} \\
&= 1 - \frac{8}{12}\hat{L}^2 + \frac{1}{12}\hat{L}^2 \cdot \hat{L}^2.
\end{aligned}$$

Using the relations above it is easily found:

$$\begin{aligned}
\hat{L}^2(\hat{L}^2\psi_1) &= 4(\hat{L}^2\psi_1) + 2(\hat{L}^2\psi_2) + 2(\hat{L}^2\psi_3) \\
&= 4(4\psi_1 + 2\psi_2 + 2\psi_3) + 2(2\psi_1 + 2\psi_2) + 2(2\psi_1 + 2\psi_3) \\
&= 24\psi_1 + 12\psi_2 + 12\psi_3.
\end{aligned}$$

Then it follows:

$$\begin{aligned}
\hat{O}_0\psi_1 &= \psi_1 - \frac{8}{12}(\hat{L}^2\psi_1) + \frac{1}{12}\hat{L}^2(\hat{L}^2\psi_1) \\
&= \psi_1 - \frac{8}{12}(4\psi_1 + 2\psi_2 + 2\psi_3) + \frac{1}{12}(24\psi_1 + 12\psi_2 + 12\psi_3) \\
&= \frac{1}{3}(\psi_1 - \psi_2 - \psi_3) \propto \frac{1}{\sqrt{3}}(\psi_1 - \psi_2 - \psi_3) \quad S\text{-state}
\end{aligned}$$

which coincides with the result (i) of Problem 9.3 after normalization.
We can proceed similarly for the remaining components. Wanting the P-state ($L = 1$):

$$\hat{O}_1 = \prod_{L(\neq 1)} \frac{\hat{L}^2 - L(L+1)}{2 - L(L+1)} = \frac{\hat{L}^2}{2} \cdot \frac{\hat{L}^2 - 6}{2 - 6} = \frac{6}{8}\hat{L}^2 - \frac{1}{8}\hat{L}^2 \cdot \hat{L}^2$$

$$\hat{O}_1\psi_1 = \frac{6}{8}(\hat{L}^2\psi_1) - \frac{1}{8}\hat{L}^2(\hat{L}^2\psi_1)$$

$$= \frac{6}{8}(4\psi_1 + 2\psi_2 + 2\psi_3) - \frac{1}{8}(24\psi_1 + 12\psi_2 + 12\psi_3) = 0$$

$$\begin{aligned}\hat{L}^2(\hat{L}^2\psi_2) &= 2(\hat{L}^2\psi_1) + 2(\hat{L}^2\psi_2)\\ &= 2(4\psi_1 + 2\psi_2 + 2\psi_3) + 2(2\psi_1 + 2\psi_2) = 12\psi_1 + 8\psi_2 + 4\psi_3\end{aligned}$$

$$\begin{aligned}\hat{O}_1\psi_2 &= \frac{6}{8}(\hat{L}^2\psi_2) - \frac{1}{8}\hat{L}^2(\hat{L}^2\psi_2)\\ &= \frac{6}{8}(2\psi_1 + 2\psi_2) - \frac{1}{8}(12\psi_1 + 8\psi_2 + 4\psi_3)\\ &= \frac{1}{2}(\psi_2 - \psi_3) \propto \frac{1}{\sqrt{2}}(\psi_2 - \psi_3) \quad P\text{-state}\end{aligned}$$

after normalization.
Wanting the D-state ($L = 2$):

$$\hat{O}_2 = \prod_{L(\neq 2)} \frac{\hat{L}^2 - L(L+1)}{6 - L(L+1)} = \frac{\hat{L}^2}{6} \cdot \frac{\hat{L}^2 - 2}{4} = \frac{1}{24}\hat{L}^2 \cdot \hat{L}^2 - \frac{2}{24}\hat{L}^2.$$

Then:

$$\begin{aligned}\hat{O}_2\psi_1 &= \frac{1}{24}\hat{L}^2(\hat{L}^2\psi_1) - \frac{2}{24}(\hat{L}^2\psi_1)\\ &= \frac{1}{24}(24\psi_1 + 12\psi_2 + 12\psi_3) - \frac{2}{24}(4\psi_1 + 2\psi_2 + 2\psi_3)\\ &= \frac{1}{3}(2\psi_1 + \psi_2 + \psi_3) \propto \frac{1}{\sqrt{6}}(2\psi_1 + \psi_2 + \psi_3) \quad D\text{-state}\end{aligned}$$

after normalization.
Once the effect of $\hat{L}^2$ on the basis functions is known, use of the projector (62) is the simplest way of obtaining the correct combination having the desired value of L.

9.9. Construct the ${}^1P$ state out of the $2p3d$ configuration of two non-equivalent electrons by the projection method.
We saw in Section 9.3.1 (ii) what are the possible allowed states arising from the $2p3d$ configuration. The basis functions are given by (47), while the effect of $\hat{L}^2$ on these functions is given by (50), which we report below for convenience:

$$\hat{L}^2\psi_1 = 6\psi_1 + \sqrt{12}\psi_2$$

$$\hat{L}^2\psi_2 = 8\psi_2 + \sqrt{12}(\psi_1 + \psi_3)$$

$$\hat{L}^2\psi_3 = 6\psi_3 + \sqrt{12}\psi_2.$$

To build the ^1P state out of the $2p3d$ configuration we must annihilate the D and F components. The projector for $k = 1$ will be:

$$\hat{O}_1 = \prod_{L(\neq 1)} \frac{\hat{L}^2 - L(L+1)}{2 - L(L+1)} = \frac{\hat{L}^2 - 6}{2-6} \cdot \frac{\hat{L}^2 - 12}{2-12} = \frac{1}{40}(72 - 18\hat{L}^2 + \hat{L}^2 \cdot \hat{L}^2).$$

Now:

$$\begin{aligned} \hat{L}^2(\hat{L}^2\psi_1) &= \hat{L}^2(6\psi_1 + \sqrt{12}\psi_2) = 6\hat{L}^2\psi_1 + \sqrt{12}\hat{L}^2\psi_2 \\ &= 6(6\psi_1 + \sqrt{12}\psi_2) + \sqrt{12}(8\psi_2 + \sqrt{12}\psi_1 + \sqrt{12}\psi_3) \\ &= 48\psi_1 + 14\sqrt{12}\psi_2 + 12\psi_3. \end{aligned}$$

Acting with $\hat{O}_1$ on the first function, it is hence obtained:

$$\begin{aligned} \hat{O}_1\psi_1 &= \frac{72}{40}\psi_1 - \frac{18}{40}(\hat{L}^2\psi_1) + \frac{1}{40}\hat{L}^2(\hat{L}^2\psi_1) \\ &= \frac{72}{40}\psi_1 - \frac{18}{40}(6\psi_1 + \sqrt{12}\psi_2) + \frac{1}{40}(48\psi_1 + 14\sqrt{12}\psi_2 + 12\psi_3) \\ &= \psi_1\left(\frac{72}{40} - \frac{108}{40} + \frac{48}{40}\right) + \sqrt{12}\psi_2\left(-\frac{18}{40} + \frac{14}{40}\right) + \psi_3\left(\frac{12}{40}\right) \\ &= \frac{3}{10}(\psi_1 + \psi_3) - \frac{\sqrt{3}}{5}\psi_2 \propto \sqrt{\frac{3}{10}}(\psi_1 + \psi_3) - \sqrt{\frac{2}{5}}\psi_2 \qquad P\text{-state} \end{aligned}$$

after normalization. This result coincides with that of equation (57) found previously.

– 10 –

Valence Bond Theory and the Chemical Bond

10.1 INTRODUCTION

We saw in Chapter 7 how increasingly sophisticated wavefunctions can be constructed for molecules starting from the Hartree–Fock approximation. However, the independent particle model, of which Hartree–Fock is the most refined expression, treats the molecule as a sea of uncorrelated electrons moving in the field of nuclei of given symmetry. The one-configuration approach yields at its best a single determinant wavefunction of delocalized molecular orbitals, whose energies bear some relation to the negative of the experimentally detectable ionization potentials (the so called Koopmans' theorem), but are otherwise the expression of the nature and limitations of the basis set. Molecular orbitals are many-centre one-electron functions reflecting molecular symmetry, and may change their form depending on unitary transformations among the basic orbitals. We saw that all physical properties of the system are embodied in the fundamental invariant ρ, the Fock–Dirac density matrix, which has semiempirically been extended to include correlation effects in density functional theory. What is lacking in the MO approach is any direct relation with the chemical bond and its stereochemistry. Even if molecular geometries can be obtained theoretically, within the correlation error, by optimizing bond lengths and bond angles, MO theory in its first approximation fails to describe bond dissociation, even in the simplest case of the 2-electron bond in H_2. The conventional chemical idea of a molecule as made by inner shells, chemical bonds and lone pairs is absent in a MO description of the molecule, though chemical intuition might help in avoiding brute force calculations. Even if the chemical bond is difficult to be defined exactly, we can measure experimentally the length of the $O-H$ bonds in H_2O and the angle they make in the molecule. It is certainly more familiar to chemists and molecular physicists the idea that a molecule is made by atoms that are bound together by some kind of forces. An interesting discussion on the origin of the chemical bond was given by Kutzelnigg (1990).

The idea of the covalent bond stems directly from the pioneering work by Heitler and London (1927), where they describe in a correct qualitative way bond dissociation in the ground state of the H_2 molecule. Heitler–London (HL) theory appears as the first step in a possible perturbative improvement to the wavefunction (see Chapters 11 and 12), where polarization and correlation corrections can easily be accounted for in second order, yielding results that are almost in perfect agreement with the most advanced theoretical calculations and with experimental results. HL theory can be considered as the elementary formulation of the so called valence bond (VB) theory in terms of covalent VB structures.

These ideas were next extended by Pauling (1933) to the VB description of the π electron bonds in aromatic and conjugated hydrocarbons. The "resonance" between Kekulé structures, a great intuition of an experimental organic chemist[1], stems directly from the quantum mechanical treatment of the interaction between VB structures describing localized π bonds in benzene.

One of the greatest problems of VB theory, the preparation of suitably directed hybrids which should then be involved in the chemical bond, was solved in recent advances of the theory (Cooper et al., 1987), allowing for optimization of large basis sets. The other problem is connected with the non-orthogonality of VB structures, and this still remains a problem, especially in the evaluation of the matrix elements of the Hamiltonian.

Emphasis in this Chapter will always be on *elementary* VB methods and on how they can qualitatively help in studying electronic molecular structure, in a strict correspondence between quantum mechanical VB structures and chemical formulae.

---

[1] Kekulé, Friedrich August von Stradonitz 1829–1896, German organic chemist, Professor at the Universities of Gand (Belgium), Heidelberg and Bonn.

The content of this Chapter will be the following. We begin by introducing the Born–Oppenheimer approximation, which is essential for the existence of potential energy surfaces and, hence, for the very concept of the chemical bond. Next, the possibility of forming the 2-electron bond in H_2 is examined, showing the failure of the simple MO approach in describing dissociation. Heitler–London theory is then introduced as the simplest way of solving the dissociation problem, and the equivalence between MO-CI and full VB (covalent+ionic) wavefunctions for H_2 is fully discussed. The orthogonality catastrophe occurring in the covalent VB theory of H_2 is examined, and the way of overcoming it suggested in detail.

After this introduction, the general formulation of elementary VB theory is presented, comparing VB and MO methods, then giving a qualitative VB description of many simple molecules. Pauling VB theory of π electron systems is presented in Section 5, with applications to a few important conjugated and aromatic molecules, and its theoretical failures and possible corrections are discussed. Finally, the problem of hybridization and of directed valency is briefly discussed, particularly with reference to the H_2O molecule, with a short outline of the most recent advances in ab-initio VB theory. Problems and solved problems conclude the Chapter as usual.

10.2 THE BORN–OPPENHEIMER APPROXIMATION

It concerns the separation, in molecules, of the *slow* motion of the nuclei from the *fast* motion of electrons. Let the molecular wave equation be:

$$\hat{H}\Psi = W\Psi, \tag{1}$$

where $\hat{H}$ is the molecular Hamiltonian[2]:

$$\begin{aligned}\hat{H} &= \sum_{\alpha} -\frac{1}{2M_\alpha}\nabla_\alpha^2 + \left\{\sum_i -\frac{1}{2}\nabla_i^2 + V_{en} + V_{ee}\right\} + V_{nn} \\ &= \sum_{\alpha} -\frac{1}{2M_\alpha}\nabla_\alpha^2 + \hat{H}_e + V_{nn}\end{aligned} \tag{2}$$

and $\hat{H}_e$ the electronic Hamiltonian:

$$\hat{H}_e = \sum_i -\frac{1}{2}\nabla_i^2 + V_{en} + V_{ee}. \tag{3}$$

The molecular wavefunction:

$$\Psi = \Psi(\mathbf{x}, \mathbf{q}) \tag{4}$$

is a function of the electronic coordinates **x** *and* of the nuclear coordinates **q**.

---

[2] M_α is the mass of nucleus α in units of the electron mass.

According to Born and Oppenheimer (1927), the heavier nuclei move so slowly that, in the average, electrons see only the position of nuclei and not their velocity. Therefore, Born–Oppenheimer assume that the electronic wavefunction Ψ_e will depend on the electron coordinates **x**, being only *parametric* in the q which describe the nuclear configuration:

$$\Psi \approx \Psi_e(\mathbf{x}; q)\Psi_n(\mathbf{q}). \tag{5}$$

The electronic wavefunction Ψ_e is assumed normalized and satisfying the electronic wave equation:

$$\hat{H}_e\Psi_e = E_e(q)\Psi_e \tag{6}$$

$$\langle\Psi_e|\Psi_e\rangle = \int d\mathbf{x}\,\Psi_e^*\Psi_e = 1, \tag{7}$$

where $E_e(q)$ is the electronic energy, which depends on the configuration q of the nuclei.

Considering $\Psi_e\Psi_n$ as a nuclear variation function with $\Psi_e =$ *fixed*, Longuet-Higgins (1961) showed that the best nuclear function satisfies the eigenvalue equation (Problem 10.1):

$$\left\{\sum_\alpha -\frac{1}{2M_\alpha}\nabla_\alpha^2 + \hat{U}_e(q)\right\}\Psi_n(q) = W\Psi_n(q), \tag{8}$$

where $\hat{U}_e(q)$ is a potential energy *operator* for the motion of the nuclei in the electron distribution of the molecule:

$$\begin{aligned}\hat{U}_e(q) = E_e(q) &+ V_{nn}\\ &-\sum_\alpha \frac{1}{2M_\alpha}\int dx\,\Psi_e^*\nabla_\alpha^2\Psi_e\\ &-\sum_\alpha \frac{1}{M_\alpha}\int dx\,\Psi_e^*\nabla_\alpha\Psi_e\cdot\nabla_\alpha.\end{aligned} \tag{9}$$

The last two terms in (9) describe the coupling between the motion of the nuclei and that of the electrons and are called *vibronic* terms. Since they are small in comparison with the first two terms in (9) (being of the order of $1/M_\alpha \approx 10^{-3}$), they can be overlooked in a first approximation. In this way, it is possible to define a *potential energy surface* for the motion of the nuclei in the field provided by the nuclei themselves and by the molecular electron charge distribution:

$$U_e(q) \approx E_e(q) + V_{nn} = E(q). \tag{10}$$

We shall refer to (10) as to the molecular energy in the Born–Oppenheimer approximation. In this approximation, the nuclear wave equation is:

$$\left\{\sum_\alpha -\frac{1}{2M_\alpha}\nabla_\alpha^2 + U_e(q)\right\}\Psi_n(q) = W\Psi_n(q), \tag{11}$$

where $U_e(q)$ acts as the "effective" potential for the nuclei. Equation (11) determines the nuclear motion (e.g. molecular vibrations) in the Born–Oppenheimer approximation, which is so familiar in spectroscopy. The *adiabatic* approximation includes the third term in (9), which describes the effect on Ψ_e of the nuclear Laplacian ∇_α^2, while the last term in (9) gives the effect on Ψ_e of the nuclear linear momentum $(-i\nabla_\alpha)$. Both these terms can be included perturbatively as small corrections, and are responsible for interesting structural effects in vibrational spectroscopy (Jahn–Teller and Renner effects). According to Jahn and Teller (1937), a non-linear polyatomic molecule in a degenerate ground state (usually, with high symmetry) is not stable, and the molecule necessarily distorts into a structure of lower symmetry where degeneracy is removed. A typical example is the photoionization of the CH_4 molecule:

$$\begin{aligned} CH_4(T_d, {}^1A_1) &\xrightarrow{h\nu} CH_4^+(T_d, {}^2T_2) \longrightarrow \text{Jahn–Teller instability} \\ &\longrightarrow CH_4^+(D_{4h}, {}^2A_{2u}). \end{aligned} \tag{12}$$

The CH_4^+ ion rearranges its geometry, through a tetragonal distortion, in a square planar configuration where the degeneracy of the ${}^2T_2$ electronic state is removed. Theoretical calculations of the Jahn–Teller distortion in CH_4^+ were done by Dixon (1971). The Jahn–Teller effect in XH_4^+ ions (X = C, Si, Ge, Sn) was observed experimentally through the splitting of the t_2 vibrational band in photoelectron spectra (Potts and Price, 1972).

Similar is the Renner effect (Renner, 1934), where the degenerate electronic states of a linear triatomic molecule are unstable, so that the molecule bends until degeneracy is removed.

10.3 THE CHEMICAL BOND IN H_2

We shall now examine the formation of the 2-electron chemical bond in the H_2 molecule in terms of elementary MO and VB theories using a minimal basis set of AOs centred at the two nuclei A and B. With reference to Figure 10.1, the molecular Hamiltonian for H_2 in the Born–Oppenheimer approximation will be:

$$\hat{H} = \hat{H}_e + \frac{1}{R} = \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} + \frac{1}{R}, \tag{13}$$

where $\hat{H}_e$ is the electronic Hamiltonian,

$$\hat{h} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} \tag{14}$$

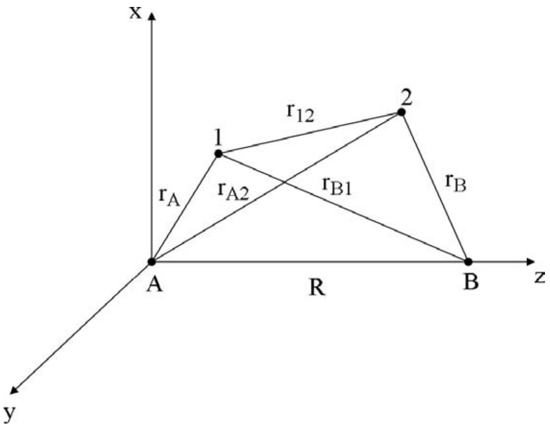


Figure 10.1 Reference system for the H_2 molecule.

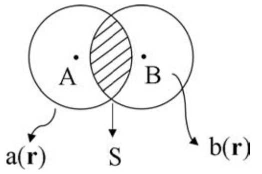


Figure 10.2 The overlap between $a(\mathbf{r})$ and $b(\mathbf{r})$ is the dashed area.

the 1-electron molecular Hamiltonian, and atomic units (a.u.) are used throughout.

In the first approximation, the two AOs are spherical $1s$ orbitals $a(\mathbf{r}_1)$ and $b(\mathbf{r}_2)$ centred at A and B, respectively, having an overlap S (the dashed area of Figure 10.2):

$$a(\mathbf{r}_1) = \frac{1}{\sqrt{\pi}} \exp(-r_{A1}) \tag{15}$$

$$b(\mathbf{r}_2) = \frac{1}{\sqrt{\pi}} \exp(-r_{B2}) \tag{16}$$

$$S = \langle a|b\rangle = \int d\mathbf{r}\, a(\mathbf{r})b(\mathbf{r}) = S(R). \tag{17}$$

The orbitals (15) and (16) are normalized $1s$ STOs with orbital exponent $c_0 = 1$.

10.3.1 Failure of the MO Theory for Ground State H_2

The one-configuration MO description of ground state H_2 is given by the 2-electron (normalized) singlet Slater determinant of doubly occupied σ_g MOs:

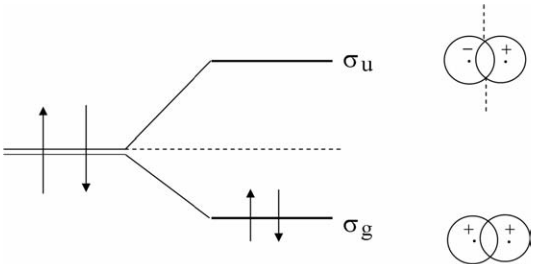


Figure 10.3 MO diagram of ground state H$_2$.

$$\Psi\left(\text{MO}, {}^1\Sigma_g^+\right) = \|\sigma_g\bar{\sigma}_g\| = \sigma_g(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)\frac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)] \tag{18}$$

where σ_g is the (normalized) bonding MO:

$$\sigma_g = \frac{a+b}{\sqrt{2+2S}}. \tag{19}$$

The corresponding (normalized) *antibonding* σ_u MO:

$$\sigma_u = \frac{b-a}{\sqrt{2-2S}} \tag{20}$$

is empty in the ground state (Figure 10.3).

We observe from Figure 10.3 that the splitting of the doubly degenerate atomic level under the interaction is non-symmetric for $S \neq 0$, the antibonding level being *more* repulsive and the bonding *less* attractive than the symmetric case occurring for $S = 0$. We further notice that the LCAO coefficients are in this case completely determined by symmetry. The MO energy for the ground state will be:

$$\begin{aligned} E\left(\text{MO}, {}^1\Sigma_g^+\right) &= \left\langle \Psi\left(\text{MO}, {}^1\Sigma_g^+\right) \middle| \hat{H} \middle| \Psi\left(\text{MO}, {}^1\Sigma_g^+\right) \right\rangle \\ &= \left\langle \sigma_g\sigma_g \middle| \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} + \frac{1}{R} \middle| \sigma_g\sigma_g \right\rangle \\ &= 2h_{\sigma_g\sigma_g} + \left(\sigma_g^2|\sigma_g^2\right) + \frac{1}{R}, \end{aligned} \tag{21}$$

where:

$$\begin{aligned} 2h_{\sigma_g\sigma_g} &= \frac{h_{aa} + h_{bb} + h_{ba} + h_{ab}}{1+S} \\ &= 2E_H + \frac{(a^2|V_B) + (b^2|V_A) + (ab|V_B) + (ba|V_A)}{1+S} \end{aligned} \tag{22}$$

$$(\sigma_g^2|\sigma_g^2) = \frac{\frac{1}{4}[(a^2|a^2) + (b^2|b^2)] + \frac{1}{2}(a^2|b^2) + (ab|ab) + (a^2|ba) + (b^2|ab)}{(1+S)^2}. \tag{23}$$

We have used for the 2-electron integrals the charge density notation:

$$\left(\overset{1}{ab} \mid \overset{2}{ab}\right) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\{a(\mathbf{r}_2)b^*(\mathbf{r}_2)\}}{r_{12}} \big\{a(\mathbf{r}_1)b^*(\mathbf{r}_1)\big\}. \tag{24}$$

The different terms in equations (22) and (23) have the following physical meaning:

$$(a^2|V_B) = \big(a^2| - r_B^{-1}\big) \tag{25}$$

is the attraction by the B nucleus of electron 1 distributed with the 1-centre density $a^2(\mathbf{r}_1)$;

$$(ab|V_B) = \big(ab| - r_B^{-1}\big) \tag{26}$$

the attraction by the B nucleus of electron 1 distributed with the 2-centre density $a(\mathbf{r}_1)b(\mathbf{r}_1)$;

$$(a^2|a^2) \tag{27}$$

the 1-centre electrostatic repulsion between the densities $a^2(\mathbf{r}_1)$ and $a^2(\mathbf{r}_2)$ both on A;

$$(a^2|b^2) \tag{28}$$

the 2-centre Coulomb integral, describing the electrostatic repulsion between the 1-centre densities $a^2(\mathbf{r}_1)$ on A and $b^2(\mathbf{r}_2)$ on B;

$$(ab|ab) \tag{29}$$

the 2-centre exchange integral, describing the electrostatic interaction between the 2-centre densities $a(\mathbf{r}_1)b(\mathbf{r}_1)$ and $a(\mathbf{r}_2)b(\mathbf{r}_2)$ shared between A and B;

$$(a^2|ab) \tag{30}$$

the 2-centre ionic (or hybrid) integral, describing the electrostatic repulsion between densities $a^2(\mathbf{r}_1)$ and $a(\mathbf{r}_2)b(\mathbf{r}_2)$.

The 2-centre integrals are evaluated in spheroidal coordinates $\mu = \frac{r_A+r_B}{R}$, $\nu = \frac{r_A-r_B}{R}$, φ in Chapter 13. We give here, for completeness, their analytic expression as a function of the internuclear distance R:

$$S = \langle a|b\rangle = \langle b|a\rangle = (ab|1) = \exp(-R)\left(1 + R + \frac{R^2}{3}\right) = S(R) \tag{31}$$

$$(a^2|r_B^{-1}) = \frac{1}{R} - \frac{\exp(-2R)}{R}(1+R) \tag{32}$$

$$(ab|r_B^{-1}) = \exp(-R)(1+R) \tag{33}$$

$$(a^2|b^2) = \frac{1}{R} - \frac{\exp(-2R)}{R}\left(1 + \frac{11}{8}R + \frac{3}{4}R^2 + \frac{1}{6}R^3\right) \tag{34}$$

$$(a^2|ab) = \frac{\exp(-R)}{R}\left(\frac{5}{16} + \frac{1}{8}R + R^2\right) - \frac{\exp(-3R)}{R}\left(\frac{5}{16} + \frac{1}{8}R\right) \tag{35}$$

$$\begin{aligned}(ab|ab) = \frac{1}{5}\Bigg\{&\exp(-2R)\left(\frac{25}{8} - \frac{23}{4}R - 3R^2 - \frac{1}{3}R^3\right)\\ &+ \frac{6}{R}[S^2(\gamma + \ln R) + S'^2 Ei(-4R) - 2SS' Ei(-2R)]\Bigg\},\end{aligned} \tag{36}$$

where:

$$S' = S(-R) = \exp(-R)\left(1 - R + \frac{R^2}{3}\right) \tag{37}$$

$$\gamma = 0.577\,215\,664\,9\cdots$$

is the Euler constant, and

$$Ei(-x) = -\int_x^\infty dt \frac{e^{-t}}{t} = -E_1(x) \tag{38}$$

the exponential integral function (Abramowitz and Stegun, 1965) defined for $x > 0$.

A few values to 7 significant figures of the 2-electron 2-centre integrals (34)–(36) are given in Table 10.1 as a function of R. The remaining 1-electron 2-centre integrals (31)–(33) were already given for H_2^+ in Table 5.10 of Chapter 5.

The interaction energy is obtained by subtracting to the molecular energy (21) the energy of the two ground state H atoms:

$$\Delta E\left({}^1\Sigma_g^+\right) = E\left({}^1\Sigma_g^+\right) - 2E_H = \Delta E^{\text{cb}} + \Delta E^{\text{exch-ov}}\left({}^1\Sigma_g^+\right), \tag{39}$$

where:

$$\Delta E^{\text{cb}} = \left(a^2\middle|V_B\right) + \left(b^2\middle|V_A\right) + (a^2|b^2) + \frac{1}{R} \tag{40}$$

is the semiclassical Coulombic interaction, and

$$\Delta E^{\text{exch-ov}}\left({}^1\Sigma_g^+\right) = \frac{(ab - Sa^2|V_B) + (ba - Sb^2|V_A)}{1+S}$$

$$+\left\{\frac{1}{4}\left[(a^2|a^2)+(b^2|b^2)\right]-\left(\frac{1}{2}+2S+S^2\right)(a^2|b^2)+(ab|ab)\right.$$

$$\left.+(a^2|ab)+(b^2|ba)\right\}/(1+S)^2 \tag{41}$$

the quantum mechanical component describing the exchange-overlap interaction between the charge distributions of the two H atoms, with its 1-electron (upper part) and 2-electron (lower part) contributions. The exchange-overlap (or penetration) component is a purely electronic quantum mechanical term arising from the Pauli principle: it depends on the nature of the spin coupling and is seen to give the largest contribution to the bond energy (the molecular energy at its minimum, in this case the energy of the chemical bond in the MO approximation). The MO description of this term is however affected by a large *correlation error*, which becomes evident at large distances, and is such that the simple MO wavefunction (18) cannot describe correctly the dissociation of $H_2(^1\Sigma_g^+)$ into two neutral H atoms in their ground state. Expression (39) for the MO interaction energy gives in fact:

$$\lim_{R\to\infty}\Delta E\big(\mathrm{MO},{}^1\Sigma_g^+\big)=\frac{1}{2}(a^2|a^2)=\frac{5}{16}E_h \tag{42}$$

corresponding to the erroneous dissociation:

$$\mathrm{H}_2\big({}^1\Sigma_g^+\big)\longrightarrow \mathrm{H}(^2S)+\frac{1}{2}\mathrm{H}^-(^1S). \tag{43}$$

In equation (42), $(a^2|a^2)$ is the 1-centre 2-electron repulsion integral between the 1-centre charge distributions $a^2(\mathbf{r}_1)$ and $a^2(\mathbf{r}_2)$ (both electrons on atom A) arising from the 2-electron part of $\Delta E^{\text{exch-ov}}(^1\Sigma_g^+)$. We shall see later in this Chapter that this large correlation

Table 10.1.

Numerical values (E_h) of the 2-electron 2-centre integrals occurring in the H_2 calculation as a function of R ($c_0=1$)

R/a_0	$(a^2\|b^2)$	$(a^2\|ab)$	$(ab\|ab)$
1.0	5.545214×10^{-1}	5.070449×10^{-1}	4.366526×10^{-1}
1.2	5.295794×10^{-1}	4.669873×10^{-1}	3.789989×10^{-1}
1.4	5.035210×10^{-1}	4.258827×10^{-1}	3.232912×10^{-1}
1.6	4.771690×10^{-1}	3.850683×10^{-1}	2.715583×10^{-1}
1.8	4.511638×10^{-1}	3.455494×10^{-1}	2.250001×10^{-1}
2.0	4.259743×10^{-1}	3.080365×10^{-1}	1.841565×10^{-1}
3.0	3.198035×10^{-1}	1.607424×10^{-1}	5.850796×10^{-2}
4.0	2.475539×10^{-1}	7.698167×10^{-2}	1.562720×10^{-2}
5.0	1.995691×10^{-1}	3.495304×10^{-2}	3.717029×10^{-3}
6.0	1.665926×10^{-1}	1.531146×10^{-2}	8.140232×10^{-4}
8.0	1.249979×10^{-1}	2.738738×10^{-3}	3.289596×10^{-5}

Table 10.2.

Numerical results (E_h) for MO calculations on ground state $H_2(^1\Sigma_g^+)$

	$c_0 = 1$, $R_e = 1.6a_0$[a]	$c_0 = 1.1695$, $R_e = 1.4a_0$[b]	HF, $R_e = 1.4a_0$[c]
$2h_{\sigma\sigma}$	$-1 - 1.277\,02$	$-1 - 1.485\,85$	
$(\sigma^2\|\sigma^2)$	$0.552\,94$	$0.643\,78$	
ΔE_h	$-0.724\,08$	$-0.842\,07$	$-0.847\,47$
$\frac{1}{R}$	$0.625\,00$	$0.714\,29$	$0.714\,29$
ΔE	$-0.099\,08$	$-0.127\,78$	$-0.133\,18$

[a] Hellmann (1937). [b] Coulson (1937). [c] Coulson (1938).

error, which is typical of the single determinant description of doubly occupied MOs, can be removed by configuration interaction (CI) between the configuration σ_g^2 and the doubly excited one σ_u^2.

In Table 10.2 are collected some numerical results for MO calculations on the ground state $^1\Sigma_g^+$ of the H_2 molecule in the bond region.

The accurate theoretical value for the bond energy at $R_e = 1.4a_0$ from Kołos and Wolniewicz (1965) is $\Delta E(^1\Sigma_g^+) = -0.174\,474 E_h$, as seen in Chapter 7.

The first column of Table 10.2 gives the MO results corresponding to the MO wavefunction (18), a calculation first done by Hellmann (1937). It can be seen that the resulting bond is too long (+14%) and the bond energy too small, no more than 57% of the correct one. So, the MO description in terms of *undistorted* $1s$ AOs ($c_0 = 1$) is largely insufficient even in the bond region.

The second column gives the MO results by Coulson (1937a), where the orbital exponent c_0 was variationally optimized at the different values at R. At the correct bond distance, $R_e = 1.4a_0$, the AOs in the molecule are sensibly *contracted* ($c_0 \approx 1.17$, spherical polarization), the bond energy being improved to about 73% of the true. Coulson's best variational values are $c_0 = 1.197$, $R_e = 1.38a_0$, $\Delta E = -0.128\,184 E_h$, respectively 98.6% and 73.4% of the correct values.

The third column gives the nearly HF values obtained by Coulson (1938b) using a 5-term expansion of the MOs in spheroidal coordinates. Coulson's calculation was later improved by Goodisman (1963), who used nine terms for each MO expansion, getting $R_e = 1.4a_0$ and $\Delta E = -0.133\,40 E_h$. This value is only $\Delta E = 0.000\,23 E_h$ above the correct HF/2D one given by Pyykkö and coworkers (Sundholm et al., 1985), $\Delta E = -0.133\,63 E_h$.

Table 10.3 gives the dependence on the internuclear distance R of the interaction energy and its Coulombic and exchange-overlap components ($10^{-3} E_h$) for the $^1\Sigma_g^+$ ground state of H_2 according to the MO wavefunction of equation (18) with $c_0 = 1$ in the $1s$ AOs (15) and (16).

Introducing the values for the 2-centre integrals, it can be seen that the Coulombic interaction energy has the analytic expression:

$$\Delta E^{\text{cb}} = \frac{\exp(-2R)}{R}\left(1 + \frac{5}{8}R - \frac{3}{4}R^2 - \frac{1}{6}R^3\right), \tag{44}$$

Table 10.3.

MO interaction energy and its components ($10^{-3}E_h$) for ground state H_2 ($c_0 = 1$)

R/a_0	ΔE^{cb}	$\Delta E^{\text{exch-ov}}$	$\Delta E(^1\Sigma_g^+)$
1.0	95.863	−81.761	14.102
1.2	28.879	−88.267	−59.388
1.4	−2.273	−88.670	−90.943
1.6	−15.354	−83.726	−99.079
1.8	−19.385	−74.410	−93.794
2.0	−19.079	−61.725	−80.803
3.0	−6.920	24.162	17.243
4.0	−1.6074	106.25	104.64
5.0	−0.3220	166.00	165.68
6.0	−0.0596	204.92	204.86
8.0	−0.001 79	244.42_5	244.23

which has a minimum of $\Delta E^{\text{cb}} = -19.6106 \times 10^{-3}E_h$ at $R_e = 1.8725a_0$, that can be found analytically by solving the quartic equation:

$$2R^4 + 7R^3 - 12R^2 - 12R - 6 = 0. \tag{45}$$

In the limit of the united atom, He(^1S), $B \to A$, $b \to a$, $S \to 1$, and the 2-centre integrals tend to their 1-centre counterpart (Section 7.3 of Chapter 13). The exchange-overlap component of the interaction energy tends to zero, so that the electronic energy becomes:

$$\begin{aligned}\lim_{R\to 0} E_e(\text{MO}, {}^1\Sigma_g^+) &= 2E_H + \lim_{R\to 0} \Delta_e E^{\text{cb}} + \lim_{R\to 0} \Delta_e E^{\text{exch-ov}} \\ &= 2E_H + \left[2\left(a^2|r_A^{-1}\right) + (a^2|a^2)\right] + \frac{1}{4}(a^2|a^2)\left(\frac{2}{4} - \frac{7}{2} + 3\right) \\ &= -1 - 2 + \frac{5}{8} = -3 + \frac{5}{8} = -\frac{19}{8}.\end{aligned} \tag{46}$$

On the other hand, for the united atom He(^1S):

$$E_e(\text{He}, {}^1S) = -Z^2 + \frac{5}{8}Z = -4 + \frac{5}{4} = -\frac{22}{8} \tag{47}$$

so that $E_e(R \to 0)$ is in error by $-\frac{3}{8} = -0.375E_h$. The variational optimization of c_0 ($c_0 = 1.6875$) removes this considerable error.

10.3.2 The Heitler–London Theory for H_2

The Heitler–London (HL) theory for H_2 is the simplest example of valence bond (VB) theory applied to the covalent part of the wavefunction for H_2. In VB theory, derived from the original work by Heitler and London (1927), the formation of a *covalent* bond between two atoms is possible if the atoms have, in their valence shell, orbitals containing *unpaired* electrons: the pairing to a singlet coupled state of two electrons with opposite spin yields the formation of a chemical bond between the two atoms. A basic requirement, which must always be satisfied, is that the resultant wavefunction must satisfy Pauli's exclusion principle or, in other words, it must be *antisymmetric* with respect to electron interchange.

For the ${}^1\Sigma_g^+$ ground state of H_2 in the minimum basis set (ab) of $1s$ AOs, these requirements are met by the HL wavefunction written as linear combination of the *two* Slater determinants:

$$\begin{aligned}\Psi\big(\mathrm{HL}, {}^1\Sigma_g^+\big) &= N\{\|a\bar{b}\| - \|\bar{a}b\|\}\\ &= \frac{a(\mathbf{r}_1)b(\mathbf{r}_2) + b(\mathbf{r}_1)a(\mathbf{r}_2)}{\sqrt{2+2S^2}}\frac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)].\end{aligned} \tag{48}$$

The HL energy for the ground state will be:

$$\begin{aligned}E\big(\mathrm{HL}, {}^1\Sigma_g^+\big) &= \big\langle\Psi\big(\mathrm{HL}, {}^1\Sigma_g^+\big)\big|\hat{H}\big|\Psi\big(\mathrm{HL}, {}^1\Sigma_g^+\big)\big\rangle\\ &= \left\langle\frac{ab+ba}{\sqrt{2+2S^2}}\right|\hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} + \frac{1}{R}\left|\frac{ab+ba}{\sqrt{2+2S^2}}\right\rangle\\ &= \frac{h_{aa} + h_{bb} + S(h_{ba} + h_{ab}) + (a^2|b^2) + (ab|ab)}{1+S^2} + \frac{1}{R}.\end{aligned} \tag{49}$$

But:

$$\begin{aligned}h_{aa} &= E_A + \big(a^2\big|V_B\big), \qquad & h_{bb} &= E_B + \big(b^2\big|V_A\big)\\ h_{ba} &= E_A S + (ab|V_B), \qquad & h_{ab} &= E_B S + (ba|V_A)\end{aligned} \tag{50}$$

so that:

$$\begin{aligned}E\big(\mathrm{HL}, {}^1\Sigma_g^+\big) = E_A + E_B&\\ &+ \big\{\big(a^2\big|V_B\big) + \big(b^2\big|V_A\big) + S[(ab|V_B) + (ba|V_A)] + (a^2|b^2)\\ &+ (ab|ab)\big\}\big/(1+S^2) + \frac{1}{R},\end{aligned} \tag{51}$$

where the first term is the sum of the energies of the individual ground state H atoms, and the second the interatomic energy for the ground state. All terms in (51) have the same meaning as for the MO expression.

The HL interaction energy is:

$$\Delta E\big(\mathrm{HL}, {}^1\Sigma_g^+\big) = E\big(\mathrm{HL}, {}^1\Sigma_g^+\big) - 2E_H = \Delta E^{\mathrm{cb}} + \Delta E^{\text{exch-ov}}\big({}^1\Sigma_g^+\big), \tag{52}$$

where ΔE^{cb} is the *same* as that for the MO expression (40), but where $\Delta E^{\text{exch-ov}}$ now simplifies to:

$$\begin{aligned}\Delta E^{\text{exch-ov}}\left({}^1\Sigma_g^+\right) &= \frac{S[(ab|V_B)+(ba|V_A)]+(ab|ab)-\Delta E_e^{\mathrm{cb}}S^2}{1+S^2}\\ &= S\frac{(ab-Sa^2|V_B)+(ba-Sb^2|V_A)}{1+S^2}+\frac{(ab|ab)-S^2(a^2|b^2)}{1+S^2}\\ &= \Delta E_1^{\text{exch-ov}}\left({}^1\Sigma_g^+\right)+\Delta E_2^{\text{exch-ov}}\left({}^1\Sigma_g^+\right). \end{aligned} \tag{53}$$

The exchange-overlap component (53) differs from the corresponding MO counterpart (41) in two respects: (i) the 1-electron part, $\Delta E_1^{\text{exch-ov}}({}^1\Sigma_g^+)$, differs from its MO counterpart by the factor $S(1+S)(1+S^2)^{-1}$, which shows the greater importance of *overlap* in the HL theory (generally, in VB theory); and (ii) the 2-electron part, $\Delta E_2^{\text{exch-ov}}({}^1\Sigma_g^+)$, is now remarkably simpler than its MO counterpart, and is characterized by the disappearance of the ionic and the atomic 2-electron integrals. At variance with the MO wavefunction (18), the HL wavefunction (48) allows now for a *correct* dissociation of the H_2 molecule into neutral ground state atoms:

$$\lim_{R\to\infty}\Delta E\left(\mathrm{HL},{}^1\Sigma_g^+\right)=0 \tag{54}$$

$$\mathrm{H}_2\left({}^1\Sigma_g^+\right)\longrightarrow 2\mathrm{H}({}^2S). \tag{55}$$

In the 1-electron part, $\Delta E_1^{\text{exch-ov}}({}^1\Sigma_g^+)$, appears, as already seen in the MO result (41), the exchange-overlap density $a(\mathbf{r}_1)b(\mathbf{r}_1)-Sa^2(\mathbf{r}_1)$, which has the interesting property of giving a zero contribution to the electronic charge:

$$\int d\mathbf{r}_1\left[a(\mathbf{r}_1)b(\mathbf{r}_1)-Sa^2(\mathbf{r}_1)\right]=S-S=0, \tag{56}$$

even if contributing in a relevant way to the exchange-overlap energy and, therefore, to the bond energy.

The HL function for the excited triplet state, ${}^3\Sigma_u^+$, is given by three functions having the *same* spatial part and differing for the spin part:

$$\begin{aligned}\Psi\left(\mathrm{HL},{}^3\Sigma_u^+\right) &= \begin{matrix}\|ab\| & S=1,\ M_S=1\\ N\{\|a\bar{b}\|+\|\bar{a}b\|\} & 0\\ \|\bar{a}\bar{b}\| & -1\end{matrix}\\ &= \frac{a(\mathbf{r}_1)b(\mathbf{r}_2)-b(\mathbf{r}_1)a(\mathbf{r}_2)}{\sqrt{2-2S^2}}\begin{cases}\alpha(s_1)\alpha(s_2)\\ \frac{1}{\sqrt{2}}\left[\alpha(s_1)\beta(s_2)+\beta(s_1)\alpha(s_2)\right]\\ \beta(s_1)\beta(s_2).\end{cases}\end{aligned} \tag{57}$$

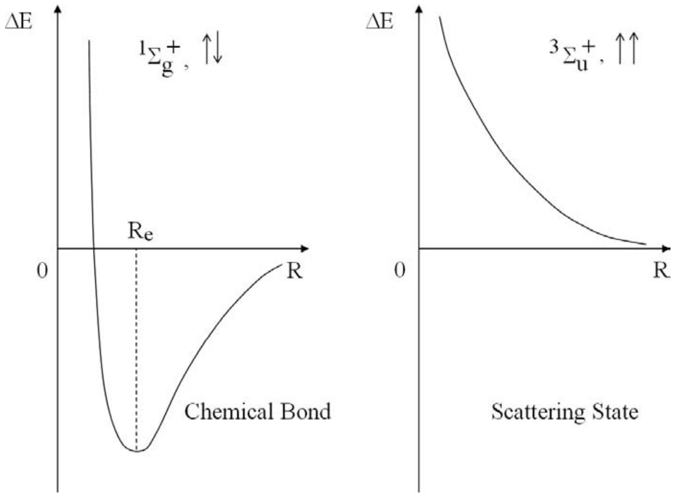


Figure 10.4 Schematic R-dependence of the HL interaction energies for H_2 for (i) left, singlet ground state, and (ii) right, excited triplet state.

The exchange-overlap component of the interaction energy for the triplet is *different* from that of the singlet ground state, and is given by:

$$\Delta E^{\text{exch-ov}}\left({}^3\Sigma_u^+\right) = -\frac{S[(ab|V_B) + (ba|V_A)] + (ab|ab) - \Delta E_e^{\text{cb}} S^2}{1 - S^2} > 0 \qquad (58)$$

so that it is *repulsive* for any R. Since $\Delta E^{\text{exch-ov}}({}^3\Sigma_u^+)$ is larger than ΔE^{cb}, the HL triplet interaction energy is always repulsive, describing a scattering (non bonded) state. The qualitative behaviour of the two states for H_2 is sketched in Figure 10.4.

Table 10.4 gives the dependence on the internuclear distance R of the interaction energy and its exchange-overlap component ($10^{-3} E^h$) for the ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ states of H_2 according to the HL wavefunctions in the minimum basis with $c_0 = 1$. The ΔE^{cb} component is the *same* as that for the MO wavefunction. In parenthesis are given the accurate theoretical values of Kołos and Wolniewicz (1965) obtained using an 80-term wavefunction expanded in spheroidal coordinates of the two electrons and containing explicitly r_{12} and the appropriate dependence on the hyperbolic functions of the ν-variables (see Section 7.10.3 of Chapter 7).

It can be seen from Table 10.4 that the HL results for both states of H_2 are only in *qualitative* agreement with the accurate theoretical results of Kołos and Wolniewicz (KW). For the ${}^1\Sigma_g^+$ ground state, the HL value at the correct $R_e = 1.4a_0$ is only 60.5% of the KW value, while at $R_e = 8a_0$ the HL result is only 33% of KW. For the ${}^3\Sigma_u^+$ excited state, all the HL values severely overestimate the accurate KW results. This is not surprising, however, since we have already said that the HL wavefunction can be considered only as the first approximation describing the interaction between *undistorted* H atoms. Accounting for polarization and dispersion (correlation) effects, what can be done in second order

Table 10.4.

HL interaction energies and their exchange-overlap components ($10^{-3}E_h$) for ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ states of H_2 ($c_0 = 1$) compared with accurate results[a]

R/a_0	$\Delta E^{\text{exch-ov}}$		ΔE	
	${}^1\Sigma_g^+$	${}^3\Sigma_u^+$	${}^1\Sigma_g^+$	${}^3\Sigma_u^+$
1.0	−92.286	609.045	3.576 (−124.54)[a]	704.91 (378.48)[a]
1.2	−100.865	478.110	−71.99 (−164.93)	506.99 (281.04)
1.4	−103.201	373.392	−105.47 (−174.47)	371.12 (215.85)
1.6	−100.356	290.217	−115.71 (−168.58)	274.86 (168.28)
1.8	−93.664	224.566	−113.05 (−155.07)	205.18 (131.71)
2.0	−84.473	173.037	−103.55 (−138.13)	153.96 (102.94)
3.0	−34.754	44.364	−41.674 (−57.31)	37.44 (27.99)
4.0	−9.678	10.397	−11.285 (−16.37)	8.790 (6.622)
5.0	−2.203	2.244	−2.525 (−3.763)	1.922 (1.315)
6.0	−0.4495	0.452	−0.5092 (−0.815)	0.392 (0.1875)
8.0	−0.0156	0.0156	−0.0174 (−0.053)	0.0138 (−0.0196)

[a] Kołos and Wolniewicz (1965).

of Rayleigh–Schroedinger perturbation theory (Chapter 12), greatly improves agreement with the accurate KW results, as shown by us elsewhere (Magnasco and Costa, 2005).

The results of Tables 10.3 and 10.4 for the ${}^1\Sigma_g^+$ ground state of H_2 are plotted against R in Figure 10.5. The qualitatively correct behaviour of the HL calculation during dissociation is evident from Figure 10.5, as is the incorrect MO behaviour in the same region of internuclear distance, with its exceedingly large correlation error, which asymptotically reaches the value of $312.5 \times 10^{-3}E_h$ (horizontal dashed line in Figure 10.5).

At variance with the ${}^1\Sigma_g^+$ ground state, Problem 10.2 shows the complete equivalence between MO and HL wavefunctions for the ${}^3\Sigma_u^+$ excited state.

10.3.3 Equivalence Between MO-CI and Full VB for Ground State H_2 and Improvements in the Wavefunction

In the minimal basis set (ab), it is possible to improve the HL *covalent* wavefunction for ground state H_2 by the variational mixing with the *ionic* wavefunction having the same symmetry:

$$\Psi\left(\text{ION}, {}^1\Sigma_g^+\right) = N\{\|a\bar{a}\| + \|b\bar{b}\|\}$$

$$= \frac{a(\mathbf{r}_1)a(\mathbf{r}_2) + b(\mathbf{r}_1)b(\mathbf{r}_2)}{\sqrt{2+2S^2}} \frac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)] \tag{59}$$

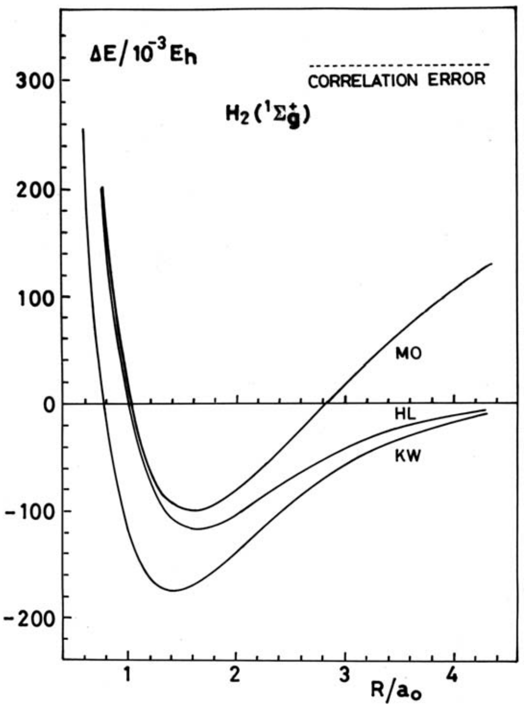


Figure 10.5 Plot vs R of MO, HL and KW interaction energies for the $^1\Sigma_g^+$ ground state of H_2.

which describes the two equivalent ionic VB structures H^-H^+ and H^+H^-. The complete VB wavefunction will be in general:

$$\Psi\left(\mathrm{VB}, {}^1\Sigma_g^+\right) = c_1\Psi\left(\mathrm{HL}, {}^1\Sigma_g^+\right) + c_2\Psi\left(\mathrm{ION}, {}^1\Sigma_g^+\right), \tag{60}$$

where c_1 and c_2 are variational coefficients to be determined by the Ritz method. At $R = 1.6a_0$, $c_1/c_2 \approx 0.138$, and the covalent (HL) structure gives the main contribution to the energy of the chemical bond.

It is possible to obviate the MO error by means of configuration interaction (CI). The possible electron configurations for H_2 are given in Figure 10.6.

We can mix only functions having the same symmetry, so that the interconfigurational wavefunction for ground state H_2 will be:

$$\Psi\left(\mathrm{MO-CI}, {}^1\Sigma_g^+\right) = c_1\Psi\left(\sigma_g^2, {}^1\Sigma_g^+\right) + c_2\Psi\left(\sigma_u^2, {}^1\Sigma_g^+\right). \tag{61}$$

This function describes correctly the dissociation of the H_2 molecule, and is completely equivalent to the full VB (HL + ION) function (60), provided all variational parameters are completely optimized (Problem 10.3):

$$\Psi\left(\mathrm{MO-CI}, {}^1\Sigma_g^+\right)$$

$$= N\left\{(ab+ba) + \frac{(1-S)+\lambda(1+S)}{(1-S)-\lambda(1+S)}(aa+bb)\right\}\frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha). \qquad (62)$$

For R large, $\lambda = c_2/c_1 \to -1$ (see Figure 10.7), $S \approx 0$ and $\Psi(\mathrm{MO-CI}, {}^1\Sigma_g^+) \to \Psi(\mathrm{HL}, {}^1\Sigma_g^+)$, the covalent HL structure which dissociates correctly. For intermediate values of R, the interconfigurational function $\Psi(\mathrm{MO-CI})$ reduces the weight of the ionic structures, which is 1 in the MO wavefunction.

Further improvements can be found by optimizing the molecular energy with respect to the non-linear parameter c_0, the orbital exponent of the $1s$ AOs ($c_0 = 1$ in the original HL theory). In such a way, it is possible to account for part of the *spherical distortion* of the AOs during the formation of the bond. The HL wavefunction with optimized c_0 satisfies the virial theorem:

$$2\langle T\rangle = -\langle V\rangle - R\frac{dE}{dR}, \qquad (63)$$

guaranteeing the correct partition of the expectation value of the molecular energy into its kinetic $\langle T\rangle$ and potential energy $\langle V\rangle$ components, which is not true for the original HL wavefunction with $c_0 = 1$. The dependence of c_0 on R is given in Figure 10.8.

The effect of improving the quality of the basic AOs (ab) on the bond energy ΔE at $R_e = 1.4a_0$ for the ${}^1\Sigma_g^+$ ground state of H_2, and the residual error with respect to the accurate value (Kołos and Wolniewicz, 1965), is shown in Table 10.5 for the covalent HL and in Table 10.6 for the full VB (HL + ION) wavefunctions.

We can see from Table 10.5 that admitting part of the spherical distortion of the H orbitals (second row) reduces the error by $33.58mE_h$ ($1mE_h = 10^{-3}E_h$), while the inclusion of some $p\sigma$ polarization (third row) improves the result by a further $8.69mE_h$. The best that can be done at the HL level with two non-linear parameters is the Inui result (fourth row of Table 10.5), where the error is reduced by another $1.41mE_h$.

The full VB results (Table 10.6) show a sensible improvement of $8.84mE_h$ for the Weinbaum wavefunction (second row), what means that admitting ionic structures partly accounts for higher polarizations. It is worth noting that the error with the second function of Table 10.6 is quite close to that of the third function of Table 10.5, where partial dipole polarization of the orbitals is admitted. The best bond energy value obtained by admitting the ionic structures in the two-parameter Inui wavefunction is however still $21.14mE_h$ above the correct value.

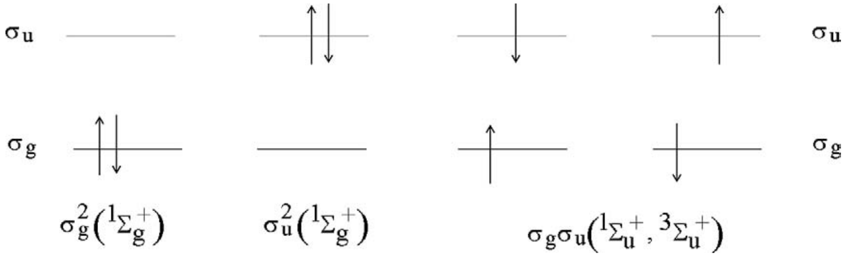


Figure 10.6 Ground state and excited electron configurations in H_2.

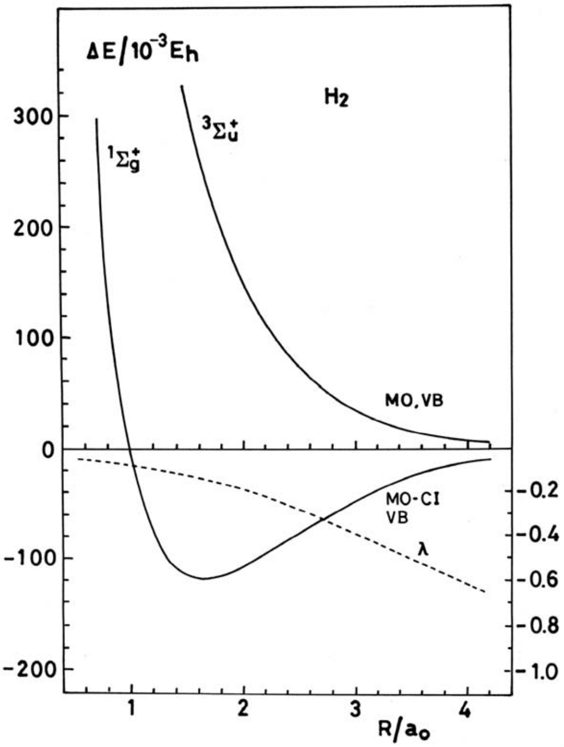


Figure 10.7 Plot vs R of interaction energies and mixing parameter λ (right scale) for ground and excited state of H_2.

For a further comparison we give in Table 10.7 the SDCI bond energy results for ground state H_2 at $R_e = 1.4a_0$, taken from Wright and Barclay (1987), who gradually added GTO polarization functions centred at the two nuclei to a starting $(9s) \to [4s]$ contracted GTO basis on each H atom. It can be seen that the SDCI value with only spherical functions is not far from the full VB Inui value (fourth row of Table 10.6), while convergence towards the correct value when including polarization functions with $l = 1, 2, 3$ is rather slow. Nonetheless, the final $4s3p2d1f$ result is within $0.5mE_h$ of the accurate KW result, and even better than the best 13-term result including r_{12} quoted in the classical paper by James and Coolidge (1933), $\Delta E = -173.45 \times 10^{-3} E_h$. In this last case, however, some inaccuracy is expected in the integral values.

We end this Section by quoting the interesting work by Coulson and Fischer (1949). They introduced the *semilocalized* AOs:

$$a' = \frac{a + \lambda b}{\sqrt{1 + \lambda^2 + 2\lambda S}}, \qquad b' = \frac{b + \lambda a}{\sqrt{1 + \lambda^2 + 2\lambda S}}, \tag{64}$$

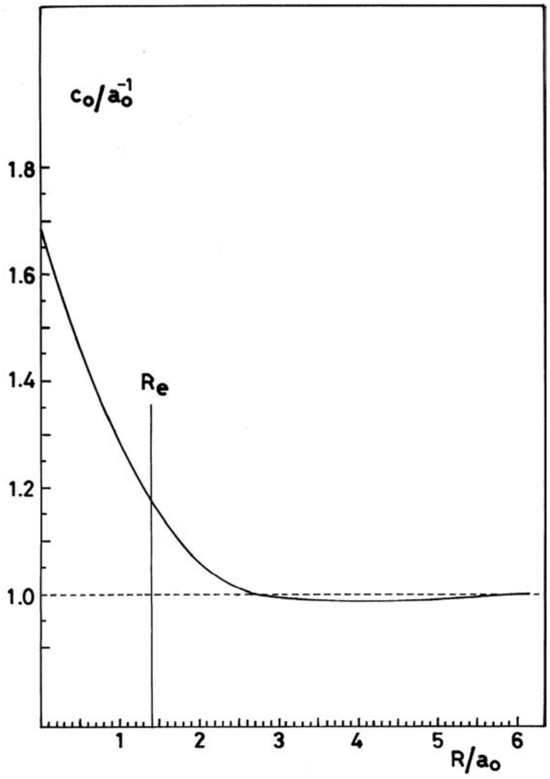


Figure 10.8 Dependence on R of optimized c_0 for ground state H_2.

that are normalized:

$$\langle a'|a'\rangle = \langle b'|b'\rangle = 1 \tag{65}$$

and have a non-orthogonality S':

$$S' = \langle a'|b'\rangle = \langle b'|a'\rangle = \frac{S\lambda^2 + 2\lambda + S}{1 + \lambda^2 + 2\lambda S}. \tag{66}$$

If $\lambda < 1$, a' is localized near nucleus A, and b' near nucleus B. We note that the Coulson–Fischer semilocalized AOs are 2-centre AOs containing a single *linear* variational parameter, while Inui AOs (Section 10.3 of Chapter 7) are 2-centre Guillemin–Zener AOs containing two *non-linear* variational parameters.

If we construct a HL symmetrical space function with Coulson–Fischer AOs (64), then the suitably normalized space part (omitting spin for short) will be:

$$\Psi' = \frac{a'(\mathbf{r}_1)b'(\mathbf{r}_2) + b'(\mathbf{r}_1)a'(\mathbf{r}_2)}{\sqrt{2 + 2S'^2}}, \tag{67}$$

Table 10.5.

Effect of improving the basic AOs in the covalent HL wavefunction on the bond energy ΔE at $R_e = 1.4a_0$ for ground state H_2, and residual error with respect to the accurate value

a	Basic AO	$\Delta E/10^{-3}E_h$	Error$/10^{-3}E_h$
1. $1s_A \propto \exp(-r_A)$ $(c_0 = 1)$	H $1s^a$	-105.47	69.00
2. $1s_A \propto \exp(-c_0 r_A)$ $(c_0 = 1.1695)$	STO $1s^b$	-139.05	35.42
3. $1s_A + \lambda' 2p\sigma_A$ $(c_0 = 1.19,\ c_p = 2.38,$ $\lambda' = 0.105)$	Dipole polarized AO (sp hybrid)^c	-147.74	26.73
4. $\exp(-\alpha r_A - \beta r_B)$ $(\alpha = 1.0889,\ \beta = 0.1287)$	2-centre GZ^d AO^e	-149.15	25.32
5. Accurate	f	-174.47	0

[a] Heitler and London (1927). [b] Wang (1928). [c] Rosen (1931). [d] Guillemin and Zener (GZ) (1929). [e] Inui (1938). [f] Kołos and Wolniewicz (1965).

Table 10.6.

Effect of improving the basic AOs in the full VB (HL + ION)[a] wavefunction on the bond energy ΔE at $R_e = 1.4a_0$ for ground state H_2, and residual error with respect to the accurate value

a	Basic AO	$\Delta E/10^{-3}E_h$	Error$/10^{-3}E_h$
1. $1s_A \propto \exp(-r_A)$ $(c_0 = 1,\ \lambda = 0.1174^a)$	H $1s^b$	-106.56	67.91
2. $1s_A \propto \exp(-c_0 r_A)$ $(c_0 = 1.193,\ \lambda = 0.2564)$	STO $1s^c$	-147.89	26.58
3. $1s_A + \lambda' 2p\sigma_A$ $(c_0 = 1.19,\ c_p = 2.38,$ $\lambda' = 0.07,\ \lambda = 0.1754)$	Dipole polarized AO (sp hybrid)^d	-151.49	22.98
4. $\exp(-\alpha r_A - \beta r_B)$ $(\alpha = 1.0889,\ \beta = 0.1287,$ $\lambda \approx 1)$	2-centre GZ AO^e	-153.33	21.14
5. Accurate	f	-174.47	0

[a] λ is the relative weight ION/COV. [b] Figari (1985). [c] Figari (1985). [d] Weinbaum (1933). [e] Ottonelli and Magnasco (1995). [f] Kołos and Wolniewicz (1965).

where S' is given by (66). Then:

(i) $\lambda = 0$ gives the ordinary HL wavefunction:

$$\Psi'(\lambda = 0) = \frac{a(\mathbf{r}_1)b(\mathbf{r}_2) + b(\mathbf{r}_1)a(\mathbf{r}_2)}{\sqrt{2+2S^2}}, \tag{68}$$

where *no* ionic structures are present;

Table 10.7.

SDCI bond energy[a] of ground state H_2 at $R_e = 1.4a_0$, and residual error with respect to the accurate value[b] for various GTO basis sets

GTO basis set	Number of functions	$\Delta E/10^{-3}E_h$	$\text{Error}/10^{-3}E_h$
$4s$	8	−154.32	20.15
$4s3p$	26	−171.83	2.64
$4s3p2d$	50	−173.75	0.72
$4s3p2d1f$	70	−173.97	0.50
Accurate[b]	80	−174.47	0

[a] Wright and Barclay (1987). [b] Kołos and Wolniewicz (1965).

(ii) $\lambda = 1$ gives the ordinary MO wavefunction:

$$\Psi'(\lambda = 1) = \frac{[a(\mathbf{r}_1) + b(\mathbf{r}_1)][b(\mathbf{r}_2) + a(\mathbf{r}_2)]}{2 + 2S}, \tag{69}$$

where the ionic structures have now the same weight of the covalent structure, which is the origin of the correlation error;

(iii) The variational optimization of λ at any given R gives the correct mixing between covalent and ionic structures, the same result that can be obtained by optimizing the linear parameter in (60). So, optimization of λ removes the correlation error and improves upon the HL result.

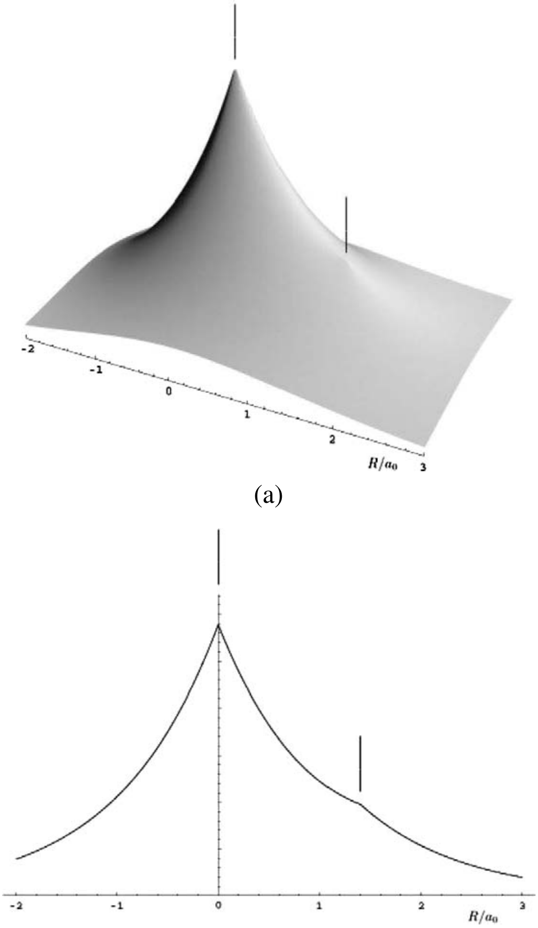
It can be shown (Magnasco and Peverati, 2004) that full optimization of c_0 and λ in the Heitler–London–Coulson–Fischer wavefunction (67) at $R_e = 1.4a_0$ ($c_0 = 1.2$, $\lambda = 0.135$, $S = 0.6744$) enhances interorbital overlap by over 18%, yielding a bond energy $\Delta E = -0.1478E_h$ which is practically coincident with that resulting from the Full-VB calculation with the original basis set. This is better than Rosen dipole polarized result of Table 10.5 and within 85% of the accurate bond energy of Kołos and Wolniewicz (1965). The resulting Coulson–Fischer orbital:

$$a' = 0.912\,81 s_A + 0.123\,11 s_B$$

is plotted in the 3-dimensional graph of Figure 10.9 with its section in the zx-plane. The cusp at nucleus A (origin of the coordinate system) and the small cusp at nucleus B due to delocalization are apparent from Figure 10.9. The exceptional performance of the Coulson–Fischer orbitals will be further discussed later in Section 10.7.

10.3.4 The Orthogonality Catastrophe in the Covalent VB Theory for Ground State H_2

In 1951 Slater pointed out that the *orthogonal* atomic orbitals (OAOs), first introduced by Wannier (1937) in solid state physics and next by Löwdin (1950) in molecular problems,



(a)

(b)

Figure 10.9 Coulson–Fischer optimized AO for ground state H_2 at $R_e = 1.4a_0$ (a) and its section in the zx-plane (b).

do not give a simple way of overcoming the non-orthogonality problem in the Heitler–London method. A HL calculation of the H_2 molecule ground state using these OAOs shows that no bond can be formed between H atoms since the molecular energy has no energy minimum. We saw before (first column of Table 10.4) that the HL exchange-overlap component $\Delta E^{\text{exch-ov}}$ of the bond energy is always *attractive* for the ${}^1\Sigma_g^+$ ground state of H_2, this being due to the 1-electron part of this quantum component. If we set $S = 0$ in equation (53), we see that:

$$\Delta E^{\text{exch-ov}}\left({}^1\Sigma_g^+, S = 0\right) = (ab|ab), \tag{70}$$

the 2-electron exchange integral, which is always positive. At the expected bond length of $R_e = 1.4a_0$, $\Delta E^{\text{cb}} = -2.273 \times 10^{-3} E_h$ (Table 10.3), $(ab|ab) = 323.3 \times 10^{-3} E_h$ (Table 10.1), so that $\Delta E(^1\Sigma_g^+) \approx 321 \times 10^{-3} E_h$, and we have a strong *repulsion* between the H atoms. This *orthogonality catastrophe* can however be overcome by admitting with a substantial weight the ionic structures in a complete VB calculation, as we shall see below. Let us now, in fact, investigate in greater detail the mixing of covalent (HL) and ionic VB structures for ground state H_2, starting either from ordinary (non-orthogonal) AOs or from Löwdin OAOs. For a correct comparison, it will be convenient to use values of the molecular integrals correct to 9 significant figures.

(i) Normalized *non-orthogonal* basis.

For $c_0 = 1$, $R = 1.4a_0$, the 1-electron 2-centre integrals can be taken from Table 10.10 of Chapter 5 and the 2-electron ones from Table 10.1 of this Chapter, but are given below with 9-figure accuracy. We then have:

$$\begin{aligned}
&S = 0.752\,942\,730 \\
&h_{aa} = h_{bb} = -1.110\,039\,890, \qquad h_{ba} = h_{ab} = -0.968\,304\,078 \\
&(a^2|b^2) = 0.503\,520\,926, \qquad (ab|ab) = 0.323\,291\,175, \\
&(a^2|ab) = 0.425\,882\,670.
\end{aligned} \tag{71}$$

Let (space part only):

$$\psi_1(\text{HL}) = \frac{ab + ba}{\sqrt{2 + 2S^2}}, \qquad \psi_2(\text{ION}) = \frac{aa + bb}{\sqrt{2 + 2S^2}}, \tag{72}$$

be the covalent (HL) and ionic VB wavefunctions for H_2, respectively. They are strongly non-orthogonal:

$$S_{12} = \langle \psi_1 | \psi_2 \rangle = \frac{2S}{1 + S^2} = 0.961\,046\,392, \tag{73}$$

showing that there is a strong linear dependence between them (at $R = 0$, they become identical). The matrix elements (E_h) of the molecular Hamiltonian $\hat{H}$ are:

$$\begin{aligned}
H_{11} &= \langle \psi_1 | \hat{H} | \psi_1 \rangle \\
&= (1 + S^2)^{-1}[h_{aa} + h_{bb} + S(h_{ba} + h_{ab})] \\
&\quad + (1 + S^2)^{-1}[(a^2|b^2) + (ab|ab)] + \frac{1}{R} \\
&= -0.347\,425\,747 + 0.527\,665\,403 + 0.714\,285\,714 \\
&= -1.105\,473\,880,
\end{aligned} \tag{74}$$

which is the result of the third column of Table 10.4 when truncated to the fifth decimal place.

$$\begin{aligned}H_{22} &= \langle\psi_2|\hat{H}|\psi_2\rangle\\ &= (1+S^2)^{-1}[h_{aa}+h_{bb}+S(h_{ba}+h_{ab})]\\ &\quad + (1+S^2)^{-1}\frac{1}{2}[(a^2|a^2)+(b^2|b^2)+2(ab|ab)]+\frac{1}{R}\\ &= -2.347\,425\,747+0.605\,192\,564+0.714\,285\,714\\ &= -1.027\,947\,468,\end{aligned} \tag{75}$$

so that the energy of the ionic state ($H^-H^+ + H^+H^-$) is higher than that of H−H.

$$\begin{aligned}H_{12} &= \langle\psi_1|\hat{H}|\psi_2\rangle\\ &= (1+S^2)^{-1}[S(h_{aa}+h_{bb})+(h_{ba}+h_{ab})]\\ &\quad + (1+S^2)^{-1}[(a^2|ab)+(b^2|ba)]+\frac{1}{R}S_{12}\\ &= -2.302\,730\,674+0.543\,591\,149+0.686\,461\,708\\ &= -1.072\,677\,817,\end{aligned} \tag{76}$$

so that covalent and ionic structures are also strongly interacting.

The pseudo-secular equation for the (non-orthogonal) ionic-covalent "resonance" in ground state H_2 will hence be:

$$\begin{vmatrix} H_{11}-E & H_{12}-ES_{12}\\ H_{12}-ES_{12} & H_{22}-E\end{vmatrix}=0, \tag{77}$$

which can be expanded to the quadratic equation in E:

$$\left(1-S_{12}^2\right)E^2-(H_{11}+H_{22}-2S_{12}H_{12})E+\left(H_{11}H_{22}-H_{12}^2\right)=0. \tag{78}$$

The *lowest* root E_1 will be:

$$E_1=\frac{H_{11}+H_{22}-2S_{12}H_{12}}{2(1-S_{12}^2)}-\frac{\Delta}{2(1-S_{12}^2)} \tag{79}$$

where:

$$\Delta=\left\{(H_{22}-H_{11})^2+4(H_{12}-H_{11}S_{12})(H_{12}-H_{22}S_{12})\right\}^{1/2}>0. \tag{80}$$

The numerical value of E_1 is:

$$E_1=-0.468\,873\,311-0.637\,683\,279=-1.106\,556\,590, \tag{81}$$

corresponding to a bond energy of:

$$\Delta E_1 = E_1 - 2E_H = -0.106\,556\,590 E_h, \tag{82}$$

in agreement with the first row of Table 10.6.

The mixing coefficients in the non-orthogonal basis are calculated as usual from:

$$\begin{cases} (H_{11} - E_1)c_1 + (H_{12} - E_1 S_{12})c_2 = 0 \\ c_1^2 + c_2^2 + 2c_1c_2S_{12} = 1 \end{cases} \tag{83}$$

giving:

$$\lambda = \left(\frac{c_2}{c_1}\right)_1 = \frac{E_1 - H_{11}}{H_{12} - E_1 S_{12}} = -0.117\,359\,290, \tag{84}$$

so that we finally obtain:

$$\Psi\left(\text{VB}, {}^1\Sigma_g^+\right) = \frac{\psi_1 + \lambda\psi_2}{\sqrt{1 + \lambda^2 + 2\lambda S_{12}}} = 0.898\,262\,463\psi_1 + 0.105\,419\,445\psi_2. \tag{85}$$

The relative weights of the non-orthogonal structures are then:

$$\%\text{HL} = c_1^2 + c_1c_2S_{12} = 89.79\%, \qquad \%\text{ION} = c_1c_2S_{12} + c_2^2 = 10.21\%. \tag{86}$$

Over the non-orthogonal basis the contribution of the two ionic structures is about 10%, as small as physically expected. It is worth noting that the *single* HL wavefunction built from the overlap-enhanced Coulson–Fischer AOs (64) with the optimum value $\lambda = 0.058\,883\,153$ gives a molecular energy $E = -1.106\,556\,590 E_h$, which coincides exactly to all figures with the Full-VB result (82). As a general rule, enhancing atomic overlap reduces the importance of the ionic structures. For the minimal basis set, we have therefore the complete *equivalence*:

$$E\left({}^1\Sigma_g^+\right) = \underset{\text{Full-VB (3 structures)}}{-1.106\,556\,590 E_h} = \underset{\substack{\text{Coulson–Fischer HL with} \\ \lambda = 0.058\,883\,153}}{-1.106\,556\,590 E_h}. \tag{87}$$

So, in the fully optimized Coulson–Fischer covalent wavefunction the ionic structures *disappear*.

(ii) Normalized *orthogonalized* basis.

To get the normalized orthogonal (OAO) basis, we do a Löwdin symmetrical orthogonalization (Chapter 2) of the original basis set, which gives:

$$\begin{aligned}\bar{a} &= 1.383\,585\,021a - 0.628\,290\,845b \\ \bar{b} &= 1.383\,585\,021b - 0.628\,290\,845a.\end{aligned} \tag{88}$$

We note (Slater, 1963) that Löwdin OAOs (88) are nothing but the Coulson–Fischer semi-localized AOs (64) when λ is chosen to be a solution of the quadratic equation[3]:

$$S\lambda^2 + 2\lambda + S = 0 \tag{89}$$

$$\lambda_1 = -\frac{1-(1-S^2)^{1/2}}{S}, \qquad \lambda_2 = -\frac{1+(1-S^2)^{1/2}}{S}. \tag{90}$$

Choosing the first root, λ_1, we obtain the relations (that can be checked either analytically or numerically):

$$\left(1+\lambda_1^2+2\lambda_1 S\right)^{1/2} = \frac{A+B}{2}, \qquad \lambda_1\left(1+\lambda_1^2+2\lambda_1 S\right)^{1/2} = \frac{A-B}{2}, \tag{91}$$

where (Löwdin)

$$A = (1+S)^{-1/2}, \qquad B = (1-S)^{-1/2}. \tag{92}$$

We now transform all integrals (71) to the OAO basis, obtaining:

$$\begin{aligned}&\bar{S} = 0, \qquad h_{\bar{a}\bar{a}} = -0.879\,663\,802, \qquad h_{\bar{b}\bar{a}} = -0.305\,967\,614 \\ &(\bar{a}^2|\bar{b}^2) = 0.426\,039\,142, \qquad (\bar{a}\bar{b}|\bar{a}\bar{b}) = 0.009\,878\,391, \\ &(\bar{a}^2|\bar{a}\bar{b}) = -0.005\,066\,793, \qquad (\bar{a}^2|\bar{a}^2) = 0.706\,541\,235.\end{aligned} \tag{93}$$

Löwdin's orthogonalization has the effect of reducing to some extent the 1-electron integrals, while drastically reducing the 2-electron integrals involving the 2-centre charge density $\bar{a}(\mathbf{r})\bar{b}(\mathbf{r})$.

The covalent (HL) and ionic VB structures in the OAO basis will be:

$$\bar{\psi}_1 = \frac{\bar{a}\bar{b}+\bar{b}\bar{a}}{\sqrt{2}} \qquad \bar{\psi}_2 = \frac{\bar{a}\bar{a}+\bar{b}\bar{b}}{\sqrt{2}}, \tag{94}$$

with the matrix elements:

$$\begin{aligned}\bar{H}_{11} &= \langle\bar{\psi}_1|\hat{H}|\bar{\psi}_1\rangle \\ &= h_{\bar{a}\bar{a}} + h_{\bar{b}\bar{b}} + (\bar{a}^2|\bar{b}^2) + (\bar{a}\bar{b}|\bar{a}\bar{b}) + \frac{1}{R}\end{aligned}$$

---

[3] We discovered a wrong sign in the denominator of equation (4-13) in Slater (1963) book.

$$
\begin{aligned}
&= -1.759\,327\,605 + 0.435\,917\,533 + 0.714\,285\,714 \\
&= -0.609\,124\,357, \qquad (95)
\end{aligned}
$$

so that:

$$\overline{H}_{11} - 2E_h = 0.390875649 \qquad (96)$$

describes *strong* repulsion. *The HL structure over the OAO basis does not allow to describe the formation of any bond in* H_2.

$$
\begin{aligned}
\overline{H}_{22} &= \langle \overline{\psi}_2 | \hat{H} | \overline{\psi}_2 \rangle \\
&= h_{\overline{a}\overline{a}} + h_{\overline{b}\overline{b}} + \frac{1}{2}[(\overline{a}^2|\overline{a}^2) + (\overline{b}^2|\overline{b}^2) + 2(\overline{a}\overline{b}|\overline{a}\overline{b})] + \frac{1}{R} \\
&= -1.759\,327\,605 + 0.716\,419\,626 + 0.714\,285\,714 \\
&= -0.328\,622\,265 \qquad (97)
\end{aligned}
$$

$$\overline{H}_{22} - 2E_h = 0.671\,377\,735 \qquad (98)$$

so that we get an even greater repulsion for the ionic state.

$$
\begin{aligned}
\overline{H}_{12} &= \langle \overline{\psi}_1 | \hat{H} | \overline{\psi}_2 \rangle \\
&= h_{\overline{b}\overline{a}} + h_{\overline{a}\overline{b}} + [(\overline{a}^2|\overline{a}\overline{b}) + (\overline{b}^2|\overline{b}\overline{a})] \\
&= -0.611\,935\,227 - 0.010\,133\,586 = -0.622\,068\,813, \qquad (99)
\end{aligned}
$$

which is sensibly smaller than the corresponding term (76) over the non-orthogonal basis.

The secular equation for the (orthogonalized) ionic-covalent "resonance" in ground state H_2 will hence be:

$$\begin{vmatrix} \overline{H}_{11} - E & \overline{H}_{12} \\ \overline{H}_{12} & \overline{H}_{22} - E \end{vmatrix} = 0, \qquad (100)$$

which expands to the quadratic equation in E:

$$E^2 - (\overline{H}_{11} + \overline{H}_{22})E + \left(\overline{H}_{11}\overline{H}_{22} - \overline{H}_{12}^2\right) = 0. \qquad (101)$$

The *lowest* root E_1 will be:

$$E_1 = \frac{\overline{H}_{11} + \overline{H}_{22}}{2} - \frac{\overline{\Delta}}{2}, \qquad (102)$$

where:

$$\overline{\Delta} = \left\{(\overline{H}_{22} - \overline{H}_{11})^2 + 4\overline{H}_{12}^2\right\}^{1/2} > 0. \qquad (103)$$

The numerical value of E_1 is now:

$$E_1 = -0.468\,873\,311 - 0.637\,683\,279 = -1.106\,556\,590 \tag{104}$$

$$\Delta E_1(^1\Sigma_g^+) = -0.106\,556\,590, \tag{105}$$

in perfect agreement with the value (82) obtained with the non-orthogonal basis. In this way, the chemical bond in H_2 has been restored through a strong CI with the ionic state!

The CI coefficients in the orthogonal basis are calculated from:

$$\begin{cases} (\overline{H}_{11} - E_1)\overline{c}_1 + \overline{H}_{12}\overline{c}_2 = 0 \\ \overline{c}_1^2 + \overline{c}_2^2 = 1 \end{cases} \tag{106}$$

giving:

$$\overline{\lambda} = \left(\frac{\overline{c}_2}{\overline{c}_1}\right)_1 = \frac{E_1 - \overline{H}_{11}}{\overline{H}_{12}} = 0.799\,641\,812, \tag{107}$$

a value which is about 7 times larger than the corresponding non-orthogonal value (84). The "resonance" between ionic and covalent VB structures in the OAO basis will be described by the wavefunction:

$$\overline{\Psi}(\text{VB}, {}^1\Sigma_g^+) = \frac{\overline{\psi}_1 + \overline{\lambda}\overline{\psi}_2}{\sqrt{1+\overline{\lambda}^2}} = 0.781\,005\,253\overline{\psi}_1 + 0.624\,524\,455\overline{\psi}_2, \tag{108}$$

where the structures have now the relative weights:

$$\%\text{HL} = \overline{c}_1^2 = 61\%, \qquad \%\text{ION} = \overline{c}_2^2 = 39\%. \tag{109}$$

In the orthogonalized basis, the contribution of the two ionic structures is about 4 times larger than the true value, a mathematical effect of the variational principle which has to restore the physical reality in the formation of the bond in H_2, that is its dependence on the effective overlap between the two H atoms[4].

Exactly the same effects were observed in an ab-initio OAO calculation of the short-range interaction in the H_2–H_2 system (Magnasco and Musso, 1968), where a small amount (less than 1%) of the charge-transfer states $H_2^-H_2^+$ and $H_2^+H_2^-$ was seen to give interaction energies which are in substantial agreement with those obtained from the complete VB treatment (Magnasco and Musso, 1967b).

---

[4] It is worth noting that exactly the same result can be obtained in terms of just the single covalent (HL) structure constructed from Coulson–Fischer AOs built from Löwdin OAOs (Magnasco and Peverati, 2004) for $\tilde{\lambda} = 0.499\,627\,110$. In the semilocalized Coulson–Fischer description, for this value of $\tilde{\lambda}$ the ionic structures disappear.

10.4 ELEMENTARY VALENCE BOND METHODS

In this Section we shall introduce elementary VB methods as an extension of the HL theory of H_2, comparing their feasibility with the corresponding MO formulation of the same problems. The theory will be mostly used in a qualitative way, just to outline how chemical intuition can be used to construct ad hoc VB wavefunctions for some simple representative molecules. Deviation from the so called "perfect-pairing approximation" (Coulson, 1961) will be discussed in terms of "resonance" between different structures. In a few cases (allyl radical, XeF_2, π electron system of the benzene molecule) symmetry arguments will enable us to draw conclusions on bonding and electron distribution without doing any effective calculation. The different nature of the multiple bonds in N_2, CO and O_2 will be evident from the VB description of their π systems, as well as the difference between Pauli repulsion in He_2 and the relatively strong σ bond in He_2^+. The general aim of the Section will be to show how brute force calculations can be avoided if chemical intuition can be used from the outset to concentrate effort on the physically relevant part of the electron bonding in molecules.

10.4.1 General Formulation of VB Theory

Originating from the work of Heitler and London (1927) on H_2 we have thoroughly discussed in the previous Section, VB theory was further developed by Slater and Pauling (1930–1940), McWeeny (1954a, 1954b), Goddard III (1967, 1968) up to the recent advances in the theory by Cooper et al. (1987). A modern group theoretical approach was also given by Gallup (1973, 2002). The most useful formulation for us is based on use of Slater determinants (dets).

As we have already said at the beginning of the previous Section, for describing the formation of a covalent bond between atoms A and B, each having orbitals a and b singly occupied by electrons with opposite spin, we start by writing the Slater det $\|a\bar{b}\|$[5], then interchange spin between the orbitals forming the bond, obtaining in this way a second Slater det $\|\bar{a}b\|$, which must be added to the first with the minus sign (singlet)[6]. It can be easily verified that in this way we obtain a molecular state where the total spin takes a definite value, and which is therefore eigenstate of $\hat{S}_z$ and $\hat{S}^2$ with eigenvalues M_S and S, respectively (covalent VB structure, $S = 0$ for the singlet).

The corresponding VB structures will be:

$$\Psi\left({}^1\Sigma_g^+\right) = N\{\|a\bar{b}\| - \|\bar{a}b\|\} \tag{110}$$

$$\Psi\left({}^3\Sigma_u^+\right) = N'\{\|a\bar{b}\| + \|\bar{a}b\|\}, \tag{111}$$

where N and N' are normalization factors. The first is the singlet ($S = M_S = 0$) VB structure describing a σ chemical bond (*attraction* between A and B), the second the triplet

---

[5] Called the *parent* det since all other dets can be derived from it by suitable spin interchanges.

[6] The plus sign will give the corresponding triplet state (as for H_2).

state ($S = 1$, $M_S = 0$) describing *repulsion* between A and B. By expanding the dets we see that the singlet and triplet functions can be written in the original HL form:

$$\Psi\left({}^1\Sigma_g^+\right) = \frac{ab + ba}{\sqrt{2 + 2S^2}} \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha) \qquad S = M_S = 0 \tag{112}$$

$$\Psi\left({}^3\Sigma_u^+\right) = \frac{ab - ba}{\sqrt{2 - 2S^2}} \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha) \qquad S = 1,\ M_S = 0 \tag{113}$$

with the corresponding components with $M_S = \pm 1$ for the latter (equation (57) of the previous Section).

Functions (110)–(113) are fully antisymmetric in the interchange of the space-spin coordinates of the two electrons and therefore satisfy the Pauli exclusion principle.

To each VB structure is usually assigned a Rumer *diagram*, which describes in a visible way the formation of a covalent bond between the two atoms A and B:

$$\Psi\left({}^1\Sigma_g^+\right) \Rightarrow \mathrm{A} - \mathrm{B} \tag{114}$$

the shared Lewis electron pair.

If both electrons are on A, or B, we have the ionic structures, in which doubly occupied AOs appear, and which are described by single Slater dets, which are already eigenfunctions of $\hat{S}^2$ with $S = 0$:

$$\Psi\left({}^1\Sigma_g^+\right) = \|a\bar{a}\| = aa\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha) \qquad A^-B^+ \tag{115}$$

$$\Psi\left({}^1\Sigma_g^+\right) = \|b\bar{b}\| = bb\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha) \qquad A^+B^-. \tag{116}$$

The relative weight of the different structures having the same symmetry is determined by the Ritz method by solving the appropriate secular equations arising from the linear combination of the VB structures. This may be not easy because of the possible non-orthogonalities between the structures themselves. It is important to note, and we shall see it later in this Section, that often VB structures are non-orthogonal even if they are built from orthonormal spin orbitals. As nearer are the molecular energies pertaining to each individual VB structure the mixing coefficients will tend to become nearer to each other, becoming *identical* in the case of "full resonance" between *equivalent* structures. In the calculation of the relative weights we must correctly take into account the non-orthogonality between the structures, as we did for H_2 in the previous Section of this Chapter.

We now schematize the elementary VB method and compare it with the corresponding schematization of the MO approach.

(i) Schematization of the VB method.

Basis of (spatial) atomic orbitals (AOs) → Atomic spin-orbitals (ASOs) → Antisymmetrized products (APs), i.e. Slater dets of order equal to the number of electrons (defined M_S) → VB structures, eigenstates of $\hat{S}^2$, defined S → Symmetry combination of VB structures → Multideterminant functions describing at the Full-VB level the electronic states of the molecule.

(ii) Schematization of the MO method.

Basis of atomic orbitals (AOs) → Molecular orbitals (MO) by the LCAO method, classified according to symmetry-defined types → Single Slater det of doubly occupied MOs (for singlet states), or combination of different dets with even singly occupied MOs (for non-singlet states) → MO-CI, among all dets with the same symmetry → Multideterminant functions describing at the MO-CI level the electronic states of the molecule.

Starting from the *same* basis of AOs, VB and MO methods are entirely equivalent at the end of each process, but may be deeply different at the early stages of each approach. The MO method has been more widely used, compared to the VB method, because for closed-shell molecules ($S = 0$, singlet) a single Slater det may be often sufficient as a first approximation, and for the further reasons we shall indicate below.

(iii) Advantages of the VB method.

1. The VB structures are related to the existence of chemical bonds in the molecule, the most important corresponding to the rule of "perfect pairing".
2. The principle of maximum overlap, better the minimum of the exchange-overlap bond energy (Magnasco and Costa, 2005), determines the stereochemistry of the bonds in a polyatomic molecule, hence the directed valency.
3. It allows for a correct dissociation of the chemical bonds, what is of paramount importance in chemical reactions.
4. It gives a sufficiently accurate description of spin densities, even at the most elementary level.
5. For small molecules, it is possible to account for about 80% of electronic correlation and to get bond distances within $0.02a_0$.

(iv) Disadvantages of the VB method.

1. Non-orthogonal basic AOs → Non-orthogonal VB structures → Difficulties in the evaluation of the matrix elements of the Hamiltonian (Slater rules are no longer valid).
2. The number of covalent VB structures of given S increases rapidly with the number n ($2n = N$) of the bonds, according to the Wigner formula:

$$f_S^N = \binom{2n}{n-S} - \binom{2n}{n-S-1} = \frac{(2S+1)(2n)!}{(n+S+1)!(n-S)!}. \tag{117}$$

An example for the π electron systems of a few polycyclic hydrocarbons is given in Table 10.8.

Table 10.8 makes it immediately evident the striking difference between the numbers of the second (Hückel) and the last column (VB). The situation is even worst if, besides covalent structures, we take ionic structures into account. In this

Table 10.8.

Comparison between the order of Hückel and VB secular equations for the singlet state of some polycyclic hydrocarbons

Molecule	$2n$	n	f_0^N
Benzene	6	3	5
Naphthalene	10	5	42
Anthracene	14	7	429
Coronene	24	12	208 012

case, the total number of structures, covalent plus all possible ionic, is given by the Weyl formula (Weyl, 1931; Mulder, 1966; McWeeny and Jorge, 1988):

$$f(N,m,S) = \frac{2S+1}{m+1}\binom{m+1}{\frac{N}{2}+S+1}\binom{m+1}{\frac{N}{2}-S}, \tag{118}$$

where N is the number of electrons, m the number of basic AOs, and S the total spin.

As an example, for the π electron system of benzene:

$$N=6, \qquad m=6, \qquad S=0 \qquad f(6,6,0)=175$$

singlet (covalent + ionic) VB structures.

$$N=6, \qquad m=6, \qquad S=1 \qquad f(6,6,1)=189$$

triplet (covalent + ionic) VB structures.

With a DZ basis set ($m = 12$), for $N = 6$ the singlet structures are:

$$N=6, \qquad m=12, \qquad S=0 \qquad f(6,12,0)=15730.$$

The total number of all possible VB structures is hence seen to increase very rapidly with the size of the basic AOs.

(v) Advantages of the MO method.
1. As a first approximation, singlet molecular states can be described in terms of a single Slater det of doubly occupied MOs.
2. The non-orthogonality of the basic AOs does not make any problem.
3. MOs are always orthogonal, even inside the same symmetry.
4. Electron configurations of molecules are treated on the same foot as are those for atoms.

(vi) Disadvantages of the MO method.
1. MO are delocalized over the different nuclei in the molecule and are not suitable for a direct chemical interpretation.

2. The single det cannot describe correctly the dissociation of the 2-electron bond.
3. The ionic part of the wavefunction is overestimated.
4. The single det of doubly occupied MOs does not describe whatever correlation between electrons with opposite spin.
5. MO spin densities are often inaccurate (see the allyl radical).

10.4.2 Construction of VB Structures for Multiple Bonds

It is convenient to use for the *parent* det (that describes which bonds are formed in the molecule) a shorthand notation, as the following example shows for the description of the triple bond in N_2:

$$\Psi\left({}^1\Sigma_g^+\right) = (\sigma_A\overline{\sigma}_B x_A\overline{x}_B y_A\overline{y}_B). \tag{119}$$

Equation (119) specifies the formation of a σ bond between orbitals $2p_{zA}$ and $2p_{zB}$ (possibly allowing for some sp hybridization, the z axis being directed from A to B along the bond), and two π bonds (perpendicular to the z axis) between $2p_{xA}$, $2p_{xB}$, and $2p_{yA}$, $2p_{yB}$. We have omitted for short the remaining eight electrons which are assumed to make a generalized "core" which, in the first approximation, is assumed to be "frozen" during the formation of the bond. In such a way, attention is focused on the physically relevant part of the triple bond. The advantage of this "short" notation (119) may be appreciated when compared with the "full" notation, which should involve the normalized Slater det of order 14 (the number of electrons in N_2):

$$\Psi = \| \underbrace{1s_A\overline{1s}_A 1s_B\overline{1s}_B 2s_A\overline{2s}_A 2s_B\overline{2s}_B}_{\text{core}} | \underbrace{\sigma_A\overline{\sigma}_B x_A\overline{x}_B y_A\overline{y}_B}_{\text{triple bond}} \|. \tag{120}$$

For the moment, we shall not take into consideration hybridization, that is the mixing between $2s$ and $2p\sigma$ AO onto the *same* centre. The parent (119) is a normalized Slater det which is eigenstate of $\hat{S}_z$ with $M_S = 0$, but not as yet eigenstate of $\hat{S}^2$. To obtain the singlet VB structure (eigenstate of $\hat{S}^2$ with $S = 0$) we must do in the parent det all possible spin interchanges between the AOs forming the bonds (σ or π), taking into account that for each interchange we must change the sign of the det which is being added (minus sign for an odd number of interchanges, plus sign for an even number). The complete covalent VB function for ground state N_2 is hence made by the linear combination of the following eight Slater dets:

$$\begin{aligned}\Psi\left({}^1\Sigma_g^+\right) = \frac{1}{\sqrt{8}}\big\{&(\sigma_A\overline{\sigma}_B x_A\overline{x}_B y_A\overline{y}_B)\\ &- (\overline{\sigma}_A\sigma_B x_A\overline{x}_B y_A\overline{y}_B) - (\sigma_A\overline{\sigma}_B\overline{x}_A x_B y_A\overline{y}_B) - (\sigma_A\overline{\sigma}_B x_A\overline{x}_B\overline{y}_A y_B)\\ &+ (\overline{\sigma}_A\sigma_B\overline{x}_A x_B y_A\overline{y}_B) + (\overline{\sigma}_A\sigma_B x_A\overline{x}_B\overline{y}_A y_B) + (\sigma_A\overline{\sigma}_B\overline{x}_A x_B\overline{y}_A y_B)\\ &- (\overline{\sigma}_A\sigma_B\overline{x}_A x_B\overline{y}_A y_B)\big\}\end{aligned} \tag{121}$$

which belongs to the eigenvalue $S = 0$ as can be easily shown by using Dirac's formula for $\hat{S}^2$. It is worth noting that all doubly occupied orbitals do not contribute to S, and can therefore be omitted in the calculation of the total spin. The normalization factor in (121) assumes orthonormal Slater dets. We give in the following other simple examples.

10.4.3 The Allyl Radical ($N = 3$)

Consider the π system of the allyl radical $C_3H_5^\bullet$ as given in Figure 10.10, where attention has to be focused only on the π electron system (top in Figure 10.10), and where below each chemical structure we write the parent det.

We see that the parent is the *same* in the two resonant VB structures (which are fully equivalent), but the linear combination of Slater dets is *different*, since in ψ_1 we have a bond between a and b, in ψ_2 between b and c:

$$\psi_1 = \frac{1}{\sqrt{2}}\left[(a\bar{b}c) - (\bar{a}bc)\right] \quad S = M_S = \frac{1}{2} \tag{122}$$

$$\psi_2 = \frac{1}{\sqrt{2}}\left[(a\bar{b}c) - (ab\bar{c})\right] \quad S = M_S = \frac{1}{2}. \tag{123}$$

As said before, the notation omits the description of the twenty electrons of the "frozen core", formed by the electrons of the three inner shells of the C atoms, the two C—C bonds and the five C—H bonds. Even assuming orthonormal spin-orbitals, as we shall do, the two covalent structures describing the doublet state of the radical are non-orthogonal:

$$S_{12} = \langle\psi_1|\psi_2\rangle = \frac{1}{2}. \tag{124}$$

It will be shown in Problem 10.4 that if we Schmidt orthogonalize ψ_1 to ψ_2, the resulting orthogonalized set is in one-to-one correspondence with the two spin doublets found

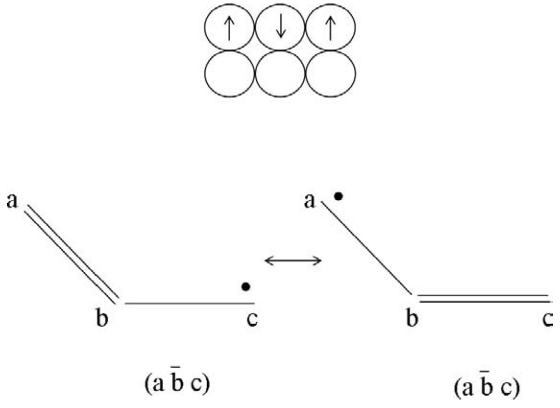


Figure 10.10 The two resonant chemical structures of the π electrons in allyl radical.

in Chapter 6 using pure spin functions. In other words the two VB structures ψ_1 and ψ_2 constructed using the physically appealing elementary method are not linearly independent, while Schmidt orthogonalization gives two linearly independent functions which, however, have lost their simple graphical representation.

The electronic structure of the π system in the allyl radical is hence given by the resonant VB function:

$$\Psi = \psi_1 c_1 + \psi_2 c_2 \tag{125}$$

where, because of symmetry:

$$c_1 = c_2 = \frac{1}{\sqrt{3}} \tag{126}$$

since:

$$\langle \Psi | \Psi \rangle = c_1^2 + c_2^2 + 2c_1 c_2 S_{12} = 3c_1^2 = 1. \tag{127}$$

Knowing Ψ from (125), we can immediately calculate the π electron and spin density distributions in the allyl radical, an interesting example of population analysis in multideterminant wavefunctions. The 1-electron distribution function from (125) will be:

$$\begin{aligned}
\rho_1 &= 3\iint d\mathbf{x}_2\, d\mathbf{x}_3 \Psi\Psi^* = c_1^2\left[3\iint d\mathbf{x}_2\, d\mathbf{x}_3 \psi_1\psi_1^*\right] \\
&\quad + c_2^2\left[3\iint d\mathbf{x}_2\, d\mathbf{x}_3 \psi_2\psi_2^*\right] + c_1c_2\left[3\iint d\mathbf{x}_2\, d\mathbf{x}_3 (\psi_1\psi_2^* + \psi_2\psi_1^*)\right] \\
&= c_1^2\left[\frac{1}{2}(a^2+c^2)\alpha\alpha^* + \frac{1}{2}b^2\beta\beta^* + \frac{1}{2}a^2\beta\beta^* + \frac{1}{2}(b^2+c^2)\alpha\alpha^*\right] \\
&\quad + c_2^2\left[\frac{1}{2}(a^2+c^2)\alpha\alpha^* + \frac{1}{2}b^2\beta\beta^* + \frac{1}{2}(a^2+b^2)\alpha\alpha^* + \frac{1}{2}c^2\beta\beta^*\right] \\
&\quad + c_1c_2\left\{2\left[\frac{1}{2}(a^2+c^2)\alpha\alpha^* + \frac{1}{2}b^2\beta\beta^*\right]\right\},
\end{aligned} \tag{128}$$

where we used Slater's rules for orthonormal determinants.

We then have:

$$\begin{aligned}
\rho_1^\alpha &= \text{coefficient of } \alpha\alpha^* \text{ in } \rho_1 \\
&= a^2\left(\frac{1}{2}c_1^2 + c_2^2 + c_1c_2\right) + b^2\left(\frac{1}{2}c_1^2 + \frac{1}{2}c_2^2\right) + c^2\left(c_1^2 + \frac{1}{2}c_2^2 + c_1c_2\right)
\end{aligned} \tag{129}$$

$$\rho_1^\beta = \text{coefficient of } \beta\beta^* \text{ in } \rho_1$$

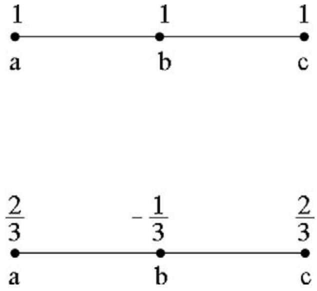


Figure 10.11 π electron (top) and spin density (bottom) VB distributions in allyl radical.

$$= a^2\left(\frac{1}{2}c_1^2\right) + b^2\left(\frac{1}{2}c_1^2 + \frac{1}{2}c_2^2 + c_1c_2\right) + c^2\left(\frac{1}{2}c_2^2\right) \tag{130}$$

$$\begin{aligned} P(\mathbf{r}) &= \rho_1^\alpha(\mathbf{r}) + \rho_1^\beta(\mathbf{r}) = \left(c_1^2 + c_2^2 + c_1c_2\right)\left(a^2 + b^2 + c^2\right) \\ &= a^2 + b^2 + c^2 \end{aligned} \tag{131}$$

$$\begin{aligned} Q(\mathbf{r}) &= \rho_1^\alpha(\mathbf{r}) - \rho_1^\beta(\mathbf{r}) = a^2\left(c_2^2 + c_1c_2\right) - b^2(c_1c_2) + c^2\left(c_1^2 + c_1c_2\right) \\ &= \frac{2}{3}a^2 - \frac{1}{3}b^2 + \frac{2}{3}c^2. \end{aligned} \tag{132}$$

(131) shows that the allyl radical has a *uniform* charge distribution of its π electrons (as it must be for an *alternant* hydrocarbon), while if atoms a and c have spin α there is some spin β at the central atom b. At variance with MO theory (Section 8.4 of Chapter 7), VB theory correctly predicts the existence of some β-spin at the central atom when some α-spin is present at the external atoms, a result which agrees with the experimental ESR spectra of the radical.

The π electron and spin density VB distributions in the allyl radical are shown in Figure 10.11.

The relative weights of the two resonant (non-orthogonal) structures in the ground state of the allyl radical will be:

$$\%\psi_1 = c_1^2 + c_1c_2S_{12} = \frac{1}{3} + \frac{1}{3}\cdot\frac{1}{2} = \frac{1}{2} \tag{133}$$

$$\%\psi_2 = c_2^2 + c_2c_1S_{12} = \frac{1}{3} + \frac{1}{3}\cdot\frac{1}{2} = \frac{1}{2} \tag{134}$$

as expected on symmetry grounds.

10.4.4 Cyclobutadiene ($N = 4$)

Consider the π system of cyclobutadiene as given in Figure 10.12.

Even in this case, the parent det is the *same* in either resonant VB structures but the π bonds are *different*, so that the singlet ($S = M_S = 0$) structures are:

$$\psi_1 = \frac{1}{2}\left[(a\bar{b}c\bar{d}) - (\bar{a}bc\bar{d}) - (a\bar{b}\bar{c}d) + (\bar{a}b\bar{c}d)\right] \tag{135}$$

$$\psi_2 = \frac{1}{2}\left[(a\bar{b}c\bar{d}) - (\bar{a}\bar{b}cd) - (ab\bar{c}\bar{d}) + (\bar{a}b\bar{c}d)\right]. \tag{136}$$

Even these VB structures are non-orthogonal, since the first and the fourth det in each structure are equal:

$$S_{12} = \langle \psi_1 | \psi_2 \rangle = \frac{1}{2}. \tag{137}$$

The electronic structure of the π system in cyclobutadiene is given by the resonant VB function:

$$\Psi = \psi_1 c_1 + \psi_2 c_2 \tag{138}$$

where again, by symmetry:

$$c_1 = c_2 = \frac{1}{\sqrt{3}} \tag{139}$$

since:

$$\langle \Psi | \Psi \rangle = c_1^2 + c_2^2 + 2c_1c_2S_{12} = 3c_1^2 = 1. \tag{140}$$

A calculation similar to that in the allyl radical shows that now:

$$\rho_1^\alpha = (a^2 + b^2 + c^2 + d^2)\left(\frac{c_1^2}{4} + \frac{c_1^2}{4} + \frac{c_2^2}{4} + \frac{c_2^2}{4} + \frac{2}{4}c_1c_2\right)$$

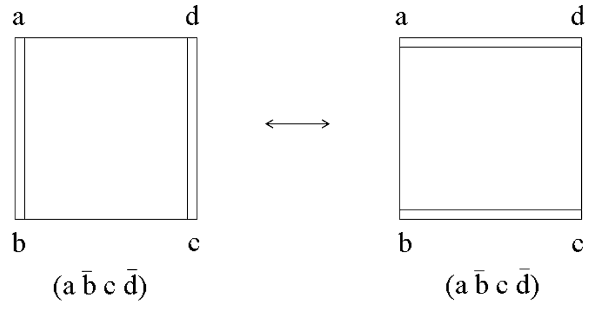


Figure 10.12 The two resonant chemical structures of the π electrons in cyclobutadiene.

$$
\begin{aligned}
&= (a^2+b^2+c^2+d^2)\frac{1}{2}(c_1^2+c_2^2+c_1c_2)\\
&= \frac{1}{2}(a^2+b^2+c^2+d^2) = \rho_1^\beta
\end{aligned}
\tag{141}
$$

so that:

$$
P(\mathbf{r}) = \rho_1^\alpha(\mathbf{r}) + \rho_1^\beta(\mathbf{r}) = a^2+b^2+c^2+d^2 \tag{142}
$$

$$
Q(\mathbf{r}) = \rho_1^\alpha(\mathbf{r}) - \rho_1^\beta(\mathbf{r}) = 0 \tag{143}
$$

and the electron charge distribution of the π electrons in cyclobutadiene is *uniform*, as expected for alternant hydrocarbons, whereas the spin density is zero (singlet state).

10.4.5 VB Description of Simple Molecules

We shall now give a few further examples of the VB description of chemical bonds in simple molecules, assuming in the first approximation that (i) only valence electrons are considered, (ii) all electrons not directly involved in the formation of the bond of interest are assumed "frozen", and (iii) hybridization is not taken into account. This allows us for the *qualitative* VB description of a few diatomic molecules and for the study of the electronic structure and charge distribution of XeF_2 and O_3, while for the H_2O molecule hybridization becomes crucial in the VB study of directed valency. *Quantitative* calculations would imply the evaluation of the matrix elements of the Hamiltonian between these structures and the solution of the related secular equations.

(i) $LiH(^1\Sigma^+)$.

$$
\begin{array}{lcc}
\mathrm{Li}(^2S)\colon\ 1s_{\mathrm{Li}}^2 s & \mathrm{H}(^2S)\colon\ h & \\
\text{Covalent structure} & \text{Ionic structures} & \\
\mathrm{Li{-}H} & \mathrm{Li^+H^-} & \mathrm{Li^-H^+} \\
(s\,\bar{h}) & (h\,\bar{h}) & (s\,\bar{s})
\end{array}
\tag{144}
$$

where:

$$
\begin{aligned}
(s\,\bar{h}) &= \|1s_{\mathrm{Li}}\overline{1s}_{\mathrm{Li}}\,s\,\bar{h}\|\\
(h\,\bar{h}) &= \|1s_{\mathrm{Li}}\overline{1s}_{\mathrm{Li}}\,h\,\bar{h}\|\\
(s\,\bar{s}) &= \|1s_{\mathrm{Li}}\overline{1s}_{\mathrm{Li}}\,s\,\bar{s}\|
\end{aligned}
\tag{145}
$$

are the short notations for the 4-electron normalized Slater dets. $(s\,\bar{h})$ is the *parent* for the covalent function for Li−H. The full singlet VB structure describing resonance between covalent and ionic structures in Li−H will be:

$$
\Psi(^1\Sigma^+) \propto \left[(s\,\bar{h}) - (\bar{s}h)\right] + \lambda_1(h\,\bar{h}) + \lambda_2(s\,\bar{s}), \tag{146}
$$

where λ_1 and λ_2 must be determined by the Ritz method. Because of the different electronegativities of Li and H, it is expected that $\lambda_1 \gg \lambda_2$.

(ii) FH($^1\Sigma^+$).

$$\begin{array}{cc} \mathrm{F}(^2P)\text{: } 1s_{\mathrm{F}}^2 2s_{\mathrm{F}}^2 2p\pi_{\mathrm{F}}^4 2p\sigma_{\mathrm{F}} & \mathrm{H}(^2S)\text{: } h \\ \text{Covalent structure} & \text{Ionic structures} \\ \mathrm{F{-}H} & \mathrm{F^-H^+} \quad \mathrm{F^+H^-} \\ (\sigma_{\mathrm{F}}\,\overline{h}) & (\sigma_{\mathrm{F}}\,\overline{\sigma}_{\mathrm{F}}) \quad (h\,\overline{h}) \end{array} \tag{147}$$

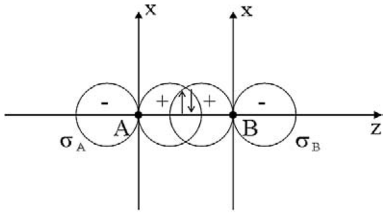
$$\Psi(^1\Sigma^+) \propto \left[(\sigma_{\mathrm{F}}\,\overline{h}) - (\overline{\sigma}_{\mathrm{F}} h)\right] + \lambda_1(\sigma_{\mathrm{F}}\,\overline{\sigma}_{\mathrm{F}}) + \lambda_2(h\,\overline{h}) \tag{148}$$

with $\lambda_1 > \lambda_2$.

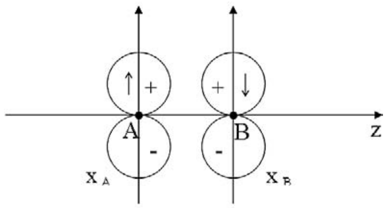
(iii) $\mathrm{N_2}\left(^1\Sigma_g^+\right)$ N≡N triple bond.

$$\mathrm{N_A}(^4S)\text{:} \quad 1s_{\mathrm{N_A}}^2 2s_{\mathrm{N_A}}^2 \sigma_A x_A y_A \quad \sigma = 2p\sigma = 2p_z \tag{149}$$

$$\mathrm{N_B}(^4S)\text{:} \quad 1s_{\mathrm{N_B}}^2 2s_{\mathrm{N_B}}^2 \sigma_B x_B y_B \quad x = 2p\pi_x = 2p_x. \tag{150}$$



Covalent σ-bond: $(\sigma_A\bar{\sigma}_B)$ - $(\bar{\sigma}_A\sigma_B)$



Covalent π_x-bond: $(x_A\bar{x}_B)$ - $(\bar{x}_A x_B)$

Figure 10.13 Covalent σ and π_x bonds in $\mathrm{N_2}$.

The triple bond in N_2 will be described by the *parent*:

$$\left(\sigma_A\overline{\sigma}_B\, x_A\overline{x}_B\, y_A\overline{y}_B\right) \tag{151}$$

while the full singlet ($S = M_S = 0$) VB covalent structure will be given by the combination of the eight Slater dets of equation (121). We can likely introduce ionic VB structures N^-N^+, N^+N^- in terms of $(\sigma_A\overline{\sigma}_A)$, $(\sigma_B\overline{\sigma}_B)$, $(x_A\overline{x}_A)$, $(x_B\overline{x}_B)$, and so on.

(iv) $CO\left({}^1\Sigma^+\right)$.

$$C({}^3P):\quad 1s_C^2 2s_C^2\, \sigma_C x_C y_C^0 \quad \text{or} \quad x_C^0 y_C \tag{152}$$

$$O({}^3P):\quad \underbrace{1s_O^2 2s_O^2}_{\text{core}}\, \underbrace{\sigma_O x_O y_O^2}_{\text{valence}} \quad \text{or} \quad x_O^2 y_O. \tag{153}$$

The three most important covalent VB structures in $CO({}^1\Sigma^+)$ all have a heteropolar σ bond between σ_C and σ_O. The peculiarity of CO (isoelectronic with N_2) comes from its π system, as shown in Figure 10.14. In (a), we have a heteropolar π_x bond between x_C and x_O, not shown in the figure, a lone pair y_O^2, while y_C^0 is empty. In (b), a heteropolar π_y bond between y_C and y_O, a lone pair x_O^2, and x_C^0 is empty. This will induce an *electron transfer* from the doubly occupied lone pair orbitals to the empty orbitals of the other atom, giving (c) as the most probable structure showing that an *ionic triple bond* is formed in CO. The bond is ionic, with polarity C^-O^+, since now seven electrons are on carbon, seven electrons on oxygen. Of course, the truth will be given by the variational determination of the mixing coefficients between the three VB structures associated with the parents of Figure 10.14. This will reduce strongly the molecular dipole moment of CO, being in the opposite sense of the σ and π heteropolar effects going in the sense C^+O^-. This

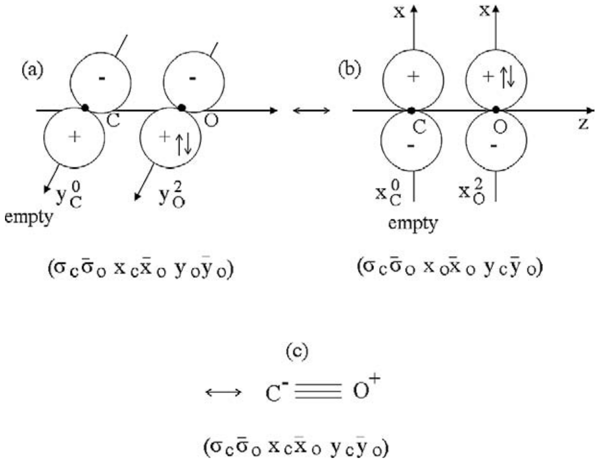


Figure 10.14 Parent dets in ground state CO.

is experimentally observed, and the result of accurate theoretical calculations (Maroulis, 1996), which give $\mu(\mathrm{C^-O^+}) = -0.04ea_0$.

Therefore, the VB function describing the mixing of the *covalent* structures of Figure 10.14, will be:

$$\Psi_1(\mathrm{COV}, {}^1\Sigma^+) = \psi_1 c_1 + \psi_2 c_2 + \psi_3 c_3, \tag{154}$$

where:

$$\begin{aligned}\psi_1 = \frac{1}{2}\big[&(\sigma_\mathrm{C}\bar{\sigma}_\mathrm{O}x_\mathrm{C}\bar{x}_\mathrm{O}y_\mathrm{O}\bar{y}_\mathrm{O}) - (\bar{\sigma}_\mathrm{C}\sigma_\mathrm{O}x_\mathrm{C}\bar{x}_\mathrm{O}y_\mathrm{O}\bar{y}_\mathrm{O})\\ &- (\sigma_\mathrm{C}\bar{\sigma}_\mathrm{O}\bar{x}_\mathrm{C}x_\mathrm{O}y_\mathrm{O}\bar{y}_\mathrm{O}) + (\bar{\sigma}_\mathrm{C}\sigma_\mathrm{O}\bar{x}_\mathrm{C}x_\mathrm{O}y_\mathrm{O}\bar{y}_\mathrm{O})\big]\end{aligned} \tag{155}$$

$$\begin{aligned}\psi_2 = \frac{1}{2}\big[&(\sigma_\mathrm{C}\bar{\sigma}_\mathrm{O}x_\mathrm{O}\bar{x}_\mathrm{O}y_\mathrm{C}\bar{y}_\mathrm{O}) - (\bar{\sigma}_\mathrm{C}\sigma_\mathrm{O}x_\mathrm{O}\bar{x}_\mathrm{O}y_\mathrm{C}\bar{y}_\mathrm{O})\\ &- (\sigma_\mathrm{C}\bar{\sigma}_\mathrm{O}x_\mathrm{O}\bar{x}_\mathrm{O}\bar{y}_\mathrm{C}y_\mathrm{O}) + (\bar{\sigma}_\mathrm{C}\sigma_\mathrm{O}x_\mathrm{O}\bar{x}_\mathrm{O}\bar{y}_\mathrm{C}y_\mathrm{O})\big],\end{aligned} \tag{156}$$

while ψ_3 is given by the linear combination of eight Slater dets as in (121) with $A = C$, $B = O$.

To Ψ_1 we must add variationally the corresponding *ionic* function $\Psi_2(\mathrm{ION}, {}^1\Sigma^+)$ describing the polarity of σ and π bonds in CO.

(v) Pauli repulsion between closed shells.

A typical example is the interaction between two ground state He atoms which, each having the closed-shell electron configuration $1s^2$, cannot give any chemical bond and therefore, in the first approximation[7] (one-determinant, no correlation), must repel each other. In this case, VB and MO descriptions coincide.

$$\mathrm{He}_2\big({}^1\Sigma_g^+\big) \qquad 1s_\mathrm{A} = a, \qquad 1s_\mathrm{B} = b$$

$$\Psi\big(\mathrm{VB}, {}^1\Sigma_g^+\big) = \|a\bar{a}b\bar{b}\| = \|\sigma_g\bar{\sigma}_g\sigma_u\bar{\sigma}_u\| = \Psi\big(\mathrm{MO}, {}^1\Sigma_g^+\big) \tag{157}$$

as can be seen immediately from the properties of determinants and the Pauli principle (Problem 10.5). The electron density contributed by the 4 electrons of the two atoms is:

$$\begin{aligned}P(\mathbf{r}) &= 2\sigma_g^2(\mathbf{r}) + 2\sigma_u^2(\mathbf{r})\\ &= \frac{2}{1-S^2}(a^2+b^2) - \frac{2S}{1-S^2}\left(\frac{ab}{S} + \frac{ba}{S}\right)\\ &= q_A a^2(\mathbf{r}) + q_B b^2(\mathbf{r}) + q_{AB}\frac{a(\mathbf{r})b(\mathbf{r})}{S} + q_{BA}\frac{b(\mathbf{r})a(\mathbf{r})}{S}\end{aligned} \tag{158}$$

---

[7] Attraction forces due to interatomic electron correlation are described at the multiconfiguration level.

with:

$$q_A = q_B = \frac{2}{1-S^2} > 2, \qquad q_{AB} = q_{BA} = -\frac{2S^2}{1-S^2} < 0, \tag{159}$$

a result similar to that observed for triplet H_2 (Problem 7.4 of Chapter 7). In $He_2(^1\Sigma_g^+)$, as in $H_2(^3\Sigma_u^+)$, electrons escape from the bond region originating repulsion (the overlap charge is *negative*). Recent ab-initio calculations of the Pauli repulsion in He_2 (Magnasco and Peverati, 2004) show that a simple optimized $1s$ basis set gives fair values at $R = 3a_0$ ($c_0 = 1.691$, $\Delta E = 12.964 \times 10^{-3} E_h$) and $R = 4a_0$ ($c_0 = 1.688$, $\Delta E = 1.073 \times 10^{-3} E_h$), which compare favourably either with the accurate theoretical SCF calculations by Liu and McLean (1973) ($\Delta E = 13.52 \times 10^{-3} E_h$, $\Delta E = 1.355 \times 10^{-3} E_h$, respectively) or even better with the experimental results by Feltgen et al. (1982). In the latter case, however, it is expected that our actual 1-determinant underestimation of the interaction will compensate, in part, for the effect of the attractive London forces.

A like repulsion is observed between closed-shell molecules, or between pairs of saturated bonds or electron lone pairs in molecules (Pauli repulsion). Pauli repulsion between C—H bonds is at the origin of the torsional barrier in ethane C_2H_6, as shown by Musso and Magnasco (1982) using an improved bond orbital wavefunction supplemented by small correction terms accounting for electron delocalization. The theory was then analyzed in terms of localized singlet VB structures revealing bonding and charge transfer occurring between the four electrons involved in each excitation (Magnasco and Musso, 1982), and successfully extended to the study of nineteen flexible molecules possessing a single internal rotation angle about a B—N, C—C, C—N, C—O, N—N, N—O, O—O central bond (Musso and Magnasco, 1984). The molecules possess 16 to 34 electrons and a variety of functional groups differing in their chemical structure (CH_3, NH_2, OH, NO, CHO, CH=CH_2, NH=, and some of their F-derivatives).

(vi) 3-electron bonds.

While the bond in H_2^+ can be considered as the prototype of the 1-electron bond, we saw that the great part of σ or π chemical bonds is made by 2-electron bonds, agreeing with Lewis' idea of the bond electron pair. There are, however, cases where we observe the formation of 3-electron bonds like, for example, in He_2^+ and O_2.

(a) The 3-electron σ bond in He_2^+.

At variance with the Pauli repulsion in $He_2(^1\Sigma_g^+)$, it is possible to form a rather strong chemical bond between a neutral $He(1s^2)$ atom and a $He^+(1s)$ ion: $He_2^+(^2\Sigma_u^+)$ exists and is fairly stable (Huber and Herzberg, 1979), $\Delta E = -90.78 \times 10^{-3} E_h$ at $R_e = 2.04a_0$ (compare $\Delta E = -102.6 \times 10^{-3} E_h$ at $R_e = 2a_0$ for ground state H_2^+). For the VB theory, He_2^+ is the prototype of the 3-electron σ bond.

$$He_2^+(^2\Sigma_u^+)$$

$$He(^1S)\colon\ 1s^2 \qquad He^+(^2S)\colon\ 1s \qquad 1s_A = a, \qquad 1s_B = b. \tag{160}$$

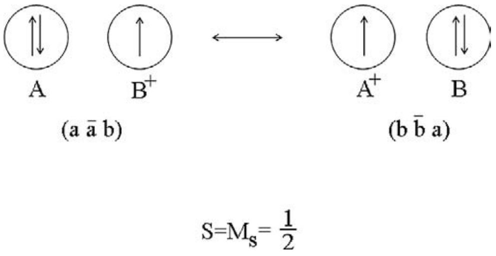


Figure 10.15 Parent dets in ground state He_2^+.

In this case, the parents coincide with the VB structures (they are eigenfunctions of $\hat{S}^2$ with $S = M_S = 1/2$). By symmetry, the two structures must have equal weight, so that the complete VB function with the correct symmetry (u under inversion) will be:

$$\Psi_1(^2\Sigma_u^+) = \frac{1}{\sqrt{2}}\left[\|a\bar{a}b\| - \|b\bar{b}a\|\right] \quad S = \frac{1}{2},\ M_S = \frac{1}{2} \tag{161}$$

$$\Psi_2(^2\Sigma_u^+) = \frac{1}{\sqrt{2}}\left[\|a\bar{a}\bar{b}\| - \|b\bar{b}\bar{a}\|\right] \quad S = \frac{1}{2},\ M_S = -\frac{1}{2}. \tag{162}$$

It is clear that for each component of the doublet:

$$\begin{aligned} \hat{\imath}\Psi_1 &= \frac{1}{\sqrt{2}}\left[\|b\bar{b}a\| - \|a\bar{a}b\|\right] = -\Psi_1 \\ \hat{\imath}\Psi_2 &= \frac{1}{\sqrt{2}}\left[\|b\bar{b}\bar{a}\| - \|a\bar{a}\bar{b}\|\right] = -\Psi_2 \end{aligned} \tag{163}$$

so that Ψ is odd (u) under inversion. As for He_2 it might be shown that:

$$\Psi_1(\text{VB}, {}^2\Sigma_u^+) = \|\sigma_g\bar{\sigma}_g\sigma_u\| \tag{164}$$

$$\Psi_2(\text{VB}, {}^2\Sigma_u^+) = \|\sigma_g\bar{\sigma}_g\bar{\sigma}_u\| \tag{165}$$

so that, even in this case, VB and MO descriptions coincide.

Recent ab-initio calculations on He_2^+ ($^2\Sigma_u^+$) (Magnasco and Peverati, 2004) show that the simple optimized $1s$ basis set gives a fair representation of the potential energy curve in the bond region, with a calculated bond energy of $\Delta E = -90.50 \times 10^{-3} E_h$ at $R = 2.06a_0$ ($c_0 = 1.832$), in excellent agreement with the experimental results quoted above (Huber and Herzberg, 1979) and the results of accurate theoretical calculations by Liu (1971).

(b) The 3-electron π bonds in O_2.

$O_2(^3\Sigma_g^-)$	One 2-electron σ bond	Two 3-electron π bonds

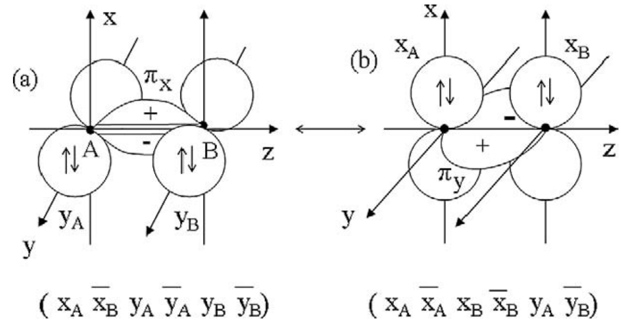


Figure 10.16 Parent dets in singlet ground state O_2.

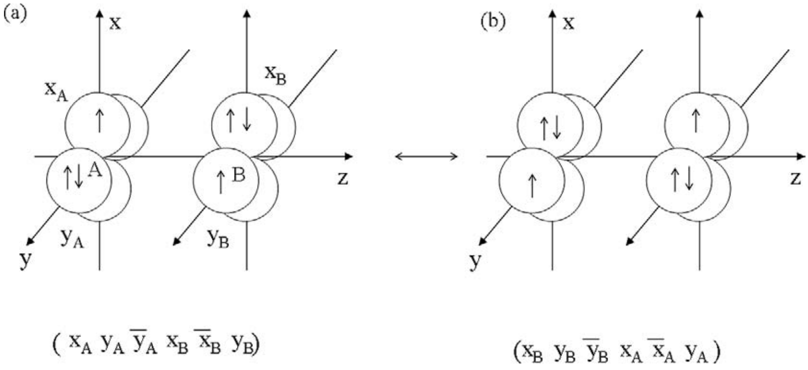


Figure 10.17 Parent dets in triplet ground state O_2.

$$O_A(^3P): \quad 1s_A^2 2s_A^2 \sigma_A x_A y_A^2 \quad \text{or} \quad x_A^2 y_A \tag{166}$$

$$O_B(^3P): \quad \underbrace{1s_B^2 2s_B^2}_{\text{core}} \underbrace{\sigma_B x_B y_B^2}_{\text{valence}} \quad \text{or} \quad x_B^2 y_B. \tag{167}$$

There are four possible covalent VB structures for ground state O_2.

- Two equivalent *singlet* ($S = M_S = 0$) structures.

The singlet VB structures associated with the parents of Figure 10.16 (a π_x bond with two y-lone pairs, a π_y bond with two x-lone pairs) cannot be very stable because of the strong Pauli repulsion between electron lone pairs having the same symmetry (the lone pairs lie in the *same* yz- or zx-plane).

- Two equivalent *triplet* ($S = 1$) structures.

The triplet VB structures associated with the parents of Figure 10.17 are expected to be much more stable, since the two lone pairs are now in *perpendicular* planes with a strong reduction of repulsive effects and, what is more interesting, the possibility of forming two equivalent 3-electron π bonds (Wheland, 1937). Omitting the doubly occupied orbitals, in an ultrashort notation, the VB function describing the covalent triplet state of ground state O_2 will be:

$$\Psi(\text{VB}, {}^3\Sigma_g^-) = \begin{cases} \frac{1}{\sqrt{2}}[(x_A y_B) + (x_B y_A)] & S = 1, M_S = 1 \\ \frac{1}{2}[(x_A \overline{y}_B) + (\overline{x}_A y_B) + (x_B \overline{y}_A) + (\overline{x}_B y_A)] & 0 \\ \frac{1}{\sqrt{2}}[(\overline{x}_A \overline{y}_B) + (\overline{x}_B \overline{y}_A)]. & -1 \end{cases} \tag{168}$$

It can be verified (Problem 8.16 of Chapter 8) that Ψ simultaneously satisfies the following eigenvalue equations:

$$\begin{aligned} \hat{S}^2\Psi &= 1(1+1)\Psi, & \hat{L}_z\Psi &= 0 \cdot \Psi \\ \hat{\sigma}\Psi &= -\Psi, & \hat{\imath}\Psi &= \Psi \end{aligned} \tag{169}$$

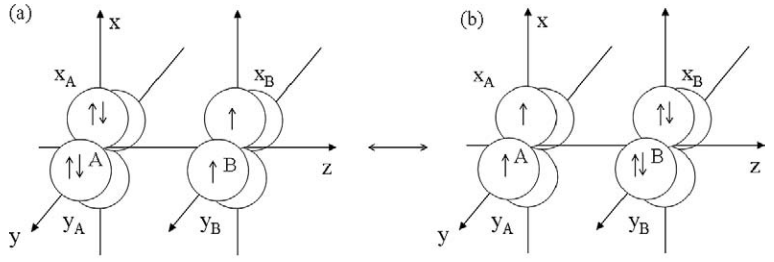
so that Ψ correctly describes a ${}^3\Sigma_g^-$ state (σ is chosen as the symmetry zx plane). At variance with the MO wavefunction, the VB function (168) correctly describes the dissociation of $O_2({}^3\Sigma_g^-)$ into two neutral $O({}^3P)$ atoms.

(c) Ionic structures in triplet O_2.

For the triplet ground state of the O_2 molecule we can have the O^-O^+ and O^+O^- ionic structures shown in Figure 10.18.

These ionic structures, which we saw to have erroneously a weight equal to that of the covalent structure in the MO wavefunction of H_2, are expected to have some importance in O_2 in view of the acceptable energetic cost needed to form O^-O^+ (and O^+O^-) from the neutral atoms. In fact:

$$O({}^3P)2p^4 \rightarrow O^+({}^4S)2p^3 + e^- \qquad \text{I.P.} = 13.6 \text{ eV} \tag{170}$$



$(x_A \overline{x}_A y_A \overline{y}_A x_B y_B)$ $(x_A y_A x_B \overline{x}_B y_B \overline{y}_B)$

Figure 10.18 Parent dets for ionic structures in triplet O_2.

$$O(^3P)2p^4 + e^- \to O^-(^2P)2p^5 \qquad \text{E.A.} = 1.5 \text{ eV} \tag{171}$$

so that, at the bond distance $R_e = 2.28a_0$, we have in the first approximation:

$$\text{I.P.} - \text{E.A.} - \frac{1}{R_e} = 13.6 - 1.5 - \frac{27.21}{2.28} = 0.17 \text{ eV} = 6.1 \times 10^{-3} E_h, \tag{172}$$

where the last term is surely overestimated at this value of R since we do not take into account charge-overlap effects damping the Coulomb attraction between the ions. A VB calculation at R_e (McWeeny, 1990) with a DZ-GTO basis set yields:

$$\Psi = 0.59\psi_{\text{cov}} - 0.23\psi_{\text{ion}} \tag{173}$$

with a rather large ionic contribution to the VB wavefunction. However, this may be not unexpected since it is well known that DZ basis sets tend to overestimate the polarity of the molecule. The Pauli repulsion still existing between electron lone pairs even in orthogonal planes, but on the same atom, does not certainly contribute to the stability of the ionic structures in triplet O_2. The symmetry of the ionic VB structures associated with the parents of Figure 10.18 is studied in detail in Problem 10.6.

(vii) XeF_2 ($D_{\infty h}$).

XeF_2 is a centrosymmetric linear molecule (symmetry $D_{\infty h}$) with an experimental $\text{Xe}-\text{F} = 4a_0$, which has been studied by Coulson (1964).

$$\text{Xe}(^1S)\text{: } 5s^2 5p\pi^4 5p\sigma^2 \qquad N = 54 \text{ electrons} \tag{174}$$

$$\text{F}(^2P)\text{: } 2s^2 2p\pi^4 2p\sigma \qquad N = 9 \text{ electrons.} \tag{175}$$

The heavy rare gas Xe is easily ionizable, while F atom has a high electron affinity:

$$\text{Xe}(^1S) \to \text{Xe}^+(^2P) + e^- \qquad \text{I.P.} = 12.1 \text{ eV} \tag{176}$$

$$\text{F}(^2P) + e^- \to \text{F}^-(^1S) \qquad \text{E.A.} = 3.5 \text{ eV.} \tag{177}$$

As we have seen for O_2, in a first approximation, the electrostatic energy needed to form Xe^+F^- at $R_e = 4a_0$, will be:

$$\text{I.P.(Xe)} - \text{E.A.(F)} - \frac{1}{R_e} = 12.1 - 3.5 - \frac{27.21}{4} = 1.8 \text{ eV} = 66.1 \times 10^{-3} E_h. \tag{178}$$

This rather large energy will be recovered by the formation of a *covalent* Xe^+-F bond on the other part of the molecule. We have hence complete resonance between the two VB structures: $\text{F}-\text{Xe}^+\text{F}^- \Leftrightarrow \text{F}^-\text{Xe}^+ - \text{F}$.

$$\underset{\Psi_1}{\mathrm{F{-}\overset{+}{Xe}\quad F^-}} \longleftrightarrow \underset{\Psi_2}{\mathrm{F^-\quad \overset{+}{Xe}{-}F}}$$

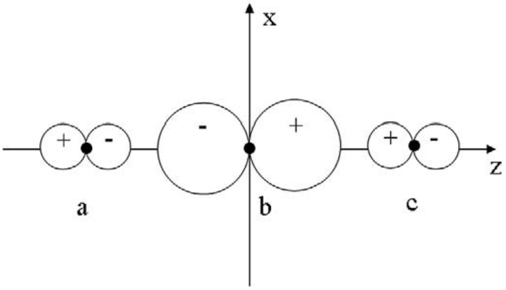


Figure 10.19 $2p\sigma$(F) and $5p\sigma$(Xe) AOs and VB structures involved in covalent bonding in XeF_2.

The two structures, normalized and orthogonal, are:

$$\psi_1 = \frac{1}{\sqrt{2}}\big[(a\bar{b}c\bar{c}) - (\bar{a}bc\bar{c})\big] \tag{179}$$

$$\psi_2 = \frac{1}{\sqrt{2}}\big[(a\bar{a}b\bar{c}) - (a\bar{a}\bar{b}c)\big] \tag{180}$$

with:

$$\langle\psi_1|\psi_2\rangle = 0. \tag{181}$$

The function describing complete resonance between the two covalent structures will therefore be:

$$\Psi = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2). \tag{182}$$

It is now possible to calculate the electron charge distribution in XeF_2 as we did for the allyl radical. Using Slater rules for orthonormal det, it is easily obtained:

$$\rho_1^{\alpha} = \underbrace{\frac{1}{2}\left[\frac{1}{2}(a^2+c^2) + \frac{1}{2}(b^2+c^2)\right]}_{\text{from } \psi_1\psi_1^*} + \underbrace{\frac{1}{2}\left[\frac{1}{2}(a^2+b^2) + \frac{1}{2}(a^2+c^2)\right]}_{\text{from } \psi_2\psi_2^*} \tag{183}$$

$$\rho_1^{\beta} = \frac{1}{2}\left[\frac{1}{2}(b^2+c^2) + \frac{1}{2}(a^2+c^2)\right] + \frac{1}{2}\left[\frac{1}{2}(a^2+c^2) + \frac{1}{2}(a^2+b^2)\right], \tag{184}$$

namely:

$$\rho_1^\alpha = \rho_1^\beta = \frac{1}{4}(3a^2 + 2b^2 + 3c^2). \tag{185}$$

Therefore, according to this VB description, XeF_2 has the following electron charge distribution:

$$P(\mathbf{r}) = \rho_1^\alpha(\mathbf{r}) + \rho_1^\beta(\mathbf{r}) = \frac{3}{2}a^2(\mathbf{r}) + b^2(\mathbf{r}) + \frac{3}{2}c^2(\mathbf{r}) \tag{186}$$

$$\mathrm{tr}P(\mathbf{r}) = \int d\mathbf{r}\, P(\mathbf{r}) = \frac{3}{2} + \frac{2}{2} + \frac{3}{2} = 4. \tag{187}$$

The corresponding electron and formal charge on the atoms in the molecule are given in Figure 10.20.

In a first approximation, the formal charge $\delta = 1/2$ gives a linear quadrupole moment equal to:

$$\mu_2 = -\frac{1}{2}|\delta|(2R_{\mathrm{XeF}})^2 = -16ea_0^2 = -2.1 \times 10^{-25}\ \mathrm{esu\,cm^2} \tag{188}$$

which is within 10% of the experimentally observed value of -1.9×10^{-25} esu cm^2. This value of the quadrupole moment is very large when compared to that of other molecules (for instance, CO_2 has $\mu_2 = -0.3 \times 10^{-25}$ esu cm^2), and is due to the fact that, in the molecule, the fluorine atoms carry a substantial net negative charge.

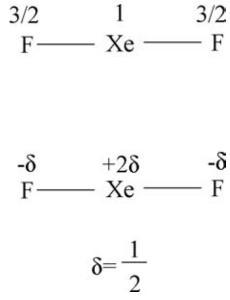


Figure 10.20 Electron (top) and formal charges (bottom) in XeF_2.

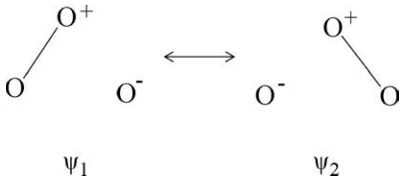


Figure 10.21 Resonance between ionic structures in the π electron system of ozone.

A like calculation can be done for the π system of the triangular $O_3(^1A_1)$ molecule ($2\theta = 117°$, $R_{OO} = 2.41a_0$). The resonance between the equivalent ionic structures (each containing a covalent bond) (Figure 10.21) yields a π formal charge $\delta = 1/2$, which gives a π contribution to the dipole moment of $\mu_\pi = [2\mu_B^2(1 - \cos 2\theta)]^{1/2} = 2.05ea_0$. Since the accurate μ value is sensibly lower than this (Xie et al., 2000), $\mu = \mu_\sigma + \mu_\pi = -0.22ea_0$, we can reasonably expect an even larger, and of opposite sign, contribution by the σ-skeleton of the molecule.

10.5 PAULING VB THEORY FOR CONJUGATED AND AROMATIC HYDROCARBONS

We have used so far VB theory mostly for a qualitative description of the chemical bond in molecules. Use of symmetry arguments for the resonance of equivalent structures has allowed us, in some cases, to determine the electron and spin density distributions in simple molecules without doing any effective calculation of the relative weight of the structures. However, to do effective, even if approximate, energy calculations we are required to evaluate the matrix elements between structures. This is the main object of any VB theory once the proper wavefunctions have been prepared according to the general rules given in the preceding Sections. The general formulation of this problem is rather difficult because of the non-orthogonality of the atomic basis set and non-orthogonality of the VB structures themselves. A great simplification might be reached if we assume that the basic AOs are orthonormal, even if this may be not true for structures. This is a very delicate point, however, since we saw in Section 10.3.4 of this Chapter that assumed, or forced, orthogonalization of the basic AOs yields no bonding at all for atoms described by covalent wavefunctions. It is mostly for this reason that the interesting approach introduced long ago by Pauling (1933) for the VB theory of conjugated and aromatic hydrocarbons has been criticized first and then fully dismissed.

From a theoretical point of view, we saw in the simple case of H_2 how the orthogonality drawback can be removed from the treatment of the covalent bond by admitting with a substantial weight ionic structures which restore the correct charge distribution between the interacting atoms. This way was followed by McWeeny (1954a, 1954b) in his rigorous mathematical reformulation of the conventional VB theory based on orthogonalized AOs (OVB), where he extended Pauling rules to include ionic structures. This rigorous VB treatment was also used by the author (Magnasco and Musso, 1967a, 1967b) in an ab-initio study of the short-range interaction of two H_2 molecules in their ground state. It was shown there (Magnasco and Musso, 1967b) that the orthogonality constraint disappears when the VB treatment is complete and all possible ionic structures are included in the calculation.

On the other hand, VB theory can be applied at its lowest semiempirical level much in the same way as Hückel theory for MO theory. In this case, all criticism is inappropriate, since the results are parametrized in terms of Coulomb and exchange integrals, Q and K, which are treated as fully empirical negative parameters, much in the same way as the αs and βs of Hückel theory. Even at this level, the theory is seen to give some interesting insights into the electronic structure of π electron systems, and of σ systems as well. Furthermore, the rigorous derivation of Pauling's rules under their restrictive assumptions is an interesting introduction to the evaluation of Hamiltonian matrix elements between covalent structures for the more advanced theory. For all these reasons, and for their historical importance, we shall give some space in the following to the Pauling rules for the evaluation of the matrix elements between singlet covalent structures and to their application to the π electron system of some conjugated and aromatic hydrocarbons. The Section will end with a short derivation of Pauling's formula in the case of H_2 ($N = 2$) and cyclobutadiene ($N = 4$).

10.5.1 Pauling Formula for the Matrix Elements of Singlet Covalent VB Structures

Let us restrict ourselves to the singlet ($S = M_S = 0$) states of molecules with spin degeneracy only (Pauling and Wilson, 1935). Among the different ways in which valence bonds can be drawn between pairs of orbitals, the number of independent singlet covalent bond structures (the so called *canonical structures*) which can be constructed from $2n$ singly occupied orbitals is given by the Wigner formula:

$$\text{Number of singlet covalent VB structures} = \frac{(2n)!}{n!(n+1)!}, \tag{189}$$

where n is the number of bonds.

For the case of four orbitals a, b, c, d arranged as a square ring (cyclobutadiene), the bonds can be drawn by lines in three ways, as Figure 10.22 shows, but only ψ_1 and ψ_2, having not intersecting lines, are canonical structures.

The lines drawn in Figure 10.22, denoting single covalent bonds between singly occupied AOs, are called *Rumer diagrams*. From them, it is possible to construct the so called *superposition patterns* of Figure 10.23.

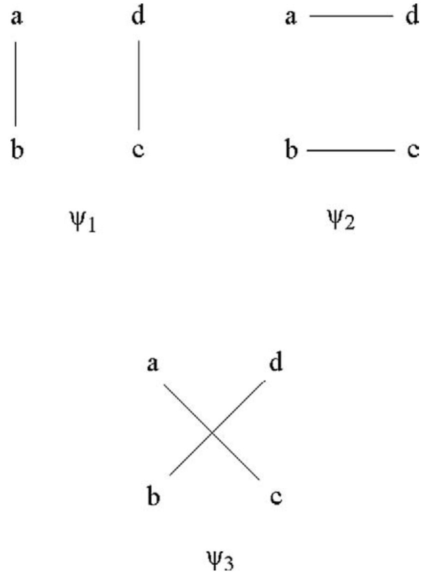
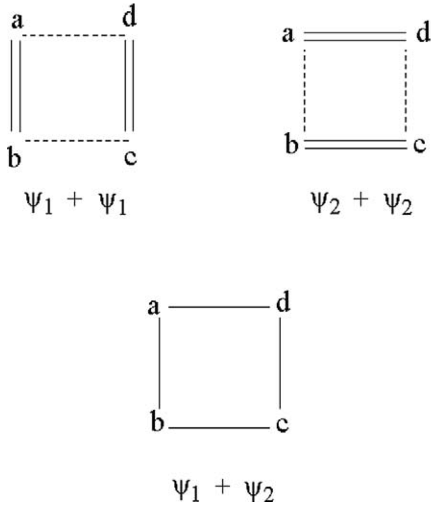


Figure 10.22 Possible covalent bonds in the four orbital problem.



$\psi_1 + \psi_1$ $\psi_2 + \psi_2$

$\psi_1 + \psi_2$

Figure 10.23 Superposition patterns for the four orbital problem.

The superposition patterns consist of closed polygons or *islands*, each formed by an even number of bonds. Based on such premises, and on the following assumptions;

1) Orthonormality of the basic AOs;
2) Consideration of singlet covalent VB structures only;
3) Consideration of single interchanges between adjacent orbitals only;

Pauling (1933) derived simple graphical rules for the evaluation of the general matrix element between structures ψ_r and ψ_s, which are embodied in the formula:

$$H_{rs} - ES_{rs} = \frac{1}{2^{n-i}}\left\{Q - E + \sum_{\substack{i,j \\ \text{bonded}}} K_{ij} - \frac{1}{2}\sum_{\substack{i,j \\ \text{non-bonded}}} K_{ij}\right\}, \tag{190}$$

where n is the number of bonds, i the number of islands in each superposition pattern, $Q(< 0)$ the Coulomb integral, $K_{ij}(< 0)$ the single interchange integral between the pair i and j. The first summation in (190) is over all *bonded* orbitals in the *same* island, the second over all *non-bonded* orbitals in *different* islands.

Pauling formula (190) can be derived by considering for each VB structure its complete form in terms of Slater dets, and calculating H_{rs} and S_{rs} from the appropriate Slater rules for orthonormal determinants. As already done in Hückel theory, in solving the secular equations it will be found convenient to put:

$$\frac{Q - E}{K} = -x \quad E = Q + xK, \tag{191}$$

where x is the bond energy in units of parameter K, $x > 0$ meaning bonding. The solution of the secular equation may be simplified by use of symmetry, if the basis of ordinary VB structures is replaced by a basis of symmetry-adapted VB structures, using the techniques explained in Chapter 8. We shall now examine in some detail a few illustrative molecular cases.

10.5.2 Cyclobutadiene

Even if the canonical VB structures and the superposition patterns for $2n = 4$ were already given in Figures 10.22 and 10.23, it will be convenient here for completeness to collect them both in Figure 10.24, completing the superposition patterns with number of islands and Pauling coefficients from the general formula (190).

Matrix elements are:

$$\begin{aligned} H_{11} - ES_{11} &= H_{22} - ES_{22} = Q - E + 2K - K = Q - E + K \\ H_{12} - ES_{12} &= H_{21} - ES_{21} = \frac{1}{2}(Q - E) + \frac{1}{2}(4K) = \frac{1}{2}(Q - E) + 2K \end{aligned} \tag{192}$$

giving the secular equation:

$$\begin{vmatrix} -x+1 & -\dfrac{x}{2}+2 \\ -\dfrac{x}{2}+2 & -x+1 \end{vmatrix} = 0 \qquad \begin{aligned} &(-x+1)^2 = \left(-\frac{x}{2}+2\right)^2 \\ &x^2 - 4 = 0 \Rightarrow\ x = \pm 2. \end{aligned} \tag{193}$$

Taking the positive root, we have for the π-energy:

$$\text{1 Kekulé} \quad E = Q + K \tag{194}$$

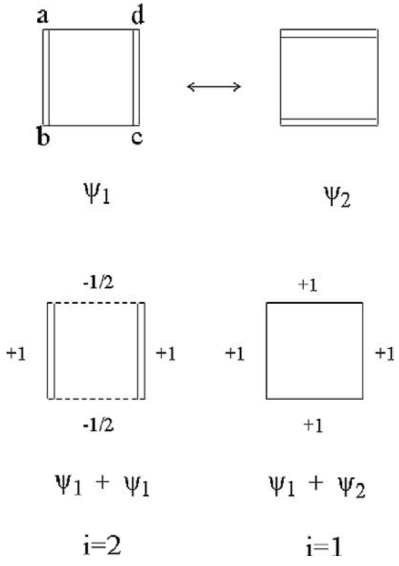


Figure 10.24 Canonical structures (top) and superposition patterns (bottom) for cyclobutadiene.

$$\text{2 Kekulé} \quad E = Q + 2K, \tag{195}$$

giving an energy lowering (resonance energy):

$$E(2K) - E(K) = K < 0. \tag{196}$$

So, resonance between the two Kekulé structures stabilizes the system.

The calculation of the coefficients proceeds as usual from the homogeneous system:

$$(-x+1)c_1 + \left(-\frac{x}{2} + 2\right)c_2 = 0 \quad \text{with } x = 2 \tag{197}$$

$$c_2 = \frac{x-1}{2-\frac{x}{2}} c_1 = c_1 \tag{198}$$

so that, neglecting non-orthogonality between the structures, we obtain:

$$c_1 = c_2 = \frac{1}{\sqrt{2}} \tag{199}$$

finally giving as weights for the two Kekulé structures:

$$50\%\psi_1 \qquad 50\%\psi_2 \tag{200}$$

as it must be for completely resonant structures. A non-empirical VB calculation on the π-electron system of cyclobutadiene was done by McWeeny (1955).

10.5.3 Butadiene

For the open chain with $2n = 4$, canonical structures and superposition patterns are given in Figure 10.25. We note that a and d are now non-adjacent atoms.

Matrix elements are:

$$\begin{aligned} &H_{11} - ES_{11} = Q - E + \frac{3}{2}K \\ &H_{22} - ES_{22} = Q - E \\ &H_{12} - ES_{12} = H_{21} - ES_{21} = \frac{1}{2}(Q-E) + \frac{3}{2}K \end{aligned} \tag{201}$$

$$\begin{vmatrix} -x + \frac{3}{2} & -\frac{x}{2} + \frac{3}{2} \\ -\frac{x}{2} + \frac{3}{2} & -x \end{vmatrix} = 0 \qquad \begin{aligned} &-x\left(-x + \frac{3}{2}\right) = \left(-\frac{x}{2} + \frac{3}{2}\right)^2 \\ &x^2 - 3 = 0 \Rightarrow x = \pm\sqrt{3} \end{aligned} \tag{202}$$

$$\begin{aligned} &\text{1 Kekulé} \quad E = Q + 1.5K \\ &K + D \qquad E = Q + 1.73K \end{aligned} \tag{203}$$

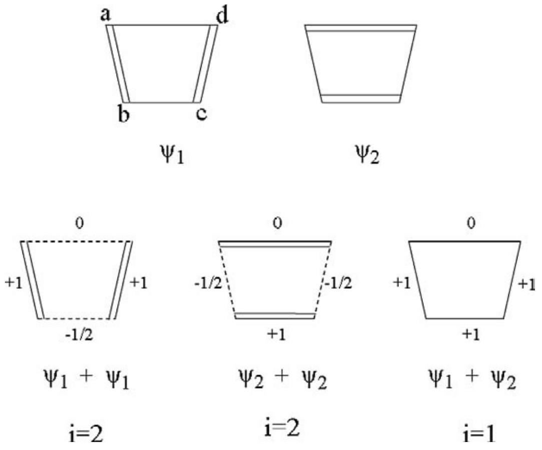


Figure 10.25 Canonical structures (top) and superposition patterns (bottom) for butadiene.

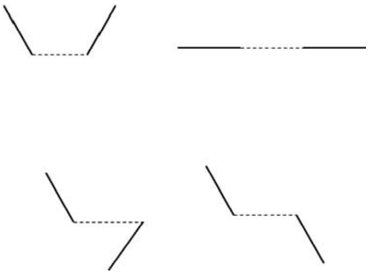


Figure 10.26 Different conformations of butadiene.

so that:

$$\text{Conjugation energy} = 0.23K < 0. \tag{204}$$

We note that ψ_2 has a "long" π-bond (a–d) and is called Dewar (D) structure. The conjugation energy stabilizes the system. We notice that the conjugation energy in open butadiene is about four times smaller than the resonance energy in the corresponding ring. As in Hückel theory, at this level of approximation we cannot distinguish between the different conformations of the open chain, which are all taken to have the same energy (Figure 10.26).

The calculation of the coefficients in butadiene, assuming orthogonality between the structures, gives:

$$\left(-x + \frac{3}{2}\right)c_1 + \left(-\frac{x}{2} + \frac{3}{2}\right)c_2 = 0 \quad \text{with } x = 1.73 \tag{205}$$

$$c_2 = \frac{x - \frac{3}{2}}{\frac{3}{2} - \frac{x}{2}} c_1 = 0.362 c_1. \tag{206}$$

Therefore, we obtain for the resonance between Kekulé and Dewar structures in butadiene:

$$\Psi = c_1(\psi_1 + 0.362\psi_2) = 0.94\psi_1 + 0.34\psi_2 \tag{207}$$

$$88\%\psi_1 \qquad 12\%\psi_2 \tag{208}$$

which shows the greater importance of the Kekulé vs the Dewar structure.

10.5.4 Allyl Radical

This is an interesting example of how to apply Pauling VB theory to an odd-electron system ($N = 3$, $S = 1/2$). We add a *phantom* atom (say d), treat the system as a four orbital system and, at the end, delete the phantom orbital from the calculation. The covalent VB structures and the corresponding superposition patterns are hence the *same* (including the phantom orbital) as those of butadiene. With reference to Figure 10.25, if d is the phantom orbital, we have:

$$\begin{aligned} H_{11} - ES_{11} &= Q - E + K - \frac{1}{2}K + \underset{\text{removed}}{K} = Q - E + \frac{1}{2}K \\ H_{22} - ES_{22} &= Q - E + K - \frac{1}{2}K - \frac{1}{2}\underset{\text{removed}}{K} = Q - E + \frac{1}{2}K \\ H_{12} - ES_{12} &= \frac{1}{2}(Q - E + K + K + \underset{\text{removed}}{K}) = \frac{1}{2}(Q - E) + K \end{aligned} \tag{209}$$

$$\begin{vmatrix} -x + \frac{1}{2} & -\frac{x}{2} + 1 \\ -\frac{x}{2} + 1 & -x + \frac{1}{2} \end{vmatrix} = 0 \qquad \begin{aligned} &\left(-x + \frac{1}{2}\right)^2 = \left(-\frac{x}{2} + 1\right)^2 \\ &\frac{3}{4}x^2 = \frac{3}{4} \Rightarrow x = \pm 1 \end{aligned} \tag{210}$$

$$\begin{aligned} &1\,K && E = Q + \frac{1}{2}K \\ &K + D && E = Q + K \end{aligned} \tag{211}$$

$$\text{Conjugation energy} = 0.5K < 0. \tag{212}$$

The stabilization due to the conjugation of the π-bonds in the allyl radical is hence larger for $N = 3$ than for $N = 4$ (butadiene): $\Delta E = 0.5K$ instead of $0.23K$.

The calculation of the coefficients gives:

$$\left(-x + \frac{1}{2}\right)c_1 + \left(-\frac{x}{2} + 1\right)c_2 = 0 \quad \text{with } x = 1 \tag{213}$$

$$c_2 = \frac{x - \frac{1}{2}}{1 - \frac{x}{2}} c_1 = c_1 \qquad c_1 = c_2 = \frac{1}{\sqrt{2}} \tag{214}$$

if we neglect non-orthogonality between the structures. This gives for the relative weight of the VB structures:

$$50\%\psi_1 \qquad 50\%\psi_2 \tag{215}$$

as expected for full resonance.

It is interesting to note that the *same* result is obtained if we correctly admit non-orthogonality between the structures. Since:

$$S_{12} = \langle\psi_1|\psi_2\rangle = \frac{1}{2}$$

$$\Psi = \psi_1 c_1 + \psi_2 c_2 = \frac{1}{\sqrt{3}}(\psi_1 + \psi_2) \quad c_1 = c_2 = \frac{1}{\sqrt{3}}$$

we have:

$$\%\psi_1 = c_1^2 + c_1 c_2 S_{12} = \frac{1}{3}\left(1 + \frac{1}{2}\right) = \frac{1}{3} \cdot \frac{3}{2} = \frac{1}{2}$$

$$\%\psi_2 = c_2^2 + c_2 c_1 S_{12} = \frac{1}{3}\left(1 + \frac{1}{2}\right) = \frac{1}{3} \cdot \frac{3}{2} = \frac{1}{2}$$

as it must be.

10.5.5 Benzene

The five canonical structures (2 Kekulé + 3 Dewar) for singlet benzene ($2n = 6$) are given in the top row of Figure 10.27, while the bottom row of the same figure gives the distinct superposition patterns.

By symmetry, all exchange integrals are equal, $K_{ij} = K$. From the superposition patterns of Figure 10.27, we obtain immediately all necessary matrix elements between the structures.

$$\begin{aligned} H_{11} - ES_{11} &= H_{22} - ES_{22} = Q - E + \frac{3}{2}K \\ H_{12} - ES_{12} &= \frac{1}{4}(Q - E) + \frac{3}{2}K \end{aligned} \tag{216}$$

$$\begin{aligned} H_{33} - ES_{33} &= H_{44} - ES_{44} = H_{55} - ES_{55} = Q - E \\ H_{34} - ES_{34} &= H_{35} - ES_{35} = H_{45} - ES_{45} = \frac{1}{4}(Q - E) + \frac{3}{2}K \end{aligned} \tag{217}$$

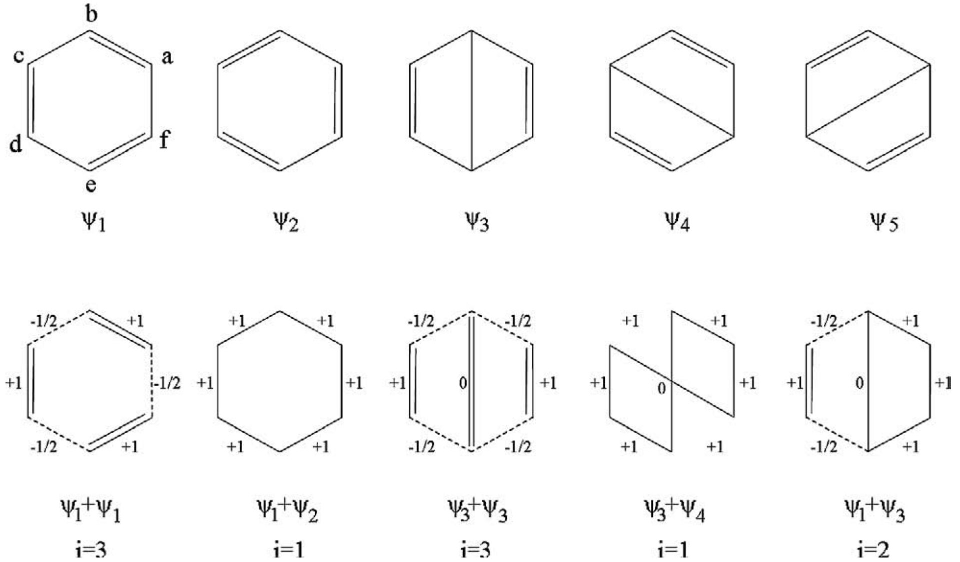


Figure 10.27 Canonical structures (top) and superposition patterns (bottom) for benzene.

$$\begin{aligned} H_{13} - ES_{13} &= H_{14} - ES_{14} = H_{15} - ES_{15} \\ &= H_{23} - ES_{23} = H_{24} - ES_{24} = H_{25} - ES_{25} \\ &= \frac{1}{2}(Q - E) + \frac{3}{2}K. \end{aligned} \tag{218}$$

(216) are the matrix elements between Kekulé structures, (217) between Dewar structures, (218) the cross-terms between Kekulé and Dewar structures.

We now examine the different possible cases.

(i) Resonance between Kekulé structures.

$$\Psi = \psi_1 c_1 + \psi_2 c_2 \tag{219}$$

giving the secular equation:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0, \tag{220}$$

namely:

$$\begin{vmatrix} -x + \frac{3}{2} & -\frac{x}{4} + \frac{3}{2} \\ -\frac{x}{4} + \frac{3}{2} & -x + \frac{3}{2} \end{vmatrix} = 0 \qquad \begin{aligned} &\left(-x + \frac{3}{2}\right)^2 = \left(-\frac{x}{4} + \frac{3}{2}\right)^2 \\ &5x^2 - 12x = x(5x - 12) = 0 \end{aligned} \tag{221}$$

with the roots:

$$x = 0 \Rightarrow E = Q \tag{222}$$

$$x = \frac{12}{5} \Rightarrow E = Q + \frac{12}{5}K = Q + 2.4K. \tag{223}$$

Taking into account the equivalence of the two Kekulé structures, and renouncing to the excited root ($x = 0$), we can write immediately:

$$\begin{aligned} H_{\Psi\Psi} - ES_{\Psi\Psi} &= \langle \psi_1 + \psi_2 | \hat{H} - E | \psi_1 + \psi_2 \rangle \\ &= 2(H_{11} - ES_{11}) + 2(H_{12} - ES_{12}) \\ &= (-2x + 3) + \left(-\frac{1}{2}x + 3 \right) = -\frac{5}{2}x + 6 = 0 \Rightarrow x = \frac{12}{5}. \end{aligned} \tag{224}$$

(ii) Resonance between Dewar structures.

$$\Psi = \psi_3 c_3 + \psi_4 c_4 + \psi_5 c_5 \tag{225}$$

giving the secular equation:

$$\begin{vmatrix} -x & -\frac{x}{4} + \frac{3}{2} & -\frac{x}{4} + \frac{3}{2} \\ -\frac{x}{4} + \frac{3}{2} & -x & -\frac{x}{4} + \frac{3}{2} \\ -\frac{x}{4} + \frac{3}{2} & -\frac{x}{4} + \frac{3}{2} & -x \end{vmatrix} = 0. \tag{226}$$

Expanding the determinant gives:

$$x^3 + 2x^2 - 4x - 8 = (x + 2)^2 (x - 2) = 0 \tag{227}$$

with the roots:

$$x = -2(\text{twice}) \Rightarrow E = Q - 2K \tag{228}$$

$$x = 2 \Rightarrow E = Q + 2K. \tag{229}$$

Taking into account the fact that the three Dewar structures are equivalent by symmetry, we get for the lowest root:

$$\begin{aligned} H_{\Psi\Psi} - ES_{\Psi\Psi} &= \langle \psi_3 + \psi_4 + \psi_5 | \hat{H} - E | \psi_3 + \psi_4 + \psi_5 \rangle \\ &= 3(H_{33} - ES_{33}) + 6(H_{34} - ES_{34}) \\ &= -3x - \frac{6}{4}x + \frac{18}{2} = -\frac{9}{2}x + 9 = 0 \Rightarrow x = 2 \end{aligned} \tag{230}$$

as before.

(iii) Resonance between Kekulé and Dewar structures.

Taking into account symmetry, we can write immediately:

$$\Psi = c_1(\psi_1 + \psi_2) + c_2(\psi_3 + \psi_4 + \psi_5) = c_1\Psi_K + c_2\Psi_D, \tag{231}$$

where Ψ_K and Ψ_D are un-normalized. The secular equation is:

$$\begin{vmatrix} H_{KK} - ES_{KK} & H_{KD} - ES_{KD} \\ H_{KD} - ES_{KD} & H_{DD} - ES_{DD} \end{vmatrix} = 0, \tag{232}$$

where:

$$\begin{aligned} H_{KK} - ES_{KK} &= -\frac{5}{2}x + 6 \\ H_{DD} - ES_{DD} &= -\frac{9}{2}x + 9 \end{aligned} \tag{233}$$

were already calculated, and:

$$\begin{aligned} H_{KD} - ES_{KD} &= \langle\psi_1 + \psi_2|\hat{H} - E|\psi_3 + \psi_4 + \psi_5\rangle \\ &= 6(H_{13} - ES_{13}) = 6\left(-\frac{x}{2} + \frac{3}{2}\right) = -3x + 9. \end{aligned} \tag{234}$$

Therefore:

$$\begin{vmatrix} -\frac{5}{2}x + 6 & -3x + 9 \\ -3x + 9 & -\frac{9}{2}x + 9 \end{vmatrix} = 0 \quad x^2 + 2x - 12 = 0 \tag{235}$$

with the roots:

$$x = -1 + \sqrt{13} = 2.6055 \Rightarrow E = Q + 2.6055K \tag{236}$$

$$x = -1 - \sqrt{13} = -4.6055 \Rightarrow E = Q - 4.6055K. \tag{237}$$

(iv) Full VB calculation.

$$\Psi = \psi_1 c_1 + \psi_2 c_2 + \psi_3 c_3 + \psi_4 c_4 + \psi_5 c_5. \tag{238}$$

Without use of symmetry, (238) gives the secular equation:

$$\begin{array}{c}
\begin{array}{cc} K-K \qquad\qquad\qquad & \qquad\qquad K-D \end{array} \\
\left|\begin{array}{cc|ccc}
-x+\frac{3}{2} & -\frac{x}{4}+\frac{3}{2} & -\frac{x}{2}+\frac{3}{2} & -\frac{x}{2}+\frac{3}{2} & -\frac{x}{2}+\frac{3}{2} \\
-\frac{x}{4}+\frac{3}{2} & -x+\frac{3}{2} & -\frac{x}{2}+\frac{3}{2} & -\frac{x}{2}+\frac{3}{2} & -\frac{x}{2}+\frac{3}{2} \\
\hline
-\frac{x}{2}+\frac{3}{2} & -\frac{x}{2}+\frac{3}{2} & -x & -\frac{x}{4}+\frac{3}{2} & -\frac{x}{4}+\frac{3}{2} \\
-\frac{x}{2}+\frac{3}{2} & -\frac{x}{2}+\frac{3}{2} & -\frac{x}{4}+\frac{3}{2} & -x & -\frac{x}{4}+\frac{3}{2} \\
-\frac{x}{2}+\frac{3}{2} & -\frac{x}{2}+\frac{3}{2} & -\frac{x}{4}+\frac{3}{2} & -\frac{x}{4}+\frac{3}{2} & -x
\end{array}\right| = 0. \\
\begin{array}{cc} K-D \qquad\qquad\qquad & \qquad\qquad D-D \end{array}
\end{array} \tag{239}$$

Elementary, but lengthy, manipulations of the determinant (multiplication by a number, addition or subtraction of rows and columns) give the expanded form:

$$x^5+6x^4-40x^2-48x = x(x+2)^2(x^2+2x-12) = 0 \tag{240}$$

giving the five real roots (in ascending order):

$$x = -1+\sqrt{13}, \quad 0, \quad -2, \quad -2, \quad -1-\sqrt{13}. \tag{241}$$

The lowest root, $x = -1+\sqrt{13}$, is the energy pertaining to the ground state of the π-electron system of benzene, described by the "resonance" between Kekulé and Dewar VB structures.

(v) Use of C_{6v} symmetry.

As already done for Hückel theory, we can use C_{6v} symmetry for the complete factorization of the secular equation for the five canonical structures of benzene, an interesting application of symmetry in VB theory.

Let us, for convenience, rename the structures as:

$$\psi_1 = A, \quad \psi_2 = B, \quad \psi_3 = C, \quad \psi_4 = D, \quad \psi_5 = E. \tag{242}$$

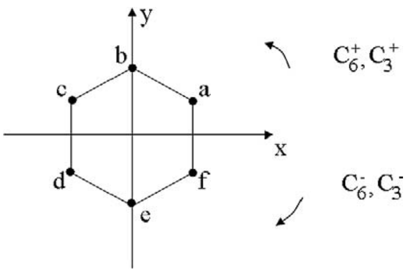


Figure 10.28 The benzene ring.

With reference to Figure 10.28, we keep π bonds *fixed*, so that $\hat{R}\chi$ simply permutes identical carbon nuclei in the molecule. The transformation table of the AOs in the active representation is:

$\hat{R}\chi$	I	C_6^+	C_6^-	C_3^+	C_3^-	C_2	σ_a	σ_b	σ_c	σ_{ab}	σ_{bc}	σ_{cd}
a	a	f	b	e	c	d	a	c	e	b	d	f

giving the transformation table of the VB structures (top of Figure 10.27) under C_{6v} symmetry:

$\hat{R}\psi$	I	C_6^+	C_6^-	C_3^+	C_3^-	C_2	σ_a	σ_b	σ_c	σ_{ab}	σ_{bc}	σ_{cd}
A	A	B	B	A	A	B	B	B	B	A	A	A
B	B	A	A	B	B	A	A	A	A	B	B	B
C	C	D	E	E	D	C	D	C	E	E	D	C
D	D	E	C	C	E	D	C	E	D	D	C	E
E	E	C	D	D	C	E	E	D	C	C	E	D

The table of characters of the point group C_{6v} is:

C_{6v}	I	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1
B_1	1	-1	1	-1	1	-1
B_2	1	-1	1	-1	-1	1
E_1	2	1	-1	-2	0	0
E_2	2	-1	-1	2	0	0
$\chi(\Gamma)$	5	0	2	3	1	3

where $\chi(\Gamma)$ are the characters of the *reducible* representation Γ. $\chi(\Gamma)$ can be written immediately, without making use of the full representative matrices, simply by counting how many structures are left unchanged in the column of the transformation table corresponding to the operation $\hat{R}$. By decomposing Γ into its *irreducible* components under C_{6v} (Chapter 8), we find:

$$\Gamma = 2A_1 + B_2 + E_2. \tag{243}$$

Using the full projector:

$$\hat{P}^i_{\lambda\lambda} = \frac{l_i}{h}\sum_R \mathbf{D}^i(R)^*_{\lambda\lambda}\hat{R}, \tag{244}$$

from the full table of C_{6v} in the form of representative matrices of the operations $\hat{R}$ (Problem 8.13 of Chapter 8), we find that the symmetry-adapted VB structures, in un-normalized form, are:

$$\begin{aligned} &A_1\colon\quad A+B \propto \Psi_K, \qquad C+D+E \propto \Psi_D \\ &B_2\colon\quad A-B \\ &E_2\colon\quad 2C-D-E \propto x^2-y^2, \qquad D-E \propto xy. \end{aligned} \tag{245}$$

In this symmetry-adapted basis, which transforms as the irreducible representations of C_{6v}, the 5×5 secular equation (239) factorizes into a 2×2 block (symmetry A_1), a 1×1 block (B_2), while the 2×2 E_2 block further factorizes into its components $E_2^{x^2-y^2}$ and E_2^{xy}, which are orthogonal and *not* interacting with respect to $\hat{H}$, as shown in Figure 10.29.

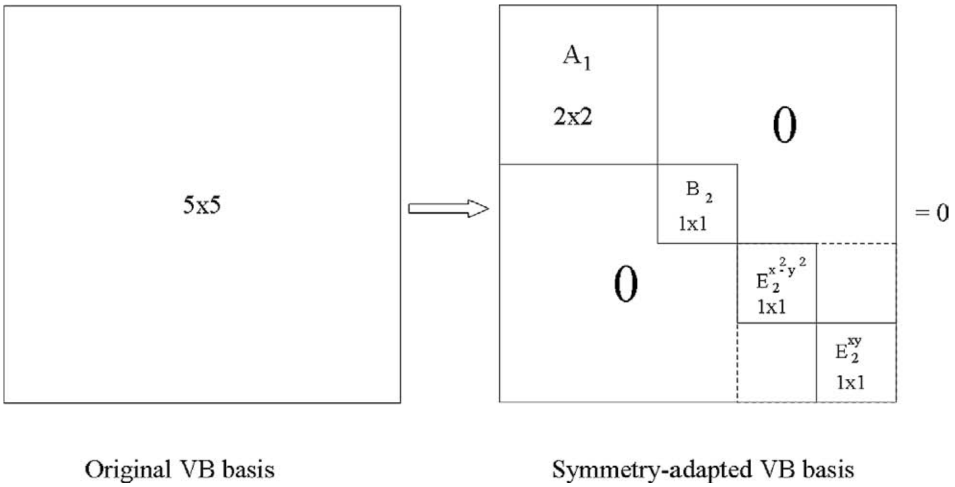


Figure 10.29 Factorization of the full VB secular equation into its C_{6v} symmetry blocks.

Therefore, we have:

$$\begin{aligned}
&A_1: && D_2 = x^2 + 2x - 12 = 0\\
&B_2: && D_1 = -x + \frac{3}{2} + \frac{x}{4} - \frac{3}{2} = -\frac{3}{4}x = 0\\
&E_2^{x^2-y^2}: && D_1 = -x + \frac{x}{4} - \frac{3}{2} = -\frac{3}{4}x - \frac{3}{2} = 0\\
&E_2^{xy}: && D_1 = -x + \frac{x}{4} - \frac{3}{2} = -\frac{3}{4}x - \frac{3}{2} = 0
\end{aligned} \tag{246}$$

which corresponds to the factorization (240) giving the real roots:

$$\begin{aligned}
&A_1: && -1 + \sqrt{13}, \quad -1 - \sqrt{13}\\
&B_2: && 0\\
&E_2: && -2,\ -2 \text{ (twofold degenerate).}
\end{aligned} \tag{247}$$

(vi) Weights of VB structures and resonance energies.

The coefficients of Kekulé and Dewar structures are calculated from the homogeneous system of equation (235):

$$\left(-\frac{5}{2}x+6\right)c_1+(-3x+9)c_2=0 \quad \text{with } x=2.6055 \tag{248}$$

$$c_2=\frac{\frac{5}{2}x-6}{-3x+9}c_1=0.4341c_1. \tag{249}$$

Assuming orthogonality between the structures:

$$\langle\Psi|\Psi\rangle=2c_1^2+3c_2^2=1 \qquad N=\left(2c_1^2+3c_2^2\right)^{1/2} \tag{250}$$

$$c_1=0.6243, \qquad c_2=0.2710 \tag{251}$$

so that we obtain:

$$\begin{aligned}&38.9\% = \text{weight of each Kekulé structure}\\&7.3\% = \text{weight of each Dewar structure}\end{aligned} \tag{252}$$

in surprising agreement with a recent ab-initio VB calculation by Cooper et al. (1986b) giving for these weights 40.3% and 6.5%, respectively.

As we already saw before in this Chapter, the *resonance energy* is defined (Pauling) as the difference between the π energy obtained from the linear combination of the VB structures and that corresponding to the most stable single VB structure. It is this resonance energy which explains, according to Pauling, the *stabilization* of the aromatic sextet of π electrons in benzene (compare the delocalization energy in Hückel MO theory).

The π energies and the resonance energies corresponding to the different combinations of VB structures in benzene are given in Table 10.9.

For a basis of non-orthogonal AOs, the introduction of the 170 ionic structures (Gerratt, 1987), 60 singly polar, 90 doubly polar, 20 triply polar, for a total of $170+5$ singlet ($S=M_S=0$) structures, does not alter in an appreciable way these conclusions. Ta-

Table 10.9.

π energies and resonance energies for VB structures in benzene

Structure	Ψ^a	π energy	Resonance energy^b
1 Kekulé	ψ_1	$Q+1.5K$	0
2 Kekulé	$\psi_K=\psi_1+\psi_2$	$Q+2.4K$	0.9
1 Dewar	ψ_3	Q	–
3 Dewar	$\psi_D=\psi_3+\psi_4+\psi_5$	$Q+2K$	0.5
2K + 3D	$0.6243\psi_K+0.2710\psi_D$	$Q+2.6K$	1.1

^{a}Un-normalized. ^{b}In units of K: $\Delta x=\Delta E/K$.

Table 10.10.

Resonance and delocalization energies for a few conjugated and aromatic hydrocarbons

Molecule	Resonance energy[a]	Delocalization energy[b]	Experiment[c] kcal mol^{-1}
Butadiene	0.23	0.47	3.5
Hexatriene	0.48	0.99	–
Benzene	1.10	2.00	37
Naphthalene	2.04	3.68	75
Diphenyl	2.37	4.38	79
Anthracene	2.95	5.32	105
Fenanthrene	3.02	5.45	110

[a] In units of K. [b] In units of β. [c] From heats of hydrogenation.

ble 10.10 compares resonance (VB) and delocalization (MO) energies for a few conjugated and aromatic hydrocarbons.

MO and VB results are seen to be in fair qualitative agreement. Resonance energy is sensibly larger for rings rather than for open chains, the reason being in the larger number of Kekulé structures of similar energy (larger resonance energy) that we have in closed chain (rings) molecules. The revised VB theory over OAOs was applied in non-empirical calculations of the lower π-electron levels of benzene by McWeeny (1955).

10.5.6 Naphthalene

We shall now give a short outline of the VB theory of naphthalene (Pauling and Wheland, 1933, PW; Sherman, 1934), just to show how dramatically increases the number of allowed structures and the difficulty of the calculation.

According to the Wigner rule for $n = 5$ and $S = 0$:

$$f_0^5 = \frac{(2S+1)(2n)!}{(n+S+1)!(n-S)!} = \frac{10!}{6!5!} = 42 \tag{253}$$

there are 42 singlet covalent VB structures for naphthalene, of which 3 are Kekulé and 39 Dewar structures involving "long" bonds. 16 of these Dewar structures involve *one* "long" bond, 19 *two* "long" bonds, and 4 *three* "long" bonds, improperly called by PW singly, doubly, and triply excited structures, respectively (Figure 2 of PW). The first VB calculation on naphthalene was done by Pauling and Wheland (1933) under certain simplifying assumptions, while the complete secular equation for the 42 canonical structures was set up and solved rigorously within the Pauling approximations by Sherman (1934). Sherman used molecular symmetry to factor out the secular equation into a 16 × 16, a 14 × 14, and two 6 × 6 blocks. For the ground state of the molecule, it was sufficient to consider only the 16 × 16 block, whose matrix elements are fully given in Table 10.1 of his paper.

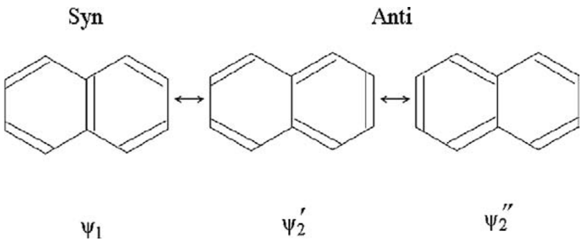


Figure 10.30 The three Kekulé structures of naphthalene.

In the following, we shall however refer to the simpler approach by PW, who assumed equal all structures within each block (which is not strictly true, but of sufficient accuracy). The PW grouping of structures is hence the following:

$$\begin{array}{ccccccccccc} 1 & + & 2 & + & 16 & + & 19 & + & 4 & = & 42 \\ \psi_1 & & \psi_2 & & \psi_3 & & \psi_4 & & \psi_5 & & \end{array} \tag{254}$$

giving the VB wavefunction:

$$\Psi = \psi_1 c_1 + \psi_2 c_2 + \psi_3 c_3 + \psi_4 c_4 + \psi_5 c_5. \tag{255}$$

The most important structures are of course the three Kekulé structures of Figure 10.30, one *syn* and two equivalent *anti*.

It must be noted that, even if each structure of Figure 10.30 has the *same* energy, the $12'$ (and $12''$) interactions are *different* from $2'2''$. The three Kekulé structures yield the secular equation (Sherman, 1934):

$$\begin{vmatrix} -x+2 & -\dfrac{x}{2}+\dfrac{13}{4} \\ -\dfrac{x}{2}+\dfrac{13}{4} & -\dfrac{17}{8}x+\dfrac{43}{8} \end{vmatrix} = 0, \tag{256}$$

which can be expanded to give the quadratic equation:

$$10x^2 - 34x + 1 = 0 \tag{257}$$

having the lowest root:

$$x = \frac{17 + 3\sqrt{31}}{10} = 3.3703. \tag{258}$$

The calculation of the coefficients for this root gives:

$$c_2 = \frac{x-2}{\frac{13}{4}-\frac{x}{2}} c_1 = 0.8757 c_1, \tag{259}$$

Table 10.11.

π energies and resonance energies for the VB structures of naphthalene[a]

Structure	π energy	Resonance energy[b]
ψ_1	$Q+2K$	0
$\psi_1+\psi_2$	$Q+3.37K$	1.37
$\psi_1+\psi_2+\psi_3$	$Q+3.98K$	1.98 (2.004)[c]
Ψ, eq. (255)	$Q+4.02K$	2.02 (2.04)[c]

[a] Pauling and Wheland (1933). [b] In units of K. [c] Sherman (1934).

Table 10.12.

Relative weights of the VB structures of naphthalene[a]

Structure	Coefficients	Individual weight	Total weight %
$\psi_1(1)$	0.4954	24.54	24.54
$\psi_2(2)$	0.4217	17.78	35.57
$\psi_3(16)$	0.1499	2.247	35.95
$\psi_4(19)$	0.0455_2	0.207	3.93
$\psi_5(4)$	0.0038_{15}	0.002_5	0.01

[a] Pauling and Wheland (1933).

so that, assuming orthogonality between the structures:

$$\Psi = 0.6282\psi_1 + 0.5501\psi_2, \tag{260}$$

where (un-normalized):

$$\psi_2 = \psi_2' + \psi_2'', \tag{261}$$

with the relative weights:

$$39.4\%\psi_1 \qquad 30.3\%\psi_2' \qquad 30.3\%\psi_2''. \tag{262}$$

This situation is however deeply modified when the large number (16) of one "long" bond structures is admitted: PW calculations indicate that all these structures contribute to the total by more than 1/3 (36%). The PW energies for the VB structures of naphthalene are given in Table 10.11, while Table 10.12 gives the relative weights of the corresponding structures whose number is indicated in parenthesis in the first column.

Table 10.12 shows how the situation is changed when Dewar structures are admitted. There is a 15% reduction in the importance of ψ_1 (Kekulé syn), whereas the weight of $\psi_2' + \psi_2''$ (the two equivalent Kekulé anti) is reduced by about 25%. As a whole, about 60% is still contributed by the three Kekulé structures, but the one "long" bond Dewar structures, which have a moderate individual contribution (about 2.25%), contribute by over 1/3 to the total, because their number is large (16). The contribution of the two "long" bond structures is less than 4% of the total, while the contribution of the three "long" bond structures is negligible.

The situation is expected to be even worst in anthracene ($2n = 14$), where the total number of canonical structures (429) is slightly more than 10 times the number of naphthalene (42), and the number of one "long" bond Dewar structures increases 3 times (48 instead of 16). The total number of "higher-excited" Dewar structures (Sherman, 1934) increases however more than 16 times (377 instead of $19 + 4 = 23$), a trend expected to explode for larger polycyclic hydrocarbons (compare coronene!).

10.5.7 Derivation of the Pauling Formula for H$_2$ and Cyclobutadiene

We now derive the Pauling formula (190) first for the H_2 molecule ($2n = 2$) and, next, for cyclobutadiene ($2n = 4$).

(i) The H_2 molecule.

- ${}^1\Sigma_g^+$ ground state ($S = M_S = 0$).

  Under Pauling's assumptions, the covalent VB structure for ground state H_2 is:

$$\psi_1 = \frac{1}{\sqrt{2}}\big[(a\bar{b}) - (\bar{a}b)\big] = \frac{1}{\sqrt{2}}\big[\underset{1}{(a\bar{b})} + \underset{2}{(b\bar{a})}\big] \tag{263}$$

with:

$$S_{11} = \langle\psi_1|\psi_1\rangle = \frac{1}{2}(1+1) = 1. \tag{264}$$

In what follows it will be more convenient to use for ψ_1 the second form of equation (263), where the α and β spin parts of the second Slater det are put in a corresponding order as in the starting parent.

The VB matrix element for structure ψ_1 will be:

$$\begin{aligned}
H_{11} &= \langle\psi_1|\hat{H}|\psi_1\rangle \\
&= \frac{1}{2}\Big\{\underset{\text{"diagonal terms"}}{\big[\langle(a\bar{b})|\underset{11}{\hat{H}}|(a\bar{b})\rangle + \langle(b\bar{a})|\underset{22}{\hat{H}}|(b\bar{a})\rangle\big]} \\
&\qquad + \underset{\text{"off-diagonal terms"}}{\big[\langle(a\bar{b})|\underset{12}{\hat{H}}|(b\bar{a})\rangle + \langle(b\bar{a})|\underset{21}{\hat{H}}|(a\bar{b})\rangle\big]}\Big\} \\
&= \text{use Slater's rules for orthonormal determinants} \\
&= \frac{1}{2}\Bigg\{\Bigg[h_{aa} + h_{\bar{b}\bar{b}} + \left\langle a\bar{b}\middle|\frac{1}{r_{12}}\middle|a\bar{b}\right\rangle - \left\langle a\bar{b}\middle|\frac{1}{r_{12}}\middle|\bar{b}a\right\rangle + \frac{1}{R}\Bigg]
\end{aligned}$$

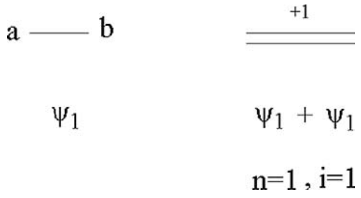


Figure 10.31 Canonical structure and superposition pattern for ground state H_2.

$$+\left[h_{bb}+h_{\overline{a}\overline{a}}+\left\langle b\overline{a}\left|\frac{1}{r_{12}}\right|b\overline{a}\right\rangle-\left\langle b\overline{a}\left|\frac{1}{r_{12}}\right|\overline{a}b\right\rangle+\frac{1}{R}\right]$$

$$+\left\langle a\overline{b}\left|\frac{1}{r_{12}}\right|b\overline{a}\right\rangle-\left\langle a\overline{b}\left|\frac{1}{r_{12}}\right|\overline{a}b\right\rangle+\left\langle b\overline{a}\left|\frac{1}{r_{12}}\right|a\overline{b}\right\rangle-\left\langle b\overline{a}\left|\frac{1}{r_{12}}\right|\overline{b}a\right\rangle\Bigg\}$$

$=$ eliminating spin, we have contributions only from "matching" spins

$$=\frac{1}{2}\left\{2\left[h_{aa}+h_{bb}+(a^2|b^2)+\frac{1}{R}\right]+(ab|ba)+(ba|ab)\right\}$$

$$=\frac{1}{2}(2Q+2K)=Q+K. \tag{265}$$

In the last two rows of (265) we used the charge density notation for the spinless form of the 2-electron integrals:

$$\begin{aligned}(a^2|b^2)&=\iint d\mathbf{r}_1\,d\mathbf{r}_2\frac{b(\mathbf{r}_2)b^*(\mathbf{r}_2)}{r_{12}}a(\mathbf{r}_1)a^*(\mathbf{r}_1)\\(ab|ab)&=\iint d\mathbf{r}_1\,d\mathbf{r}_2\frac{a(\mathbf{r}_2)b^*(\mathbf{r}_2)}{r_{12}}a(\mathbf{r}_1)b^*(\mathbf{r}_1),\end{aligned} \tag{266}$$

and put, for the Coulomb integral:

$$Q=h_{aa}+h_{bb}+(a^2|b^2)+\frac{1}{R}. \tag{267}$$

Hence, we obtain:

$$H_{11}-ES_{11}=Q-E+K=0\Rightarrow E\left({}^1\Sigma_g^+\right)=Q+K, \tag{268}$$

in agreement with the superposition pattern of Figure 10.31, corresponding to the singlet wavefunction which describes "bonded" atoms (of course, in the sense discussed at the beginning of this Section).

- ${}^3\Sigma_u^+$ triplet state ($S=1$, $M_S=0$).

This case is *not* comprised in Pauling's formula (190), but is in some way illuminating in explaining the origin of repulsion between "non-bonded" atoms.

$$\psi_1\left({}^3\Sigma_u^+, M_S = 0\right) = \frac{1}{\sqrt{2}}[(a\bar{b}) + (\bar{a}b)] = \frac{1}{\sqrt{2}}[\underset{1}{(a\bar{b})} - \underset{2}{(b\bar{a})}] \tag{269}$$

with:

$$S_{11} = \langle \psi_1 | \psi_1 \rangle = \frac{1}{2}(1+1) = 1. \tag{270}$$

Proceeding as before, we find:

$$\begin{aligned} H_{11} &= \left\langle \psi_1\left({}^3\Sigma_u^+\right) \middle| \hat{H} \middle| \psi_1\left({}^3\Sigma_u^+\right) \right\rangle \\ &= \frac{1}{2}\left\{\left[\langle (a\bar{b})| \underset{11}{\hat{H}} |(a\bar{b})\rangle + \langle (b\bar{a})| \underset{22}{\hat{H}} |(b\bar{a})\rangle\right]\right. \\ &\quad \left. - \left[\langle (a\bar{b})| \underset{12}{\hat{H}} |(b\bar{a})\rangle + \langle (b\bar{a})| \underset{21}{\hat{H}} |(a\bar{b})\rangle\right]\right\} \\ &= Q - K, \end{aligned} \tag{271}$$

so that:

$$H_{11} - ES_{11} = Q - E - K = 0 \Rightarrow E\left({}^3\Sigma_u^+\right) = Q - K. \tag{272}$$

For two "non-bonded" atoms having "random" spins, we have four possible spin states (one for singlet, three for triplet), so that the average energy will be:

$$E\left[\frac{1}{4}E\left({}^1\Sigma_g^+\right) + \frac{3}{4}E\left({}^3\Sigma_u^+\right)\right] = \frac{1}{4}(Q+K) + \frac{3}{4}(Q-K) = Q - \frac{1}{2}K, \tag{273}$$

where the exchange integral appears with the coefficient typical of "non-bonded" AOs.

(ii) Cyclobutadiene.

With reference to Figure 10.24, we rewrite here the complete expressions for the two singlet ($S = M_S = 0$) canonical structures of cyclobutadiene, keeping the dictionary order for the orbitals in the Slater dets:

$$\begin{aligned} \psi_1 &= \frac{1}{2}\left[(a\bar{b}c\bar{d}) - (\bar{a}bc\bar{d}) - (a\bar{b}\bar{c}d) + (\bar{a}b\bar{c}d)\right] \\ \psi_2 &= \frac{1}{2}\left[(a\bar{b}c\bar{d}) - (\bar{a}\bar{b}cd) - (ab\bar{c}\bar{d}) + (\bar{a}b\bar{c}d)\right] \end{aligned} \tag{274}$$

with:

$$
\begin{aligned}
S_{11} &= \langle \psi_1 | \psi_1 \rangle = \frac{1}{4}(1+1+1+1) = 1 \\
S_{12} &= \langle \psi_1 | \psi_2 \rangle = \frac{1}{4}(1+1) = \frac{1}{2}.
\end{aligned}
\tag{275}
$$

As in the previous case of H_2, we now evaluate the matrix elements between the VB structures, taking into account Pauling's assumptions and Slater's rules for orthonormal determinants (details in Problem 10.7).

$$
\begin{aligned}
H_{11} &= \langle \psi_1 | \hat{H} | \psi_1 \rangle \\
&= \frac{1}{4}\{4Q - 2[(ac|ac) + (ad|ad) + (bc|bc) + (bd|bd)] \\
&\quad + 4[(ab|ab) + (cd|cd)]\},
\end{aligned}
\tag{276}
$$

where Q is the Coulomb integral and we used the charge density notation for the 2-electron integrals. In (276):

$$
(ac|ac) = (bd|bd) = 0 \tag{277}
$$

because exchange integrals between "non-adjacent" atoms, whereas by symmetry:

$$
(ab|ab) = (ad|ad) = (bc|bc) = (cd|cd) = K. \tag{278}
$$

Hence, we finally obtain:

$$
H_{11} = Q + \underset{\substack{\text{"bonded"} \\ \text{atoms}}}{2K} - \underset{\substack{\text{"non-bonded"} \\ \text{atoms}}}{\frac{1}{2}(2K)} \tag{279}
$$

$$
H_{11} - ES_{11} = Q - E + K \tag{280}
$$

in agreement with the superposition pattern of Figure 10.24. By symmetry:

$$
H_{22} - ES_{22} = H_{11} - ES_{11}. \tag{281}
$$

For the off-diagonal element between the structures we have similarly:

$$
\begin{aligned}
H_{12} &= \langle \psi_1 | \hat{H} | \psi_2 \rangle \\
&= \frac{1}{4}\{2[Q - (ac|ac) - (bd|bd)] - 2(bd|bd) \\
&\quad + 2[(ab|ab) - (ac|ac) + (ad|ad) + (bc|bc) + (cd|cd)]\}
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{1}{2}[Q + (ab|ab) - 2(ac|ac) + (ad|ad) \\
&\quad + (bc|bc) - 2(bd|bd) + (cd|cd)] \\
&= \frac{1}{2}(Q + 4K)
\end{aligned}
\tag{282}
$$

$$
H_{12} - ES_{12} = \frac{1}{2}(Q - E + 4K) \tag{283}
$$

as prescribed by Pauling's formula.

Hence, using the full determinantal expressions for the canonical structures and Pauling's simplifying assumptions, use of Slater's rules for orthonormal determinants yields the results obtained in Section 10.5.2 for cyclobutadiene using the superposition patterns of Figure 10.24. The same could be done for benzene ($2n = 6$).

10.6 HYBRIDIZATION AND DIRECTED VALENCY IN POLYATOMIC MOLECULES

In the VB description of *diatomic* molecules discussed in Section 10.4.5, hybridization on the heavy atoms was not taken into account, at least in the first approximation. This is no longer possible in the VB description of *polyatomic* molecules, since the principle of maximum overlap (which will be examined in more detail in Section 10.6.4) requires that the covalent bond be formed between AOs properly directed one towards each other so as to avoid the formation of bent (weaker) bonds. This point is of tantamount importance for a correct description of directed valency and, therefore, of all bond stereochemistry. In the following, we shall examine further this question, with special reference to the VB calculation of the water molecule.

10.6.1 sp^2 Hybridization in H_2O

Considering the H_2O molecule in the yz-plane (H_1 in the positive part of the yz-molecular plane, see Figure 8.19 in Problem 8.6), if the O—H bond would be formed only by the $2p$ AOs ($2p_y = y$ and $2p_z = z$, for short) of oxygen and the $1s$ AOs ($1s_1 = h_1$ and $1s_2 = h_2$) of hydrogens, the principle of maximum overlap (*straight* bonds between O and H) would yield a bond angle of $2\theta = 90°$. The fact that the experimentally observed angle is larger than this ($2\theta \approx 105°$), would suggest the formation of sensibly *bent* O—H bonds, with very poor overlap between the $2p$ AOs of oxygen and the $1s$ AOs of H_1 and H_2. On the other hand, $2p$ AOs directed towards the H atoms and making an interbond angle equal to the experimentally observed value of $2\theta = 105°$, would be *non-orthogonal* (see Problem 10.8). We can restore orthogonality between the AOs on the oxygen atom by mixing in a certain quantity of $2s$ ($= s$) with the two $2p$ AOs of oxygen, obtaining in this way three sp^2 hybrids of C_{2v} symmetry (the symmetry of the H_2O molecule), directed along two equivalent O—H bonds and on the rear of the molecule in a direction bisecting the valence angle.

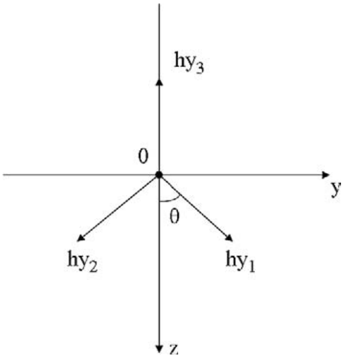


Figure 10.32 The three sp^2 hybrids of C_{2v} symmetry in H_2O.

The three hybrids hy_i $(i = 1, 2, 3)$ of Figure 10.32 allow (i) for an interbond angle greater than 90° $(\cos 2\theta < 0)$, preserving orthogonality between valence AOs onto the same atom, and (ii) for orbitals directed along the bonds, satisfying in this way the principle of maximum overlap and giving stronger straight bonds.

The three sp^2 (C_{2v}) hybrids are:

$$\begin{aligned} hy_1 &= 0.4534s + 0.5426z + 0.7071y \\ hy_2 &= 0.4534s + 0.5426z - 0.7071y \\ hy_3 &= 0.7673s - 0.6412z, \end{aligned} \tag{284}$$

giving $20.6\%s$ and $79.4\%p$ for hybrids engaged in the O—H bonds, $58.9\%s$ and $41.1\%p$ for the hybrid directed along z and forming the σ lone pair. The hybrids are easily constructed by taking into account equivalence and orthonormality requirements (Problem 10.8).

If the hybrids are written as:

$$\begin{aligned} hy_1 &= as + bp_1 \\ hy_2 &= as + bp_2 \\ hy_3 &= cs - dz, \end{aligned} \tag{285}$$

where p_1 and p_2 are two p orbitals directed towards h_1 and h_2, the transformation between the original and the hybrid AO basis is given by the *unitary* matrix $\mathbf{U}$:

$$(hy_1\, hy_2\, hy_3) = (s\, z\, y)\mathbf{U} \tag{286}$$

$$\mathbf{U} = \begin{pmatrix} \frac{1}{\sqrt{2}}d & \frac{1}{\sqrt{2}}d & c \\ \frac{1}{\sqrt{2}}c & \frac{1}{\sqrt{2}}c & -d \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \end{pmatrix} \tag{287}$$

with:

$$\mathbf{U}\mathbf{U}^\dagger = \mathbf{U}^\dagger\mathbf{U} = \mathbf{1}. \tag{288}$$

10.6.2 VB Description of H_2O

Let us now consider the VB description of ground state H_2O in terms of *directed* hybrid orbitals on O, by posing:

$$hy_1 = b_1, \qquad hy_2 = b_2, \qquad hy_3 = \sigma. \tag{289}$$

- $H_2O(^1A_1)$.

$$O(^3P)\colon\ 1s_O^2 2s_O^2 2p_{xO}^2 2p_{yO} 2p_{zO} \Rightarrow k^2\sigma^2x^2b_1b_2 \tag{290}$$

$$H(^2S)\colon\ \Rightarrow h_1h_2, \tag{291}$$

where k is the inner-shell oxygen AO, σ and x the AOs describing the two lone pairs, and b_1, b_2 the two equivalent $sp^2(C_{2v})$ hybrids on oxygen pointing towards h_1 and h_2.

In a first approximation, restricting ourselves to the four orbitals b_1, b_2, h_1, h_2, and treating H_2O as an "effective" 4-electron problem, Weyl formula gives:

$$f(4,4,0) = \frac{1}{5}\binom{5}{3}\binom{5}{2} = 20 \tag{292}$$

singlet ($S = M_S = 0$) VB structures, 2 covalent, 12 singly polar, 6 doubly polar, few of which are given in Figure 10.33, where the *parent* dets are also indicated. The most important structures are, of course, ψ_1 (perfect-pairing), the two equivalent singly polar ψ_3 and ψ_4 and the doubly polar ψ_{15}. Polar structures are expected to be important in H_2O because of the greater electronegativity of the O atom compared to the H atoms.

Considering only the most important structures in the VB wavefunction:

$$\Psi(^1A_1) = \psi_1c_1 + \frac{1}{\sqrt{2}}(\psi_3 + \psi_4)c_3 + \psi_{15}c_{15}, \tag{293}$$

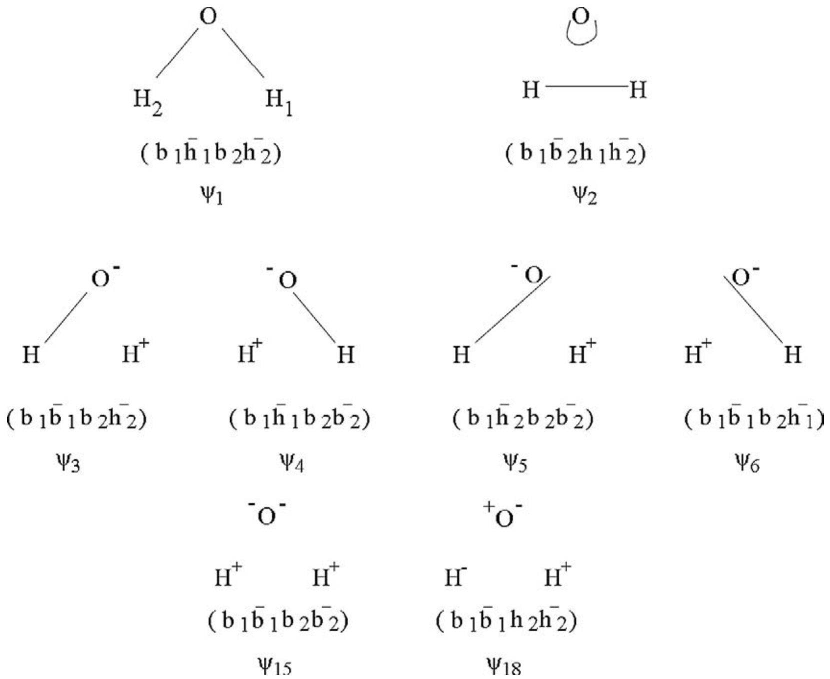


Figure 10.33 A few of the 20 singlet VB structures for ground state H_2O treated as a four-electron problem.

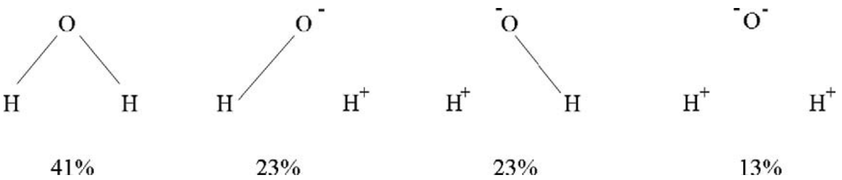


Figure 10.34 Estimated relative weights of covalent and polar VB structures in ground state H_2O.

Coulson (1961) gave an estimate of the mixing coefficients which reproduces the value of observed dipole moment ($\mu = 0.73ea_0$):

$$c_1 = 0.64, c_3 = c_4 = 0.48, c_{15} = 0.36$$

yielding the relative weights of Figure 10.34.

Even if the importance of the ionic structures in Coulson's VB description of H_2O might seem too large, subsequent ab-initio VB calculations by Raimondi et al. (1977) on CH_4 using a minimal basis of STOs in the $1s^2$ "frozen" core approximation, have confirmed the importance of mono- and bi-ionic structures in accounting for a large part of the correlation energy in this molecule. Different ab-initio VB calculations on ground state H_2O in the minimum STO basis of Ellison and Shull (1953) were done by McWeeny and Ohno (1960) and Maclagan and Schnuelle (1977), while Raimondi, Tantardini and Simonetta

(RTS) (Raimondi et al., 1974, 1975) tested the influence on energy and dipole moment of the quality of the orbitals and the number of structures included in the calculation. RTS concluded that the best value of the energy is strongly dependent on the nature of the orbitals in the basis set, while the full-electron VB calculation in the minimum basis set of 7 AOs (196 structures) is not significantly better than the $1s^2$ "frozen" core approximation involving 6 AOs (105) structures. On the other hand, the performance of the physically appealing simple VB approximation (293) does not seem to have been fully explored in ab-initio calculations. In more recent work, McWeeny and Jorge (1988) examined the effect of hybridization in a VB study of H_2O using a minimal set of 7 AOs expressed in STO-6G form, keeping a k^2x^2 "frozen" core. They concluded that, with suitably optimized hybrids, a few structures are capable of giving results close to those obtained in the full-CI limit of 50 structures.

Group function (GF) calculations for ground state H_2O were reported by Klessinger (1965), who studied the systematic variation of the molecular energy with the hybridization parameters. Best energy was obtained for orthogonal sp^2 bond hybrids having $18\%s$ and an interbond angle of $102.7°$. These values are not far from those obtained from the simple requirement of hybrid orthogonality of equation (284) (20.6% and $2\theta = 105°$).

10.6.3 Properties of Hybridization

We now summarize briefly the main properties of hybridization.

(i) Physically, hybridization describes to a certain extent the *distortion* of the orbitals involved in the bond (see H_2), a second-order effect which can be fully accounted for by enlarging the basis set to include polarization functions.

(ii) Hybridization *increases* overlap between the AOs forming the bond, yielding a strong bond (more correctly, it increases the exchange-overlap component of the bond energy).

(iii) Hybridization restores orthogonality of the AOs onto the *same* atom, allowing for interhybrid angles greater than 90°. The hybrid AOs can in this way reorient themselves in an optimum way, maximizing the overlap in the formation of the bonds and avoiding the formation of weaker bent bonds. The proof of this statement was first given by Coulson (1961), and will be fully given in Problem 10.9 with reference to Figure 10.35.

(iv) Hybridization can give in this way the AOs the appropriate directional character for forming covalent bonds, and is therefore of fundamental importance in bond stereochemistry.

(v) According to Mulliken (1951), "a little hybridization goes a long way". Even without changes in valency (*isovalent* hybridization), hybridization allows for a better disposition in space of electron lone pairs, projecting them in regions of space external to the bond region, what has a considerable effect on the electric dipole moment of the molecule (see Coulson's atomic dipoles).

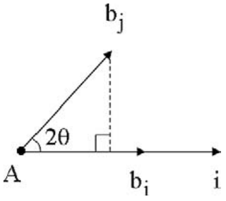


Figure 10.35 Resolution of the bond hybrid b_j into orthogonal components.

Table 10.13.

Possible sp^3 hybrids equivalent under different symmetries

Hybrid	Name	$2\theta/^\circ$	Number of hybrids	Symmetry
$sp\pi^2$	Digonal	180	2	$D_{\infty h}$
$sp^2\pi$	Trigonal	120	3	D_{3h}, C_{3v}
sp^3	Tetrahedral	109.5	4	T_d

(vi) For the carbon atom, promotion of an electron from $2s$ to $2p$ increases *covalency* from 2 to 4, so that it is possible to obtain four sp^3 hybrid orbitals, each singly occupied, symmetrically disposed in space and making interhybrid angles greater than 90°:

$$s^2p^2 \Rightarrow sp^3 \Rightarrow \text{four hybrids of different symmetries.} \tag{294}$$

The analytical form of the different equivalent hybrids pointing in the i-th direction is:

$$\begin{aligned} b_i &= \frac{s+p_i}{\sqrt{2}} && \text{digonal} \left(\%s = \frac{1}{2}\right) \\ b_i &= \frac{s+\sqrt{2}p_i}{\sqrt{3}} && \text{trigonal} \left(\%s = \frac{1}{3}\right) \\ b_i &= \frac{s+\sqrt{3}p_i}{2} && \text{tetrahedral} \left(\%s = \frac{1}{4}\right). \end{aligned} \tag{295}$$

Possible equivalent sp^n hybrids are given in Table 10.13 and Figure 10.36.

These *equivalent* hybrids are those describing the bonds in BeH_2 and CO_2 ($D_{\infty h}$), BH_3 (D_{3h}) and CH_4 (T_d). As already seen for H_2O, sp^n hybrids of lower symmetry are possible as well. They are only partly equivalent, such as sp^3 or $sp^2\pi$ (C_{2v}) in H_2O, sp^3 (C_{3v}) in NH_3 or CH_3X molecules. In the case of ammonia, three equivalent hybrids form the three N—H bonds with the three H atoms, while a fourth, non equivalent, hybrid will describe the electron lone pair directed along the symmetry z-axis. Torkington (1951) gave formulae for sp^3 hybrids equivalent under C_{2v} and C_{3v} symmetry, whereas Musso et al. (1973) gave formulae for sp^3 hybrids of C_1 (no symmetry) and C_s (one symmetry plane) symmetry. From the latter formulae, Torkington results for C_{2v} (two symmetry planes) and C_{3v} (three symmetry planes) are easily recovered under the appropriate symmetry restrictions.

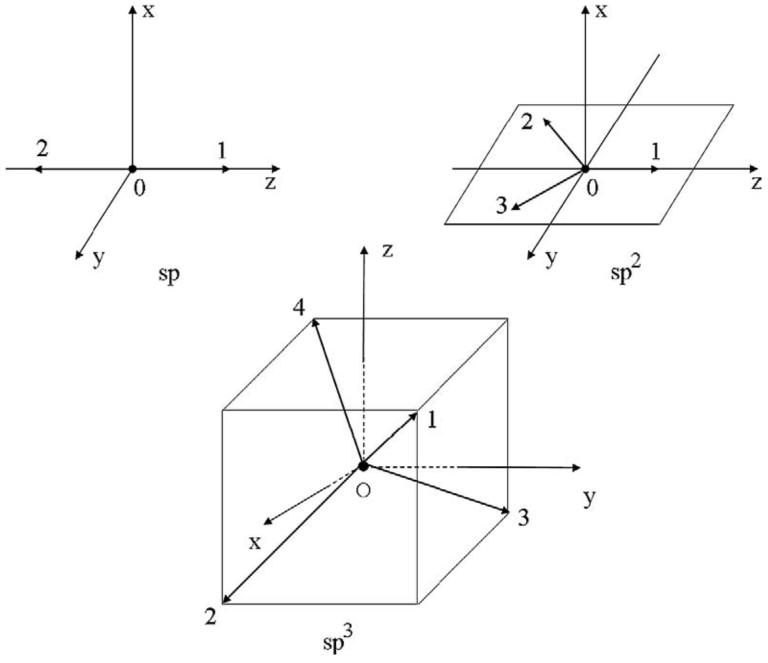


Figure 10.36 Equivalent sp^n hybrids of $D_{\infty h}$, D_{3h} and T_d symmetries.

A striking example of point (ii) above in the case of two equivalent sp hybrids will conclude this Section. With reference to Figure 10.37, assuming all elementary overlaps between s and $p\sigma$ AOs to be positive, the overlap between two general sp hybrids making an angle 2θ with respect to the bond direction z will be:

$$\begin{aligned} S_{bb} &= \langle b_A | b_B \rangle \\ &= S_{ss}\cos^2\omega + \left(S_{\sigma\sigma}\cos^2 2\theta + S_{\pi\pi}\sin^2 2\theta\right)\sin^2\omega \\ &\quad + S_{s\sigma}\sin 2\omega\cos 2\theta, \end{aligned} \tag{296}$$

where ω denotes the hybridization parameter.

For hybrids directed along the bond, $\theta = 0°$, so that:

$$S_{bb} = S_{ss}\cos^2\omega + S_{\sigma\sigma}\sin^2\omega + S_{s\sigma}\sin 2\omega. \tag{297}$$

Table 10.14 gives the hybrid overlap S_{bb} for different C=C hybrids in ethylene, for $R = 2.55a_0$ and elementary overlaps between STOs with $c_s = c_p = 1.625$:

$$S_{ss} = 0.4322, \qquad S_{\sigma\sigma} = 0.3262, \qquad S_{s\sigma} = 0.4225. \tag{298}$$

Table 10.14 shows that hybrid overlap is sensibly larger than each elementary overlap S_{ss}, $S_{\sigma\sigma}$ and $S_{s\sigma}$. Considering the largest individual overlap, $S_{ss} = 0.4322$, hybrid overlap

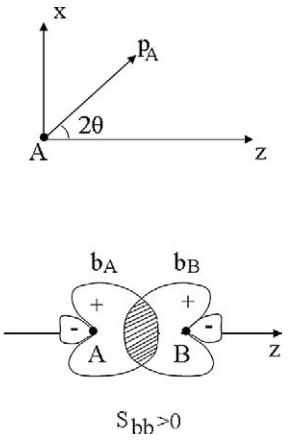


Figure 10.37 Overlap between two sp hybrids along the bond direction.

Table 10.14.

Overlap between sp bond hybrids according to different hybridizations

Hybrid	sp^n	$\cos\omega$	$\omega/°$	S_{bb}
Digonal	sp	$\frac{1}{\sqrt{2}}$	45	0.8017
Trigonal	sp^2	$\frac{1}{\sqrt{3}}$	54.7	0.7600
Tetrahedral	sp^3	$\frac{1}{2}$	60	0.7186

is increased by over 85.5% for sp, 75.8% for sp^2, and 66.3% for sp^3. The numbers show unequivocally the phantastic increase in overlap due to sp hybridization.

10.6.4 The Principle of Maximum Overlap in VB Theory

The principle of maximum overlap was often assumed as one of the fundamental rules of chemical bonding since the early applications of quantum mechanics to the study of the electronic structure of molecules (Hückel, 1930; Pauling, 1931a; Coulson, 1937b). The principle states that "bonding is stronger for AOs having maximum overlap", and has the important consequence that *straight* bonds are stronger.

We shall outline here a simple VB model, recently presented by us (Magnasco and Costa, 2005), which shows that, in the valence bond description of the chemical bond, "covalent bonding is strongest for AOs maximizing the strength[8] of the complete exchange-overlap component of the bond energy". This was suggested by the fact (i) that the HL description

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[8] We recall that the bond strength is the negative of the bond energy D_e at the bond length R_e.

of the covalent bond seems an adequate first approximation for describing the strength of a chemical bond and its dependence on orientation, and (ii) that Table 10.4 in this Chapter shows that the exchange-overlap component of the first-order HL interaction energy for ground state H_2 has a sensible minimum at the bond length, $R_e = 1.4a_0$. The overlap S_{AB} between p_A, a directed $2p$ orbital on A making an angle θ with the interbond axis A–B directed from A to B along z, and s_B, a spherical orbital on B a distance R apart, is:

$$S_{AB} = \langle s_B | p_A \rangle = S \cos\theta, \tag{299}$$

where S is an overlap integral characteristic of the bond A–B, which depends on R but is independent of θ. It is immediately evident that S_{AB} has a maximum value when p_A points in the direction of s_B ($\theta = 0°$). The HL 1- and 2-electron exchange-overlap components of the bond energy, equation (53), will take the simple form:

$$\Delta E_1^{\text{exch-ov}} = S_{AB} \frac{(h_{s_B p_A} - S_{AB} h_{p_A p_A}) + (h_{p_A s_B} - S_{AB} h_{s_B s_B})}{1 + S_{AB}^2} \tag{300}$$

$$\Delta E_2^{\text{exch-ov}} = \frac{(p_A s_B | p_A s_B) - S_{AB}^2 (p_A^2 | s_B^2)}{1 + S_{AB}^2}. \tag{301}$$

For the matrix elements of the "effective" 1-electron operator $\hat{h}$ over the exchange-overlap densities $(p_A s_B - S_{AB} p_A^2)$ and $(s_B p_A - S_{AB} s_B^2)$ we can make assumptions similar to those of Hückel theory including overlap (Magnasco, 2002, 2004a):

$$\begin{aligned} h_{p_A p_A} &= \left(p_A^2 | \hat{h}\right) = \alpha_p, \qquad h_{s_B s_B} = \left(s_B^2 | \hat{h}\right) = \alpha_s \\ h_{s_B p_A} &= (p_A s_B | \hat{h}) = \beta_{AB} = \beta \cos\theta, \end{aligned} \tag{302}$$

where α_p, α_s, β are all negative quantities, and β is a bond integral, characteristic of the bond A–B but independent of the orientation θ. When the angular dependence on θ is singled out from expressions (300) and (301), it is easily shown that the stationarity condition for $E^{\text{exch-ov}}$ against θ is obtained from:

$$\frac{dE^{\text{exch-ov}}}{d\theta} = \frac{\sin 2\theta}{(1 + S^2 \cos^2\theta)^2} \left[a + b \cos^2\theta (2 + S^2 \cos^2\theta)\right] = 0, \tag{303}$$

while the second angular derivative is positive at the stationary point $\theta = 0$:

$$\left(\frac{d^2 E^{\text{exch-ov}}}{d\theta^2}\right)_{\theta=0} = \frac{2}{(1 + S^2)^2} \left[a + b(2 + S^2)\right] > 0. \tag{304}$$

In the equations above, a and b are positive constants involving 1- and 2-electron integrals independent of angle θ. Equations (303) and (304) then say that the HL exchange-overlap strength of the covalent bond formed between the AOs p_A and s_B has a maximum (a minimum of negative energy) for the straight bond ($\theta = 0°$), which has the physically appealing expression:

$$E^{\text{exch-ov}}(\theta = 0) = \frac{S[2\beta - S(\alpha_p + \alpha_s)] + [(\sigma_A s_B|\sigma_A s_B) - S^2(\sigma_A^2|s_B^2)]}{1 + S^2}, \qquad (305)$$

the exact counterpart of equation (53) for ground state H_2. Here, σ_A and π_A (involved in the constants a, b) are the components of p_A along the bond direction and perpendicular to it.

We may conclude that the principle of maximum overlap of elementary valence theory (Coulson, 1961) should more appropriately be replaced by the principle of *maximum exchange-overlap* in the formation of the covalent bond. A similar conclusion is obtained in elementary Hückel theory including overlap (Magnasco, 2005).

10.7 AN OUTLINE OF RECENT ADVANCES IN VB THEORY

In the next two Sections we shall give a short outline of some recent advances in valence bond theory, first summarizing the main lines of research in the field (Section 10.7.1), next giving some details of the spin-coupled VB theory.

10.7.1 Modern VB Theories

In a broad sense, we can refer to the content of this Section as to "Modern VB theories" since we want to present here those lines of research aimed at an ab-initio VB theory after the semiempirical Pauling's approach given in Section 10.5. The research in the field may be roughly summarized into six main lines as follows.

(i) As already outlined in Section 10.5, the first attempt to put the theory on a sound basis so as to allow for ab-initio calculations was done long ago by McWeeny, who, after a critique of the VB methods existing at that time (McWeeny, 1954a), reformulated the theory (McWeeny, 1954b) in terms of Löwdin orthogonalized atomic orbitals (OAOs) fully including polar (ionic) structures. The construction of suitable spin eigenfunctions and the evaluation of matrix elements between structures is fully described there, together with an extension of usual Pauling's rules to include the presence of ionic structures. This revised VB theory was then applied by McWeeny (1955) in non-empirical calculations of the lower π-electron levels of cyclobutadiene and benzene. This theory was also used by the author and coworkers (Magnasco and Musso, 1967a, 1967b) in ab-initio studies of short-range intermolecular interactions in H_2–H_2.

(ii) Direct use of Löwdin rules (Löwdin, 1955a) for the evaluation of matrix elements between Slater determinants of non-orthogonal orbitals. This was the approach mostly followed by Simonetta's group in Milan in the seventies. An a-priori VB theory, which could be applied to states of any multiplicity, was formulated in a general form including both spin and orbital degeneracy (Simonetta et al., 1968). Structures were related to products of spin functions found by means of extended Rumer diagrams, the spin functions corresponding to each diagram being the product of $(N - 2S)$ spins coupled in pairs and $2S$ parallel coupled ("leading term"). All possible ways of coupling electrons in pairs were considered. Calculations in the σ–π approximation using STO bases were done for simple hydrocarbons, molecules, radicals and ions. An application to benzyl radical with inclusion of an increasing number of ionic structures was found to give excellent results for the hyperfine coupling constants of the radical calculated from VB spin densities (Raimondi et al., 1972).

The theory was next applied at the ab-initio level to small molecules and radicals, using minimal basis sets of STOs. Calculations were done on ground state ($^2\Pi$) energy, proton and ^{13}C hyperfine splittings of the CH radical (Tantardini and Simonetta, 1972, 1973), and on different electronic states of CH_2 (Tantardini et al., 1973).

The quality of the orbitals in the basis set (Slater, Slater with optimized orbital exponents, Hartree–Fock AOs) and the number of structures included in the calculation was then examined in minimum basis set ab-initio VB calculations on LiH, CH, CH_2, CH_3, NH_3 and H_2O by Raimondi et al. (1974). Confirming previous results on H_2 and LiH by Yokoyama (1972), it was shown there that a relatively small number of structures could give fair results if the basic AOs were carefully chosen. The problems arising in the VB treatment when attempting to extend the basis set were discussed, for the same set of molecules, by Raimondi et al. (1975). They came to the conclusion that there was the need for a general method of going beyond the minimal basis set, then making a selection of the resulting VB structures according to chemical intuition. In this way, connection with Gerratt's work (Gerratt, 1971), where use is made of "best" orbitals to build spin-coupled VB functions (next point in this Section), arose quite naturally.

(iii) As just discussed in (ii), the classical valence bond method, considered as a simple extension of the Heitler–London theory, becomes quickly impracticable if use of extended basis sets is needed to obtain highly accurate results. Goddard (1967a, 1967b, 1968a, 1968b) and Gerratt (1971) proposed independently a general theory where use of group theoretical arguments is made from the outset to obtain an energy expansion corresponding to a linear combination of structures for a single orbital configuration, then optimizing both orbitals and expansion coefficients to obtain the best possible one-configuration approximation. The non-orthogonal orbitals resulting therefrom were called unrestricted general valence bond (GVB) orbitals by Goddard or spin-coupled self-consistent-field (SC-SCF) orbitals by Gerratt. Gerratt's theory and its further extension will be further discussed in the next Section.

As far as the numerical results are concerned, Goddard made a preliminary calculation on the magnetic hyperfine structure of the Li atom (Goddard III, 1967c), followed by GVB calculations for several molecules, including H_2 (Goddard III, 1967b), Li_2, CH_3, CH_4 (Goddard III, 1968b), LiH (Palke and Goddard III, 1969), LiH, H_3, BH, H_2O, C_2H_6, O_2 (Hunt et al., 1972) and O_2 (Moss et al., 1975). The calculations gave a fairly correct torsional barrier in ethane, and an accurate description of the relative position of the $^3\Sigma_g^-$ and $^1\Sigma_g^+$ electronic states of O_2. Particular attention was paid to the shape of the optimized GVB orbitals, which show enhanced overlap over the entire internuclear distances.

By Gerratt, calculations were done using an extension of his original approach on H_2 (Wilson and Gerratt, 1975), LiH, BH, Li_2, HF (Pyper and Gerratt, 1977), the potential energy curves of different electronic states of BeH (Gerratt and Raimondi, 1980), the dipole moment of ground state LiH (Cooper et al., 1985), the reaction $B^+ + H_2$ (Cooper et al., 1986a), and a review (Cooper et al., 1987) where the results on small molecular systems, containing up to 10 electrons, were presented. Again it was found that the orbitals resulting from the optimized procedure are of the Coulson–Fischer enhanced-overlap type, and that relatively short expansions usually lead to wavefunctions of high quality. The spin-coupled functions typically yield 85% of the observed binding energies and equilibrium bond distances accurate to 0.01Å. 200–700 structures are usually sufficient to reproduce the first 10 states of a given symmetry to an accuracy of about 0.01 eV.

The explicit introduction of r_{12} into the Coulson–Fischer wavefunction was examined by Clarke et al. (1994). Similar VB-SCF and VB-CI methods were later proposed by Van Lenthe and Balint-Kurti (1983).

(iv) Gallup, Gallup et al. (1973, 1982) largely uses group theoretical techniques with Young idempotents to project out functions of appropriate symmetry from a set of arbitrary orbital products, but not optimizing the orbitals. His presentation is complicated to some extent by the abstract formalism of the permutation group and its algebras, but, according to the author, this formulation allows to develop an optimal algorithm for the evaluation of matrix elements of the Hamiltonian involving non-orthogonal orbitals. The theory was presented in some detail by Gallup (2002) in a recent textbook on valence bond methods, and fully implemented in a commercial program package (CRUNCH) developed by the author and his students.

(v) McWeeny (1988b, 1990) recasted classical VB theory in a spin-free form which seems to provide a practicable route to ab-initio calculations of molecular electronic structure even for extended basis sets. The formalism is, in part, similar to that explained in some detail in the next Section, being based on the construction of symmetry-adapted functions obtained by applying Wigner projectors to suitable products of space orbitals, and coupling them with the associated "dual" spin functions carrying an f_S^N-dimensional irrep of the S_N group. To maintain contact with classical VB theory, however, the spin functions are chosen to be of the Weyl–Rumer form and *not* of the standard Kotani's form as those used by Gerratt et al. (1971, 1987). The Weyl–Rumer functions for $|M_S| = S$ correspond to the lowest path in the standard branching diagram, where $(N-2S)/2$ spins are coupled in pairs while all remaining spins are parallel coupled (see also Serber, 1934a, 1934b). A standard variational approach allows to determine best expansion coefficients and orbitals in the expansion of the wavefunction over all possible symmetry-adapted orbital products. The matrix elements are easily evaluated (even within the memory of a fast personal computer) provided efficient algorithms are used for systematically generating permutations and for handling Rumer diagrams. The method should be sufficient for dealing with molecular systems containing up to 10 electrons outside a closed-shell core, and simple calculations on the H_2–H_2 system (McWeeny, 1988a), and on the H_2O and O_2 molecules (McWeeny and Jorge, 1988; McWeeny, 1990) seem to confirm the conclusions of Cooper et al. (1987) that, using strongly overlapping optimized orbitals, a small number of "classical" covalent structures can give results close to those occurring in a Full-CI calculation with the same basis set.

(vi) We end by quoting Corongiu's recent approach (Corongiu, 2005, 2006) which mixes Hartree–Fock with Heitler–London theory. The method rests, essentially, in taking as a first step a variationally optimized linear combination of traditional HF and HL functions, followed by inclusion of valence and inner shells correlation. Using increasingly accurate $s, p, d, f \ldots$ sets of Gaussian functions, results for the whole potential curves, including dissociation, for the homonuclear diatomics H_2, Li_2, F_2, and the diatomic hydrides HeH, LiH, BeH, BH, CH, NH, OH, FH seem excellent over the whole range of internuclear distances, and very promising for future applications to polyatomic molecules.

It must be said that similar concepts were put forward in a qualitative way as early as 1936, by Nordheim-Pöschl (1936a, 1936b) in her doctoral dissertation at the Faculty of Mathematical and Natural Sciences of the University of Göttingen, for explaining the apparent deviations occurring in the HL description of the chemical bond in some diatomic and polyatomic molecules.

10.7.2 The Spin-Coupled VB Theory

The so-called spin-coupled VB theory was initially suggested by Gerratt (1971, 1976) and later developed mostly with Cooper and Raimondi (Gerratt and Raimondi, 1980; Cooper et al., 1987, references therein and subsequent work by these authors). In Gerratt's original approach, the most general approximate function obtainable from a spatial function Φ^N is written as a linear combination of all possible spin couplings k:

$$\Psi_{SM_S} = \sum_{k=1}^{f_S^N} \Psi_{SM_S;k} d_{Sk}, \tag{306}$$

where $\Psi_{SM_S;k}$ is the un-normalized "spin-coupled function" [9]:

$$\Psi_{SM_S;k} = \left(\frac{1}{f_S^N}\right)^{1/2} \sum_{l=1}^{f_S^N} (\hat{Y}_{lk}^S \Phi^N) \Theta_{SM_S;l}^S. \tag{307}$$

In equation (306), space and spin parts of the function are constructed separately following a suggestion by Wigner (1959). Φ^N is an arbitrary regular spatial function without any permutational symmetry, chosen in the form of products of N spatial orbitals:

$$\Phi^N(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \cdots \phi_N(\mathbf{r}_N), \tag{308}$$

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[9] The Θs of Gerratt's work replace our ηs of Chapter 6.

while $\hat{Y}^S_{lk}$ is the Young–Yamanouchi–Wigner projector:

$$\hat{Y}^S_{lk} = \left(\frac{f^N_S}{N!}\right)^{1/2} \sum_P U^S_{lk} \hat{P}^r \tag{309}$$

projecting out of Φ^N a basis transforming irreducibly under the operations of the symmetric group S_N (see Section 8.7.5 of Chapter 8).

$\Theta^N_{SM_S;l}(s_1, s_2, \cdots, s_N)$, the spin function "dual" to $(\hat{Y}^S_{lk}\Phi^N)$ in the Wigner sense, is constructed by the synthetic method due to Kotani (Section 6.6 of Chapter 6) starting with the spin functions for a single electron ($\Theta = \alpha$ for $M_S = 1/2$, $\Theta = \beta$ for $M_S = -1/2$) and building up the N-electron function by coupling the spins successively according to the usual rules for angular momentum in Quantum Mechanics (Chapter 9) with reference to the Kotani branching diagram. As already said before, indices k, l ($k, l = 1, 2, \cdots, f^N_S$, where f^N_S is the usual Wigner number of Chapter 6) can be interpreted as a series of partial resultant spins. All $\Theta^N_{SM_S;k}$ are eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$ with eigenvalues S and M_S, respectively, and form an orthonormal set of functions making a basis for the irrep of S_N ("dual" to the projected spatial part), which transforms under a permutation $\hat{P}^s$ of the spin variables according to:

$$\hat{P}^s \Theta^N_{SM_S;k} = \varepsilon_P \sum_{l=1}^{f^N_S} \Theta^N_{SM_S;l} U^S_{lk}(P), \tag{310}$$

the matrices $\varepsilon_P \mathbf{U}^S(P)$ being said by Wigner to constitute the "dual" representation[10]. The resultant functions (306) and (307) are, of course, exact eigenfunctions of the spin operators $\hat{S}^2$ and $\hat{S}_z$ with eigenvalues S and M_S, respectively:

$$\hat{S}^2 \Psi_{SM_S} = S(S+1)\Psi_{SM_S}, \qquad \hat{S}^2_z \Psi_{SM_S} = M_S \Psi_{SM_S}. \tag{311}$$

The energy corresponding to function (306) is given by:

$$\begin{aligned} E_S = \frac{1}{\Delta}\Bigg[& \sum_{\mu,\nu=1}^{N} D(\mu|\nu)\langle\phi_\mu|\hat{h}|\phi_\nu\rangle \\ & + \sum_{\mu<\nu}^{N}\sum_{\sigma<\tau}^{N} D(\mu\nu|\sigma\tau)\langle\phi_\mu\phi_\nu|g|\phi_\sigma\phi_\tau\rangle \\ & + \sum_{\mu<\nu}^{N}\sum_{\sigma<\tau}^{N} D(\mu\nu|\tau\sigma)\langle\phi_\mu\phi_\nu|g|\phi_\tau\phi_\sigma\rangle\Bigg], \end{aligned} \tag{312}$$

where $D(\mu|\nu)$, $D(\mu\nu|\sigma\tau)$ are elements of the one- and two-electron density matrices, $\langle\phi_\mu|\hat{h}|\phi_\nu\rangle$ and $\langle\phi_\mu\phi_\nu|g|\phi_\sigma\phi_\tau\rangle$ the usual one- and two-electron integrals and Δ the nor-

---

[10] ε_P is the usual parity of the permutation, equal to $+1$ or -1 according to whether P is even or odd.

malization integral. The linear coefficients $\{d_{Sl}\}$ or, better, their normalized counterpart $\{c_{Sl} = d_{Sl}(\Delta_{ll}^{S})^{1/2}\}$, are found by solving a pseudosecular equation of order f_S^N at most. The variation problem is next completed by optimizing the energy (312) with respect to the form of the orbitals. This is best and most efficiently achieved by using gradient techniques (Gerratt and Raimondi, 1980). Best orbitals ϕ_μs appear as solution of a one-electron integro-differential equation, reminiscent of the Hartree–Fock equation, but with a rather complicated one-electron operator $\hat{F}_\mu$, different for each orbital. The resulting orbital energy ε_μ can in no way be related to the experimentally observed molecular ionization potentials, but must be simply regarded as the energy of the corresponding electron in the field of nuclei and all other electrons. The virtual (unoccupied) orbitals resulting therefrom have the same *distorted* atomic form of the occupied ones and have *negative* orbital energies. This is at variance with what occurs in conventional MO theory, where the excited MOs usually correspond to *positive* orbital energies, being, consequently, highly diffuse and, as such, not well suited for use in the CI procedure.

We want to stress at this point that the general expression of the spin-coupled function $\Psi_{SM_S;k}$ of equation (307) can be recast into the more familiar form in terms of Slater determinants. In fact, using the explicit form (309) of the projector $\hat{Y}^S$, we have:

$$\begin{aligned}
\Psi_{SM_S;k} &= \left(\frac{1}{f_S^N}\right)^{1/2} \sum_{l=1}^{f_S^N} \left(\hat{Y}_{lk}^S \Phi^N\right) \Theta_{SM_S;l}^N \\
&= \left(\frac{1}{N!}\right)^{1/2} \sum_P \left(\hat{P}^r \Phi^N\right) \left\{\sum_{l=1}^{f_S^N} U_{lk}^S(P) \Theta_{SM_S;l}^N\right\} \\
&= \left(\frac{1}{N!}\right)^{1/2} \sum_P \left(\hat{P}^r \Phi^N\right) \left\{\varepsilon_P \left(\hat{P}^s \Theta_{SM_S;l}^N\right)\right\} \\
&= (N!)^{1/2} \hat{A}\left(\Phi^N \Theta_{SM_S;l}^N\right),
\end{aligned} \tag{313}$$

where $\hat{A}$ is the usual antisymmetrizer:

$$\hat{A} = \frac{1}{N!} \sum_P \varepsilon_P \hat{P}, \qquad \hat{P} = \hat{P}^r \hat{P}^s \tag{314}$$

$\hat{P}^r$ being a permutation of spatial variables, $\hat{P}^s$ of spin variables only.

The original form of Gerratt's theory, however, suffers from the limitation of being constructed from a single configuration and, in some cases, cannot predict the correct dissociation of the bonds. Pyper and Gerratt (1977) introduced a two-configuration wavefunction where both orbital expansion coefficients and interconfigurational coefficients were simultaneously optimized, giving in this way a very accurate description of the whole potential energy curve for the simple molecules LiH, BH, Li_2 and HF. Gerratt's theory was later extended in two respects, (i) by considering the expansion of the spatial functions Φ into different sets of orthonormal functions for each electron coordinate, the different sets being not orthogonal to each other, and (ii) by making full use of Löwdin (1955a) techniques for the calculation of matrix elements of the Hamiltonian between Slater determinants of non-orthogonal orbitals using (313), in a procedure which involves the simultaneous production of up to four-electron density matrices[11]. The technical problems arising from the computation of a huge number of cofactors and the efficiency of the different strategies for the design of ab-initio VB algorithms were fully examined by Raimondi and Gianinetti (1988). In the last reformulation of the theory (1987), the spin-coupled wavefunction (306) appears as the first (and more important) term in a more general expansion of Φ into N distinct sets of non-orthogonal orbitals. The CI stage of this work makes use of the traditional VB spin functions as first formulated by Rumer (Section 10.5.1), in which the functions are constructed by coupling together pairs of individual electron spins to form *singlets*, so highlighting the phenomenon of bond formation in molecules.

10.8 PROBLEMS 10

10.1. Give a variational derivation of the Born–Oppenheimer equation (8) (Longuet-Higgins, 1961).

Answer:
Equation (8) of the main text.

Hint:
Use $\Phi = \Psi_e(x;q)\Psi_n(q)$ as nuclear variational wavefunction and optimize Ψ_n subject to the normalization condition.

10.2. Show the complete equivalence between MO and HL wavefunctions for the ${}^3\Sigma_u^+$ excited state of H_2.

Answer:

$$\Psi(\text{MO}, {}^3\Sigma_u^+) = \frac{1}{\sqrt{2}}(\sigma_g\sigma_u - \sigma_u\sigma_g) \begin{cases} \alpha\alpha \\ \dfrac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha) \\ \beta\beta \end{cases}$$

---

[11] In order to optimize the energy with non-orthogonal AOs, density matrices of order 1, 2, 3, 4 are needed. These density matrices are connected with one another, and can all be produced simultaneously, providing in this way a highly efficient recurrence scheme for their computation.

$$= \frac{ab - ba}{\sqrt{2 - 2S^2}} \begin{cases} \alpha\alpha \\ \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha) \\ \beta\beta \end{cases} = \Psi\big(\mathrm{HL}, {}^3\Sigma_u^+\big).$$

Hint:

Use the definitions, expanding σ_g and σ_u according to expressions (19) and (20) of the main text.

10.3. Show the equivalence between the MO-CI wavefunction (61) and the full VB (HL + ION) (60).

Answer:

$$\begin{aligned} \Psi(\mathrm{MO-CI}, {}^1\Sigma_g^+) &= N\big\{\Psi(\sigma_g^2, {}^1\Sigma_g^+) + \lambda\Psi(\sigma_u^2, {}^1\Sigma_g^+)\big\} \\ &= N\bigg\{(ab + ba) \\ &\quad + \frac{(1-S) + \lambda(1+S)}{(1-S) - \lambda(1+S)}(aa + bb)\bigg\}\frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha) \\ &= c_1\Psi\big(\mathrm{HL}, {}^1\Sigma_g^+\big) + c_2\Psi\big(\mathrm{ION}, {}^1\Sigma_g^+\big), \end{aligned}$$

where $\lambda = c_2/c_1$.

Hint:
Use the definitions, expanding σ_g and σ_u according to expressions (19) and (20) of the main text.

10.4. Show that the Schmidt orthogonalization of ψ_1 to ψ_2 in the case of the allyl radical yields two functions which are in one-to one correspondence with the two pure spin doublets found in Problem 6.1 of Chapter 6.

Answer:

$$\begin{aligned} \psi_1' &= \frac{\psi_1 - S_{12}\psi_2}{\sqrt{1 - S_{12}^2}} \\ &= \frac{1}{\sqrt{6}}\big[(ab\bar{c}) + (a\bar{b}c) - 2(\bar{a}bc)\big] \\ \psi_2' = \psi_2 &= \frac{1}{\sqrt{2}}\big[(a\bar{b}c) - (ab\bar{c})\big], \end{aligned}$$

to be compared with the two pure spin *doublet* functions of Chapter 6:

$$\eta_1 = \frac{1}{\sqrt{6}}(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha)$$

$$\eta_3 = \frac{1}{\sqrt{2}}(\alpha\alpha\beta - \alpha\beta\alpha).$$

Hint:
Evaluate the Schmidt transformed VB function ψ_1'.

10.5. Show the equivalence between MO and VB wavefunctions for $He_2(^1\Sigma_g^+)$.

Answer:

$$\Psi\big(\text{MO}, {}^1\Sigma_g^+\big) = \|\sigma_g\overline{\sigma}_g\sigma_u\overline{\sigma}_u\| = \|a\overline{a}b\overline{b}\| = \Psi\big(\text{VB}, {}^1\Sigma_g^+\big).$$

Hint:
Use the definitions (19) and (20) for σ_g and σ_u, and the elementary properties of determinants.

10.6. Study the symmetry of the ionic structures in triplet O_2.

In the ultrashort notation of Section 10.4.5 (vi) (b), the $M_S = 1$ component of the ionic structures in triplet O_2 can be written as:

$$\Psi(\text{ION}) = \frac{1}{\sqrt{2}}\big[(x_A y_A) + (x_B y_B)\big].$$

Answer:
$\Psi(\text{ION})$ is the $M_S = 1$ component of the state $^3\Sigma_g^-$.

Hint:
Use the operators $\hat{S}^2$, $\hat{L}_z$, $\hat{\sigma}_{zx}$ and $\hat{\imath}$, commuting with the Hamiltonian $\hat{H}$, to classify the electronic state $\Psi(\text{ION})$.

10.7. Evaluate the matrix elements between covalent VB structures for cyclobutadiene.

Answer:
Equations (279) and (282) of the main text.

Hint:
Use Slater's rules for orthonormal dets and the elementary properties of determinants.

10.8. Construct the three sp^2 hybrids of C_{2v} symmetry for H_2O.

Answer:
If the molecule is chosen to lie in the yz-plane, the three hybrids are:

$$hy_1 = as + bp_1 \qquad hy_2 = as + bp_2 \qquad hy_3 = cs - dz,$$

where, if 2θ is the interhybrid angle:

$$a = \sqrt{\frac{2\sin^2\theta - 1}{2\sin^2\theta}}, \qquad b = \sqrt{\frac{1}{2\sin^2\theta}}$$

$$c = \cot\theta, \qquad d = \sqrt{\frac{2\sin^2\theta - 1}{\sin^2\theta}}.$$

Hint:
Use equivalence and orthonormality relations between the three hybrids.

10.9. Prove that the angle made by two equivalent orthogonal hybrids is greater than 90°.

Answer:
If 2θ is the angle between the two equivalent orthogonal hybrids $b_i = s\cos\omega + p_i \sin\omega$ and $b_j = s\cos\omega + p_j \sin\omega$ (ω is the hybridization parameter), then:

$$\cos 2\theta = -\left(\frac{\cos\omega}{\sin\omega}\right)^2 < 0.$$

Hint:
Project b_j onto the direction of b_i, then use the orthogonality condition between the two hybrids.

10.9 SOLVED PROBLEMS

10.1. Variational derivation of the Born–Oppenheimer equation (Longuet-Higgins, 1961). Let:

$$\hat{H} = \sum_\alpha -\frac{1}{2M_\alpha}\nabla_\alpha^2 + \hat{H}_e + V_{nn}$$

$$\hat{H}_e = \sum_i -\frac{1}{2}\nabla_i^2 + V_{en} + V_{ee} = \sum_i -\frac{1}{2}\nabla_i^2 + \sum_{i<j}\frac{1}{r_{ij}} - \sum_\alpha\sum_i \frac{Z_\alpha}{r_{\alpha i}}$$

$$V_{nn} = \sum_{\alpha<\beta}\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}$$

$$\Phi = \Psi_e(x;q)\Psi_n(q)$$

where $\Psi_n(q)$ is the nuclear variational function whose form must be optimized, while $\Psi_e(x;q)$ is kept fixed during the variation.

The molecular wave equation is:

$$\hat{H}\Psi = W\Psi$$

and its variational approximation:

$$W = \frac{\langle\Phi|\hat{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle} = AB^{-1}.$$

Varying W subject to the normalization condition gives:

$$\delta W = \delta A \cdot B^{-1} - AB^{-1-1} \cdot \delta B = 0$$

$$\delta A - W\delta B = 0$$

being the condition because W be *stationary* against infinitesimal arbitrary variations in $\delta\Psi_n$. Now:

$$A = \langle\Psi_e\Psi_n|\hat{H}|\Psi_e\Psi_n\rangle \qquad B = \langle\Psi_e\Psi_n|\Psi_e\Psi_n\rangle$$

$$\begin{aligned}\nabla_\alpha^2(\Psi_e\Psi_n) &= \nabla_\alpha \cdot \nabla_\alpha(\Psi_e\Psi_n) = \nabla_\alpha \cdot (\Psi_e\nabla_\alpha\Psi_n + \Psi_n\nabla_\alpha\Psi_e)\\ &= \Psi_e\nabla_\alpha^2\Psi_n + \Psi_n\nabla_\alpha^2\Psi_e + 2\nabla_\alpha\Psi_e \cdot \nabla_\alpha\Psi_n\\ &= \left\{\Psi_e\nabla_\alpha^2 + \nabla_\alpha^2\Psi_e + 2\nabla_\alpha\Psi_e \cdot \nabla_\alpha\right\}\Psi_n,\end{aligned}$$

so that:

$$\begin{aligned}\hat{H}(\Psi_e\Psi_n) = \Bigg\{&\Psi_e\sum_\alpha -\frac{1}{2M_\alpha}\nabla_\alpha^2 + \sum_\alpha -\frac{1}{2M_\alpha}\nabla_\alpha^2\Psi_e\\ &-\sum_\alpha \frac{1}{M_\alpha}\nabla_\alpha\Psi_e \cdot \nabla_\alpha + \hat{H}_e\Psi_e + V_{nn}\Psi_e\Bigg\}\Psi_n.\end{aligned}$$

Hence, it follows:

$$\begin{aligned}\delta A - W\delta B &= \delta\langle\Psi_e\Psi_n|\hat{H}|\Psi_e\Psi_n\rangle - W\delta\langle\Psi_e\Psi_n|\Psi_e\Psi_n\rangle\\ &= \langle\Psi_e\delta\Psi_n|\hat{H}|\Psi_e\Psi_n\rangle - W\langle\Psi_e\delta\Psi_n|\Psi_e\Psi_n\rangle + \text{c.c.}\\ &= \int dq\, \delta\Psi_n^* \int dx\, \Psi_e^*\hat{H}(\Psi_e\Psi_n)\end{aligned}$$

$$
\begin{aligned}
&-W\int dq\,\delta\Psi_n^*\int dx\,\Psi_e^*\Psi_e\cdot\Psi_n+\text{c.c.}\\
&=\int dq\,\delta\Psi_n^*\Bigg\{\int dx\,\underbrace{\Psi_e^*\,\Psi_e}_{1}\sum_\alpha-\frac{1}{2M_\alpha}\nabla_\alpha^2\\
&\quad-\sum_\alpha\frac{1}{2M_\alpha}\int dx\,\Psi_e^*\nabla_\alpha^2\Psi_e\\
&\quad-\sum_\alpha\frac{1}{M_\alpha}\int dx\,\Psi_e^*\nabla_\alpha\Psi_e\cdot\nabla_\alpha+\int dx\,\underbrace{\Psi_e^*\,\hat{H}_e\Psi_e}_{E_e}\\
&\quad+V_{nn}\int dx\,\underbrace{\Psi_e^*\,\Psi_e}_{1}-W\int dx\,\underbrace{\Psi_e^*\,\Psi_e}_{1}\Bigg\}\Psi_n+\text{c.c.}=0.
\end{aligned}
$$

Since Ψ_n^* is arbitrary, the ket must be zero, so that:

$$
\left\{\sum_\alpha-\frac{1}{2M_\alpha}\nabla_\alpha^2+\hat{U}_e(q)\right\}\Psi_n(q)=W\Psi_n(q)
$$

is the *best* wave equation for the nuclear motion, where:

$$
\begin{aligned}
\hat{U}_e(q)&=E_e(q)+V_{nn}\\
&\quad+\sum_\alpha-\frac{1}{2M_\alpha}\int dx\,\Psi_e^*\nabla_\alpha^2\Psi_e\\
&\quad+\sum_\alpha\frac{1}{M_\alpha}\int dx\,\Psi_e^*(-i\nabla_\alpha\Psi_e)\cdot(-i\nabla_\alpha)
\end{aligned}
$$

is the "effective" potential energy *operator* for the nuclear motion, equation (9) of the main text.

10.2. Equivalence between MO and HL wavefunctions for the ${}^3\Sigma_u^+$ excited state of H_2.

The ${}^3\Sigma_u^+$ state of H_2 is obtained by exciting one electron from the σ_g^2 configuration of the ground state (Figure 10.3) to the empty σ_u MO, giving the excited $\sigma_g\sigma_u$ MO configuration. The normalized MO wavefunction describing ${}^3\Sigma_u^+$ is then:

$$
\begin{aligned}
&\Psi(\mathrm{MO},{}^3\Sigma_u^+)\\
&=\frac{1}{\sqrt{2}}\{\sigma_g(\mathbf{r}_1)\sigma_u(\mathbf{r}_2)-\sigma_u(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)\}\begin{cases}\alpha(s_1)\alpha(s_2)\\[2ex]\dfrac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2)+\beta(s_1)\alpha(s_2)]\\[2ex]\beta(s_1)\beta(s_2).\end{cases}
\end{aligned}
$$

Considering only the spatial part of the wavefunction, we have:

$$\begin{aligned}\Psi(\mathrm{MO},{}^3\Sigma_u^+) &= \frac{[a(\mathbf{r}_1)+b(\mathbf{r}_1)][b(\mathbf{r}_2)-a(\mathbf{r}_2)]-[b(\mathbf{r}_1)-a(\mathbf{r}_1)][a(\mathbf{r}_2)+b(\mathbf{r}_2)]}{2\sqrt{2-2S^2}}\\ &= \frac{(ab+bb-aa-ba)-(ba-aa+bb-ab)}{2\sqrt{2-2S^2}}\\ &= \frac{ab-ba}{\sqrt{2-2S^2}} = \Psi\left(\mathrm{HL},{}^3\Sigma_u^+\right)\end{aligned}$$

that coincides with equation (57) of the main text.

10.3. Equivalence between MO-CI and full VB (HL + ION) wavefunctions for ground state H_2.

Let:

$$\lambda = \frac{c_2}{c_1}$$

be the ratio between the linear coefficients in equation (61). Then, using (19) and (20) of the main text, we obtain:

$$\begin{aligned}\Psi\left(\mathrm{MO-CI},{}^1\Sigma_g^+\right) &= c_1\left\{\Psi\left(\sigma_g^2,{}^1\Sigma_g^+\right)+\lambda\Psi\left(\sigma_u^2,{}^1\Sigma_g^+\right)\right\}\\ &= c_1\left\{\frac{(a+b)(a+b)}{2+2S}+\lambda\frac{(b-a)(b-a)}{2-2S}\right\}\times \mathrm{SPIN}\\ &= \frac{c_1}{2}\left(\frac{aa+ba+ab+bb}{1+S}+\lambda\frac{bb-ab-ba+aa}{1-S}\right)\times \mathrm{SPIN}\\ &= \frac{c_1}{2}\left\{(ab+ba)\left(\frac{1}{1+S}-\frac{\lambda}{1-S}\right)\right.\\ &\qquad\left.+(aa+bb)\left(\frac{1}{1+S}+\frac{\lambda}{1-S}\right)\right\}\times \mathrm{SPIN}\\ &= N\left\{(ab+ba)+(aa+bb)\frac{\frac{1}{1+S}+\frac{\lambda}{1-S}}{\frac{1}{1+S}-\frac{\lambda}{1-S}}\right\}\times \mathrm{SPIN}\\ &= N\left\{\underset{\mathrm{HL}}{(ab+ba)}+\frac{(1-S)+\lambda(1+S)}{(1-S)-\lambda(1+S)}\underset{\mathrm{ION}}{(aa+bb)}\right\}\times \mathrm{SPIN}\end{aligned}$$

which is equation (62) of the main text, N being a normalization factor.

10.4. Schmidt orthogonalization of ψ_1 to ψ_2 in the case of the allyl radical.

$$\begin{cases} \psi_1' = \dfrac{\psi_1 - S_{12}\psi_2}{\sqrt{1-S_{12}^2}} & S_{12} = \dfrac{1}{2} \\ \psi_2' = \psi_2 \end{cases}$$

which gives:

$$\begin{aligned} \psi_1' &= \frac{2}{\sqrt{3}} \cdot \frac{1}{\sqrt{2}} \left\{ \left[(a\bar{b}c) - (\bar{a}bc) \right] - \frac{1}{2} \left[(a\bar{b}c) - (ab\bar{c}) \right] \right\} \\ &= \frac{1}{\sqrt{6}} \left[2(a\bar{b}c) - 2(\bar{a}bc) - (a\bar{b}c) + (ab\bar{c}) \right] \\ &= \frac{1}{\sqrt{6}} \left[(ab\bar{c}) + (a\bar{b}c) - 2(\bar{a}bc) \right] \quad S = \frac{1}{2},\ M_S = \frac{1}{2} \end{aligned}$$

whose associated spin structure is in a one-to-one correspondence with that previously found in Problem 6.1 for the *first* doublet pure spin function:

$$\eta_1 = \frac{1}{\sqrt{6}} (\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha) \quad S = \frac{1}{2},\ M_S = \frac{1}{2}.$$

The second VB structure:

$$\psi_2' = \psi_2 = \frac{1}{\sqrt{2}} \left[(a\bar{b}c) - (ab\bar{c}) \right] \quad S = \frac{1}{2},\ M_S = \frac{1}{2}$$

differs by an irrelevant (-1) phase factor from that for the *second* doublet pure spin function:

$$\eta_3 = \frac{1}{\sqrt{2}} (\alpha\alpha\beta - \alpha\beta\alpha) \quad S = \frac{1}{2},\ M_S = \frac{1}{2}.$$

The doublet nature of the two VB structures for the allyl radical ground state can be verified by applying $\hat{S}^2$ in the Dirac form for $N = 3$:

$$\hat{S}^2 = \frac{3}{4}\hat{I} + \hat{P}_{12} + \hat{P}_{13} + \hat{P}_{23}.$$

We have:

$$\begin{aligned} \hat{S}^2 \psi_1 = \frac{1}{\sqrt{2}} \Bigg\{ & \frac{3}{4}(a\bar{b}c) + (\bar{a}bc) + (a\bar{b}c) + (ab\bar{c}) \\ & - \frac{3}{4}(\bar{a}bc) - (a\bar{b}c) - (ab\bar{c}) - (\bar{a}bc) \Bigg\} \end{aligned}$$

$$
\begin{aligned}
&= \frac{3}{4}\left\{\frac{1}{\sqrt{2}}\left[(a\overline{b}c) - (\overline{a}bc)\right]\right\} = \frac{1}{2}\left(\frac{1}{2}+1\right)\psi_1 \\
\hat{S}^2\psi_2 &= \frac{1}{\sqrt{2}}\left\{\frac{3}{4}(a\overline{b}c) + (\overline{a}bc) + (a\overline{b}c) + (ab\overline{c})\right. \\
&\qquad \left. - \frac{3}{4}(ab\overline{c}) - (ab\overline{c}) - (\overline{a}bc) - (a\overline{b}c)\right\} \\
&= \frac{3}{4}\left\{\frac{1}{\sqrt{2}}\left[(a\overline{b}c) - (ab\overline{c})\right]\right\} = \frac{1}{2}\left(\frac{1}{2}+1\right)\psi_2
\end{aligned}
$$

as it must be for doublet $S = 1/2$ states.

10.5. Equivalence between MO and VB wavefunctions for $He_2(^1\Sigma_g^+)$.

The following elegant proof is due to Ottonelli (1997). We start from the single determinant MO wavefunction:

$$
\begin{aligned}
\Psi\big(\mathrm{MO}, {}^1\Sigma_g^+\big) &= \|\sigma_g\overline{\sigma}_g\sigma_u\overline{\sigma}_u\| = -\|\overset{\text{spin}\,\alpha}{\sigma_g\sigma_u}\ \overset{\text{spin}\,\beta}{\overline{\sigma}_g\overline{\sigma}_u}\| \\
&= -\left\|\frac{a+b}{\sqrt{2+2S}}\frac{b-a}{\sqrt{2-2S}}\frac{\overline{a}+\overline{b}}{\sqrt{2+2S}}\frac{\overline{b}-\overline{a}}{\sqrt{2-2S}}\right\| \\
&= -\big[4(1-S^2)\big]^{-1}|a+b\quad b-a\quad \overline{a}+\overline{b}\quad \overline{b}-\overline{a}| \\
&= -\big[4(1-S^2)\big]^{-1}\begin{vmatrix} |\mathbf{D}| & \mathbf{0} \\ \mathbf{0} & |\mathbf{D}| \end{vmatrix}\cdot|a\quad b\quad \overline{a}\quad \overline{b}| \\
&= -\big[4(1-S^2)\big]^{-1}|\det\mathbf{D}|^2\cdot|a\quad b\quad \overline{a}\quad \overline{b}| \\
&= -(1-S^2)^{-1}|a\quad b\quad \overline{a}\quad \overline{b}| = \|a\quad \overline{a}\quad b\quad \overline{b}\| = \Psi\big(\mathrm{VB}, {}^1\Sigma_g^+\big),
\end{aligned}
$$

since:

$$
\mathbf{D} = \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}, \qquad |\mathbf{D}| = \det\mathbf{D} = \begin{vmatrix} 1 & -1 \\ 1 & 1 \end{vmatrix} = 2
$$

$$
|\det\mathbf{D}|^2 = 4 \qquad (a+b\ \ b-a) = (a\ b)\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}
$$

D being a linear transformation between the basic AOs.

10.6. Symmetry of the ionic structures in triplet O_2.

In the ultrashort notation, the $M_S = 1$ component of the ionic VB structures for triplet O_2 corresponding to the parents of Figure 10.18 is described by the wavefunction:

$$\Psi(\mathrm{ION}) = \frac{1}{\sqrt{2}}\big[(x_A y_A) + (x_B y_B)\big]$$

which can be treated as a 2-electron wavefunction (see Problem 8.16 of Chapter 8).

$$\hat{S}^2\Psi = 2\Psi = 1(1+1)\Psi$$

$$\begin{aligned}\hat{L}_z\Psi &= \frac{1}{\sqrt{2}}\big[(iy_A y_A) + (x_A - ix_A) + (iy_B y_B) + (x_B - ix_B)\big]\\ &= \frac{i}{\sqrt{2}}\big[(y_A y_A) - (x_A x_A) + (y_B y_B) - (x_B x_B)\big] = 0\Psi\end{aligned}$$

since all determinants vanish because of the Pauli principle.

$$\hat{\sigma}_{zx}\Psi = \frac{1}{\sqrt{2}}\big[(x_A - y_A) + (x_B - y_B)\big] = -\Psi$$

$$\hat{\imath}\Psi = \frac{1}{\sqrt{2}}\big[(-x_B - y_B) + (-x_A - y_A)\big] = \Psi.$$

Hence, $\Psi(\mathrm{ION})$ is the component with $M_S = 1$ of the triplet ${}^3\Sigma_g^-$, as it must be.

10.7. VB matrix elements for cyclobutadiene.

With reference to (274) expressing ψ_1 and ψ_2 in terms of Slater dets, we have:

$$\begin{aligned}H_{11} &= \langle\psi_1|\hat{H}|\psi_1\rangle\\ &= \underbrace{\frac{1}{4}\Big\{\langle(a\bar{b}c\bar{d})|\underset{11}{\hat{H}}|(a\bar{b}c\bar{d})\rangle + \langle(\bar{a}bc\bar{d})|\underset{22}{\hat{H}}|(\bar{a}bc\bar{d})\rangle + \langle(a\bar{b}\bar{c}d)|\underset{33}{\hat{H}}|(a\bar{b}\bar{c}d)\rangle + \langle(\bar{a}b\bar{c}d)|\underset{44}{\hat{H}}|(\bar{a}b\bar{c}d)\rangle\Big\}}_{\text{“diagonal” elements}}\\ &\quad + \underbrace{\begin{aligned}\frac{2}{4}\Big\{&-\langle(a\bar{b}c\bar{d})\underset{12+21}{|\hat{H}|}(\bar{a}bc\bar{d})\rangle - \langle(a\bar{b}c\bar{d})\underset{13+31}{|\hat{H}|}(a\bar{b}\bar{c}d)\rangle\\ &+ \langle(a\bar{b}c\bar{d})\underset{14+41}{|\hat{H}|}(\bar{a}b\bar{c}d)\rangle + \langle(\bar{a}bc\bar{d})\underset{23+32}{|\hat{H}|}(a\bar{b}\bar{c}d)\rangle\\ &- \langle(\bar{a}bc\bar{d})\underset{24+42}{|\hat{H}|}(\bar{a}b\bar{c}d)\rangle - \langle(a\bar{b}\bar{c}d)\underset{34+43}{|\hat{H}|}(\bar{a}b\bar{c}d)\rangle\Big\}\end{aligned}}_{\text{“off-diagonal” elements}}\end{aligned}$$

$=$ use Slater's rules for orthonormal dets, considering only single interchanges and omitting for short $1/r_{12}$ in the Dirac notation

$$
\begin{aligned}
&= \frac{1}{4}\Big\{[Q - \underset{11}{\langle ac|ca\rangle} - \langle \overline{bd}|\overline{db}\rangle] + [Q - \underset{22}{\langle \bar{a}\bar{d}|\bar{d}\bar{a}\rangle} - \langle bc|cb\rangle] \\
&\qquad + [Q - \underset{33}{\langle ad|da\rangle} - \langle \bar{b}\bar{c}|\bar{c}\bar{b}\rangle] + [Q - \underset{44}{\langle \overline{ac}|\overline{ca}\rangle} - \langle bd|db\rangle]\Big\} \\
&\quad + \frac{2}{4}\Big\{\underset{12+21}{\langle a\bar{b}|b\bar{a}\rangle} + \underset{13+31}{\langle c\bar{d}|d\bar{c}\rangle} + \underset{24+42}{\langle c\bar{d}|d\bar{c}\rangle} + \underset{34+43}{\langle a\bar{b}|b\bar{a}\rangle}\Big\} \\
&= \text{eliminate spin using charge density notation} \\
&= \frac{1}{4}\Big\{4Q - 2[(ac|ac) + (ad|ad) + (bc|bc) + (bd|bd)] \\
&\qquad + 4[(ab|ab) + (cd|cd)]\Big\},
\end{aligned}
$$

where Q is the Coulomb integral arising from the product of orbital functions (zero interchanges):

$$
\begin{aligned}
Q &= \langle abcd|\hat{H}|abcd\rangle \\
&= h_{aa} + h_{bb} + h_{cc} + h_{dd} \\
&\quad + (a^2|b^2) + (a^2|c^2) + (a^2|d^2) + (b^2|c^2) + (b^2|d^2) + (c^2|d^2) \\
&\quad + V_{nn}.
\end{aligned}
$$

Since, for "non-adjacent" orbitals:

$$
(ac|ac) = (bd|bd) = 0
$$

and all other exchange integrals are equal by symmetry, we finally obtain:

$$
H_{11} = Q + 2K - \frac{1}{2}(2K) = Q + K
$$

which is the equation (279) in the main text.

For the off-diagonal element, we have:

$$
\begin{aligned}
H_{12} &= \langle \psi_1|\hat{H}|\psi_2\rangle \\
&= \frac{1}{4}\Big\{\langle (a\bar{b}c\bar{d})|\underset{11}{\hat{H}}|(a\bar{b}c\bar{d})\rangle + \langle (\bar{a}bc\bar{d})|\underset{22}{\hat{H}}|(\bar{a}\bar{b}cd)\rangle \\
&\qquad + \langle (a\bar{b}\bar{c}d)|\underset{33}{\hat{H}}|(ab\bar{c}\bar{d})\rangle + \langle (\bar{a}b\bar{c}d)|\underset{44}{\hat{H}}|(\bar{a}b\bar{c}d)\rangle\Big\} \\
&\qquad\qquad \text{"diagonal" elements} \\
&\quad + \frac{1}{4}\Big\{-\langle (a\bar{b}c\bar{d})|\underset{12}{\hat{H}}|(\bar{a}\bar{b}cd)\rangle - \langle (a\bar{b}c\bar{d})|\underset{13}{\hat{H}}|(ab\bar{c}\bar{d})\rangle \\
&\qquad + \langle (a\bar{b}c\bar{d})|\underset{14}{\hat{H}}|(\bar{a}b\bar{c}d)\rangle - \langle (\bar{a}bc\bar{d})|\underset{21}{\hat{H}}|(a\bar{b}c\bar{d})\rangle
\end{aligned}
$$

$$
\begin{aligned}
&+ \langle(\bar{a}bc\bar{d})|\underset{23}{\hat{H}}|(ab\bar{c}\bar{d})\rangle - \langle(\bar{a}bc\bar{d})|\underset{24}{\hat{H}}|(\bar{a}b\bar{c}d)\rangle \\
&- \langle(a\bar{b}\bar{c}d)|\underset{31}{\hat{H}}|(a\bar{b}c\bar{d})\rangle + \langle(a\bar{b}\bar{c}d)|\underset{32}{\hat{H}}|(\bar{a}\bar{b}cd)\rangle \\
&- \langle(a\bar{b}\bar{c}d)|\underset{34}{\hat{H}}|(\bar{a}b\bar{c}d)\rangle + \langle(\bar{a}b\bar{c}d)|\underset{41}{\hat{H}}|(a\bar{b}c\bar{d})\rangle \\
&- \langle(\bar{a}b\bar{c}d)|\underset{42}{\hat{H}}|(\bar{a}\bar{b}cd)\rangle - \langle(\bar{a}b\bar{c}d)|\underset{43}{\hat{H}}|(ab\bar{c}\bar{d})\rangle\big\}
\end{aligned}
$$

"off-diagonal" elements

$$
\begin{aligned}
&= \frac{1}{4}\big\{[Q - \underset{11}{\langle ac|ca\rangle} - \langle\overline{bd}|\overline{db}\rangle] - \underset{22}{\langle b\bar{d}|d\bar{b}\rangle} \\
&\quad - \underset{33}{\langle d\bar{b}|b\bar{d}\rangle} + [Q - \underset{44}{\langle\overline{ac}|\overline{ca}\rangle} - \langle bd|db\rangle]\big\} \\
&\quad + \frac{1}{4}\big\{\underset{12}{\langle a\bar{d}|d\bar{a}\rangle} + \underset{13}{\langle c\bar{b}|b\bar{c}\rangle} + \underset{21}{\langle b\bar{a}|a\bar{b}\rangle} - \underset{23}{\langle c\bar{a}|a\bar{c}\rangle} + \underset{24}{\langle c\bar{d}|d\bar{c}\rangle} \\
&\qquad + \underset{31}{\langle d\bar{c}|c\bar{d}\rangle} - \underset{32}{\langle a\bar{c}|c\bar{a}\rangle} + \underset{34}{\langle a\bar{b}|b\bar{a}\rangle} + \underset{42}{\langle b\bar{c}|c\bar{b}\rangle} + \underset{43}{\langle d\bar{a}|a\bar{d}\rangle}\big\} \\
&= \frac{1}{4}\big\{2[Q - (ac|ac) - (bd|bd)] - 2(bd|bd) \\
&\quad + 2[(ab|ab) - (ac|ac) + (ad|ad) + (bc|bc) + (cd|cd)]\big\} \\
&= \frac{1}{2}[Q + (ab|ab) - 2(ac|ac) + (ad|ad) + (bc|bc) - 2(bd|bd) + (cd|cd)] \\
&= \frac{1}{2}(Q + 4K)
\end{aligned}
$$

which is equation (282) of the main text.

10.8. We first study the resolution of a p_θ orbital, making an angle θ with the positive z-axis in the yz-plane, into its orthogonal components p_y and p_z (Figure 10.38).

We have:

$$\overrightarrow{OP} = \overrightarrow{OQ} + \overrightarrow{QP} = \mathbf{k}z + \mathbf{j}y = \mathbf{k}OP\cos\theta + \mathbf{j}OP\sin\theta$$

$$\frac{\overrightarrow{OP}}{OP} = \mathbf{k}\cos\theta + \mathbf{j}\sin\theta.$$

k and **j** can be replaced by $p_z = z$, and $p_y = y$. Therefore:

$$p_\theta = z\cos\theta + y\sin\theta,$$

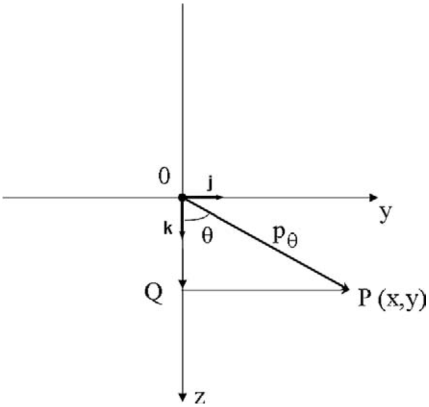

Figure 10.38 Resolution of a p_θ AO into orthogonal components.

where $\cos\theta$ and $\sin\theta$ are the direction cosines of p_θ in the yz-plane. Similarly, changing θ into $-\theta$:

$$p_{-\theta} = z\cos\theta - y\sin\theta,$$

and we have the linear transformation:

$$p_1 = z\cos\theta + y\sin\theta$$
$$p_2 = z\cos\theta - y\sin\theta$$

$$(p_1 p_2) = (yz)\mathbf{L},$$

where:

$$\mathbf{L} = \begin{pmatrix} \sin\theta & -\sin\theta \\ \cos\theta & \cos\theta \end{pmatrix}.$$

The two transformed AOs, p_1 and p_2, are *not* orthogonal:

$$\langle p_1 | p_2 \rangle = \cos^2\theta - \sin^2\theta = \cos 2\theta.$$

The transformation matrix $\mathbf{L}$ has $\det\mathbf{L} = \sin 2\theta$, and is therefore unitary only for $\theta = \pi/4$. The inverse transformation is:

$$\mathbf{L}^{-1} = \begin{pmatrix} \dfrac{1}{2\sin\theta} & \dfrac{1}{2\cos\theta} \\ -\dfrac{1}{2\sin\theta} & \dfrac{1}{2\cos\theta} \end{pmatrix}$$

giving:

$$y = \frac{1}{2\sin\theta}(p_1 - p_2), \qquad z = \frac{1}{2\cos\theta}(p_1 + p_2).$$

We can now pass to the construction of the three sp^2 hybrids equivalent under C_{2v} symmetry. We can write:

$$hy_1 = as + bp_1 = as + b\cos\theta z + b\sin\theta y$$

$$hy_2 = as + bp_2 = as + b\cos\theta z - b\sin\theta y$$

$$hy_3 = cs - dz,$$

where the coefficients a, b, c, d must satisfy the orthonormality conditions:

$$\begin{cases} a^2 + b^2 = 1 & a^2 + b^2\cos 2\theta = 0 \\ c^2 + d^2 = 1 & ac - bd\cos\theta = 0. \end{cases}$$

By solving it is found:

$$a^2 = \frac{\cos 2\theta}{\cos 2\theta - 1} = 1 - \frac{1}{2\sin^2\theta} = \frac{2\sin^2\theta - 1}{2\sin^2\theta}$$

$$b^2 = 1 - a^2 = \frac{1}{2\sin^2\theta}$$

$$c^2 = \frac{b^2}{a^2}(1 - c^2)\cos^2\theta = \frac{\cos^2\theta}{\sin^2\theta} = \cot^2\theta$$

$$d^2 = 1 - c^2 = \frac{2\sin^2\theta - 1}{\sin^2\theta},$$

whence, by choosing the positive roots:

$$a = \sqrt{\frac{2\sin^2\theta - 1}{2\sin^2\theta}}, \qquad b = \sqrt{\frac{1}{2\sin^2\theta}}$$

$$c = \cot\theta, \qquad d = \sqrt{\frac{2\sin^2\theta - 1}{\sin^2\theta}}.$$

The *unitary* matrix **U** doing the sp^2 (C_{2v}) hybridization is then:

$$(hy_1 hy_2 hy_3) = (szy)\mathbf{U},$$

where:

$$\mathbf{U}=\begin{pmatrix} a & a & c \\ b\cos\theta & b\cos\theta & -d \\ b\sin\theta & -b\sin\theta & 0 \end{pmatrix}.$$

It is possible to express **U** as a function of c and d only, using:

$$a=\frac{1}{\sqrt{2}}d, \qquad b\cos\theta=\frac{1}{\sqrt{2}}c, \qquad b\sin\theta=\frac{1}{\sqrt{2}},$$

so that we obtain for **U** the simplified form:

$$\mathbf{U}=\begin{pmatrix} \frac{1}{\sqrt{2}}d & \frac{1}{\sqrt{2}}d & c \\ \frac{1}{\sqrt{2}}c & \frac{1}{\sqrt{2}}c & -d \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \end{pmatrix}.$$

It is immediately verified that:

$$\mathbf{U}\mathbf{U}^{\dagger}=\mathbf{U}^{\dagger}\mathbf{U}=\mathbf{1}.$$

10.9. Angle between equivalent orthogonal hybrids.

With reference to Figure 10.35, let b_i, b_j be the two s, p hybrids pointing in the directions i and j, and making an interhybrid angle 2θ. If we denote by ω the single hybridization parameter (*equivalent* hybrids), we can write the hybrids as:

$$b_i=s\cos\omega+p_i\sin\omega$$

$$b_j=s\cos\omega+p_j\sin\omega.$$

We resolve p_j into its components in the direction of the i-th bond and the direction perpendicular to it:

$$p_j=p_i\cos 2\theta+p_{\perp}\sin 2\theta.$$

The condition of orthogonality between the two hybrids then gives:

$$\langle b_i|b_j\rangle=\cos^2\omega+\sin^2\omega\langle p_i|p_j\rangle=\cos^2\omega+\sin^2\omega\cos 2\theta=0,$$

and we therefore obtain:

$$\cos 2\theta = -\left(\frac{\cos\omega}{\sin\omega}\right)^2 < 0$$

which means that the angle 2θ between *real* orthogonal hybrids is *greater* than 90°.

– 11 –

Rayleigh–Schroedinger Perturbation Methods for Stationary States

11.1 INTRODUCTION

We already saw that the great majority of problems in molecular quantum mechanics is not exactly soluble, so that approximation methods are needed to work out solutions at different levels of sophistication. The most important is undoubtedly the Rayleigh variation method which was widely treated in Chapter 5. We take now into consideration the perturbation method due to Schroedinger, and known as Rayleigh–Schroedinger (RS) perturbation theory. It consists essentially in relating the actual problem to one for which a complete solution is exactly known, and in treating the difference between their Hamiltonian operators as a small perturbation. We shall be concerned here only with time-independent or stationary RS perturbation theory. Time-dependent perturbation theory is mostly of interest for spectroscopy and related time-dependent phenomena, and appropriate presentations can be found elsewhere (McWeeny, 1989; Stone, 1996). We shall follow in this Chapter essentially excellent previous work by Dalgarno (1961) and Hirschfelder et al. (1964). Perturbation techniques are specially adapted for treating the electric (and magnetic) properties of molecules (Van Vleck, 1932; Dalgarno, 1962; Davies, 1967) and molecular interactions (Stone, 1996).

11.2 RS PERTURBATION THEORY FOR STATIONARY STATES

11.2.1 RS Perturbation Equations and Energy Corrections

Let:

$$(\hat{H} - E)\psi = 0 \tag{1}$$

by the Schroedinger eigenvalue equation to be solved, and:

$$(\hat{H}_0 - E_0)\psi_0 = 0 \tag{2}$$

the already solved eigenvalue problem little different from (1). We treat the difference between the Hermitian operators $\hat{H}$ and $\hat{H}_0$ as a small *perturbation*:

$$\hat{H} - \hat{H}_0 = \lambda \hat{H}_1, \tag{3}$$

where λ is a convenient parameter giving the *orders* of the perturbation theory. In some case, λ can be identified with some experimental parameter, say the strength F of a uniform electric field such that existing in a plane condenser, and we can speak in this case of a physical perturbation, which can be removed in the laboratory by switching off the condenser. In most cases, however, the perturbation $\hat{H}_1$ is not physically accessible, as may be the electron repulsion $1/r_{12}$ in treating the He atom as a perturbation of two hydrogen-like electrons, or the interatomic potential V set in the interaction of two H atoms.

We expand E, ψ in a power series of λ, whose coefficients give corrections which must be smaller and smaller with increasing powers of λ:

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \lambda^3 E_3 + \cdots \tag{4}$$

$$\psi = \psi_0 + \lambda \psi_1 + \lambda^2 \psi_2 + \cdots \tag{5}$$

and substitute the expansions into the original eigenvalue equation (1):

$$\{(\hat{H}_0 - E_0) + \lambda(\hat{H}_1 - E_1) - \lambda^2 E_2 - \lambda^3 E_3 + \cdots\}(\psi_0 + \lambda\psi_1 + \lambda^2\psi_2 + \cdots) = 0. \tag{6}$$

If we now collect all coefficients of the same power of λ we obtain the hierarchy of RS perturbation equations:

$$\begin{aligned}
&\lambda^0 \quad (\hat{H}_0 - E_0)\psi_0 = 0\\
&\lambda \quad (\hat{H}_0 - E_0)\psi_1 + (\hat{H}_1 - E_1)\psi_0 = 0\\
&\lambda^2 \quad (\hat{H}_0 - E_0)\psi_2 + (\hat{H}_1 - E_1)\psi_1 - E_2\psi_0 = 0\\
&\lambda^3 \quad (\hat{H}_0 - E_0)\psi_3 + (\hat{H}_1 - E_1)\psi_2 - E_2\psi_1 - E_3\psi_0 = 0\\
&\qquad\qquad\qquad\qquad\qquad \cdots
\end{aligned} \tag{7}$$

The zeroth-order equation (2) has to have been solved exactly, otherwise uncontrollable errors will affect the whole chain of equations. The first-order equation in (7) is a inhomogeneous differential equation that must be solved under the first-order orthogonality condition (see next Section):

$$\langle \psi_0 | \psi_1 \rangle = 0. \tag{8}$$

Once ψ_0 and ψ_1 are known, we can next find ψ_2 by solving the second-order differential equation in (7), and so on. We shall see, however, that ψ_1 determines the energy corrections up to the third order in λ.

The energy corrections E_n of the various orders are obtained by bracketing on the left each RS equation by $\langle \psi_0|$, taking into account the fact that in each equation the first term on the left vanishes because the operators are Hermitian:

$$\begin{aligned}
&\lambda^0 \quad E_0 = \langle \psi_0 | \hat{H}_0 | \psi_0 \rangle\\
&\lambda \quad E_1 = \langle \psi_0 | \hat{H}_1 | \psi_0 \rangle\\
&\lambda^2 \quad E_2 = \langle \psi_0 | \hat{H}_1 - E_1 | \psi_1 \rangle\\
&\lambda^3 \quad E_3 = \langle \psi_1 | \hat{H}_1 - E_1 | \psi_1 \rangle\\
&\qquad\qquad \cdots
\end{aligned} \tag{9}$$

We notice that E_0 is the expectation value of the unperturbed Hamiltonian $\hat{H}_0$ over the unperturbed function ψ_0, but to avoid any error in the chain ψ_0 must be the *exact* eigenfunction of $\hat{H}_0$. E_1 is the expectation value of the perturbation $\hat{H}_1$ over ψ_0. Knowledge of ψ_0 is hence sufficient to obtain the energy up to first order, which will be denoted by:

$$E^{(1)} = E_0 + E_1. \tag{10}$$

The second-order energy correction, E_2, is instead given as an off-diagonal element of $(\hat{H}_1 - E_1)$, which is usually known as a transition integral (from ψ_0 to ψ_1 under the perturbation $\hat{H}_1$). For E_3 we can write from the last RS equation of order λ^3 by bracketing by $\langle \psi_0|$:

$$\langle \psi_0 | \hat{H}_1 - E_1 | \psi_2 \rangle - E_2 \langle \psi_0 | \psi_1 \rangle = E_3 \tag{11}$$

$$\begin{aligned}E_3 &= \langle(\hat{H}_1 - E_1)\psi_0|\psi_2\rangle - E_2\langle\psi_0|\psi_1\rangle\\&= -\langle\psi_1|\hat{H}_0 - E_0|\psi_2\rangle - E_2\langle\psi_0|\psi_1\rangle\\&= \langle\psi_1|\hat{H}_1 - E_1|\psi_1\rangle - E_2[\langle\psi_1|\psi_0\rangle + \langle\psi_0|\psi_1\rangle]\\&= \langle\psi_1|\hat{H}_1 - E_1|\psi_1\rangle.\end{aligned}$$

The possibility of shifting the orders of perturbation from the wavefunction to the operator, and vice versa, is known as Dalgarno's interchange theorem.

11.2.2 The Orthogonality Conditions

Expanding ψ to the various orders of perturbation theory ($\lambda = 1$):

$$\psi = \psi_0 + \psi_1 + \psi_2 + \cdots \tag{12}$$

The normalization condition on the wavefunction ψ gives:

$$\begin{aligned}\langle\psi|\psi\rangle &= \langle\psi_0 + \psi_1 + \psi_2 + \cdots|\psi_0 + \psi_1 + \psi_2 + \cdots\rangle\\&= \langle\psi_0|\psi_0\rangle + \{\langle\psi_0|\psi_1\rangle + \langle\psi_1|\psi_0\rangle\}\\&\quad + \{\langle\psi_0|\psi_2\rangle + \langle\psi_1|\psi_1\rangle + \langle\psi_2|\psi_0\rangle\} + \cdots = 1\end{aligned} \tag{13}$$

meaning:

$$\lambda^0 \quad \langle\psi_0|\psi_0\rangle = 1 \tag{14}$$

$$\lambda \quad \langle\psi_0|\psi_1\rangle + \langle\psi_1|\psi_0\rangle = 0 \tag{15}$$

$$\lambda^2 \quad \langle\psi_0|\psi_2\rangle + \langle\psi_1|\psi_1\rangle + \langle\psi_2|\psi_0\rangle = 0 \tag{16}$$

$$\cdots$$

Generally, we can write:

$$\sum_{k=0}^{n}\langle\psi_k|\psi_{n-k}\rangle = \delta_{0n} \tag{17}$$

giving orthogonality to the n-th order as:

$$\sum_{k=0}^{n}\langle\psi_k|\psi_{n-k}\rangle = 0 \quad n > 0. \tag{18}$$

Hence we see that we have normalization in zeroth-order, and orthogonality to all orders $n > 0$.

Considering the orthogonality condition to first order:

$$n = 1 \quad \sum_{k=0}^{1} \langle \psi_k | \psi_{1-k} \rangle = \langle \psi_0 | \psi_1 \rangle + \langle \psi_1 | \psi_0 \rangle = 0 \tag{19}$$

we see that for *real* functions:

$$2\langle \psi_0 | \psi_1 \rangle = 0 \tag{20}$$

gives the familiar orthogonality condition on the first-order wavefunction.

In general, let ψ_1 be a *complex* function:

$$\psi_1 = A + iB, \quad A = \mathcal{Re}\, \psi_1, \quad B = \mathcal{Im}\, \psi_1, \tag{21}$$

where A, B are both real functions. Then, orthogonality to first order becomes:

$$\langle \psi_0 | \psi_1 \rangle + \langle \psi_1 | \psi_0 \rangle = \{\langle \psi_0 | A \rangle + \langle A | \psi_0 \rangle\} + i\{\langle \psi_0 | B \rangle - \langle B | \psi_0 \rangle\}, \tag{22}$$

where the last term vanishes irrespective of the value of function B. The condition of *strong orthogonality* to first order takes $\langle \psi_0 | B \rangle = 0$ individually, which is most simply satisfied if the imaginary part of ψ_1 (which is otherwise arbitrary) is assumed to be identically zero.

11.2.3 First-Order Perturbation Theory for Degenerate Eigenvalues

Let E_0 be a g-fold degenerate eigenvalue of $\hat{H}_0$. Then there is a set $\{\psi_1^0, \psi_2^0, \cdots \psi_g^0\}$ of g different orthogonal (linearly independent) and normalized eigenfunctions belonging to the same eigenvalue E_0:

$$\left\langle \psi_\alpha^0 | \psi_\beta^0 \right\rangle = \delta_{\alpha\beta} \quad \alpha, \beta = 1, 2, \cdots, g. \tag{23}$$

Then the first-order RS equation can be written as:

$$(\hat{H}_0 - E_0)\psi_1 + (\hat{H}_1 - E_1)\sum_\beta \psi_\beta^0 C_\beta = 0. \tag{24}$$

Bracketing on the left by $\langle \psi_\alpha^0 |$ we obtain:

$$\left\langle \psi_\alpha^0 \middle| \hat{H}_0 - E_0 \middle| \psi_1 \right\rangle + \left\langle \psi_\alpha^0 \middle| \hat{H}_1 - E_1 \middle| \sum_\beta \psi_\beta^0 C_\beta \right\rangle = 0 \tag{25}$$

$$\sum_\beta [(H_1)_{\alpha\beta} - E_1 \delta_{\alpha\beta}] C_\beta = 0 \tag{26}$$

or, in matrix form:

$$(\mathbf{H}_1 - E_1\mathbf{1})\mathbf{C} = \mathbf{0}, \tag{27}$$

where $\mathbf{H}_1$ is the matrix representative (order g) of the perturbation $\hat{H}_1$ over the degenerate set. Equation (27) is the eigenvalue equation for matrix $\mathbf{H}_1$, the corresponding secular equation being:

$$|\mathbf{H}_1 - E_1\mathbf{1}| = 0 \tag{28}$$

giving the g roots:

$$E_1^\alpha \quad \alpha = 1, 2, \cdots, g. \tag{29}$$

Degeneracy will be fully removed in first order when *all* roots are different.

The most striking example of degenerate first-order perturbation theory is found in the Hückel theory of chain hydrocarbons (linear or cyclic), where $x = E_1/\beta$ is the first-order π interaction in units of β. We can write for the Hückel matrix:

$$\underset{N\times N}{\mathbf{H}} = \begin{pmatrix} \alpha & \beta & 0 & 0 & \cdots \\ \beta & \alpha & \beta & 0 & \cdots \\ 0 & \beta & \alpha & \beta & \cdots \\ & & \cdot\cdot\cdot\cdot\cdot & & \end{pmatrix} = \underbrace{\begin{pmatrix} \alpha & 0 & 0 & \cdots \\ 0 & \alpha & 0 & \cdots \\ 0 & 0 & \alpha & \cdots \\ & \cdot\cdot\cdot\cdot\cdot & & \end{pmatrix}}_{\mathbf{H}_0} + \underbrace{\begin{pmatrix} 0 & \beta & 0 & \cdots \\ \beta & 0 & \beta & \cdots \\ 0 & \beta & 0 & \cdots \\ & \cdot\cdot\cdot\cdot\cdot & & \end{pmatrix}}_{\mathbf{H}_1}, \tag{30}$$

where $\mathbf{H}_0$ is the diagonal matrix of the N-degenerate eigenvalue $E_0 = \alpha$, and $\mathbf{H}_1$ the traceless matrix of the π-interaction involving Hückel βs. Then, solution of the first-order secular equation gives directly the splitting of the $2p\pi$ AO levels under the interaction:

$$|\mathbf{H}_1 - E_1\mathbf{1}| = \begin{vmatrix} -E_1 & \beta & 0 & \cdots \\ \beta & -E_1 & \beta & \cdots \\ & \cdot\cdot\cdot\cdot\cdot & & \end{vmatrix} = 0$$

$$\Longrightarrow D_N = \begin{vmatrix} -x & 1 & 0 & \cdots \\ 1 & -x & 1 & \cdots \\ & \cdot\cdot\cdot\cdot\cdot & & \end{vmatrix} = 0. \tag{31}$$

11.2.4 Properties of the Perturbation Solutions

Examination of the first few terms of the RS perturbation expansion for the ground state of the system shows the following properties.

(i) Energy in first order is an upper bound to the true eigenvalue for the ground state. In fact:

$$E^{(1)} = E_0 + E_1 = \frac{\langle\psi_0|\hat{H}_0 + \hat{H}_1|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} = \frac{\langle\psi_0|\hat{H}|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} \geq E_{\text{true}} \tag{32}$$

since $E^{(1)}$ is nothing but the expectation value of the full Hamiltonian over the unperturbed ψ_0.

Table 11.1.

Energy corrections and energies up to second order (E_h) for the hydrogen-like perturbation theory of He($1s^2$)

E_0	-4	$E^{(0)}$	-4	$+37.75\%$
E_1	$+1.25$	$E^{(1)}$	-2.75	-5.3%
E_2	$-0.157\,66$	$E^{(2)}$	$-2.907\,66$	$+0.13\%$

(ii) The second-order energy correction is always negative (attractive) for the ground state.

$$E_2 = \langle\psi_0|\hat{H}_1 - E_1|\psi_1\rangle = \langle(\hat{H}_1 - E_1)\psi_0|\psi_1\rangle = -\langle\psi_1|\hat{H}_0 - E_0|\psi_1\rangle < 0, \quad (33)$$

where we have used the interchange theorem in the first-order equation and noted that the expectation value of the excitation operator ($\hat{H}_0 - E_0$) (a positive definite operator) over the function ψ_1 is always positive.

(iii) Energy in second order, $E^{(2)}$, is always lower than the true eigenvalue (it is not protected by any variational bound). As an example, Table 11.1 gives in E_h the first few energy corrections, E_n, and the energies up to order n, $E^{(n)}$, for the H-like perturbation theory of the He atom ground state (Dalgarno, 1961). The % error resulting to the various orders in comparison with the accurate value $E = -2.903\,724\,E_h$ (Pekeris, 1958) is given in the last column. It is worth noting that the interelectronic repulsion $1/r_{12}$ is *not* a small perturbation.

E_2 for He($1s^2$) was further analyzed into its non-expanded multipole contributions E_{2l} ($l = 0, 1, 2, 3, \cdots$) by Byron and Joachain (1967) and, more recently, by Magnasco et al. (1992). It is found that convergence is very slow ($E_{20} = -0.125\,334\,E_h$, $E_{21} = -0.026\,495\,E_h$, $E_{22} = -0.003\,906\,E_h$, $E_{23} = -0.001\,077\,E_h$).

(iv) The first-order correction to the wavefunction, ψ_1, determines the energy correction up to the third order. It is generally true that the n-th correction to ψ, ψ_n, determines the energy up to E_{2n+1}.

(v) Energy in third order is not an upper bound to the true eigenvalue, even if it will be closer to it than energy in second order.

Consider the energy resulting from the variational principle using $\psi_0 + \psi_1$ as (unnormalized) variational function. Then:

$$\begin{aligned}
E &= \frac{\langle\psi_0 + \psi_1|\hat{H}_0 + \hat{H}_1|\psi_0 + \psi_1\rangle}{\langle\psi_0 + \psi_1|\psi_0 + \psi_1\rangle} \\
&= \{1 + \langle\psi_1|\psi_1\rangle\}^{-1}\big\{E_0 + E_1 + [\langle\psi_1|\hat{H}_0 - E_0|\psi_1\rangle \\
&\quad + \langle\psi_1|\hat{H}_1 - E_1|\psi_0\rangle + \langle\psi_0|\hat{H}_1 - E_1|\psi_1\rangle] \\
&\quad + \langle\psi_1|\hat{H}_1 - E_1|\psi_1\rangle + E_0\langle\psi_1|\psi_1\rangle + E_1\langle\psi_1|\psi_1\rangle\big\} \\
&= E_0 + E_1 + \frac{E_2[\psi_1] + E_3}{1 + \langle\psi_1|\psi_1\rangle} \geq E_{\text{true}}, \qquad (34)
\end{aligned}$$

where:

$$E_2[\psi_1] = \langle\psi_1|\hat{H}_0 - E_0|\psi_1\rangle + \langle\psi_1|\hat{H}_1 - E_1|\psi_0\rangle + \langle\psi_0|\hat{H}_1 - E_1|\psi_1\rangle \tag{35}$$

is the second-order functional introduced by Hylleraas, which will be shown to be an upper bound to the true E_2. Expanding the denominator in (34) gives:

$$E = E_0 + E_1 + E_2[\psi_1] + E_3 + O(\lambda^4) \tag{36}$$

so that $E^{(3)}$ is not an upper bound to the true eigenvalue.

(vi) The formal expansion of ψ_1 into eigenstates of $\hat{H}_0$ gives the well known formula:

$$E_2 = -\sum_{k>0} \frac{|\langle\psi_k^0|\hat{H}_1 - E_1|\psi_0\rangle|^2}{E_k^0 - E_0} < 0 \tag{37}$$

which is known as sum-over-states expression, and is in agreement with (33). In equation (37), $\{\psi_k^0\}$ is the complete set of excited eigenstates of $\hat{H}_0$, orthogonal to ψ_0, each belonging to the eigenvalue $|E_k^0| < |E_0|$. The trouble with (37) is that the *complete* expansion must include not only the functions belonging to the *discrete* spectrum, but also those from the *continuum* (see the related discussion on the dipole polarizability of H(1*s*)). To stress this point, equation (37) is often written as:

$$E_2 = -\sum\!\!\!\!\!\!\int \frac{|\langle\psi_k^0|\hat{H}_1 - E_1|\psi_0\rangle|^2}{E_k^0 - E_0} < 0, \tag{38}$$

where the additional sign means integration over the continuous part of the spectrum. Equation (37) cannot be used as such in actual calculations.

(vii) It can be shown that, if $\tilde{\psi}_1$ is a variational approximation to the true first-order function ψ_1, orthogonal to ψ_0, the Hylleraas functional (35) gives an upper bound to the true E_2:

$$E_2[\tilde{\psi}_1] = \tilde{E}_2 \geq E_2 \tag{39}$$

which gives a variational principle for the second-order energy. All practical calculations of second-order properties are based on such a bound.

11.2.5 Expansion in Eigenstates

Consider the first-order RS equation:

$$(\hat{H}_0 - E_0)\,\psi_1 + (\hat{H}_1 - E_1)\,\psi_0 = 0 \tag{40}$$

with the orthogonality condition:

$$\langle\psi_0|\psi_1\rangle = 0. \tag{8}$$

We expand ψ_1 into the complete set $\{\psi_k^0\}$ of the eigenstates of $\hat{H}_0$ (remind the comments of the previous Section):

$$\psi_1 = \sum_{k'} |\psi_{k'}^0\rangle C_{k'} \quad k' > 0 \tag{41}$$

$$\left(\hat{H}_0 - E_{k'}^0\right) \psi_{k'}^0 = 0, \quad \left\langle \psi_k^0 \middle| \psi_{k'}^0 \right\rangle = \delta_{kk'}. \tag{42}$$

Then the first-order equation becomes:

$$\sum_{k'} C_{k'} \left(E_{k'}^0 - E_0\right) \psi_{k'}^0 + (\hat{H}_1 - E_1)\, \psi_0 = 0. \tag{43}$$

Bracketing (43) by $\langle \psi_k^0 |$:

$$\sum_{k'} C_{k'} \left(E_{k'}^0 - E_0\right) \delta_{kk'} + \left\langle \psi_k^0 \middle| \hat{H}_1 - E_1 \middle| \psi_0 \right\rangle = 0. \tag{44}$$

where the only surviving term will be $k' = k$, giving:

$$C_k = -\frac{\langle \psi_k^0 | \hat{H}_1 - E_1 | \psi_0 \rangle}{E_k^0 - E_0} \quad k > 0. \tag{45}$$

Introducing this expression for the expansion coefficient into the previous equations and putting:

$$E_k^0 - E_0 = \varepsilon_k > 0 \tag{46}$$

we obtain the *sum-over-states* expressions for first-order function and second-order energy:

$$\psi_1 = -\sum_{k>0} |\psi_k^0\rangle \frac{\langle \psi_k^0 | \hat{H}_1 - E_1 | \psi_0 \rangle}{\varepsilon_k} \tag{47}$$

$$E_2 = -\sum_{k>0} \frac{|\langle \psi_k^0 | \hat{H}_1 - E_1 | \psi_0 \rangle|^2}{\varepsilon_k} < 0. \tag{48}$$

11.2.6 Unsöld Approximation

Especially in older work it was often made use of an approximation due to Unsöld (1927) and consisting in replacing all excitation energies ε_k by an average excitation energy ΔE, then using the closure property of the complete spectrum of eigenstates:

$$E_2 = -\sum_{k>0} \frac{\langle \psi_0 | \hat{H}_1 - E_1 | \psi_k^0 \rangle \langle \psi_k^0 | \hat{H}_1 - E_1 | \psi_0 \rangle}{\varepsilon_k}$$

$$\cong -\frac{1}{\Delta E}\sum_{k}^{\text{all}}\langle\psi_0|\hat{H}_1 - E_1|\psi_k^0\rangle\langle\psi_k^0|\hat{H}_1 - E_1|\psi_0\rangle$$

$$= -\frac{1}{\Delta E}\langle\psi_0|(\hat{H}_1 - E_1)\sum_{k}^{\text{all}}|\psi_k^0\rangle\langle\psi_k^0|\hat{H}_1 - E_1|\psi_0\rangle, \tag{49}$$

where the ground state ψ_0 has been included in the summation. Since the set of $\{\psi_k^0\}$ is now complete, the closure property gives:

$$\sum_{k}^{\text{all}}|\psi_k^0\rangle\langle\psi_k^0| = \hat{1} = \delta(x - x') \tag{50}$$

the identity operator (the Dirac δ-function). Hence we obtain the Unsöld formula for E_2:

$$E_2 \cong -\frac{1}{\Delta E}\langle\psi_0|(\hat{H}_1 - E_1)^2|\psi_0\rangle \tag{51}$$

which involves the expectation value of the *square* of the perturbation over the unperturbed ψ_0. This formula allows to give no more than an order of magnitude for E_2, because of the uncertainty in the choice of the average ΔE. Kirkwood put on quantitative basis the Unsöld approach, by means of the variation-perturbation method which we are going to explain in the next Section.

11.3 VARIATIONAL APPROXIMATIONS FOR THE SECOND-ORDER ENERGY

11.3.1 Variation-Perturbation Method

Hylleraas introduced the second-order energy functional as:

$$E_2[\psi_1] = \langle\psi_1|\hat{H}_0 - E_0|\psi_1\rangle + \langle\psi_1|\hat{H}_1 - E_1|\psi_0\rangle + \langle\psi_0|\hat{H}_1 - E_1|\psi_1\rangle. \tag{35}$$

If ψ_1 is the *exact* first-order function, then:

$$\begin{aligned} E_2[\psi_1] &= \langle\psi_1|(\hat{H}_0 - E_0)\psi_1 + (\hat{H}_1 - E_1)\psi_0\rangle + \langle\psi_0|\hat{H}_1 - E_1|\psi_1\rangle \\ &= \langle\psi_0|\hat{H}_1 - E_1|\psi_1\rangle = E_2 \end{aligned} \tag{52}$$

since the first ket in the r.h.s. vanishes by definition. Otherwise, let $\widetilde{\psi}_1$ be a well-behaved variational approximation differing by the exact ψ_1 by the first-order infinitesimal quantity $\delta\psi_1$ (an error function):

$$\widetilde{\psi}_1 = \psi_1 + \delta\psi_1. \tag{53}$$

Then, introducing $\widetilde{\psi}_1$ into (35), and taking into account the fact that ψ_1 does satisfy the first-order equation, it is readily obtained:

$$E_2[\widetilde{\psi}_1] = \widetilde{E}_2 = \langle \delta\psi_1 | \hat{H}_0 - E_0 | \delta\psi_1 \rangle + \langle \psi_0 | \hat{H}_1 - E_1 | \psi_1 \rangle, \tag{54}$$

namely:

$$\widetilde{E}_2 - E_2 = \langle \delta\psi_1 | \hat{H}_0 - E_0 | \delta\psi_1 \rangle = O(\delta^2) \geq 0. \tag{55}$$

Hence we conclude that not only the difference between $\widetilde{E}_2$ and E_2 is positive, giving an upper bound to the true E_2, but also it is second order in the error function $\delta\psi_1$. This means that, as already seen for the Rayleigh variational principle, the error in $\widetilde{E}_2$ is one order of magnitude smaller than the error in the wavefunction $\widetilde{\psi}_1$.

We now add some final variational considerations on the functional $\widetilde{E}_2$. If we look for an arbitrary infinitesimal change in $\widetilde{\psi}_1$, we obtain for the change in $\widetilde{E}_2$ to first order in $\delta\widetilde{\psi}_1$:

$$\delta\widetilde{E}_2 = \langle \delta\widetilde{\psi}_1 | \hat{H}_0 - E_0 | \widetilde{\psi}_1 \rangle + \langle \delta\widetilde{\psi}_1 | \hat{H}_1 - E_1 | \psi_0 \rangle + \text{c.c.} = 0 \tag{56}$$

which gives as necessary but not sufficient condition for the stationarity of the functional $\widetilde{E}_2$ the Euler–Lagrange equation:

$$(\hat{H}_0 - E_0)\,\widetilde{\psi}_1 + (\hat{H}_1 - E_1)\,\psi_0 = 0 \tag{57}$$

which is nothing but the first-order equation for $\widetilde{\psi}_1$. To second order in $\delta\widetilde{\psi}_1$ we find:

$$\begin{aligned}\delta^2\widetilde{E}_2 &= \langle \delta^2\widetilde{\psi}_1 | \hat{H}_0 - E_0 | \widetilde{\psi}_1 \rangle + \langle \delta^2\widetilde{\psi}_1 | \hat{H}_1 - E_1 | \psi_0 \rangle + \text{c.c.} \\ &\quad + 2\langle \delta\widetilde{\psi}_1 | \hat{H}_0 - E_0 | \delta\widetilde{\psi}_1 \rangle = 2\langle \delta\widetilde{\psi}_1 | \hat{H}_0 - E_0 | \delta\widetilde{\psi}_1 \rangle \geq 0\end{aligned} \tag{58}$$

because of the Euler–Lagrange equation for $\widetilde{\psi}_1$. So, the second variation of $\widetilde{E}_2$ is positive, and the stationary value for $\widetilde{E}_2$ corresponds to a minimum for this functional. The same result can be obtained directly in terms of functional derivatives of $\widetilde{E}_2$.

In the context of double perturbation theory, involving static perturbations $\hat{V}$ and $\hat{W}$, second-order bivariational functionals were introduced for studying magnetic properties of molecules and atomic polarizabilities (see, among others, Kolker and Karplus, 1964; Kolker and Michels, 1965). In the context of symmetry-adapted perturbation theories (Jeziorski and Kołos, 1977), Battezzati and Magnasco (1977) showed that, at least in principle, the second-order MS-MA energy (Section 5.1 of Chapter 12) can be obtained from the extrema of a single unsymmetrical functional. The matter was since then reviewed to some extent by Battezzati (1989).

11.3.2 Kirkwood Approximation

Use of the Unsöld approximation in the first-order trial function suggests for $\widetilde{\psi}_1$ the form:

$$\widetilde{\psi}_1 = -\sum_{k>0} |\psi_k^0\rangle \frac{\langle \psi_k^0 | \hat{H}_1 - E_1 | \psi_0 \rangle}{\varepsilon_k}$$

$$\cong -\frac{1}{\Delta E}\underbrace{\sum_k^{\text{all}} |\psi_k^0\rangle\langle\psi_k^0|}_{\hat{1}}\,\hat{H}_1 - E_1|\psi_0\rangle$$

$$= -\frac{1}{\Delta E}(\hat{H}_1 - E_1)\,\psi_0 \tag{59}$$

by the closure property. Therefore, Kirkwood suggested to use as a first approximation to the variational function $\widetilde{\psi}_1$:

$$\widetilde{\psi}_1 = C\,\hat{H}_1\,\psi_0, \tag{60}$$

where C is a linear coefficient and $\widetilde{\psi}_1$ is not normalized. Using this form of $\widetilde{\psi}_1$ in the Hylleraas functional, optimization of the linear coefficient gives:

$$C = -\frac{\langle\psi_0|\hat{H}_1^2|\psi_0\rangle}{\langle\psi_0|\hat{H}_1(\hat{H}_0 - E_0)\hat{H}_1|\psi_0\rangle} \tag{61}$$

yielding as best second-order energy:

$$\widetilde{E}_2(\text{best}) = -\frac{|\langle\psi_0|\hat{H}_1^2|\psi_0\rangle|^2}{\langle\psi_0|\hat{H}_1(\hat{H}_0 - E_0)\hat{H}_1|\psi_0\rangle}. \tag{62}$$

Comparing with Unsöld:

$$\widetilde{E}_2(\text{Unsöld}) = -\frac{1}{\Delta E}\langle\psi_0|\hat{H}_1^2|\psi_0\rangle \tag{63}$$

we obtain the Kirkwood variational estimate of the average excitation energy as:

$$\Delta E(\text{Unsöld}) = \frac{\langle\psi_0|\hat{H}_1(\hat{H}_0 - E_0)\hat{H}_1|\psi_0\rangle}{\langle\psi_0|\hat{H}_1^2|\psi_0\rangle} > 0. \tag{64}$$

It is disappointing that the Kirkwood approximation, which suggests a $\widetilde{\psi}_1$ proportional to $\hat{H}_1$, cannot be used for the electron repulsion $1/r_{12}$ since in this case $\Delta E = 0$ and equation (62) diverges (Hirschfelder et al., 1964).

11.3.3 The Ritz Method for $\widetilde{E}_2$: Expansion in Pseudostates

The Ritz method for $\widetilde{E}_2$ is the method of the linear combinations of a *finite* set of basis functions $\{\chi\}$ applied to the function $\widetilde{\psi}_1$ rather than to ψ. We expand the first-order variational function $\widetilde{\psi}_1$ in an appropriate basis of normalized functions $\{\chi_i\}$ $i = 1, 2, \cdots N$, Schmidt-orthogonalized among themselves and orthogonal to ψ_0 (the order is brought by the coefficients but is omitted for short):

$$\widetilde{\psi}_1 = \boldsymbol{\chi}\mathbf{C} \tag{65}$$

$$\boldsymbol{\chi} = (\chi_1\,\chi_2 \cdots \chi_N) \qquad \mathbf{C} = \begin{pmatrix} C_1 \\ C_2 \\ \cdots \\ C_N \end{pmatrix} \tag{66}$$

with:

$$\langle \chi_i | \chi_{i'} \rangle = \delta_{ii'} \tag{67}$$

$$\boldsymbol{\chi}^{\dagger} \psi_0 = 0. \tag{68}$$

We introduce the matrices:

$$\mathbf{M} = \boldsymbol{\chi}^{\dagger}(\hat{H}_0 - E_0)\boldsymbol{\chi}, \qquad M_{ii'} = \langle \chi_i | \hat{H}_0 - E_0 | \chi_{i'} \rangle \tag{69}$$

the $N \times N$ Hermitian matrix of the excitation energies, and:

$$\boldsymbol{\mu} = \boldsymbol{\chi}^{\dagger} \hat{H}_1 \psi_0, \qquad \mu_i = \langle \chi_i | \hat{H}_1 | \psi_0 \rangle \tag{70}$$

the column matrix of the N transition integrals. The second-order energy functional then takes the matrix form:

$$\widetilde{E}_2 = \mathbf{C}^{\dagger}\mathbf{M}\mathbf{C} + \mathbf{C}^{\dagger}\boldsymbol{\mu} + \boldsymbol{\mu}^{\dagger}\mathbf{C}. \tag{71}$$

Optimizing $\widetilde{E}_2$ with respect to arbitrary infinitesimal changes in the linear coefficients, we get as stationarity condition:

$$\frac{\delta \widetilde{E}_2}{\delta \mathbf{C}^{\dagger}} = \mathbf{M}\mathbf{C} + \boldsymbol{\mu} = \mathbf{0}, \tag{72}$$

which gives the best coefficients as:

$$\mathbf{C} = -\mathbf{M}^{-1}\boldsymbol{\mu} \tag{73}$$

and the best second-order energy:

$$\widetilde{E}_2 = -\boldsymbol{\mu}^{\dagger}\mathbf{M}^{-1}\boldsymbol{\mu}. \tag{74}$$

The Hermitian matrix $\mathbf{M}$ can be diagonalized by a unitary transformation with a matrix $\mathbf{U}$:

$$\boldsymbol{\psi} = \boldsymbol{\chi}\mathbf{U} \qquad \mathbf{U}^{\dagger}\mathbf{M}\mathbf{U} = \boldsymbol{\varepsilon} \qquad \mathbf{U}^{\dagger}\boldsymbol{\mu} = \boldsymbol{\mu}_{\psi} \tag{75}$$

giving $\widetilde{E}_2$ in the form:

$$\widetilde{E}_2 = -\sum_{i=1}^{N} \frac{|\langle \psi_i | \hat{H}_1 | \psi_0 \rangle|^2}{\varepsilon_i} \geq E_2 \tag{76}$$

which is known as *sum-over-pseudostates* expression. This gives an upper bound to the true E_2, with a formula that strictly parallels equation (37), but involves now a *finite* number of accessible functions, the linear pseudostates, which are formally similar to the eigenstates of $\hat{H}_0$ but have sensibly better properties of convergence, as we shall see shortly.

11.4 STATIC MULTIPOLE POLARIZABILITIES FOR H$(1s)$

The simplest physical example which can display the full power of RS perturbation techniques is the ground state H atom in a static electric field F, as that existing between the plates of a plane condenser. The $1s$ H atom looses its sphericity acquiring induced electric moments that can be determined exactly by solving the appropriate RS first-order perturbation equations. This gives a useful test on the results obtained from different variational approximations to second-order energy and properties.

We begin by introducing the study of the dipole polarizability first, then finding the exact solution of the general first-order RS differential equation for the atom in the uniform electric field of strength F, and end this Section by doing comparison of exact with approximate results obtained by variation-perturbation techniques. This will unequivocally show the superiority of the approaches based on linear pseudostates in comparison to ordinary expansions in eigenstates of $\hat{H}_0$.

11.4.1 Dipole Polarizability

A H atom in its ground state is distorted in a static uniform electric field ($F_x = F_y = 0$, $F_z = F$) $\mathbf{F} = \mathbf{k}F$ acquiring an induced dipole moment $\boldsymbol{\mu}$. The interaction of $\boldsymbol{\mu}$ with the external field $\mathbf{F}$ is an additional potential energy term which can be treated as a perturbation of the Hamiltonian $\hat{H}_0$ in absence of field:

$$\hat{H} = \hat{H}_0 - \boldsymbol{\mu} \cdot \mathbf{F} = \hat{H}_0 - F\mu_z = \hat{H}_0 - Fz \tag{77}$$

if the dipole is expressed in atomic units. Either energy or moment can be expanded in a Taylor series of powers of F:

$$E(F) = E_0 + \left(\frac{dE}{dF}\right)_0 F + \frac{1}{2!}\left(\frac{d^2E}{dF^2}\right)_0 F^2 + \frac{1}{3!}\left(\frac{d^3E}{dF^3}\right)_0 F^3 + \cdots \tag{78}$$

$$\langle \mu_z \rangle = \mu_0 + \alpha F + \frac{1}{2!}\beta F^2 + \frac{1}{3!}\gamma F^3 + \cdots \tag{79}$$

But, by the Hellmann (1937)–Feynman (1939) theorem:

$$\frac{dE}{dF} = \left\langle \frac{d\hat{H}}{dF} \right\rangle = -\langle \psi | z | \psi \rangle = -\langle \mu_z \rangle \tag{80}$$

which gives from (78) and (79):

$$\begin{aligned} \frac{dE}{dF} &= \left(\frac{dE}{dF}\right)_0 + \left(\frac{d^2E}{dF^2}\right)_0 F + \frac{1}{2!}\left(\frac{d^3E}{dF^3}\right)_0 F^2 + \frac{1}{3!}\left(\frac{d^4E}{dF^4}\right)_0 F^3 + \cdots \\ &= -\mu_0 - \alpha F - \frac{1}{2!}\beta F^2 - \frac{1}{3!}\gamma F^3 - \cdots \end{aligned} \tag{81}$$

We see that the successive derivatives of E with respect to the external field F in the limit of $F \to 0$ can be related to the *electric properties* of the system:

$$-\left(\frac{dE}{dF}\right)_0 = \mu_0 \quad \text{permanent dipole moment} \tag{82}$$

$$-\left(\frac{d^2E}{dF^2}\right)_0 = \alpha \quad \text{dipole polarizability} \tag{83}$$

$$-\left(\frac{d^3E}{dF^3}\right)_0 = \beta \quad \text{first dipole hyperpolarizability} \tag{84}$$

$$-\left(\frac{d^4E}{dF^4}\right)_0 = \gamma \quad \text{second dipole hyperpolarizability} \tag{85}$$

$$\cdots$$

Taking the second derivative of E we have:

$$-\frac{d^2E}{dF^2} = \alpha + \beta F + \frac{1}{2}\gamma F^2 + \cdots \tag{86}$$

Plotting $-\frac{d^2E}{dF^2}$ against F (Figure 11.1), we see that the intercept gives α, the slope β, the curvature γ.

But equation (79) gives also:

$$\alpha = \lim_{F \to 0} \left(\frac{d\langle \mu_z \rangle}{dF}\right) \tag{87}$$

$$\beta = \lim_{F \to 0} \left(\frac{d^2\langle \mu_z \rangle}{dF^2}\right) \tag{88}$$

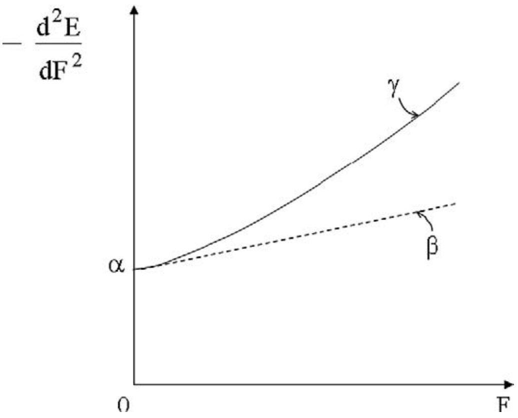

Figure 11.1 Electric properties of the H atom from the negative of the second derivative of E against F.

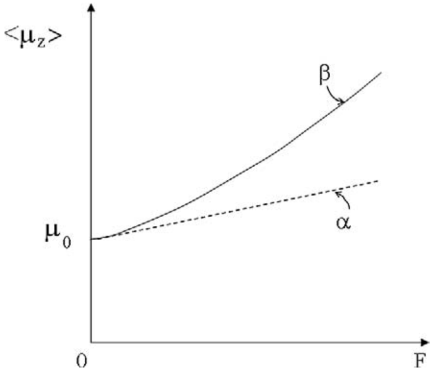

Figure 11.2 Electric properties from the plot of the average induced moment against F ($\mu_0 = 0$ for H).

$$\gamma = \lim_{F\to 0}\left(\frac{d^3\langle\mu_z\rangle}{dF^3}\right) \tag{89}$$

$$\dots$$

This is the basis of the so called Finite-Field-Method (FFM; Cohen and Roothaan, 1965; Werner and Meyer, 1976): the electric properties can also be derived by plotting $\langle\mu_z\rangle$ against F (Figure 11.2). The intercept now gives μ_0 (zero for H), the slope α, the curvature β.

The dipole polarizability α can be evaluated by taking just two points $F \pm \delta F$ according to:

$$\alpha = \left(\frac{\delta\mu_z}{\delta F}\right)_0 = \lim_{F\to 0}\frac{\mu(F+\delta F) - \mu(F-\delta F)}{2\delta F}. \tag{90}$$

11.4.2 Exact Solution of the General First-Order RS Differential Equation for H(1*s*) in a Uniform Electric Field

The electric potential Φ_i at the space point **r** due to particle i of charge q_i is:

$$\Phi_i = \frac{q_i}{r_i} = \frac{q_i}{|\mathbf{r}-\mathbf{r}_i|}, \tag{91}$$

where $\mathbf{r}_i$ is the vector position of particle i with respect to a reference system. For a set of particles, the potential at **r** will be:

$$\Phi(\mathbf{r}) = \sum_i \Phi_i. \tag{92}$$

Assuming a reference coordinate system centred at the molecular centre-of-mass (the nucleus for atoms), $\Phi(\mathbf{r})$ can be expanded in spherical coordinates (Gray, 1976; Gray and Lo, 1976; Stone and Tough, 1984; Magnasco et al., 1988) as:

$$\Phi(\mathbf{r}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} F_{lm}\, R_{lm}(\mathbf{r}), \tag{93}$$

where R_{lm} is a spherical tensor in real form:

$$R_{lm}(\mathbf{r}) = r^l\sqrt{\frac{4\pi}{2l+1}}\,Y_{lm}^{c,s}(\theta,\varphi) = r^l\sqrt{\frac{4\pi}{2l+1}}\,P_l^m(\cos\theta)\begin{cases}\cos m\varphi\\ \sin m\varphi\end{cases} \tag{94}$$

and the F_{lm} are parameters collecting successive derivatives of the potential with respect to Cartesian coordinates, say:

$$F_{00} = \Phi_0, \qquad F_{10} = \left(\frac{\partial\Phi}{\partial z}\right)_0, \qquad F_{11} = \left(\frac{\partial\Phi}{\partial x}\right)_0,$$
$$F_{1\bar{1}} = \left(\frac{\partial\Phi}{\partial y}\right)_0, \qquad \cdots \tag{95}$$

For a *uniform* electric field of strength F directed along z:

$$F_{10} = F, \qquad F_{11} = F_{1\bar{1}} = 0 \tag{96}$$

and the expansion becomes:

$$\Phi(\mathbf{r}) = F\sum_{l=0}^{\infty} R_{l0}(\mathbf{r}) = F\sum_l r^l\sqrt{\frac{4\pi}{2l+1}}\,P_l(\cos\theta). \tag{97}$$

For the electron of the H atom in a *uniform* electric field F, we then have the cylindrical *multipole* perturbation:

$$V(r,\theta) = -F\sum_l r^l\sqrt{\frac{4\pi}{2l+1}}P_l(\cos\theta) = \sum_l V_l(r,\theta), \tag{98}$$

where the 2^l-pole perturbation is:

$$V_l(r,\theta) = -F\,r^l\sqrt{\frac{4\pi}{2l+1}}P_l(\cos\theta). \tag{99}$$

Omitting the constant factor, the RS first-order equation for the 2^l-pole perturbation of the H atom in the field F will be:

$$(\hat{H}_0 - E_0)\,\psi_{1l} - F\,r^l\,P_l(\cos\theta)\psi_0 = 0. \tag{100}$$

This inhomogeneous differential equation can now be solved much in the same way as we solved the radial differential equation for the H atom. The solution was first given by Dalgarno and Lewis (1955); see also Dalgarno (1962).

The first-order RS equation can be written:

$$\left(\nabla_r^2 - \frac{\hat{L}^2}{r^2} + \frac{2}{r} - 1\right)\psi_{1l} = -2F\,r^l\,P_l(\cos\theta)\psi_0. \tag{101}$$

We take:

$$\psi_{1l} = F\,P_l(\cos\theta)R(r) \tag{102}$$

$$R(r) = \psi_0\,r^l\,f(r) = \exp(-r)\,r^l\,f(r) \quad \text{un-normalized}, \tag{103}$$

where we have omitted for short the suffix l in $f(r)$, an unknown function which must be determined. We know that:

$$\hat{L}^2 P_l = l(l+1)\,P_l \qquad \nabla^2 = \nabla_r^2 - \frac{\hat{L}^2}{r^2} \quad \nabla_r^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} \tag{104}$$

so that, taking the first and second radial derivatives of $R(r)$ and substituting in the equation above, we obtain the second-order differential equation determining $f(r)$. Little calculation gives:

$$\frac{dR}{dr} = \exp(-r)\,r^l\{f'(r) + (-1 + lr^{-1})\,f(r)\} \tag{105}$$

$$\frac{d^2R}{dr^2} = \exp(-r)\, r^l \big\{ f''(r) + (-2 + 2lr^{-1})\, f'(r) \\ + [1 - 2lr^{-1} + l(l-1)\, r^{-2}]\, f(r) \big\} \tag{106}$$

$$\nabla_r^2 R(r) = \exp(-r)\, r^l \big\{ f''(r) + [-2 + 2l(l+1)r^{-1}]\, f'(r) \\ + [1 - 2(l+1)r^{-1} + l(l+1)\, r^{-2}]\, f(r) \big\}. \tag{107}$$

Substituting in the differential equation (101) gives:

$$F\ P_l(\cos\theta)\{\nabla_r^2 - l(l+1)r^{-2} + 2r^{-1} - 1\}R = -2F\ P_l(\cos\theta)R$$

$$\exp(-r)\, r^l \big\{ f'' + [-2 + (2l+2)r^{-1}]\, f' \\ + [1 - (2l+2)r^{-1} + l(l+1)\, r^{-2}]\, f(r) \\ + [-1 + 2r^{-1} - l(l+1)\, r^{-2}]\, f(r) \big\} = -2\exp(-r)\, r^l$$

so that the differential equation for $f(r)$ is:

$$f''(r) + [-2 + (2l+2)r^{-1}]\, f'(r) - 2lr^{-1}\, f(r) + 2 = 0 \tag{108}$$

$$rf''(r) + [(2l+2) - 2r]\, f'(r) - 2l\, f(r) + 2r = 0. \tag{109}$$

The last equation can be solved by expanding $f(r)$ into the power series:

$$f(r) = \sum_{k=0}^{\infty} a_k\, r^k, \qquad f'(r) = \sum_{k=1}^{\infty} ka_k\, r^{k-1}, \qquad f''(r) = \sum_{k=2}^{\infty} k(k-1)a_k\, r^{k-2} \tag{110}$$

giving:

$$\sum_{k=2} k(k-1)\, a_k\, r^{k-1} + \sum_{k=1} (2l+2)ka_k\, r^{k-1} - \sum_{k=1} 2ka_k\, r^k \\ -2l \sum_{k=0} a_k\, r^k + 2r = 0. \tag{111}$$

We now obtain for the coefficients of the different powers of r:

$$r^0{:}\quad (2l+2)\, a_1 - 2la_0 = 0 \implies a_1 = \frac{l}{l+1}\, a_0 \quad a_0 \neq 0 \tag{112}$$

$$r^1{:}\quad 2(2-1)\, a_2 + (2l+2)\, 2a_2 - 2a_1 - 2la_1 + 2 = 0$$

$$a_2 = a_1\, \frac{l+1}{2l+3} - \frac{1}{2l+3} = \frac{1}{2l+3}\, (la_0 - 1) \tag{113}$$

$$\cdots$$

$$r^k:\quad (k+1)k\,a_{k+1} + (2l+2)(k+1)\,a_{k+1} - 2ka_k - 2la_k = 0 \tag{114}$$

$$a_{k+1} = \frac{2l+2k}{(k+1)(2l+2+k)}\,a_k \quad k = 2,\ 3, \cdots \tag{115}$$

recurrence relation for $k \geq 2$

Now:

$$\frac{a_{k+1}}{a_k} = \frac{2+\frac{2l}{k}}{k\big(1+\frac{1}{k}\big)\big(1+\frac{2l+2}{k}\big)} \tag{116}$$

$$\lim_{k\to\infty} \frac{a_{k+1}}{a_k} \approx \lim_{k\to\infty} \frac{2}{k}. \tag{117}$$

But:

$$\exp(2r) = \sum_{k=0}^{\infty} \frac{(2r)^k}{k!} \qquad a_k = \frac{2^k}{k!} \qquad a_{k+1} = \frac{2^{k+1}}{(k+1)!} \tag{118}$$

$$\frac{a_{k+1}}{a_k} = \frac{2^{k+1}}{(k+1)!}\cdot\frac{k!}{2^k} = \frac{2}{k+1} \qquad \lim_{k\to\infty}\frac{a_{k+1}}{a_k} \approx \lim_{k\to\infty}\frac{2}{k}. \tag{119}$$

When k tends to infinity, the ratio of successive terms in the series (110) is thus the same as that of successive terms in the expansion of $\exp(2r)$. Thus $f(r)$ tends to infinity as $\exp(2r)$, a solution which is *not* acceptable since $\exp(-r)f(r) \cong \exp(r)$ would diverge for $r \to \infty$. Therefore we must *truncate* the series by imposing:

$$a_{k+1} = a_{k+2} = \cdots = 0 \tag{120}$$

provided:

$$a_k = 0 \quad \text{for } k > 1. \tag{121}$$

Since:

$$a_2 = 0 \quad \text{for } a_0 = \frac{1}{l}, \qquad a_1 = \frac{1}{l+1} \tag{122}$$

it follows:

$$f(r) = a_0 + a_1 r = \frac{1}{l} + \frac{1}{l+1}r \tag{123}$$

giving finally:

$$R(r) = \psi_0 \left(\frac{r^l}{l} + \frac{r^{l+1}}{l+1} \right) \tag{124}$$

$$\psi_{1l} = F \psi_0 \left(\frac{r^l}{l} + \frac{r^{l+1}}{l+1} \right) P_l(\cos\theta) \tag{125}$$

which is the *exact* first-order solution first given by Dalgarno and Lewis (1955).

We are now in the position of evaluating the *exact* 2^l-pole *static* polarizability for ground state H. It will be sufficient to recall that the second-order energy for the l-multipole is:

$$E_{2l} = \langle \psi_0 | V_l | \psi_{1l} \rangle = -F^2 \left\langle \psi_0 \left| V_l P_l \left(\frac{r^l}{l} + \frac{r^{l+1}}{l+1} \right) \right| \psi_0 \right\rangle \tag{126}$$

giving the 2^l-pole polarizability as:

$$\alpha_l = -\left(\frac{d^2 E_{2l}}{dF^2} \right)_0 = 2 \left\langle \psi_0 \left| V_l P_l \left(\frac{r^l}{l} + \frac{r^{l+1}}{l+1} \right) \right| \psi_0 \right\rangle. \tag{127}$$

Evaluating the integral we obtain:

$$\begin{aligned}
\alpha_l &= 2 \left\langle \psi_0 \left| r^l P_l(\cos\theta) \right| P_l(\cos\theta) \left(\frac{r^l}{l} + \frac{r^{l+1}}{l+1} \right) \psi_0 \right\rangle \\
&= 2 \cdot \frac{2\pi}{\pi} \int_{-1}^{1} dx\, [P_l(x)]^2 \int_0^\infty dr\, r^2 \left(\frac{r^{2l}}{l} + \frac{r^{2l+1}}{l+1} \right) \exp(-2r) \\
&= 4 \cdot \frac{2}{2l+1} \left[\frac{(2l+2)!}{l \cdot 2^{2l+3}} + \frac{(2l+3)!}{(l+1)\, 2^{2l+4}} \right] \\
&= \frac{(2l+2)!}{(2l+1)\, 2^{2l+1}} \left(\frac{2}{l} + \frac{2l+3}{l+1} \right) = \frac{(2l+2)!}{(2l+1)\, 2^{2l+1}} \frac{(l+2)(2l+1)}{l(l+1)} \\
&= \frac{(l+2)(2l+2)!}{2^{2l+1} l(l+1)}
\end{aligned} \tag{128}$$

as it must be.

The exact values of the first five 2^l-pole static polarizabilities for the ground state H-atom are given in Table 11.2. These values are a useful reference for testing the results of variational calculations of α_l.

11.4.3 Variational Approximations

In the following, we shall be mostly concerned with different variational approximations to the dipole polarizability $\alpha_1 = \alpha$. Details of the calculations are left, as usual, to Problems 11.

Table 11.2.

Exact 2^l-pole static polarizabilities (atomic units) for H(1s) up to $l = 5$

l	1	2	3	4	5
α_l	4.5 dipole	15 quadrupole	131.25 octupole	2126.25 hexadecapole	54 573.75 32-pole

Table 11.3.

Pseudostate approximations to α for H(1s)

φ	c/a_0^{-1}	μ/ea_0	ε/E_h	α/a_0^3	%
$2p_z$ [a]	$\frac{1}{2} = 0.5$	0.7449	$\frac{3}{8} = 0.375$	2.96	66
$2p_z$ [b]	1	1	$\frac{1}{2} = 0.5$	4.0	89
$2p_z$ [c]	0.7970	0.9684	0.4191	4.48	99.5
$2p_z + 3p_z$ [d]	1	$\frac{\sqrt{6}}{6} = 0.4082$	1	$\frac{1}{3}$	4.5 Exact
	1	$\frac{\sqrt{30}}{6} = 0.9129$	$\frac{2}{5} = 0.4$	$\frac{25}{6}$	
$N\psi_0\left(z + \frac{1}{2}zr\right)$ [e]	1	$\frac{9}{2}\sqrt{\frac{2}{43}} = 0.9705$	$\frac{18}{43} = 0.4186$	4.5	Exact

[a] H-like, eigenstate of $\hat{H}_0$. [b] 1-term, Kirkwood. [c] 1-term, optimized.

[d] 2-term. Normalized STOs: $2p_z = \psi_0 z$, $3p_z = \sqrt{2/15}\psi_0 zr$.

[e] 2-term, Kirkwood generalized. Single normalized pseudostate *equivalent* to the exact ψ_1.

Table 11.4.

Expansion in discrete eigenstates of $\hat{H}_0$ (np_z functions)

n	$c = \frac{1}{n}$	μ/ea_0	ε/E_h	α/a_0^3	%
2	0.5	0.7449	0.375	2.960	65.8
3	0.333	0.2983	0.4444	3.360	74.7
4	0.25	0.1758	0.4687	3.492	77.6
5	0.2	0.1205	0.48	3.552	78.9
6	0.167	0.0896	0.4861	3.585	79.7
7	0.143	0.0701	0.4898	3.606	80.1
30	0.033	0.0076	0.4994	3.660	81.3

We first begin by comparing the results of various pseudostate calculations of α for H(1s), given in Table 11.3, with those resulting from the expansion in eigenstates of $\hat{H}_0$, given in Table 11.4.

Table 11.5.

Dipole pseudospectra of H(1s) for increasing values of N

i	α_i	ε_i	$\sum_i \alpha_i$
1	4.000000×10^{0}	5.000000×10^{-1}	4.000000
1	4.166667×10^{0}	4.000000×10^{-1}	
2	3.333333×10^{-1}	1.000000×10^{0}	4.5
1	3.488744×10^{0}	3.810911×10^{-1}	
2	9.680101×10^{-1}	6.165762×10^{-1}	
3	4.324577×10^{-2}	1.702333×10^{0}	4.5
1	3.144142×10^{0}	3.764634×10^{-1}	
2	1.091451×10^{0}	5.171051×10^{-1}	
3	2.564244×10^{-1}	9.014629×10^{-1}	
4	7.982236×10^{-3}	2.604969×10^{0}	4.5
1	3.013959×10^{0}	3.753256×10^{-1}	
2	9.536869×10^{-1}	4.785249×10^{-1}	
3	4.556475×10^{-1}	6.834311×10^{-1}	
4	7.479674×10^{-2}	1.255892×10^{0}	
5	1.910219×10^{-3}	3.706827×10^{0}	4.5

In this last case (Table 11.4), the transition moments are far too weak and the excitation energies too large, since hydrogen-like np_z $(c = 1/n)$ are too diffuse with increasing the principal quantum number n. The expansion in *discrete* eigenstates of $\hat{H}_0$ converges to the asymptotic value $\alpha = 3.66$ which is only 81.3% of the exact value 4.5. The remaining 18.7% is due to the contribution of the *continuous* part of the spectrum, which is necessary in order to make the expansion *complete*.

Comments on Table 11.3. In the last column of the Table are given the % of the exact value of α $(4.5\, a_0^3)$ obtained by the different approximations. It is immediately evident the enormous improvement in the results obtained by all pseudostate approximations (last four rows) in comparison with the extremely poor result found using the first eigenstate of $\hat{H}_0$. Moreover:

(i) Using $c = 1$ (single STO pseudostate, Kirkwood) we see that the pseudostate function is much more contracted than the eigenstate and the α value improves by about 23%, sensibly more than the limit of the discrete part of the eigenstates of $\hat{H}_0$ $(\alpha = 3.66$ with $N = 30$ terms).

(ii) Optimization of the orbital exponent in the single pseudostate gives an α value which is within 0.5% of the exact value.

(iii) Two linear pseudostates (STO $2p_z + 3p_z$ with $c = 1$) give the exact value of α (as expected, since exact α has two radial components).

(iv) Using $N > 2$ we get always the correct value of $\alpha = \sum_i \alpha_i$, but which now results from an increasingly sophisticated excited pseudospectrum $\{\alpha_i, \varepsilon_i\}$ $i = 1, 2, \cdots, N$ (see Table 11.5).

Table 11.6.

5-term quadrupole pseudospectra of H(1*s*)

i	α_i	ε_i	$\sum_i \alpha_i$
1	6.313528×10^0	5.465443×10^{-1}	
2	4.585391×10^0	4.517894×10^{-1}	
3	3.484548×10^0	7.610195×10^{-1}	
4	6.004247×10^{-1}	1.291357×10^0	
5	1.610783×10^{-2}	3.139766×10^0	15

Table 11.7.

5-term octupole pseudospectra of H(1*s*)

i	α_i	ε_i	$\sum_i \alpha_i$
1	5.948006×10^1	5.930732×10^{-1}	
2	4.062757×10^1	8.080625×10^{-1}	
3	2.332499×10^1	4.905187×10^{-1}	
4	7.603273×10^0	1.296404×10^0	
5	2.140986×10^{-1}	2.784163×10^0	131.25

(v) The single normalized pseudostate equivalent to the exact ψ_1 (last row of Table 11.3) gives a transition moment μ and an excitation energy ε differing very little from those of the 1-term optimized pseudostate (third row).

5-term quadrupole ($l = 2$) and octupole ($l = 3$) pseudospectra of H(1*s*) are given in Tables 11.6 and 11.7. 5-term pseudospectra allow for a calculation of C_6, C_8, C_{10} dispersion coefficients for the long range H–H interaction (Chapter 12) accurate to more than 6 significant figures.

All data of Tables 11.5–11.7 were taken from the PhD thesis of Massimo Ottonelli (1998).

Further techniques for evaluating atomic polarizabilities were discussed by Dalgarno (1962) and, among others, by Langhoff and Hurst (1965). Several examples of construction of dipole pseudospectra for the ground state H atom are given in Problems 11.1–11.8, while the more difficult problem of the diatomic molecule H_2 is examined in Problem 11.9.

11.5 ELECTRIC PROPERTIES OF MOLECULES

The considerations of Section 4 on the H atom can be readily extended to molecules. The Hamiltonian of a molecule in an external electric field **F** is:

$$\hat{H} = \hat{H}_0 + \sum_i q_i \Phi_i, \tag{129}$$

Table 11.8.

Real spherical tensors up to $l = 3$

$R_{00} = 1$	$R_{10} = z$	$R_{11} = x$	$R_{1\bar{1}} = y$
$R_{20} = \frac{3z^2 - r^2}{2}$	$R_{21} = \sqrt{3}zx$	$R_{2\bar{1}} = \sqrt{3}yz$	
$R_{22} = \frac{\sqrt{3}}{2}(x^2 - y^2)$	$R_{2\bar{2}} = \sqrt{3}xy$		
$R_{30} = \frac{5z^2 - 3r^2}{2}z$	$R_{31} = \sqrt{\frac{3}{8}}(5z^2 - r^2)x$	$R_{3\bar{1}} = \sqrt{\frac{3}{8}}(5z^2 - r^2)y$	
$R_{32} = \frac{\sqrt{15}}{2}(x^2 - y^2)z$	$R_{3\bar{2}} = \sqrt{15}xyz$		
$R_{33} = \sqrt{\frac{5}{8}}(x^2 - 3y^2)x$	$R_{3\bar{3}} = \sqrt{\frac{5}{8}}(3x^2 - y^2)y$		

where:

$$\Phi_i = \Phi(x_i, y_i, z_i) = \Phi(\mathbf{r}_i) \tag{130}$$

is the electric potential at the space point $\mathbf{r}_i$ where the i-th particle (electron/nucleus) of charge q_i is located. Taking as reference the molecular centre-of-mass, we saw that the potential Φ can be expanded in real spherical tensors $R_{lm}(\mathbf{r})$ as:

$$\Phi(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} F_{lm} R_{lm}(\mathbf{r}), \tag{131}$$

where the expansion coefficients are related to Cartesian derivatives of the potential evaluated at the origin of the coordinate system.

The first few spherical tensors (regular solid harmonics) up to $l = 3$ are given in Table 11.8.

The perturbation due to the external electric field can hence be written:

$$\sum_i q_i \Phi_i = \sum_l \sum_m F_{lm} \sum_i q_i R_{lm}(\mathbf{r}_i) = \sum_l \sum_m F_{lm} Q_{lm}, \tag{132}$$

where:

$$Q_{lm} = \sum_i q_i R_{lm}(\mathbf{r}_i) \tag{133}$$

is the m-component of the one-electron 2^l-pole electric moment operator of the molecule. For a molecule A with unperturbed wavefunction A_0 and i-th excited pseudostate A_i in the static electric field $\mathbf{F}$ we have:

$$\mu_{lm}(00) = \langle A_0 | Q_{lm} | A_0 \rangle \tag{134}$$

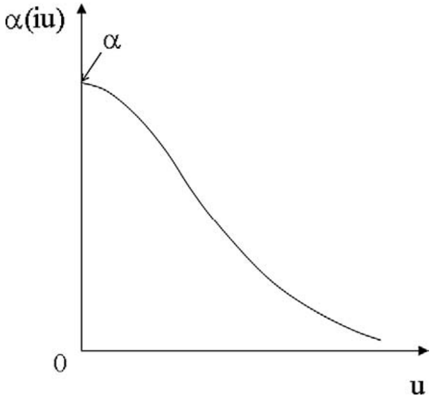

Figure 11.3 Frequency dependence of the imaginary FDP.

the m-component of the *permanent* 2^l-pole electric moment of A;

$$\mu_{lm}(0i) = \langle A_i | Q_{lm} | A_0 \rangle \tag{135}$$

the m-component of the *transition* 2^l-pole moment of A;

$$\alpha_{lm,l'm'}(i) = \frac{2\mu_{lm}(0i)\,\mu_{l'm'}(i0)}{\varepsilon_i} \tag{136}$$

the i-th pseudostate component of the static 2^l-pole $2^{l'}$-pole molecular polarizability;

$$\alpha_{lm,l'm'} = \sum_{i=1}^{N} \alpha_{lm,l'm'}(i) \tag{137}$$

the static multipole polarizability of molecule A. In spherical tensor notation α is generally specified by the four indices $lm, l'm' = a$.

The *static* polarizability can be considered as the limit to zero frequency of the corresponding frequency-dependent, or *dynamic*, polarizability (FDP):

$$\lim_{u\to 0} \alpha_{lm,l'm'}(iu) = \alpha_{lm,l'm'} \tag{138}$$

$$\alpha_{lm,l'm'}(iu) = \sum_i \varepsilon_i \frac{2\mu_{lm}(0i)\,\mu_{l'm'}(i0)}{\varepsilon_i^2 + u^2}. \tag{139}$$

The FDP at imaginary frequency iu (u = real) is plotted against u in Figure 11.3.

The number of non-zero electric properties μ and α depends on the symmetry of the molecule.

- Atoms in state S.
  All permanent moments μ are zero in the ground state.
  Polarizabilities α_l are isotropic, i.e. do depend only on l and not on m.
- Linear molecules.
  They have only axial ($m = 0$) permanent moments.
  Polarizabilities are restricted to $\alpha_{lm,l'm'} = \alpha_{ll'm}$ with $0 \le m \le \min(l, l')$, and therefore depend only on three indices.
  Example:

$$l = l' = 1$$

$\alpha_{10,10} = \alpha_{110} = \alpha_{\parallel}$	parallel (or longitudinal) polarizability
$\alpha_{11,11} = \alpha_{111} = \alpha_{\perp}$	perpendicular (or transverse) polarizability
$\dfrac{\alpha_{\parallel} + 2\alpha_{\perp}}{3} = \alpha$	isotropic polarizability
$\alpha_{\parallel} - \alpha_{\perp} = \Delta\alpha$	polarizability anisotropy.

- Centrosymmetric molecules.
  All odd moments are zero.
- Tetrahedral molecules.
  First non-zero moment is the octupole moment.

In the alternative expansion of the potential Φ in Cartesian coordinates (Buckingham, 1967; McLean and Yoshimine, 1967), the electric properties of a molecule have different notations.

- Permanent moments.

$$\text{Charge } q, \text{ dipole } \mu, \text{ quadrupole } \Theta, \text{ octupole } \Omega, \ldots \tag{140}$$

- Polarizabilities.

$$\begin{aligned}&\text{Dipole–dipole } \alpha, \text{ dipole–quadrupole } A,\\ &\text{dipole–octupole } E, \text{ quadrupole–quadrupole } C,\\ &\text{quadrupole–octupole } H, \text{ octupole–octupole } R\\ &\qquad\qquad\ldots\end{aligned} \tag{141}$$

In Cartesian notation it is sensibly more difficult to see at once which are the non-zero components, since there are linear dependences among them, which may be rather complicated for tensors of higher rank. Formulae relating spherical to Cartesian polarizabilities (and vice versa) can be found in (Stone, 1996).

11.6 PROBLEMS 11

11.1 Find the dipole polarizability α of H(1s) from the expectation value of the induced dipole moment.

Answer:

$$\alpha = \frac{9}{2}.$$

Hint:
Evaluate $\langle \psi | z | \psi \rangle$ using $\psi = \psi_0 + \psi_1$ and expand the result to first order in the electric field F.

11.2 Evaluate α for H(1s) using the single linear pseudostate $\widetilde{\psi}_1 = CF\chi$, where χ is a normalized $2p_z$ STO.

Answer:

$$\alpha = 2\,\frac{\mu^2}{\varepsilon}, \quad \mu = \langle \chi | z | \psi_0 \rangle, \quad \varepsilon = \langle \chi | \hat{H}_0 - E_0 | \chi \rangle. \tag{142}$$

Hint:
Introduce the variational function $\widetilde{\psi}_1$ into the Hylleraas functional $\widetilde{E}_2$ and optimize the *linear* coefficient C.

11.3 Evaluate the transition moment μ and the excitation energy ε of Problem 11.2.

Answer:

$$\mu = \left(\frac{2c^{1/2}}{c+1} \right)^5, \qquad \varepsilon = \frac{1}{2}\,(c^2 - c + 1). \tag{143}$$

Hint:
Evaluate the integrals in spherical coordinates.

11.4 Optimize the single pseudostate result of Problem 11.2 with respect to the non-linear parameter c (the orbital exponent).

Answer:
The required value of c $(= 0.7970)$ is the real root of the cubic equation:

$$7c^3 - 9c^2 + 9c - 5 = 0. \tag{144}$$

Hint:
Find the stationarity condition for $\widetilde{E}_2(c)$ using logarithmic derivatives of μ and ε.

11.5 Find normalization factor, non-orthogonality, transition moment and element of the excitation energy matrix for the n-power STO dipole function $\chi_n' = N_n' z r^{n-1}\psi_0$ with $c = 1$.

Answer:

$$\begin{aligned}
&N_n' = \left(\frac{3\cdot 2^{2n+1}}{(2n+2)!}\right)^{1/2}, \qquad S_{nm} = N_n' N_m' \frac{(n+m+2)!}{3\cdot 2^{n+m+1}} \\
&\mu_n' = N_n' \frac{(n+3)!}{3\cdot 2^{n+2}}, \qquad M_{nm}' = N_n' N_m' \frac{(n+m)!}{3\cdot 2^{n+m}}(2+nm).
\end{aligned} \tag{145}$$

Hint:
Use the basic integrals ($p, q \geq 0$ integers):

$$\begin{aligned}
&\langle\psi_0|z^2 r^p|\psi_0\rangle = \frac{(p+4)!}{3\cdot 2^{p+3}}, \\
&\langle\psi_0 z r^p|\hat{H}_0|\psi_0 z r^q\rangle = -\frac{(p+q+2)!}{3\cdot 2^{p+q+4}}\{p(p-q+3)+q(q-p+3)\}.
\end{aligned} \tag{146}$$

11.6 Find the single normalized pseudostate *equivalent* to the exact ψ_1 for H(1s) .

11.7 Evaluate α for H(1s) using the two normalized linear STO functions $2p_z$ and $3p_z$ ($c = 1$), and construct the corresponding dipole pseudospectrum for $N = 2$.

Answer:

$$\alpha = \alpha_1 + \alpha_2 = \frac{9}{2}$$

i	α_i	ε_i
1	$\frac{2}{6}$	1
2	$\frac{25}{6}$	$\frac{2}{5}$

Hint:
After having orthogonalized $3p_z$ to $2p_z$, construct matrices **M** and **N** over the orthonormal basis, then diagonalize the resultant 2 × 2 Hermitian matrix **M**.

11.8 Evaluate α for H(1s) using the three normalized linear STO functions $2p_z$, $3p_z$ and $4p_z$ ($c = 1$), and construct the $N = 3$ pseudospectrum.

Answer:

$$\alpha = \alpha_1 + \alpha_2 + \alpha_3 = \frac{9}{2}$$

i	α_i	ε_i
1	$3.488\,744 \times 10^{0}$	$3.810\,911 \times 10^{-1}$
2	$9.680\,101 \times 10^{-1}$	$6.165\,762 \times 10^{-1}$
3	$4.324\,577 \times 10^{-2}$	$1.702\,333 \times 10^{0}$

Hint:
Follow the technique suggested in Problem 11.7.

11.9 Construct *approximate* 4-term and 2-term pseudospectra for the dipole polarizabilities of ground state $H_2(^1\Sigma_g^+)$ at $R = 1.4\,a_0$.

Answer:

	$\alpha^{\parallel}$		$\alpha^{\perp}$	
i	$\alpha_i^{\parallel}$	$\varepsilon_i^{\parallel}$	$\alpha_i^{\perp}$	$\varepsilon_i^{\perp}$
1	4.567	0.473	2.852	0.494
2	1.481	0.645	1.350	0.699
3	0.319	0.973	0.335	1.157
4	0.011	1.701	0.022	2.207
$\sum_i \alpha_i$	6.378		4.559	

Hint:
Select, respectively, the four and two most important contributions out of the 34-term pseudospectra of $^1\Sigma_u^+$ and $^1\Pi_u$ symmetry obtained by Magnasco and Ottonelli (1996) using as ψ_0 the Kołos–Wolniewicz 54-term wavefunction for ground state H_2.

11.7 SOLVED PROBLEMS

11.1 The expectation value of the induced dipole moment can be written as:

$$\langle\psi|z|\psi\rangle = \frac{\langle\psi_0+\psi_1|z|\psi_0+\psi_1\rangle}{1+\langle\psi_1|\psi_1\rangle} = \frac{2\langle\psi_0|z|\psi_1\rangle}{1+\langle\psi_1|\psi_1\rangle}$$

$$\cong 2\langle\psi_0|z|\psi_1\rangle\{1-\langle\psi_1|\psi_1\rangle\} \cong 2\langle\psi_0|z|\psi_1\rangle \qquad (147)$$

to first order in F (contained in ψ_1). Since:

$$\psi_1 = F\psi_0 z\left(1+\frac{r}{2}\right) = F\psi_0 \cos\theta\left(r+\frac{r^2}{2}\right), \quad \psi_0 = \frac{\exp(-r)}{\sqrt{\pi}} \tag{148}$$

$$\begin{aligned}\langle\psi_0|z|\psi_1\rangle &= F\left\langle\psi_0\left|\cos^2\theta\left(r^2+\frac{r^3}{2}\right)\right|\psi_0\right\rangle \\ &= F\frac{4}{3}\int_0^\infty dr\,\left(r^4+\frac{r^5}{2}\right)\exp(-2r) = F\left(1+\frac{5}{4}\right) = \frac{9}{4}F,\end{aligned} \tag{149}$$

giving for the expectation value of the induced dipole moment:

$$\langle\psi|z|\psi\rangle \cong 2\langle\psi_0|z|\psi_1\rangle = \frac{9}{2}F. \tag{150}$$

The expansion:

$$\langle\mu_z\rangle = \mu_0 + \alpha F + \frac{1}{2!}\beta F^2 + \cdots = \alpha F + \frac{1}{2!}\beta F^2 + \cdots \tag{151}$$

gives then $\alpha = \frac{9}{2}$ as the coefficient of the term *linear* in F.

11.2 The single $2p_z$ linear pseudostate.

$$\widetilde{\psi}_1 = CF\chi \quad \chi = 2p_z = \left(\frac{c^5}{\pi}\right)^{1/2}\exp(-cr)\,r\cos\theta \tag{152}$$

$$\begin{aligned}\widetilde{E}_2 &= \langle\widetilde{\psi}_1|\hat{H}_0 - E_0|\widetilde{\psi}_1\rangle + 2\langle\widetilde{\psi}_1| - Fz|\psi_0\rangle \\ &= F^2\left\{C^2\langle\chi|\hat{H}_0 - E_0|\chi\rangle - 2C\langle\chi|z|\psi_0\rangle\right\}.\end{aligned} \tag{153}$$

$\frac{d\widetilde{E}_2}{dC} = 0$ gives:

$$C = \frac{\langle\chi|z|\psi_0\rangle}{\langle\chi|\hat{H}_0 - E_0|\chi\rangle} = \frac{\mu}{\varepsilon} \tag{154}$$

as the best value for the *linear* coefficient C. Then:

$$\widetilde{E}_2(\text{best}) = F^2\left(\frac{\mu^2}{\varepsilon^2}\cdot\varepsilon - 2\frac{\mu}{\varepsilon}\cdot\mu\right) = -F^2\frac{\mu^2}{\varepsilon} \tag{155}$$

$$-\frac{d^2\widetilde{E}_2}{dF^2} = 2\frac{\mu^2}{\varepsilon} = \alpha. \tag{156}$$

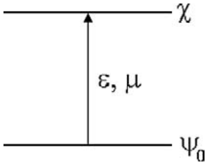

Figure 11.4 Dipole pseudostate transition from ψ_0 to χ for H(1s).

11.3 Evaluation of μ and ε in spherical coordinates.

$$\mu = \langle \chi | z | \psi_0 \rangle = (\psi_0 \chi | z) = \frac{c^{5/2}}{\pi} 2\pi \int_{-1}^{1} dx\, x^2 \int_0^\infty dr\, r^4 \exp[-(c+1)r]$$

$$= \frac{4}{3} c^{5/2} \frac{4 \cdot 3 \cdot 2}{(c+1)^5} = \left(\frac{2c^{1/2}}{c+1} \right)^5. \tag{157}$$

$$\varepsilon = \langle \chi | \hat{H}_0 - E_0 | \chi \rangle = \left\langle \chi \left| \left(-\frac{1}{2}\nabla^2 - \frac{2c}{r} \right) + \frac{2c-1}{r} - E_0 \right| \chi \right\rangle$$

$$= -\frac{c^2}{2} + (2c-1)\frac{c}{2} + \frac{1}{2} = \frac{1}{2}(c^2 - c + 1). \tag{158}$$

11.4 Optimization of the non-linear parameter c in the single pseudostate approximation. Since:

$$\widetilde{E}_2 \propto \mu^2 \varepsilon^{-1}, \tag{159}$$

taking the first c-derivative:

$$\frac{d\widetilde{E}_2}{dc} = 2\mu\varepsilon^{-1} \frac{d\mu}{dc} - \mu^2 \varepsilon^{-2} \frac{d\varepsilon}{dc} \tag{160}$$

gives as stationarity condition:

$$2 \frac{d \ln \mu}{dc} = \frac{d \ln \varepsilon}{dc}. \tag{161}$$

Now, from (157) and (158) it follows:

$$\frac{d \ln \mu}{dc} = \frac{5}{2} \frac{1-c}{c(c+1)} \tag{162}$$

$$\frac{d \ln \varepsilon}{dc} = \frac{2c-1}{c^2 - c + 1}. \tag{163}$$

Substituting in (161) then gives the cubic equation:

$$\frac{5(1-c)}{c(c+1)} = \frac{2c-1}{c^2-c+1} \Longrightarrow 7c^3 - 9c^2 + 9c - 5 = 0 \tag{164}$$

which has the real root $c = 0.7970$.

11.5 Using the basic integrals given in (146), it is easily found:

(i) Normalization factor:

$$\begin{aligned} \langle \chi_n' | \chi_n' \rangle &= N_n'^2 \langle \psi_0 | z^2 r^{2n-2} | \psi_0 \rangle = N_n'^2 \frac{(2n+2)!}{3 \cdot 2^{2n+1}} = 1 \\ &\Longrightarrow N_n' = \left(\frac{3 \cdot 2^{2n+1}}{(2n+2)!} \right)^{1/2}. \end{aligned} \tag{165}$$

(ii) Non-orthogonality:

$$\begin{aligned} S_{nm} &= \langle \chi_n' | \chi_m' \rangle = N_n' N_m' \langle \psi_0 | z^2 r^{n+m-2} | \psi_0 \rangle \\ &= N_n' N_m' \frac{(n+m+2)!}{3 \cdot 2^{n+m+1}}. \end{aligned} \tag{166}$$

(iii) Transition moment:

$$\mu_n' = \langle \chi_n' | z | \psi_0 \rangle = N_n' \langle \psi_0 | z^2 r^{n-1} | \psi_0 \rangle = N_n' \frac{(n+3)!}{3 \cdot 2^{n+2}}. \tag{167}$$

(iv) Element of the excitation energy matrix:

$$\begin{aligned} M_{nm}' &= \langle \chi_n' | \hat{H}_0 - E_0 | \chi_m' \rangle = N_n' N_m' \langle \psi_0 z r^{n-1} | \hat{H}_0 - E_0 | \psi_0 z r^{m-1} \rangle \\ &= N_n' N_m' \frac{(n+m)!}{3 \cdot 2^{n+m}} (2 + nm). \end{aligned} \tag{168}$$

We recall that the dipole functions χ_n' are normalized and orthogonal to ψ_0 by symmetry, but *not* orthogonal to each other.

11.6 We take:

$$\widetilde{\psi}_1 = CF\psi \tag{169}$$

where ψ is the exact first-order function normalized to 1:

$$\psi = N\psi_0 \left(z + \frac{r}{2} z \right). \tag{170}$$

The normalization factor will be:

$$\begin{aligned}\langle\psi|\psi\rangle &= N^2\left\langle\psi_0\left|\left(z+\frac{r}{2}z\right)^2\right|\psi_0\right\rangle = N^2\left\langle\psi_0\left|z^2+z^2r+\frac{1}{4}z^2r^2\right|\psi_0\right\rangle\\ &= N^2\left(1+\frac{5}{2}+\frac{15}{8}\right)=\frac{43}{8}N^2=1 \Longrightarrow N=\left(\frac{8}{43}\right)^{1/2}.\end{aligned}\tag{171}$$

Transition moment:

$$\begin{aligned}\mu &= \langle\psi|z|\psi_0\rangle = N\left\langle\psi_0\left|z^2+\frac{1}{2}z^2r\right|\psi_0\right\rangle\\ &= N\left(1+\frac{1}{2}\cdot\frac{5}{2}\right)=\frac{9}{4}N=\frac{9}{2}\left(\frac{2}{43}\right)^{1/2}.\end{aligned}\tag{172}$$

Excitation energy:

$$\begin{aligned}\varepsilon &= \langle\psi|\hat{H}_0-E_0|\psi\rangle = N^2\left\langle\psi_0\left(z+\frac{r}{2}z\right)\left|\hat{H}_0\right|\psi_0\left(z+\frac{r}{2}z\right)\right\rangle+\frac{1}{2}\\ &= N^2\left\{\underset{p=q=0}{\langle\psi_0z|\hat{H}_0|\psi_0z\rangle}+\frac{1}{4}\underset{p=q=1}{\langle\psi_0zr|\hat{H}_0|\psi_0zr\rangle}+\underset{p=0,\ q=1}{\langle\psi_0z|\hat{H}_0|\psi_0zr\rangle}\right\}+\frac{1}{2}\\ &= N^2\left(0-\frac{1}{4}\cdot\frac{4!}{3\cdot 2^6}\cdot 6-\frac{3!}{3\cdot 2^5}\cdot 4\right)+\frac{1}{2}=-\frac{7}{16}N^2+\frac{1}{2}=\frac{18}{43},\end{aligned}\tag{173}$$

where use was made of the general results given in (146).

11.7 2-term dipole pseudospectrum of H($1s$).

$$\widetilde{\psi}_1 = F\boldsymbol{\chi}'\mathbf{C} \quad \boldsymbol{\chi}'=(\chi_1'\,\chi_2')\tag{174}$$

where χ_1' and χ_2' are normalized $2p_z$ and $3p_z$ STOs with $c=1$:

$$\chi_1' = N_1'\psi_0 z \qquad \chi_2' = N_2'\psi_0 zr \qquad \psi_0=\frac{\exp(-r)}{\sqrt{\pi}}.\tag{175}$$

The two basis functions are normalized, orthogonal to ψ_0, but *non-orthogonal* to each other. We have from (165) and (166):

$$N_1'=1, \qquad N_2'=\sqrt{\frac{2}{15}}, \qquad S=\langle\chi_1'|\chi_2'\rangle=\sqrt{\frac{5}{6}}.\tag{176}$$

(i) We now Schmidt-orthogonalize χ_2' to χ_1':

$$\chi_1 = \chi_1', \qquad \chi_2 = \frac{\chi_2' - S\chi_1'}{\sqrt{1-S^2}} = \sqrt{6}\,\chi_2' - \sqrt{5}\,\chi_1'. \tag{177}$$

The transformed basis $\boldsymbol{\chi}$ is now *orthonormal*:

$$\langle\chi_1|\chi_1\rangle = \langle\chi_2|\chi_2\rangle = 1, \qquad \langle\chi_1|\chi_2\rangle = \langle\chi_2|\chi_1\rangle = 0. \tag{178}$$

We calculate the elements of matrices $\mathbf{M}$ and $\boldsymbol{\mu}$ over the orthonormal basis $\boldsymbol{\chi}$:

$$M_{11} = \langle\chi_1|\hat{H}_0 - E_0|\chi_1\rangle = \frac{1}{2} \tag{179}$$

$$M_{12} = \langle\chi_1|\hat{H}_0 - E_0|\chi_2\rangle = -\frac{\sqrt{5}}{10} \tag{180}$$

$$M_{22} = \langle\chi_2|\hat{H}_0 - E_0|\chi_2\rangle = \frac{9}{10} \tag{181}$$

$$\mu_1 = \langle\chi_1| - Fz|\psi_0\rangle = -F \tag{182}$$

$$\mu_2 = \langle\chi_2| - Fz|\psi_0\rangle = 0. \tag{183}$$

The matrices over the orthonormal basis $\boldsymbol{\chi}$ are then:

$$\mathbf{M} = \begin{pmatrix} \frac{5}{10} & -\frac{\sqrt{5}}{10} \\ -\frac{\sqrt{5}}{10} & \frac{9}{10} \end{pmatrix} \qquad \boldsymbol{\mu} = -F\begin{pmatrix} 1 \\ 0 \end{pmatrix}. \tag{184}$$

Then follows:

$$\mathbf{M}^{-1} = \begin{pmatrix} \frac{9}{4} & \frac{\sqrt{5}}{4} \\ \frac{\sqrt{5}}{4} & \frac{5}{4} \end{pmatrix} \tag{185}$$

so that:

$$\begin{aligned} \widetilde{E}_2 &= -\boldsymbol{\mu}^\dagger\mathbf{M}^{-1}\boldsymbol{\mu} = -\frac{F^2}{4}\,(1\;\;0)\begin{pmatrix} 9 & \sqrt{5} \\ \sqrt{5} & 5 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ &= -\frac{F^2}{4}\,(9\;\;\sqrt{5})\begin{pmatrix} 1 \\ 0 \end{pmatrix} = -F^2\,\frac{9}{4} \end{aligned} \tag{186}$$

$$\alpha = -\left(\frac{d^2\widetilde{E}_2}{dF^2}\right)_0 = \frac{9}{2} = 4.5 \tag{187}$$

which is the exact dipole solution.

(ii) The two *pseudostates* are then obtained by diagonalizing matrix **M** through the secular equation:

$$|\mathbf{M} - \varepsilon \mathbf{1}| = \begin{vmatrix} \frac{5}{10} - \varepsilon & -\frac{\sqrt{5}}{10} \\ -\frac{\sqrt{5}}{10} & \frac{9}{10} - \varepsilon \end{vmatrix} = 0 \Longrightarrow 5\varepsilon^2 - 7\varepsilon + 2 = 0 \tag{188}$$

having the roots:

$$\varepsilon_1 = 1, \qquad \varepsilon_2 = \frac{2}{5}. \tag{189}$$

Eigenvectors are:

$$\bullet \begin{cases} \left(\frac{5}{10} - \varepsilon_1\right) c_1 - \frac{\sqrt{5}}{10} c_2 = 0 \quad \varepsilon_1 = 1 \\ c_1^2 + c_2^2 = 1 \end{cases}$$

$$c_2 = -\sqrt{5}\, c_1 \Longrightarrow c_1 = \frac{1}{\sqrt{6}}, \qquad c_2 = -\frac{\sqrt{5}}{\sqrt{6}}. \tag{190}$$

$$\bullet \begin{cases} \left(\frac{5}{10} - \varepsilon_2\right) c_1 - \frac{\sqrt{5}}{10} c_2 = 0 \quad \varepsilon_2 = \frac{2}{5} \\ c_1^2 + c_2^2 = 1 \end{cases}$$

$$c_2 = \frac{1}{\sqrt{5}} c_1 \Longrightarrow c_1 = \frac{\sqrt{5}}{\sqrt{6}}, \qquad c_2 = \frac{1}{\sqrt{6}}. \tag{191}$$

The 2-term dipole pseudostates are then:

$$\begin{cases} \psi_1 = \frac{1}{\sqrt{6}}\chi_1 - \frac{\sqrt{5}}{\sqrt{6}}\chi_2 \quad \varepsilon_1 = 1 \\ \psi_2 = \frac{\sqrt{5}}{\sqrt{6}}\chi_1 + \frac{1}{\sqrt{6}}\chi_2 \quad \varepsilon_2 = \frac{2}{5}. \end{cases} \tag{192}$$

(iii) Construction of the 2-term dipole pseudospectrum.

$$\boldsymbol{\psi} = \boldsymbol{\chi}\mathbf{U} \quad \mathbf{U} = \begin{pmatrix} \dfrac{1}{\sqrt{6}} & \dfrac{\sqrt{5}}{\sqrt{6}} \\ -\dfrac{\sqrt{5}}{\sqrt{6}} & \dfrac{1}{\sqrt{6}} \end{pmatrix}. \tag{193}$$

Since $\mathbf{U}\mathbf{U}^\dagger = \mathbf{U}^\dagger\mathbf{U} = \mathbf{1}$, $\mathbf{U}$ is a unitary matrix. Over the pseudostate basis $\boldsymbol{\psi}$:

$$\mathbf{M}_\psi = \mathbf{U}^\dagger\mathbf{M}\mathbf{U} = \boldsymbol{\varepsilon} = \begin{pmatrix} 1 & 0 \\ 0 & \frac{2}{5} \end{pmatrix} \quad \text{diagonal} \tag{194}$$

$$\boldsymbol{\mu}_\psi = \mathbf{U}^\dagger\boldsymbol{\mu} = -\frac{F}{6}\begin{pmatrix} \sqrt{6} \\ \sqrt{30} \end{pmatrix}. \tag{195}$$

$\widetilde{E}_2$ in the $\boldsymbol{\psi}$ basis can be written as the sum-over-pseudostates:

$$\begin{aligned} \widetilde{E}_2 &= -\boldsymbol{\mu}_\psi^\dagger \mathbf{M}_\psi^{-1}\boldsymbol{\mu}_\psi = -\frac{F^2}{36} \quad (\sqrt{6}\,\sqrt{30})\begin{pmatrix} 1 & 0 \\ 0 & \frac{5}{2} \end{pmatrix}\begin{pmatrix} \sqrt{6} \\ \sqrt{30} \end{pmatrix} \\ &= -\frac{F^2}{36}(6+75) = -F^2\left(\frac{1}{6}+\frac{25}{12}\right) = -F^2\,\frac{9}{4}, \end{aligned} \tag{196}$$

so that the 2-term dipole pseudospectrum will be:

$$\alpha = \alpha_1 + \alpha_2 = \underset{7.4\%}{\frac{2}{6}} + \underset{92.6\%}{\frac{25}{6}} = 4.5 \tag{197}$$

giving the table:

i	α_i	ε_i
1	$\frac{2}{6}$	1
2	$\frac{25}{6}$	$\frac{2}{5}$

(198)

$\{\alpha_i, \varepsilon_i\}$ $i = 1, 2$ is the 2-term dipole pseudospectrum for H(1s), which will be used for the calculation of the C_6 dispersion coefficient for the H–H interaction in Chapter 12.

11.8 3-term dipole pseudospectrum for H(1s).

$$\widetilde{\psi}_1 = F\boldsymbol{\chi}'\mathbf{C} \quad \boldsymbol{\chi}' = (\chi_1'\,\chi_2'\,\chi_3') \tag{199}$$

where χ_1', χ_2', χ_3' are now normalized $2p_z$, $3p_z$, $4p_z$ STOs with $c = 1$:

$$\chi_1' = N_1'\psi_0 z \qquad \chi_2' = N_2'\psi_0 zr \qquad \chi_3' = N_3'\psi_0 zr^2. \tag{200}$$

Proceeding in the same way as in Problem 11.7 we must now do the calculation *numerically*, and we finally find:

$$\alpha = \alpha_1 + \alpha_2 + \alpha_3 \tag{201}$$

yielding the 3-term dipole pseudospectrum for H$(1s)$ already given as answer to this Problem. The exact value of α for H$(1s)$ is obtained this time as the sum of 3 pseudostate contributions, $\alpha = \sum_{i=1}^{3} \alpha_i$, while the 3-term dipole pseudospectrum $\{\alpha_i, \varepsilon_i\}$ $i = 1, 2, 3$ will give an improved evaluation of the dispersion constant C_{11} for the biatomic system H–H. More refined dipole pseudospectra for H$(1s)$ were collected in Table 11.5, while 5-term quadrupole and octupole pseudospectra are given in Tables 11.6 and 11.7, respectively.

11.9 Dipole polarizabilities of ground state H$_2$.

Magnasco and Ottonelli (1996) gave a pseudostate decomposition of the accurate Kołos–Wolniewicz (KW) (Kołos and Wolniewicz, 1967) *static* dipole polarizabilities for ground state H$_2$. They chose as unperturbed ψ_0 the 54-term ${}^1\Sigma_g^+$ KW wavefunction (Kołos and Wolniewicz, 1964) giving $E_0 = -1.174\,470\,E_h$ at $R = 1.4\,a_0$ (the bottom of the potential energy curve), and for the excited states the 34-term ${}^1\Sigma_u^+$ and ${}^1\Pi_u$ functions selected by KW as a basis for their polarizability calculation. The polarizability data reported in Table I of Kołos–Wolniewicz work cannot be used as such for computing the C_6 dispersion coefficients in the homodimer, because of the lack of the excitation energies corresponding to each polarizability contribution. Magnasco and Ottonelli hence independently developed explicit expressions for all necessary matrix elements, following the original James-Coolidge work (1933), and using the basic integrals developed in their previous work on H$_2$ (Magnasco et al., 1993). The linear coefficients in ψ_0 were obtained by minimization of the molecular energy by the Ostrowski method (Kołos and Wolniewicz, 1964), while the coefficients in the excited pseudostates were obtained by the Givens–Householder diagonalization of $(\hat{H}_0 - E_0)$ after Schmidt orthogonalization of the basis functions. The results are collected in Table 2 of their 1996 paper (Magnasco and Ottonelli, 1996).

Out of these very accurate results, the 4-term pseudospectra given as answer in Problem 11.9 were obtained by simple selection of the most important four contributions to the dipole polarizabilities. The results of these reduced 4-term pseudospectra are remarkably good, the calculated value for the parallel component, $\alpha^{\parallel} = 6.378$, being 99.9% of the accurate value (6.383), and that for the perpendicular component, $\alpha^{\perp} = 4.559$, 99.6% of the accurate value (4.577) reported in the original paper. As a *completeness* test, the sum-rule gives $S(0) = \sum_i \alpha_i \varepsilon_i^2 = 1.972$ for $\alpha^{\parallel}$, and 1.911 for $\alpha^{\perp}$, instead of $N = 2$ as obtained for the complete pseudospectrum.

The reduced 2-term pseudospectra are obtained by just taking the first two rows in the previous 4-term values. The dipole polarizabilities for H$_2$ obtained in this simple way are still rather satisfactory, at least in a first approximation, being about 95% for $\alpha^{\parallel}$ (6.048 instead of 6.378) and 92% for $\alpha^{\perp}$ (4.202 instead of 4.577). The loss in accuracy in the 2-term calculation is greater for the perpendicular component, where the contributions are more "disperse". We observe that both reduced spectra were not optimized. These results will be used in Chapter 12 to evaluate the corresponding C_6 dispersion coefficients for the H_2–H_2 dimer.

– 12 –

Atomic and Molecular Interactions

12.1 INTRODUCTION

The energies occurring when two molecules interact are extremely small, their ratio with respect to the energy E_0 of the individual molecules being of the order of 10^{-5}. The appropriate energy units are therefore small fractions of the atomic unit of energy, say $10^{-3}E_h$ for interactions in the region of the chemical bond, and $10^{-6}E_h$ in that of the Van der Waals bond. Any attempt to calculate intermolecular energies from the energy of the whole system $A + B$ from which we must then subtract the energies of the separate molecules is expected to meet enormous difficulties, even at the simplest level. It is also difficult to handle errors due to: (i) truncation of the basis set, (ii) lack of correlation if each molecule is described at the Hartree–Fock level, and (iii) basis set superposition. It seems therefore preferable to treat the interaction between two molecules as a *small* perturbation, extending Rayleigh–Schroedinger (RS) perturbation theory to include exchange and overlap effects, at least in first order. In the following Sections, after introducing elementary RS perturbation theory by taking as first-order perturbation the interatomic potential V for the H–H$^+$

and H–H interactions, we shall introduce elements of Murrell–Shaw–Musher–Amos (MS-MA) perturbation theory for the interaction between molecules, mostly with the aim of investigating the physical nature of the interaction up to second order in the intermolecular potential V.

12.2 INTERATOMIC INTERACTIONS

In the next two Sections we shall examine from the standpoint of perturbation theory the interatomic interactions occurring between the two simplest atomic systems, (i) the interaction between a ground state H atom and a proton (H–H$^+$), and (ii) the interaction between two ground state H atoms (H–H). We shall start by considering up to second order the RS perturbation theory of a ground state H atom perturbed (i) by a proton H$^+$, or (ii) by another ground state H atom, taking as first-order perturbation the interatomic potential V and as unperturbed Hamiltonian $\hat{H}_0$ the sum of the Hamiltonians of the separate systems. This partition is unsymmetrical as far as nuclear and electron interchange are concerned, the problems connected with this lack of symmetry being considered in Section 4 by taking the Heitler–London (HL) theory as a first-order RS perturbation theory including exchange. This gives an introduction to MS-MA perturbation theory allowing to cover the region of the chemical bond. RS Coulombic interatomic energies are first considered with non-expanded V, then by expanding V into inverse powers of the internuclear distance R, giving what is known as the multipolar expansion of the potential. Second-order energies are treated in terms of linear pseudostates.

12.3 RS PERTURBATION THEORY OF THE H–H$^+$ INTERACTION

With the aim of studying the effectiveness of linear pseudostate techniques in the calculation of non-expanded molecular interactions, we shall consider in this Section the second-order Coulombic interaction in the simplest molecular system, the hydrogen molecular-ion H_2^+. From this point of view, the system can be considered as the resultant of the interaction between a ground state H atom and a proton a distance R apart. Effects due to nuclear symmetry will not be considered here, a short outline of the problem being given in the context of the H–H interaction.

12.3.1 Non-Expanded Interaction Energies up to Second Order

Let r, r_B be the distances of the electron from the nuclei A and B, with A chosen as origin of the coordinate system, R the internuclear distance measured along z from A to B, and θ the angle between r and R.

Then:

$$\hat{H}_0 = -\frac{1}{2}\nabla^2 - \frac{1}{r} \tag{1}$$

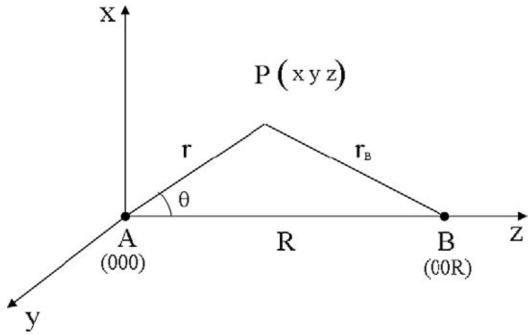

Figure 12.1 Interatomic reference system for the H–H$^+$ interaction.

is the unperturbed Hamiltonian of atom A in atomic units, with:

$$\psi_0 = \frac{\exp(-r)}{\sqrt{\pi}} \tag{2}$$

the unperturbed AO describing the ground state of the H atom, with the unperturbed ground state energy:

$$E_0 = -\frac{1}{2}. \tag{3}$$

The proton at B originates a perturbation which is the interatomic potential:

$$V = \frac{1}{R} - \frac{1}{r_B} = \frac{1}{R} + U^B, \tag{4}$$

where $U^B = -1/r_B$ is the molecular electrostatic potential (MEP).

The Coulombic energy in first order (the electrostatic energy) is always repulsive:

$$E_1^{\mathrm{cb}} = E_1^{\mathrm{es}} = \langle \psi_0 | V | \psi_0 \rangle = \frac{\exp(-2R)}{R}(1+R), \tag{5}$$

so that the only *attractive* contribution (not taking into consideration nuclear interchange) results in second order of RS perturbation theory from the induction (or polarization) energy:

$$E_2^{\mathrm{cb}} = E_2^P = \langle \psi_0 | V | \psi_1^P \rangle = E_2^{\mathrm{ind}} \tag{6}$$

which describes the *distortion* of the spherical charge distribution of the H atom by the electric field originated by the proton at B.

ψ_1^P is the so-called first-order polarization function (Chipman et al., 1973) which satisfies the RS inhomogeneous differential equation:

$$(\hat{H}_0 - E_0)\psi_1^P + (V - E_1^P)\psi_0 = 0 \tag{7}$$

which must be solved under the orthogonality condition:

$$\langle \psi_0 | \psi_1^P \rangle = 0. \tag{8}$$

In a short notation, we shall omit in the following the apex P in our notation.

Variational approximations to E_2 (Chapter 11) can be found in terms of the usual Hylleraas functional and, using the Ritz method in terms of the finite set of N linear pseudostates $\{\psi_i\}$ $i = 1, 2, \cdots N$ normalized and orthogonal among themselves and to ψ_0, the approximate $\widetilde{E}_2$ is given by the sum-over-pseudostates expression:

$$\widetilde{E}_2 = -\sum_{i=1}^{N} \frac{|\langle \psi_i | V | \psi_0 \rangle|^2}{\varepsilon_i} \geq E_2. \tag{9}$$

Posing:

$$\psi_0 = a_0, \qquad \psi_i = a_i \quad \text{(monoexcitations on A)}$$

$$\langle a_i | a_0 \rangle = \delta_{0i}, \tag{10}$$

the variational approximation $\widetilde{E}_2$ to the induction energy can be written in a charge density notation as:

$$\widetilde{E}_2^{\text{ind}} = -\sum_{i=1}^{N} \frac{|(a_0 a_i | U^B)|^2}{\varepsilon_i}. \tag{11}$$

To investigate on the nature of the excited pseudostates on A it is convenient to expand U^B for large R (Section 12.3.2):

$$U^B = -\sum_{l=0}^{\infty} \frac{R_{l0}(\mathbf{r})}{R^{l+1}} \qquad R \gg r \tag{12}$$

giving for the transition integral the expanded form:

$$(a_0 a_i | U^B) = -\sum_{l=0}^{\infty} \frac{(a_0 a_i | R_{l0})}{R^{l+1}}. \tag{13}$$

The coefficients of the power R^{-l-1} represent the 2^l-pole transition moments *induced* on atom A by the presence of B. In order that they be different from zero, it is hence necessary that each excited pseudostate a_i has the same transformation properties of the spherical tensor $R_{l0}(\mathbf{r}) = r^l P_l(\cos\theta)$, or, respectively, of the angular part of $p_z, d_z, f_z, g_z, \cdots$ $(l = 1, 2, 3, 4, \cdots)$ orbitals. The second-order expanded induction energy is therefore:

$$\widetilde{E}_2^{\text{ind}} = -\sum_{l=0}^{\infty} \widetilde{E}_{2l}^{\text{ind}} = -\sum_{l=0}^{\infty} \frac{C_{2l+2}}{R^{2l+2}}, \tag{14}$$

where the induction coefficients are given by:

$$\begin{aligned} C_2 &= 0 & l &= 0 \\ C_{2l+2} &= \frac{1}{2}\alpha_l & l &\geq 1 \end{aligned} \tag{15}$$

with:

$$\alpha_l = \sum_{i=1}^{N} \alpha_l(i) = \sum_{i=1}^{N} \frac{2|(a_0 a_i|r^l P_l)|^2}{\varepsilon_i} \tag{16}$$

the static 2^l-pole polarizability of the H-atom ground state resolved into the contributions of N pseudostates. The long-range induction in H_2^+ is hence expressible in terms of a second-order electric property of the H atom, its static 2^l-pole polarizability. It is interesting to note that the calculation of each multipole component of the induction energy requires the *whole* static polarizability of the atom, a quantity that can be measured by experiment.

The convergence of the one-centre non-expanded multipolar contributions (E_h) to the second-order induction energy in H_2^+ at the distance of the chemical bond ($R = 2\,a_0$) and of the Wan der Waals bond ($R = 12.5\,a_0$) is shown in Table 12.1 (Siciliano, 1993) as a function of the number N of the linear STO pseudostates ($c = 1$) forming the pseudospectrum of H($1s$).

We can see that while two one-centre pseudostates on A are already sufficient to give practically exact values for all multipole components of the induction energy with $l > 0$

Table 12.1.

Convergence of non-expanded multipole contributions (E_h) to $\widetilde{E}_2^{\text{ind}}$ for H_2^+ as a function of the number N of linear STO pseudostates ($c = 1$)^a

N	$l = 0$	1	2	3
$R = 2\,a_0$				
1	-4.193×10^{-3}	-4.733×10^{-2}	-6.122×10^{-3}	-8.042×10^{-4}
5	-7.942×10^{-3}	-4.897×10^{-2}	-8.406×10^{-3}	-2.407×10^{-3}
10	-7.964×10^{-3}	-4.905×10^{-2}	-8.553×10^{-3}	-2.505×10^{-3}
30	$-7.970_1 \times 10^{-3}$	$-4.907_3 \times 10^{-2}$	-8.587×10^{-3}	-2.530×10^{-3}
40	$-7.970_4 \times 10^{-3}$	$-4.907_4 \times 10^{-2}$	$-8.588_1 \times 10^{-3}$	-2.532×10^{-3}
Exact^b	$-7.970_5 \times 10^{-3}$	$-4.907_5 \times 10^{-2}$	-8.589×10^{-3}	$-2.533_5 \times 10^{-3}$
$R = 12.5\,a_0$				
1	-6.519×10^{-20}	-8.192×10^{-5}	-1.769×10^{-6}	-1.007×10^{-7}
2	-3.204×10^{-18}	-9.216×10^{-5}	-1.966×10^{-6}	-1.101×10^{-7}
10	-1.340×10^{-13}	-9.216×10^{-5}	-1.966×10^{-6}	-1.101×10^{-7}
20	$-1.484_3 \times 10^{-13}$	-9.216×10^{-5}	-1.966×10^{-6}	-1.101×10^{-7}
Exact^b	-1.513×10^{-13}	-9.216×10^{-5}	-1.966×10^{-6}	-1.101×10^{-7}

^{a} Siciliano (1993). ^{b} Magnasco and Figari (1987a).

at the Van der Waals minimum ($R = 12.5\,a_0$), a sensibly larger number of pseudostates is needed in order to describe with a sufficient accuracy the same non-expanded multipoles at the bond distance ($R = 2\,a_0$). This difficulty of convergence is due to the fact that U^B is a Coulomb potential localized near nucleus B, which modifies a_0 in its tail near B, so that, even including a large number of excited states localized on A, it is very difficult to reproduce the *cusp* on B that exists in the correct first-order function.

12.3.2 Expanded Interaction Energies up to Second Order

In the long-range region, ($R \gg r$) the interatomic potential V:

$$V = \frac{1}{R} - \frac{1}{r_B} = \frac{1}{R} - \left\{x^2 + y^2 + (z-R)^2\right\}^{-1/2} = \frac{1}{R} - \frac{1}{R}\left(1 - \frac{2z}{R} + \frac{r^2}{R^2}\right)^{-1/2} \tag{17}$$

can be expanded into multipoles on A, using the Taylor series (u = small):

$$(1+u)^{-1/2} \cong 1 - \frac{1}{2}u + \frac{3}{8}u^2 - \frac{5}{16}u^3 + O(u^4) \tag{18}$$

	Factor
$u = -\frac{2z}{R} + \frac{r^2}{R^2}$	$-\frac{1}{2}$
$u^2 = \frac{4z^2}{R^2} - \frac{4zr^2}{R^3} + \frac{r^4}{R^4}$	$\frac{3}{8}$
$u^3 = -\frac{8z^3}{R^3} + \frac{12z^2r^2}{R^4}$	$-\frac{5}{16}$

Collecting all terms in the same power in R^{-n} up to R^{-3} gives:

$$(1+u)^{-1/2} \cong 1 + \frac{z}{R} + \frac{3z^2 - r^2}{2R^2} + \frac{5z^3 - 3zr^2}{2R^3} + O(R^{-4}) \tag{19}$$

giving the first three terms of the multipole expansion for the interatomic potential V in long range:

$$V \cong -\frac{z}{R^2} - \frac{3z^2 - r^2}{2R^3} - \frac{5z^3 - 3zr^2}{2R^4} + O(R^{-5}) = -\sum_{l=1}^{\infty} \frac{R_{l0}(\mathbf{r})}{R^{l+1}} \tag{20}$$

which is the result used in the previous Section. All expansion coefficients of the multipole series for induction are given exactly in terms of the multipole static polarizabilities α_l of ground state H.

12.4 RS PERTURBATION THEORY OF THE H–H INTERACTION

In this Section, we shall mostly consider the Coulombic interaction between two ground state H atoms, leaving in the last part a short discussion of the very important effects due to nuclear and electron interchange.

12.4.1 Non-Expanded Interaction Energies up to Second Order

With reference to Figure 12.2, representing the trapezium of the interparticle distances, we again choose R as the internuclear distance measured along z.

In atomic units, the unperturbed Hamiltonian (two separate H atoms) will be:

$$\hat{H}_0 = \hat{H}_0^A + \hat{H}_0^B \tag{21}$$

while the perturbation V is the interatomic potential:

$$V = -\frac{1}{r_{B1}} - \frac{1}{r_{A2}} + \frac{1}{r_{12}} + \frac{1}{R}. \tag{22}$$

We recall that the partition of the total Hamiltonian $\hat{H}$, which is symmetrical in the interchange of identical nuclei and identical electrons, into unsymmetrical $\hat{H}_0$ and V gives rise to what is known as the symmetry problem. At the end of this Section we shall briefly digress on how to take symmetry effects into account, at least in first order, considering the Heitler–London theory as a first-order RS perturbation theory including exchange.

For the moment, we shall limit ourselves to an ordinary RS perturbation theory up to second order, by considering as unperturbed ψ_0 the simple two-electron product function:

$$\psi_0 = \overset{1}{a_0}\,\overset{2}{b_0}, \tag{23}$$

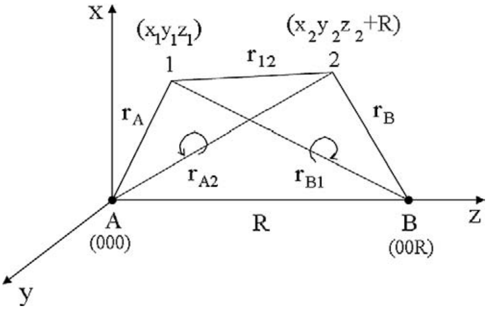

Figure 12.2 Interatomic reference system for the H–H interaction.

where $a_0 = 1s_A$, $b_0 = 1s_B$ are the AOs describing the unperturbed ground states of the separate atoms, with the unperturbed energy:

$$E_0 = E_0^A + E_0^B \tag{24}$$

the sum of the ground state energies of the individual atoms A and B ($E_0 = -1E_h$).

If we introduce a set of excited linear pseudostates $\{a_i\}$ for A and $\{b_j\}$ for B ($i, j \neq 0$) normalized and orthogonal to the respective unperturbed functions, the RS perturbation expansion up to second order in V gives:

$$E_0 = \langle\psi_0|\hat{H}_0|\psi_0\rangle = \langle a_0 b_0|\hat{H}_0^A + \hat{H}_0^B|a_0 b_0\rangle = E_0^A + E_0^B \tag{25}$$

$$E_1^{\text{cb}} = \langle\psi_0|V|\psi_0\rangle = \langle a_0 b_0|V|a_0 b_0\rangle = E_1^{\text{es}} \tag{26}$$

$$\begin{aligned} E_2^{\text{cb}} = &-\sum_i \frac{|\langle a_i b_0|V|a_0 b_0\rangle|^2}{\varepsilon_i} - \sum_j \frac{|\langle a_0 b_j|V|a_0 b_0\rangle|^2}{\varepsilon_j} \\ &-\sum_i \sum_j \frac{|\langle a_i b_j|V|a_0 b_0\rangle|^2}{\varepsilon_i + \varepsilon_j} = E_2^{\text{ind}} + E_2^{\text{disp}}. \end{aligned} \tag{27}$$

E_1^{es} is the *electrostatic* first-order interaction between undistorted H atoms (the semiclassical term of the HL theory).

E_2^{cb} is given by two contributions, (i) the induction (distortion or polarization) energy $E_2^{\text{ind}} = E_2^{\text{ind},A} + E_2^{\text{ind},B}$ which describes the distortion of A (B) by the undistorted electric field of B (A) and involves, respectively, *single* excitations on A (or B), and (ii) the dispersion energy (interatomic electron correlation) E_2^{disp} which describes the mutual distortions induced by A on B and vice versa, and which involves the coupling of simultaneous *double* excitations on A and B.

Introducing the explicit form for the interatomic potential V, we get for the transition integrals:

$$\begin{aligned} \langle \overset{1}{a_i}\, \overset{2}{b_0}\, |V|\, \overset{1}{a_0}\, \overset{2}{b_0}\rangle &= \left\langle \overset{1}{a_i}\, \overset{2}{b_0} \left| -\frac{1}{r_{B1}} - \frac{1}{r_{A2}} + \frac{1}{r_{12}} + \frac{1}{R} \right| \overset{1}{a_0} \overset{2}{b_0} \right\rangle \\ &= \left\langle a_i \left| -\frac{1}{r_{B1}} + \int d\mathbf{r}_2 \frac{[b_0(\mathbf{r}_2)]^2}{r_{12}} \right| a_0 \right\rangle = \left(a_0 a_i | U^B\right), \end{aligned} \tag{28}$$

where we have introduced the charge density notation, and U^B is the electrostatic potential at $\mathbf{r}_1$ on A due to nucleus and undistorted electron of B, having the explicit form:

$$U^B(\mathbf{r}_1) = -\frac{\exp(-2r_{B1})}{r_{B1}}(1 + r_{B1}) \tag{29}$$

which shows the charge-overlap nature of this potential which is localized near nucleus B and vanishes exponentially far from it. We get similarly for A polarizing B:

$$\langle \overset{1}{a_0}\, \overset{2}{b_j}\, |V|\, \overset{1}{a_0}\, \overset{2}{b_0}\rangle = \left\langle b_j \middle| -\frac{1}{r_{A2}} + \int d\mathbf{r}_1 \frac{[a_0(\mathbf{r}_1)]^2}{r_{12}} \middle| b_0 \right\rangle = (b_0 b_j | U^A) \tag{30}$$

$$U^A(\mathbf{r}_2) = -\frac{\exp(-2r_{A2})}{r_{A2}}(1 + r_{A2}). \tag{31}$$

For the transition integral involving biexcitations we have:

$$\begin{aligned}
\langle \overset{1}{a_i}\, \overset{2}{b_j}\, |V|\, \overset{1}{a_0}\, \overset{2}{b_0}\rangle &= \left\langle \overset{1}{a_i}\, \overset{2}{b_j} \middle| \frac{1}{r_{B1}} - \frac{1}{r_{A2}} + \frac{1}{r_{12}} + \frac{1}{R} \middle| \overset{1}{a_0} \overset{2}{b_0} \right\rangle \\
&= \left\langle a_i b_j \middle| \frac{1}{r_{12}} \middle| a_0 b_0 \right\rangle = (a_0 a_i | b_0 b_j) \\
&= \iint d\mathbf{r}_1\, d\mathbf{r}_2 \frac{P^A(0i|\mathbf{r}_1;\mathbf{r}_1) P^B(0j|\mathbf{r}_2;\mathbf{r}_2)}{r_{12}},
\end{aligned} \tag{32}$$

so that we see that it represents the electrostatic repulsion of the two electrons described by the transition densities $\{a_0(\mathbf{r}_1)\, a_i(\mathbf{r}_1)\} = P^A(0i|\mathbf{r}_1;\mathbf{r}_1)$ on A and $\{b_0(\mathbf{r}_2)\, b_j(\mathbf{r}_2)\} = P^B(0j|\mathbf{r}_2;\mathbf{r}_2)$ on B.

We then finally get for the first few orders of unexpanded RS perturbation theory in charge density notation:

$$(i) \quad E_1^{\mathrm{cb}} = E_1^{\mathrm{es}} = \left(a_0^2 \middle| -r_B^{-1}\right) + \left(b_0^2 \middle| -r_A^{-1}\right) + \left(a_0^2 \middle| b_0^2\right) + \frac{1}{R} \tag{33}$$

which is nothing but the semiclassical energy result of Heitler–London theory;

$$(ii) \quad \widetilde{E}_2^{\mathrm{ind,A}} = -\sum_i^{(A)} \frac{|(a_0 a_i | U^B)|^2}{\varepsilon_i} \tag{34}$$

where the electric field due to the unperturbed atom B distorts atom A from its spherical symmetry, the like being true for $\widetilde{E}_2^{\mathrm{ind,B}}$ with $A, i \leftrightarrow B, j$;

$$(iii) \quad \widetilde{E}_2^{\mathrm{disp}} = -\sum_i^{(A)} \sum_j^{(B)} \frac{|(a_0 a_i | b_0 b_j)|^2}{\varepsilon_i + \varepsilon_j} \tag{35}$$

is the non-expanded dispersion energy due to the mutual polarization of A and B, where the two transition densities on A and B are coupled by the interatomic electron repulsion $1/r_{12}$ (interelectron correlation).

12.4.2 Expanded Interaction Energies up to Second Order

As we did for the H–H$^+$ interaction, we now consider for the interatomic potential V the analytical form (see Figure 12.2):

$$\begin{aligned} V &= \frac{1}{R} - \frac{1}{r_{B1}} - \frac{1}{r_{A2}} + \frac{1}{r_{12}} \\ &= \frac{1}{R} - \left\{x_1^2 + y_1^2 + (z_1 - R)^2\right\}^{-1/2} - \left\{x_2^2 + y_2^2 + (z_2 + R)^2\right\}^{-1/2} \\ &\quad + \left\{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2 - R)^2\right\}^{-1/2}. \end{aligned} \tag{36}$$

Expanding in long range ($R \gg r_1, r_2$) each interparticle distance and adding altogether terms up to $O(R^{-4})$:

$$-\frac{1}{r_{B1}} = -\frac{1}{R} - \frac{z_1}{R^2} - \frac{3z_1^2 - r_1^2}{2R^3} + O(R^{-4}) \tag{37}$$

$$-\frac{1}{r_{A2}} = -\frac{1}{R} + \frac{z_2}{R^2} - \frac{3z_2^2 - r_2^2}{2R^3} + O(R^{-4}) \tag{38}$$

$$\begin{aligned} \frac{1}{r_{12}} &= \frac{1}{R} + \frac{z_1 - z_2}{R^2} + \frac{3z_1^2 - r_1^2}{2R^3} + \frac{3z_2^2 - r_2^2}{2R^3} \\ &\quad + \frac{x_1x_2 + y_1y_2 - 2z_1z_2}{R^3} + O(R^{-4}) \end{aligned} \tag{39}$$

we see that there is a lot of cancellation between lower order terms, and we obtain for V the expanded multipole form:

$$V \cong \frac{1}{R^3}(x_1x_2 + y_1y_2 - 2z_1z_2) + O(R^{-4}) \tag{40}$$

so that the first non-vanishing contribution to the expanded interatomic potential for *neutral* H atoms is the dipole–dipole interaction which goes as R^{-3} (compare Coulson, 1958).

It is easily seen that with such an expanded V:

$$E_1^{\text{cb}} = E_1^{\text{es}} = 0 \tag{41}$$

$$\widetilde{E}_2^{\text{ind,A}} = \widetilde{E}_2^{\text{ind,B}} = 0, \tag{42}$$

so that the leading surviving term in long range is the London dispersion attraction:

$$\widetilde{E}_2^{\text{disp}} = -\frac{1}{R^6} \sum_i^{(A)} \sum_j^{(B)} \frac{|\langle a_i b_j | x_1x_2 + y_1y_2 - 2z_1z_2 | a_0 b_0 \rangle|^2}{\varepsilon_i + \varepsilon_j}$$

$$= -\frac{6}{R^6}\sum_i^{(A)}\sum_j^{(B)}\frac{|(a_0a_i|z_1)|^2|(b_0b_j|z_2)|^2}{\varepsilon_i+\varepsilon_j}, \tag{43}$$

where we have taken into account the spherical symmetry of atoms A and B, which gives:

$$(a_0a_i|x_1) = (a_0a_i|y_1) = (a_0a_i|z_1) \quad \text{on A} \tag{44}$$

$$(b_0b_j|x_2) = (b_0b_j|y_2) = (b_0b_j|z_2) \quad \text{on B}. \tag{45}$$

The latter expression for the expanded dispersion energy can be written in the well-known London form:

$$\tilde{E}_2^{\text{disp}} = -\frac{6}{R^6}\cdot\frac{1}{4}\sum_i^{(A)}\sum_j^{(B)}\frac{\varepsilon_i\varepsilon_j}{\varepsilon_i+\varepsilon_j}\alpha_i^A\alpha_j^B = -\frac{6}{R^6}C_{11} = -\frac{C_6}{R^6}, \tag{46}$$

where:

$$C_{11} = \frac{1}{4}\sum_i\sum_j\frac{\varepsilon_i\varepsilon_j}{\varepsilon_i+\varepsilon_j}\alpha_i^A\alpha_j^B \tag{47}$$

is the London dispersion constant for the induced dipole–induced dipole interaction. Recall that:

$$\alpha_i^A = 2\frac{|(a_0a_i|z_1)|^2}{\varepsilon_i} \tag{48}$$

is the contribution of the i-th excited pseudostate to the static dipole polarizability of atom A:

$$\alpha^A = \sum_i \alpha_i^A. \tag{49}$$

Including the interaction of higher multipoles, we can generalize the London formula to the expression for the 2^{l_a}-pole 2^{l_b}-pole dispersion coefficients for the H–H interaction:

$$C_{2n}(l_a,l_b) = \binom{2l_a+2l_b}{2l_a}\frac{1}{4}\sum_i^{(A)}\sum_j^{(B)}\frac{\varepsilon_{l_a}^A(i)\varepsilon_{l_b}^B(j)}{\varepsilon_{l_a}^A(i)+\varepsilon_{l_b}^B(j)}\alpha_{l_a}^A(i)\alpha_{l_b}^B(j) \tag{50}$$

so that the H–H dispersion coefficient for a given $n = l_a + l_b + 1$ is given by:

$$C_{2n} = \sum_{l_a=1}^{n-2} C_{2n}(l_a, n-l_a-1). \tag{51}$$

Table 12.2.

The first three London dispersion coefficients for H–H

N	$C_6/E_h a_0^6$	$C_8/E_h a_0^8$	$C_{10}/E_h a_0^{10}$	
1	6	115.7143	2016[a]	1063.125[b]
2	6.4821	124.0932	2145.819	1132.610
3	6.4984	124.3865	2150.391	1135.107
4	6.4990_0	124.3984	2150.602	1135.209
5	6.4990_2	124.3990	2150.613_5	1135.214

[a] Dipole–octupole. [b] Quadrupole–quadrupole.

Table 12.3.

Relative importance of the Coulombic components of non-expanded induction and dispersion energies for H–H and comparison with the multipolar expansion of E_2^{cb} up to the R^{-10} term ($10^{-3}\ E_h$)

R/a_0	E_2^{ind}	E_2^{disp}	$\dfrac{E_2^{\text{ind}}}{E_2^{\text{disp}}}$	$-\dfrac{C_6}{R^6}-\dfrac{C_8}{R^8}-\dfrac{C_{10}}{R^{10}}$	Region
	a	b		b	
1	−129.40	−17.30	7.5		Chemical bond
1.4	−68.02	−11.78	5.8		
2	−25.58	−7.44	3.4	−3796	
3	−4.33	−3.14	1.4	−83.52	Medium range
4	−0.63	−1.26	0.5	−6.62	
6	−0.011	−0.19	0.06	−0.27	Van der Waals region
8	-0.2×10^{-3}	-33.80×10^{-3}	0.006	-35.30×10^{-3}	
10	-0.004×10^{-3}	-8.04×10^{-3}	0.0005	-8.07×10^{-3}	

[a] Exact non-expanded calculation by Chałasinski and Jeziorski (1974).
[b] Accurate variational calculations by Kreek and Meath (1969).

In Table 12.2 (Magnasco and Figari, 1987b) we give the first three London dispersion coefficients up to $2n = 10$ calculated as a function of the number N of linear STO pseudostates ($c = 1$).

The results with $N = 5$ pseudostates are exact to all figures given. The results for $N = 1$ coincide with Kirkwood, while those for $N = 2$ are already better than those of the single non-linear optimized pseudostate.

Table 12.3 gives the comparison of non-expanded second-order energies with the expanded results up to the R^{-10} term in different regions of the internuclear distances R. It is evident from Table 12.3 that the expanded energies diverge at small R.

12.4.3 HL Theory as a First-Order Perturbation Theory Including Exchange

Consider the Born–Oppenheimer Hamiltonian for the H_2 molecule:

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} + \frac{1}{R}, \quad \hat{h} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B}. \tag{52}$$

$\hat{H}$ is *symmetric* under the interchanges $1 \leftrightarrow 2$ and $A \leftrightarrow B$ (electron and nuclear interchange). Take the two non-orthogonal spatial functions:

$$\chi_1 = \overset{1}{a_0}\,\overset{2}{b_0} \qquad \chi_2 = \overset{1}{b_0}\,\overset{2}{a_0} \tag{53}$$

$$S_{12} = \langle \chi_1 | \chi_2 \rangle = \langle a_0 b_0 | b_0 a_0 \rangle = S_{00}^2, \quad S_{00} = \langle a_0 | b_0 \rangle = \langle b_0 | a_0 \rangle. \tag{54}$$

Each function, separately, does not possess any symmetry with respect to either electron or nuclear interchange, and cannot, therefore, represent an approximation to a physically observable electronic state, which must reflect the symmetry of the Hamiltonian $\hat{H}$ (being hence either symmetric or antisymmetric with respect to the quantum mechanical exchange operator, say $\hat{P}$, which commutes with $\hat{H}$). Since $\hat{H}$ does not contain spin, spin can be omitted at the moment, restricting our analysis to the space-part of the wavefunction, being added at the end to get a function satisfying the Pauli principle. Partitioning $\hat{H}$ into unsymmetrical $\hat{H}_0$ and V, the commutation relation:

$$[\hat{H}, \hat{P}] = [\hat{P}, \hat{H}] \tag{55}$$

implies the paradoxical relation:

$$[\hat{H}_0, \hat{P}] = [\hat{P}, \hat{V}] \tag{56}$$

where the perturbation orders are mixed. To get out of this paradox we have two ways:

(i) Set up *first* the secular equation involving the *full* symmetrical Hamiltonian and the two spatially non-orthogonal functions $\overset{1}{a_0}\,\overset{2}{b_0}$ and $\overset{1}{b_0}\,\overset{2}{a_0}$ (electrons always in dictionary order) giving the *same* expectation value of $\hat{H}$ ($\hat{H}_{11} = \hat{H}_{22}$); or

(ii) Start from the beginning using a fully symmetrized (un-normalized) ψ_0:

$$\psi_0 = \frac{a_0 b_0 + b_0 a_0}{2} = \hat{P} a_0 b_0 \quad (\text{for } {}^1\Sigma_g^+ \text{ ground state}), \tag{57}$$

where the projector $\hat{P}$ satisfies the usual properties:

$$\hat{P} = \frac{1}{2}(\hat{I} + \hat{P}_{12}) \quad \hat{P}^2 = \hat{P}, \ \hat{P}^\dagger = \hat{P} \tag{58}$$

and *later* dissecting $\hat{H}$ into $\hat{H}_0 + V$.

We now examine separately these two approaches.

(i) The Hermitian matrix yielding to the secular equation is:

$$\begin{pmatrix} H_{11}-E & H_{12}-ES_{12} \\ H_{12}-ES_{12} & H_{22}-E \end{pmatrix} = \begin{pmatrix} H_{11}-E & H_{12}-ES_{12} \\ H_{12}-ES_{12} & H_{11}-E \end{pmatrix} \tag{59}$$

since:

$$H_{11} = \left\langle a_0b_0 \left| \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} + \frac{1}{R} \right| a_0b_0 \right\rangle = h_{a_0a_0} + h_{b_0b_0} + (a_0^2|b_0^2) + \frac{1}{R} \tag{60}$$

$$\begin{aligned} H_{22} &= \left\langle b_0a_0 \left| \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} + \frac{1}{R} \right| b_0a_0 \right\rangle \\ &= h_{b_0b_0} + h_{a_0a_0} + (b_0^2|a_0^2) + \frac{1}{R} = H_{11} \end{aligned} \tag{61}$$

$$\begin{aligned} H_{12} &= \left\langle a_0b_0 \left| \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} + \frac{1}{R} \right| b_0a_0 \right\rangle \\ &= h_{a_0b_0}S_{00} + h_{b_0a_0}S_{00} + (a_0b_0|a_0b_0) + \frac{1}{R}S_{00}^2 \end{aligned} \tag{62}$$

$$S_{12} = \langle a_0b_0|b_0a_0\rangle = S_{00}^2. \tag{63}$$

Dissecting now the full Hamiltonian into the unsymmetrical components $\hat{H}_0 + V$, with:

$$\hat{H}_0 = \hat{H}_0^A + \hat{H}_0^B = \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{A1}}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{B2}}\right) \tag{64}$$

$$E_0 = \varepsilon_A + \varepsilon_B = 2\varepsilon_0 \tag{65}$$

$$V = -\frac{1}{r_{B1}} - \frac{1}{r_{A2}} + \frac{1}{r_{12}} + \frac{1}{R}, \tag{66}$$

we obtain:

$$V_{11} = \langle a_0b_0|V|a_0b_0\rangle = \left(a_0^2\right| - r_B^{-1}\left.\right) + \left(b_0^2\right| - r_A^{-1}\left.\right) + \left(a_0^2|b_0^2\right) + \frac{1}{R} \tag{67}$$

$$\begin{aligned} V_{12} &= \langle a_0b_0|V|b_0a_0\rangle \\ &= \left(b_0a_0\right| - r_B^{-1}\left.\right)S_{00} + \left(a_0b_0\right| - r_A^{-1}\left.\right)S_{00} + (a_0b_0|a_0b_0) + \frac{1}{R}S_{00}^2, \end{aligned} \tag{68}$$

so that:

$$H_{11} = E_0 + V_{11} \tag{69}$$

$$H_{12} = E_0 S_{00}^2 + V_{12}. \tag{70}$$

Writing:

$$E = E_0 + E_1, \tag{71}$$

our starting matrix becomes:

$$\begin{aligned}
&\begin{pmatrix} (E_0 + V_{11}) - (E_0 + E_1) & (E_0 S_{00}^2 + V_{12}) - (E_0 + E_1) S_{00}^2 \\ (E_0 S_{00}^2 + V_{12}) - (E_0 + E_1) S_{00}^2 & (E_0 + V_{11}) - (E_0 + E_1) \end{pmatrix} \\
&\quad = \begin{pmatrix} E_0 - E_0 & E_0 S_{00}^2 - E_0 S_{00}^2 \\ E_0 S_{00}^2 - E_0 S_{00}^2 & E_0 - E_0 \end{pmatrix} \\
&\qquad + \begin{pmatrix} V_{11} - E_1 & V_{12} - E_1 S_{00}^2 \\ V_{12} - E_1 S_{00}^2 & V_{11} - E_1 \end{pmatrix},
\end{aligned} \tag{72}$$

where the first matrix is the null matrix and the second the correct first-order matrix including exchange.

The first-order secular equation including exchange is therefore:

$$\begin{vmatrix} V_{11} - E_1 & V_{12} - E_1 S_{00}^2 \\ V_{12} - E_1 S_{00}^2 & V_{11} - E_1 \end{vmatrix} = 0 \tag{73}$$

whose roots give directly the first-order energies including exchange for the singlet $({}^1\Sigma_g^+)$ and triplet $({}^3\Sigma_u^+)$ states of the H_2 molecule.

Expanding the determinant we have:

$$V_{11} - E_1 = \pm(V_{12} - E_1 S_{00}^2). \tag{74}$$

- Lowest root:

$$E_1({}^1\Sigma_g^+) = \frac{V_{11} + V_{12}}{1 + S_{00}^2} = V_{11} + \frac{V_{12} - S_{00}^2 V_{11}}{1 + S_{00}^2}, \tag{75}$$

where:

$$V_{11} = \left(a_0^2 \middle| -r_B^{-1}\right) + \left(b_0^2 \middle| -r_A^{-1}\right) + \left(a_0^2 \middle| b_0^2\right) + \frac{1}{R} = E_1^{\text{cb}} = E_1^{\text{es}} \tag{76}$$

is the semiclassical term of the HL theory (the non-expanded first-order Coulombic or electrostatic energy); and:

$$\begin{aligned}\frac{V_{12}-S_{00}^2V_{11}}{1+S_{00}^2} &= \frac{S_{00}}{1+S_{00}^2}\left\{S_{00}\left[\left(a_0b_0-S_{00}a_0^2\right|-r_B^{-1}\right)+\left(b_0a_0-S_{00}b_0^2\right|-r_A^{-1}\left.\right)\right] \\ &\quad +\left[\left(a_0b_0|a_0b_0\right)-S_{00}^2\left(a_0^2|b_0^2\right)\right]\right\} \qquad (77)\end{aligned}$$

the quantum term of HL theory (first-order exchange-overlap or penetration energy), which is a strongly attractive term determining the chemical bond.

- Highest root:

$$E_1(^3\Sigma_u^+)=\frac{V_{11}-V_{12}}{1-S_{00}^2}=V_{11}-\frac{V_{12}-S_{00}^2V_{11}}{1-S_{00}^2} \qquad (78)$$

he second term being the quantum component for the excited triplet state, a strongly repulsive term in short range.

(ii) If we write for convenience:

$$\varphi_0=\overset{1}{a_0}\,\overset{2}{b_0} \qquad (79)$$

for the unsymmetrical product function, we can use the fully symmetrized ψ_0 (for the $^1\Sigma_g^+$ state):

$$\psi_0=\hat{P}\varphi_0=\frac{a_0b_0+b_0a_0}{2} \qquad (80)$$

as a variational function with the full $\hat{H}$:

$$E=\frac{\langle\psi_0|\hat{H}|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle}=\frac{\langle\hat{P}\varphi_0|\hat{H}|\hat{P}\varphi_0\rangle}{\langle\hat{P}\varphi_0|\hat{P}\varphi_0\rangle}=\frac{\langle\hat{P}\varphi_0|\hat{H}|\varphi_0\rangle}{\langle\hat{P}\varphi_0|\varphi_0\rangle} \qquad (81)$$

and, dissecting $\hat{H}$ into $\hat{H}_0+V$:

$$\begin{aligned}E&=\frac{\langle\hat{P}\varphi_0|\hat{H}_0+V|\varphi_0\rangle}{\langle\hat{P}\varphi_0|\varphi_0\rangle}=\frac{\langle\hat{P}\varphi_0|(\hat{H}_0-E_0)+E_0+V|\varphi_0\rangle}{\langle\hat{P}\varphi_0|\varphi_0\rangle} \\ &=E_0+E_1+\Delta, \qquad (82)\end{aligned}$$

where:

$$E_1=\frac{\langle\hat{P}\varphi_0|V|\varphi_0\rangle}{\langle\hat{P}\varphi_0|\varphi_0\rangle} \qquad (83)$$

is the HL first-order interaction including exchange, and the last term:

$$\Delta = \frac{\langle \hat{P}\varphi_0 | \hat{H}_0 - E_0 | \varphi_0 \rangle}{\langle \hat{P}\varphi_0 | \varphi_0 \rangle} \tag{84}$$

vanishes if the unsymmetrized φ_0 is an *exact* eigenfunction of $\hat{H}_0$ with eigenvalue E_0 (what is the case for H_2). For *approximate* wavefunctions, we must hence consider the correction term:

$$\Delta = \Delta^A + \Delta^B \tag{85}$$

$$\Delta^A = \frac{\langle \hat{P}\varphi_0 | \hat{H}_0^A - E_0^A | \varphi_0 \rangle}{\langle \hat{P}\varphi_0 | \varphi_0 \rangle} \tag{86}$$

$$\Delta^B = \frac{\langle \hat{P}\varphi_0 | \hat{H}_0^B - E_0^B | \varphi_0 \rangle}{\langle \hat{P}\varphi_0 | \varphi_0 \rangle}, \tag{87}$$

where:

$$E_0^A = \frac{\langle a_0 | \hat{H}_0^A | a_0 \rangle}{\langle a_0 | a_0 \rangle} \tag{88}$$

is the expectation value of $\hat{H}_0^A$ over the approximate a_0 (not necessarily an eigenfunction of $\hat{H}_0^A$). The Δ-term depends in this case on the interatomic (or intermolecular) overlap and may be quite large in short range.

This last approach, which makes use of a symmetrized ψ_0, is known as Murrell–Shaw–Musher–Amos (MS-MA: Murrell and Shaw, 1967; Musher and Amos, 1967) perturbation theory, and was fully analyzed by Chipman et al. (1973).

12.4.4 Accurate Theoretical Results for Simple Molecular Systems

In the theory of atomic or molecular interactions it is often assumed as a first reasonable approximation (Magnasco and McWeeny, 1991) to add to E_1^{es} the first-order exchange-overlap (penetration) $E_1^{\text{exch-ov}}$ term, which can be evaluated using just a_0 and b_0, and adding further the E_2^{cb} term (without second-order exchange), which introduces the main Coulombic second-order effects describing distortion and correlation between the atomic (or molecular) charge distributions.

As an example, the main contributions to the energies of the chemical bond and to the Van der Waals (VdW) bond in H_2^+ and H_2 are reported in Table 12.4.
Table 12.4 deserves the following comments.

(i) H_2^+ molecule-ion.
The main correction to the attractive HL bond energy for the $^2\Sigma_g^+$ ground state is the (attractive) distortion energy (mostly dipole) of the charge distribution. The main

Table 12.4.

Main contributions to the energies of the chemical bond ($10^{-3}\,E_h$) and the VdW bond ($10^{-6}\,E_h$) in H_2^+ and H_2

H_2^+ molecule-ion			
(i)	$R = 2a_0$	Chemical bond	
	$E_1(^2\Sigma_g^+)$	−53.8	
	$E_{21}^{\mathrm{ind},a}$	−49.0	
		−102.8	Accurate −102.6
(ii)	$R = 12.5\,a_0$	VdW bond	
	$E_1(^2\Sigma_u^+)$	+31	
	E_{21}^{ind}	−92	
		−61	Accurate −60.8
H_2 molecule			
(i)	$R = 1.4\,a_0$	Chemical bond	
	$E_1(^1\Sigma_g^+)$	−105.5	
	$E_2^{\mathrm{ind},b}$	−68.0	
		−173.5	Accurate −174.5
(ii)	$R = 8\,a_0$	VdW bond	
	$E_1(^3\Sigma_u^+)$	+14	
	$E_2^{\mathrm{disp},c}$	−34	
		−20	Accurate −20.1

[a] Dipole contribution. Assuming cancellation between the remaining attractive multipole contributions and the repulsive second-order exchange effects.

[b] Exact induction. Assuming cancellation between attractive dispersion (−11.8) and repulsive second-order exchange effects.

[c] Non-expanded dispersion.

correction to the repulsive HL energy for the $^2\Sigma_u^+$ excited state is the (attractive) distortion energy (mostly dipole) of the charge distribution. At variance with H_2 (*neutral* molecule), induction is a long-range effect in H_2^+ (*charged* molecule-ion).

(ii) H_2 molecule.
The main correction to the attractive HL bond energy for the $^1\Sigma_g^+$ ground state is still the (attractive) distortion energy of the charge distribution. The main correction to the repulsive HL energy for the $^3\Sigma_u^+$ excited state of H_2 is the (attractive) dispersion due to interatomic electron correlation. At the distance of the VdW minimum, induction is negligible for the neutral molecule.

The values reported as accurate in Table 12.4 are taken from Peek (1965) for H_2^+, Kołos and Wolniewicz (1965) for $H_2(^1\Sigma_g^+)$, and Kołos and Rychlewski (1990) for $H_2(^3\Sigma_u^+)$.

We notice that the *expanded* dispersion up to $2n = 10$ gives at $R = 8\,a_0$ for H_2 (Kreek and Meath, 1969):

$\widetilde{E}_2^{\text{disp}}$	-24.4	-6.9	-1.6	-0.9	$= -33.8 \times 10^{-6}\,E_h$
Multipoles	$1,1$	$1,2+2,1$	$1,3+3,1$	$2,2$	

a value which is in very good agreement with the corresponding *non-expanded* value of $-34 \times 10^{-6}\,E_h$.

12.5 AN OUTLINE OF A PERTURBATION THEORY FOR MOLECULAR INTERACTIONS

As we said previously (Magnasco and McWeeny, 1991), in the perturbation theory of molecular interactions the majority of the physically meaningful effects can be described in second order, provided the Coulombic energies (electrostatic, induction, dispersion) are supplemented by terms arising from symmetry and intermolecular electron exchange. First-order effects, which are dominant in short range, can be described by antisymmetrizing the product ψ_0 of the (individually antisymmetric) unperturbed wavefunctions of the separate molecules (say A_0 and B_0). The small second-order effects can then be calculated by seeking variational approximations to induction and dispersion energies (as we did for H_2^+ and H_2) eventually including later second-order exchange, using, for instance, MS-MA perturbation theory. Even if MS-MA is just one of the possible exchange perturbation theories, it owes its simplicity to the fact that the energy corrections can be calculated without solving perturbation equations involving the antisymmetrizer $\hat{A}$ (an operator which implies interchange of electrons between *different* molecules). We sketch briefly in the following the relevant equations, while for details the reader is referred to the original work (Magnasco and McWeeny, 1991, and references therein).

12.5.1 MS-MA Perturbation Theory of Molecular Interactions

If V is the intermolecular potential and $\hat{H}_0$ the unperturbed Hamiltonian (sum of the Hamiltonians $\hat{H}_0^A$ and $\hat{H}_0^B$ of the isolated molecules), then it is assumed that the unperturbed product ψ_0 of isolated-molecule functions:

$$\psi_0 = A_0 B_0 \tag{89}$$

will satisfy the zeroth order (unperturbed) equation:

$$(\hat{H}_0 - E_0)\psi_0 = 0. \tag{90}$$

The interaction energy in second order of the MS-MA expansion is obtained *directly*[1], after antisymmetrizing ψ_0, as:

$$E^{int} = E_1 + E_2, \tag{91}$$

where:

$$E_1 = \frac{\langle \hat{A}\psi_0 | V | \psi_0 \rangle}{\langle \hat{A}\psi_0 | \psi_0 \rangle} = E_1^{\text{cb}} + E_1^{\text{exch-ov}} \tag{92}$$

is the first-order interaction with its Coulombic and exchange-overlap (penetration) components:

$$E_1^{\text{cb}} = \langle \psi_0 | V | \psi_0 \rangle \tag{93}$$

$$E_1^{\text{exch-ov}} = \frac{\langle \hat{P}\psi_0 | V - E_1^{\text{cb}} | \psi_0 \rangle}{1 + \langle \hat{P}\psi_0 | \psi_0 \rangle}, \tag{94}$$

and E_2 the second order interaction:

$$E_2 = \frac{\langle \hat{A}\psi_1^P | V - E_1 | \psi_0 \rangle}{\langle \hat{A}\psi_0 | \psi_0 \rangle} = E_2^{\text{cb}} + E_2^{\text{exch-ov}} \tag{95}$$

with:

$$E_2^{\text{cb}} = \left\langle \psi_1^P \middle| V \middle| \psi_0 \right\rangle = E_2^{\text{ind}} + E_2^{\text{disp}} \tag{96}$$

$$E_2^{\text{exch-ov}} = \frac{\langle \hat{P}\psi_1^P | V - E_1 | \psi_0 \rangle - E_2^{\text{cb}} \langle \hat{P}\psi_0 | \psi_0 \rangle}{1 + \langle \hat{P}\psi_0 | \psi_0 \rangle}. \tag{97}$$

In these formulae, $\hat{A}$ is the partial (idempotent) antisymmetrizer:

$$\hat{A} = Q^{-1}(1 + \hat{P}) \tag{98}$$

$$Q^{-1} = \frac{N_A! N_B!}{N!}, \tag{99}$$

$\hat{P}$ the operator interchanging electrons between *different* molecules:

$$\hat{P} = -\sum_i^{(A)} \sum_j^{(B)} \hat{P}_{ij} + \sum_{i<i'}^{(A)} \sum_{j<j'}^{(B)} \hat{P}_{ij} \hat{P}_{i'j'} + \cdots \tag{100}$$

---

[1] That is *not* taking the small difference of two very large quantities as in the variational calculation of the whole system A + B.

and ψ_1^P the first-order polarization function satisfying the inhomogeneous differential equation:

$$(\hat{H}_0 - E_0)\psi_1^P + \left(V - E_1^{\text{cb}}\right)\psi_0 = 0 \tag{101}$$

with the constraint:

$$\left\langle \psi_0 \middle| \psi_1^P \right\rangle = 0. \tag{102}$$

Variational approximations to (101) can be given by minimizing the corresponding Hylleraas functional in terms of the first-order variational function $\widetilde{\psi}_1^P$:

$$\widetilde{E}_2^{\text{cb}} = \left\langle \widetilde{\psi}_1^P \middle| \hat{H}_0 - E_0 \middle| \widetilde{\psi}_1^P \right\rangle + \left\langle \widetilde{\psi}_1^P \middle| V \middle| \psi_0 \right\rangle + \left\langle \psi_0 \middle| V \middle| \widetilde{\psi}_1^P \right\rangle \geq E_2^{\text{cb}}. \tag{103}$$

This problem has already been fully discussed for the simpler cases of the H–H$^+$ and the H–H interaction.

The main difficulty with the application of MS-MA theory to large molecular systems lies in the evaluation of the matrix elements occurring in (94) and (97), since the usual rules based on Slater determinants are not directly applicable, and we must resort to the difficult evaluation of the different electron interchanges (mostly, single and double) by means of the expansion (100).

A simpler result is obtained if we make the assumptions (i) that the approximate free-molecule functions are available in the form of single Slater determinants of Hartree–Fock wavefunctions for A and B, and (ii) that suitable pseudostates can be generated by separate diagonalization of the excitation energy operators $(\hat{H}_0^A - E_0^A)$ and $(\hat{H}_0^B - E_0^B)$ over a basis of excited functions, individually antisymmetrized, $\{A_i\}$ for A and $\{B_j\}$ for B. In this case, (i) the first-order term, E_1 in (92), must be corrected by the addition of the term:

$$\Delta = \frac{\langle \hat{A}\psi_0 | \hat{H}_0 - E_0 | \psi_0 \rangle}{\langle \hat{A}\psi_0 | \psi_0 \rangle} = \Delta^A + \Delta^B \tag{104}$$

which must be added to the exchange-overlap component in (94) and is at least of order $O(S^2)$, if S is an overlap integral between an occupied orbital of A and one of B, but is of order $O(S^4)$ for the Hartree–Fock wavefunctions of A and B; and (ii) the second-order RS term (96) is replaced by the upper bound:

$$\widetilde{E}_2^{\text{cb}} = -\sum_{\substack{i \\ \text{(not both zero)}}}^{(A)} \sum_{j}^{(B)} \frac{|\langle A_i B_j | V | A_0 B_0 \rangle|^2}{\varepsilon_i + \varepsilon_j} \geq E_2^{\text{cb}}. \tag{105}$$

Under these assumptions, explicit general formulae were given (Magnasco and McWeeny, 1991) for equations (93), (94), (96) and (104) in terms of appropriate static and transition density matrices on A and B.

12.5.2 First-Order Exchange-Overlap Energy

The exchange overlap-energy is a quantum mechanical contribution which depends on the nature of the spin coupling of the interacting molecules (for a general discussion see Dacre and McWeeny, 1970). For closed-shell molecules the resultant total spin is zero, and the first-order contribution to the exchange-overlap component of the interaction can be expressed in *closed form* if $\hat{A}\psi_0$ is approximated as a single determinant of Hartree–Fock spin-orbitals of the individuals molecules.

First-order exchange overlap can then be expressed in terms of two contributions of opposite sign.

(i) The *attractive* contribution is due to pure 2-electron exchange between A and B:

$$\begin{aligned} K &= -\frac{1}{2}\iint d\mathbf{r}_1\, d\mathbf{r}_2 \frac{P^B(00|\mathbf{r}_1;\mathbf{r}_2)}{r_{12}} P^A(00|\mathbf{r}_2;\mathbf{r}_1) \\ &= -\frac{1}{2}\int d\mathbf{r}_1 \hat{K}^B(00|\mathbf{r}_1) P^A(00|\mathbf{r}_1;\mathbf{r}_1'), \end{aligned} \tag{106}$$

where the prime on $\mathbf{r}_1'$ must be removed *after* the action of the operator and *before* integration, and $\hat{K}^B$ is the undistorted exchange potential operator:

$$\hat{K}^B(00|\mathbf{r}_1) = \int d\mathbf{r}_2 K^B(00|\mathbf{r}_1;\mathbf{r}_2)\hat{P}_{\mathbf{r}_1\mathbf{r}_2} \tag{107}$$

an integral operator with kernel:

$$K^B(00|\mathbf{r}_1;\mathbf{r}_2) = \frac{P^B(00|\mathbf{r}_1;\mathbf{r}_2)}{r_{12}};$$

(ii) The *repulsive* contribution is due to the Pauli repulsion between the overlapping static electron distributions of the two molecules, and is given by:

$$\begin{aligned} E_{\text{ov}} &= \int d\mathbf{r}_1 \left[-U^B(\mathbf{r}_1) - \frac{1}{2}\hat{K}^B(00|\mathbf{r}_1) \right] P^A_{\text{ov}}(00|\mathbf{r}_1;\mathbf{r}_1') \\ &\quad + \frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{P^B_{\text{ov}}(00|\mathbf{r}_2;\mathbf{r}_2) - \frac{1}{2}P^B_{\text{ov}}(00|\mathbf{r}_1;\mathbf{r}_2)\hat{P}_{\mathbf{r}_1\mathbf{r}_2}}{r_{12}} P^A_{\text{ov}}(00|\mathbf{r}_1;\mathbf{r}_1') \\ &\quad + (A \leftrightarrow B, 1 \leftrightarrow 2), \end{aligned} \tag{108}$$

where:

$$U^B(\mathbf{r}) = -V^B(\mathbf{r}) - J^B(00|\mathbf{r}) \tag{109}$$

is the Coulomb potential (MEP) at $\mathbf{r}$ due to nuclei and undistorted electrons of molecule B, and:

$$P_{\text{ov}}(00|\mathbf{r};\mathbf{r}') = P_{\text{ov}}^{A}(00|\mathbf{r};\mathbf{r}') + P_{\text{ov}}^{B}(00|\mathbf{r};\mathbf{r}') \tag{110}$$

is the overlap density, whose partition between A and B is only apparently additive, since each component contains the effect of the *whole* intermolecular overlap. The two overlap components are defined as:

$$P_{\text{ov}}^{A}(00|\mathbf{r};\mathbf{r}') = 2\sum_{i}^{(A)}\sum_{p}^{\text{all}} \Phi_i(\mathbf{r})\Delta_{ip}\Phi_p^*(\mathbf{r}') \tag{111}$$

$$P_{\text{ov}}^{B}(00|\mathbf{r};\mathbf{r}') = 2\sum_{j}^{(B)}\sum_{q}^{\text{all}} \Phi_j(\mathbf{r})\Delta_{jq}\Phi_q^*(\mathbf{r}'), \tag{112}$$

and have diagonal elements with the property[2] (Problem 12.1):

$$\int d\mathbf{r}P_{\text{ov}}^{A}(00|\mathbf{r};\mathbf{r}) = \int d\mathbf{r}P_{\text{ov}}^{B}(00|\mathbf{r};\mathbf{r}) = 0. \tag{113}$$

In equation (111), i runs over the occupied MOs of A, p over *all* occupied MOs of A and B, and Δ_{ip} is an element of the matrix:

$$\boldsymbol{\Delta} = -\mathbf{S}(\mathbf{1}+\mathbf{S})^{-1} \tag{114}$$

which depends in a complicated way on the intermolecular overlap between the occupied MOs of A and B (the like being true for P_{ov}^{B}).

The overlap energy, E_{ov} of equation (108), expresses the interaction of the overlap density of one molecule with the Coulomb-exchange potential of the other, plus the Coulomb-exchange interaction of the overlap densities of the two molecules (Magnasco, 1982). All terms in E_{ov} are rigorously zero for non-overlapping molecules. For clusters of *many* interacting molecules the overlap energy is the source of first-order non-additivity observed for intermolecular forces.

Partition (110) allows for the precise definition of (i) the additional density which must supplement the ordinary and exchange electron densities of each molecule when overlap occurs, and (ii) the error Δ occurring when A_0 and B_0 are not the *exact* eigenstates of $\hat{H}_0$, but rather *approximations* satisfying the eigenvalue equation for some model Hamiltonian $\hat{H}_0$ (e.g. the one constructed in terms of the usual one-electron Fock operators of the isolated molecule). It can be shown that, if $\hat{F}^A(00|\mathbf{r})$ is the Fock operator for A, the Δ^A contribution to Δ in (104) is given by:

$$\Delta^A = \int d\mathbf{r}_1 \hat{F}^A(00|\mathbf{r}_1)P_{\text{ov}}^{A}(00|\mathbf{r}_1;\mathbf{r}_1')$$

---

[2] A generalization of what found in the Heitler–London theory of H_2.

$$+\frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{P^A_{\text{ov}}(00|\mathbf{r}_2;\mathbf{r}_2) - \frac{1}{2}P^A_{\text{ov}}(00|\mathbf{r}_1;\mathbf{r}_2)\hat{P}_{\mathbf{r}_1\mathbf{r}_2}}{r_{12}} P^A_{\text{ov}}(00|\mathbf{r}_1;\mathbf{r}'_1). \tag{115}$$

Since P^A_{ov} is at least of order $O(S^2)$, it can be seen that the first term in (115) is of order $O(S^2)$ and vanishes for Hartree–Fock A_0 (Magnasco et al., 1990; see Problem 12.2), while the second term is of order $O(S^4)$ and survives in any case.

12.5.3 Non-Expanded RS Intermolecular Energies

The non-expanded intermolecular potential V between molecules A and B in terms of interparticle distances takes the simple form:

$$V = \sum_i \sum_j \frac{q_i q_j}{r_{ij}}, \tag{116}$$

where r_{ij} is the distance between particle i (nucleus or electron) of charge q_i of A and particle j of charge q_j of B (Figure 12.3).

As we already did in treating the exchange-overlap component of the interaction energy in the preceding Section, reduction from the many-electron wavefunctions occurring in the RS terms (93) and (96) is best dealt with in terms of static and transition charge density matrices, that allow to write for the general transition matrix element of V (Longuet-Higgins, 1956; compare equation (32) of Section 12.4.1):

$$\langle A_i B_j | V | A_0 B_0 \rangle = \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\gamma^A(0i|\mathbf{r}_1;\mathbf{r}_1)\gamma^B(0j|\mathbf{r}_2;\mathbf{r}_2)}{r_{12}}, \tag{117}$$

where:

$$\gamma^A(0i|\mathbf{r}) = \delta_{0i}\sum_\alpha Z_\alpha \delta(\mathbf{r}-\mathbf{r}_\alpha) - P^A(0i|\mathbf{r};\mathbf{r}) \tag{118}$$

is the transition charge density (nuclei + electrons) operator at $\mathbf{r}$ associated to the transition $0 \to i$ on molecule A.

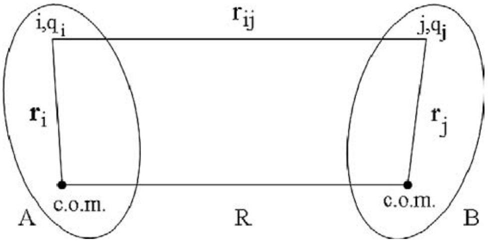

Figure 12.3 Interparticle distances in the intermolecular potential V.

Using the properties of the Dirac δ-function (Problem 12.3, see Chapter 1) it is easily found:

$$\begin{aligned}\langle A_i B_j|V|A_0 B_0\rangle = &-\delta_{0j}\sum_\beta Z_\beta \int d\mathbf{r}_1 \frac{P^A(0i|\mathbf{r}_1;\mathbf{r}_1)}{r_{1\beta}}\\ &-\delta_{0i}\sum_\alpha Z_\alpha \int d\mathbf{r}_2 \frac{P^B(0j|\mathbf{r}_2;\mathbf{r}_2)}{r_{2\alpha}}\\ &+\iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{P^A(0i|\mathbf{r}_1;\mathbf{r}_1)P^B(0j|\mathbf{r}_2;\mathbf{r}_2)}{r_{12}}\\ &+\delta_{0i}\delta_{0j}\sum_\alpha\sum_\beta \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}},\end{aligned} \tag{119}$$

so that the following general results are obtained for the Coulombic component of the intermolecular energy up to second order:

(i) First-order Coulombic (electrostatic) energy:

$$\begin{aligned}E_1^{\mathrm{cb}} = E_1^{\mathrm{es}} &= \langle A_0 B_0|V|A_0 B_0\rangle\\ &= \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\gamma^A(00|\mathbf{r}_1;\mathbf{r}_1)\gamma^B(00|\mathbf{r}_2;\mathbf{r}_2)}{r_{12}} \qquad (120)\\ &= -\sum_\beta Z_\beta \int d\mathbf{r}_1 \frac{P^A(00|\mathbf{r}_1;\mathbf{r}_1)}{r_{1\beta}}\\ &\quad -\sum_\alpha Z_\alpha \int d\mathbf{r}_2 \frac{P^B(00|\mathbf{r}_2;\mathbf{r}_2)}{r_{2\alpha}}\\ &\quad +\iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{P^A(00|\mathbf{r}_1;\mathbf{r}_1)P^B(00|\mathbf{r}_2;\mathbf{r}_2)}{r_{12}}\\ &\quad +\sum_\alpha\sum_\beta \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}\end{aligned} \tag{121}$$

is the interaction between nuclei and undistorted electron charge distribution of A and B.

(ii) Second-order distortion (polarization) of A by B:

$$\begin{aligned}E_2^{\mathrm{ind,A}} &= -\sum_i \frac{|\langle A_i B_0|V|A_0 B_0\rangle|^2}{\varepsilon_i}\\ &= -\sum_i \frac{|\int d\mathbf{r}_1 U^B(00|\mathbf{r}_1)P^A(0i|\mathbf{r}_1;\mathbf{r}_1)|^2}{\varepsilon_i},\end{aligned} \tag{122}$$

where:

$$U^B(00|\mathbf{r}_1) = -\sum_\beta \frac{Z_\beta}{r_{1\beta}} + \int d\mathbf{r}_2 \frac{P^B(00|\mathbf{r}_2;\mathbf{r}_2)}{r_{12}} \tag{123}$$

is the MEP at $\mathbf{r}_1$ due to nuclei and undistorted electrons of B (compare with equations (28) and (29) of Section 12.4).

(iii) Second-order distortion (polarization) of B by A:

$$\begin{aligned} E_2^{\text{ind,B}} &= -\sum_j \frac{|\langle A_0 B_j | V | A_0 B_0 \rangle|^2}{\varepsilon_j} \\ &= -\sum_j \frac{\left| \int d\mathbf{r}_2 U^A(00|\mathbf{r}_2) P^B(0j|\mathbf{r}_2;\mathbf{r}_2) \right|^2}{\varepsilon_j}, \end{aligned} \tag{124}$$

where:

$$U^A(00|\mathbf{r}_2) = -\sum_\alpha \frac{Z_\alpha}{r_{2\alpha}} + \int d\mathbf{r}_1 \frac{P^A(00|\mathbf{r}_1;\mathbf{r}_1)}{r_{12}} \tag{125}$$

is the MEP at $\mathbf{r}_2$ due to undistorted fields of A.

(iv) Second-order dispersion (intermolecular electron correlation):

$$\begin{aligned} E_2^{\text{disp}} &= -\sum_i \sum_j \frac{|\langle A_i B_j | V | A_0 B_0 \rangle|^2}{\varepsilon_i + \varepsilon_j} \\ &= -\sum_i \sum_j \frac{\left| \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{P^A(0i|\mathbf{r}_1;\mathbf{r}_1) P^B(0j|\mathbf{r}_2;\mathbf{r}_2)}{r_{12}} \right|^2}{\varepsilon_i + \varepsilon_j} \end{aligned} \tag{126}$$

is the second-order contribution arising from the instantaneous interaction of the electron density fluctuations mutually induced in the two molecules.

Now, let us define:

$$\Pi^A(\mathbf{r}_1;\mathbf{r}'_1|iu) = \sum_i \varepsilon_i \frac{2\, P^A(0i|\mathbf{r}_1;\mathbf{r}_1) P^A(i0|\mathbf{r}'_1;\mathbf{r}'_1)}{\varepsilon_i^2 + u^2} \tag{127}$$

as the A-dynamic propagator which determines the linear response of the charge density at $\mathbf{r}_1$ to an oscillating perturbation (at imaginary frequency iu, with u a real quantity) applied at $\mathbf{r}'_1$. Then equation (126) can be rewritten as the coupling of two electrostatic interactions ($1/r_{12}$ and $1/r_{1'2'}$) involving four space points in the two molecules with a strength factor which depends on how readily density fluctuations propagate from $\mathbf{r}'_1$ to $\mathbf{r}_1$ on A, $\mathbf{r}'_2$ to $\mathbf{r}_2$ on B (Figure 12.4).

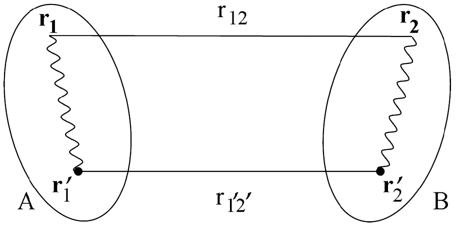

Figure 12.4 Origin of intermolecular dispersion.

Non-expanded dispersion can then be written in the two fully equivalent general forms:

$$
\begin{aligned}
E_2^{\text{disp}} &= -\sum_i\sum_j \frac{1}{\varepsilon_i+\varepsilon_j}\iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{P^A(0i|\mathbf{r}_1;\mathbf{r}_1)P^B(0j|\mathbf{r}_2;\mathbf{r}_2)}{r_{12}} \\
&\quad\times \iint d\mathbf{r}'_1 d\mathbf{r}'_2 \frac{P^A(i0|\mathbf{r}'_1;\mathbf{r}'_1)P^B(j0|\mathbf{r}'_2;\mathbf{r}'_2)}{r_{1'2'}} \\
&= -\iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}} \iint d\mathbf{r}'_1 d\mathbf{r}'_2 \frac{1}{r_{1'2'}} \\
&\quad\times \frac{1}{4}\sum_i\sum_j \frac{\varepsilon_i\varepsilon_j}{\varepsilon_i+\varepsilon_j}\Pi^A(\mathbf{r}_1;\mathbf{r}'_1|i)\Pi^B(\mathbf{r}_2;\mathbf{r}'_2|j) \qquad (128) \\
&= -\iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}} \iint d\mathbf{r}'_1 d\mathbf{r}'_2 \frac{1}{r_{1'2'}} \\
&\quad\times \frac{1}{2\pi}\int_0^\infty du\,\Pi^A(\mathbf{r}_1;\mathbf{r}'_1|iu)\Pi^B(\mathbf{r}_2;\mathbf{r}'_2|iu), \qquad (129)
\end{aligned}
$$

where use was made of the integral transform (Problem 12.4):

$$
\frac{1}{\varepsilon_i+\varepsilon_j} = \frac{2}{\pi}\int_0^\infty du \frac{\varepsilon_i}{\varepsilon_i^2+u^2}\cdot\frac{\varepsilon_j}{\varepsilon_j^2+u^2} \qquad \varepsilon_i,\varepsilon_j > 0. \tag{130}
$$

We shall refer to (128) and (129) as of generalizations of the London formula (London, 1930) and the Casimir–Polder formula (Casimir and Polder, 1948), respectively.

In equation (128), $\Pi^A(\mathbf{r}_1;\mathbf{r}'_1|i)$ is the i-th pseudostate component of the limit to zero frequency of the dynamic propagator (127):

$$
\lim_{u\to 0}\Pi^A(\mathbf{r}_1;\mathbf{r}'_1|iu) = \Pi^A(\mathbf{r}_1;\mathbf{r}'_1) = \sum_i \Pi^A(\mathbf{r}_1;\mathbf{r}'_1|i). \tag{131}
$$

In analogy with what happens for polarizabilities, we shall call $\Pi^A(\mathbf{r}_1;\mathbf{r}'_1)$ the "static propagator" of molecule A, a quantity that should replace polarizabilities in non-expanded interactions.

The general polarization propagator (127), and the corresponding frequency dependent polarizabilities (FDPs) that it determines, can be calculated by time-dependent perturbation techniques (TDHF or MC-TDHF, see McWeeny, 1989). General formulae in terms of two-electron integrals between elementary charge distributions on A and B, and the corresponding elements of the transition density matrices have been developed in terms of an atomic orbital basis, but will not be reported here where we are simply interested in the physical interpretation of molecular dispersion.

The consequence of expanding in long range the interelectron distances $1/r_{12}$ and $1/r_{1'2'}$ in (128) and (129) will be examined in the last two Sections.

12.5.4 Expanded Dispersion Interactions Between Molecules

An important difference occurring between atomic and molecular interactions is that the former depend only on the internuclear distance R, while the latter depend on the distance R between their centres-of-mass as well as on the relative orientation of the two molecules. This orientation is, in general, specified by the six Euler angles ($\Omega_A = \alpha_A, \beta_A, \gamma_A$; $\Omega_B = \alpha_B, \beta_B, \gamma_B$) that bring a body-fixed (intramolecular) reference frame into self-coincidence with the space-fixed (intermolecular or laboratory) coordinate system by successive rotations about definite axes[3] (Brink and Satchler, 1993). It is often convenient to specify the relative orientation of the two molecules in terms of just *five* independent angles ($\theta_A, \theta_B, \varphi, \chi_A, \chi_B$) related to the Euler angles, giving the orientation of the axis of highest symmetry (principal axis) in each molecule and the torsional angles χ_A and χ_B about these axes (Figure 12.5).

We shall mostly restrict ourselves to consideration of the long-range dispersion interaction between two axially symmetric linear molecules, whose relative orientation is specified by the three angles $\theta_A, \theta_B, \varphi$ (Figure 12.6), related to Euler's angles by:

$$\alpha_A = 0, \quad \beta_A = -\theta_A, \quad \gamma_A = 0 \qquad \alpha_B = 0, \quad \beta_B = -\theta_B, \quad \gamma_B = \varphi. \qquad (132)$$

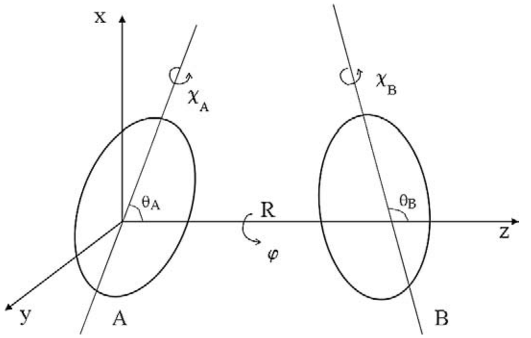

Figure 12.5 Relative angles specifying the orientation of the two molecules.

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[3] The transformation from a set of orthogonal axes $(x\,y\,z)$ to the *rotated* set $(x'\,y'\,z')$ is made in three steps: (i) the original set is first transformed into $(x_1\,y_1\,z)$ by rotation over an angle α about the z-axis, next (ii) to $(x_1'\,y_1\,z')$ by rotation of β about the y_1-axis, and finally (iii) to $(x'\,y'\,z')$ by a rotation through angle γ about the z'-axis.

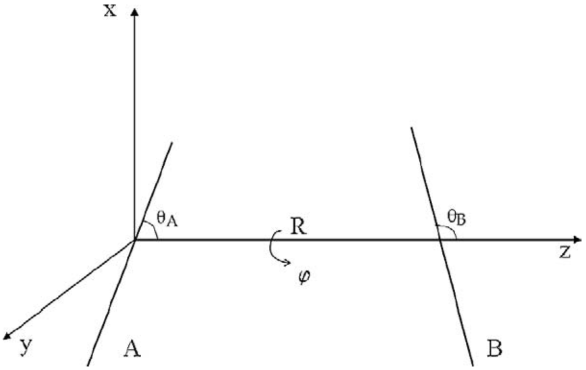

Figure 12.6 Relative angles specifying the orientation of two linear molecules.

Spherical tensor expansion of $(r_{12} \cdot r_{1'2'})^{-1}$ in long range[4] (Wormer, 1975; Ottonelli, 1998) explicitates the dependence of the dispersion energy on intermolecular distance R and molecular orientation Ω_A, Ω_B. Introducing the expansion into the dispersion energy expressions (128) and (129) and turning to real spherical harmonics, the long-range dispersion interaction between two linear molecules can be written as:

$$E_2^{\text{disp}} = -\sum_n R^{-n} C_n(\theta_A, \theta_B, \varphi), \tag{133}$$

where:

$$n = l_a + l_b + l'_a + l'_b + 2 \tag{134}$$

(l_a, l'_a), (l_b, l'_b) being the angular quantum numbers specifying the elementary multipole polarizabilities of A and B. The C_ns are angle-dependent dispersion coefficients whose general expression can be found elsewhere (Spelsberg et al., 1993; Ottonelli, 1998; Magnasco and Ottonelli, 1999). Explicit expressions for $n = 6$ are examined in the next Section, together with a short account of the simpler case of the atom–linear molecule interaction.

An elementary two-state model of expanded second-order energies based on classical electrostatics has been recently derived by the author for atom–atom and atom–linear molecule interactions (Magnasco, 2004a, 2004b). The orientation dependence of these interactions was singled out avoiding explicit calculation of matrix elements and any use of RS perturbation theory.

12.5.5 Angle-Dependent C_6 Dispersion Coefficients for Simple Molecular Systems

A real spherical tensor approach to the expanded molecular coefficients for general molecules in long range was proposed by Magnasco et al. (1988; see also Stone and Tough,

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[4] An asymptotic expansion in the sense of Erdèlyi (1956).

1984), and several cases explicitly considered in Magnasco et al. (1990). Partial expressions in Cartesian coordinates were earlier derived by Buckingham (1967). The expression for the angle-dependent C_6 dispersion coefficient for two linear molecules was first given by Hirschfelder et al. (1954; see also Briggs et al., 1971). For the homodimer it takes the form:

$$\begin{aligned} C_6(\theta_A,\theta_B,\varphi) &= (2B+4D)+3(B-D)\big(\cos^2\theta_A+\cos^2\theta_B\big) \\ &\quad + (A-2B+D)(\sin\theta_A\sin\theta_B\cos\varphi-2\cos\theta_A\cos\theta_B)^2, \end{aligned} \tag{135}$$

where A, $B=C$, D are the three dispersion constants, which in Casimir–Polder form are:

$$A=\frac{1}{2\pi}\int_0^\infty du\alpha_{110}^A(iu)\alpha_{110}^B(iu) \tag{136}$$

$$B=\frac{1}{2\pi}\int_0^\infty du\alpha_{110}^A(iu)\alpha_{111}^B(iu) \tag{137}$$

$$C=\frac{1}{2\pi}\int_0^\infty du\alpha_{111}^A(iu)\alpha_{110}^B(iu)=B \tag{138}$$

$$D=\frac{1}{2\pi}\int_0^\infty du\alpha_{111}^A(iu)\alpha_{111}^B(iu). \tag{139}$$

Magnasco et al. (1990) gave an alternative, yet equivalent (Ottonelli, 1998), expression in terms of frequency-dependent isotropic polarizabilities $\alpha(iu)$ and polarizability anisotropies $\Delta\alpha(iu)$ of the two molecules:

$$\begin{aligned} C_6(\theta_A,\theta_B,\varphi) &= \frac{1}{2\pi}\int_0^\infty du\big\{6\alpha^A\alpha^B \\ &\quad + \big[\big(3\cos^2\theta_B-1\big)\alpha^A\Delta\alpha^B+\big(3\cos^2\theta_A-1\big)\Delta\alpha^A\alpha^B\big] \\ &\quad + \big[4\cos^2\theta_A\cos^2\theta_B-\big(\cos^2\theta_A+\cos^2\theta_B\big) \\ &\quad - \sin 2\theta_A\sin 2\theta_B\cos\varphi \\ &\quad + \sin^2\theta_A\sin^2\theta_B\cos^2\varphi\big]\Delta\alpha^A\Delta\alpha^B\big\}. \end{aligned} \tag{140}$$

The angle-dependent dispersion coefficients C_n are however most conveniently expressed in terms of associated Legendre polynomials (Meyer, 1976; Spelsberg et al., 1993; Magnasco and Ottonelli, 1999) as:

$$C_n(\theta_A,\theta_B,\varphi) = \sum_{L_AL_BM} C_n^{L_AL_BM}P_{L_A}^M(\cos\theta_A)P_{L_B}^M(\cos\theta_B)\cos M\varphi \tag{141}$$

$$= \sum_{L_AL_BM} C_n\gamma_n^{L_AL_BM}P_{L_A}^M(\cos\theta_A)P_{L_B}^M(\cos\theta_B)\cos M\varphi, \tag{142}$$

Table 12.5.

The $L_A L_B M$-components of the C_6 dispersion coefficients for (i) two identical linear molecules ($B = C$), and (ii) an atom and a linear molecule

L_A	L_B	M	(i)	(ii)
0	0	0	$\frac{2}{3}(A+4B+4D)$	$2A+4B$
0	2	0	$\frac{2}{3}(A+B-2D)$	$2A-2B$
2	0	0	$\frac{2}{3}(A+B-2D)$	
2	2	0	$2(A-2B+D)$	
2	2	1	$-\frac{4}{9}(A-2B+D)$	
2	2	2	$\frac{1}{18}(A-2B+D)$	

where the expansion has a finite number of terms, $C_n = C_n^{000}$ is an isotropic dispersion coefficient and $\gamma_n^{L_A L_B M} = C_n^{L_A L_B M}/C_n$ an anisotropy coefficient.

In this formula, the elementary contributions (l_a, l'_a) on A and (l_b, l'_b) on B were coupled to resultant L_A on A and L_B on B according to:

$$\begin{aligned} &|l_a - l'_a| \le L_A \le l_a + l'_a \\ &|l_b - l'_b| \le L_B \le l_b + l'_b \quad \text{in steps of 2} \\ &0 \le M \le \min(L_A, L_B) \\ &n = l_a + l'_a + l_b + l'_b + 2. \end{aligned} \tag{143}$$

The coefficients $C_n^{L_A L_B M}$ are given in terms of Wigner 3-j symbols (Brink and Satchler, 1993) and irreducible dispersion constants[5] by a rather complicated formula that can be found elsewhere (Magnasco and Ottonelli, 1999). The $L_A L_B M$-components of the C_6 dispersion coefficients for (i) two identical linear molecules, and (ii) an atom and a linear molecule are given in Table 12.5.

The elementary dispersion constants A, $B = C$, D have been defined in equations (136)–(139). For identical molecules, the (020) and (200) coefficients are equal, while coefficients with $M \neq 0$ are not independent but related to that with $M = 0$ by the relations:

$$C_6^{221} = -\frac{2}{9} C_6^{220}, \qquad C_6^{222} = \frac{1}{36} C_6^{220}. \tag{144}$$

---

[5] A linear combination of elementary dispersion constants C_{ab} determined by symmetry.

12.5.6 Isotropic C_6 Dispersion Coefficients from Dipole Polarizability Pseudospectra

In this Section, we shall examine some results of the calculation of isotropic C_6 dispersion coefficients from dipole polarizability pseudospectra of the individual molecules. Once the orientation dependence (the geometrical part of the calculation of a dispersion coefficient) of the C_6 coefficients has been singled out in terms of anisotropy coefficients (Table 12.5), the typically quantum mechanical part of the calculation concerns the evaluation of the elementary dispersion constant C_{ab}, whose general expression is given in terms of the equivalent London (static) or Casimir–Polder (FDPs) forms:

$$\begin{aligned} C_{ab} &= \frac{1}{4}\sum_i\sum_j \frac{\varepsilon_a(i)\varepsilon_b(j)}{\varepsilon_a(i)+\varepsilon_b(j)}\alpha_a(i)\alpha_b(j) && (145)\\ &= \frac{1}{2\pi}\int_0^\infty du\alpha_a(iu)\alpha_b(iu), && (146) \end{aligned}$$

where $a = (l_a m_a, l'_a m'_a)$ and $b = (l_b m_b, l'_b m'_b)$ are labels specifying the polarizabilities of A and B.

Anisotropy coefficients, because of their smaller value, are usually more difficult to calculate than isotropic coefficients.

It seems pertinent to summarize here how the London dispersion constants can be calculated from monomer polarizability pseudospectra. We give the receipt in eight points.

1. Choose an appropriate basis of normalized functions $\boldsymbol{\chi}'$ orthogonal to ψ_0.
2. Schmidt-orthogonalize the functions among themselves obtaining the basis $\boldsymbol{\chi}$.
3. Construct matrices **M** and **N** over the orthonormal basis $\boldsymbol{\chi}$.
4. Diagonalize (Jacobi or Givens–Householder) the Hermitian matrix **M** by a unitary transformation: the (positive) non-zero eigenvalues give the excitation energies of each pseudostate.
5. The corresponding eigenvectors are the required linear pseudostates $\boldsymbol{\psi}$.
6. Matrix transformations giving linear pseudostates are:

$$\boldsymbol{\psi} = \overset{\substack{\text{orthonormal}\\ \text{basis}\\ \downarrow}}{\boldsymbol{\chi}}\ \underset{\substack{\uparrow\\ \text{unitary matrix}\\ \text{of the eigenvectors}}}{\mathbf{U}} \quad = \quad \overset{\substack{\text{non-orthogonal}\\ \text{basis}\\ \downarrow}}{\boldsymbol{\chi}'}\ \underset{\substack{\uparrow\\ \text{Schmidt-}\\ \text{orthogonalization}\\ \text{matrix}}}{\mathbf{O}}\ \mathbf{U} \qquad \boldsymbol{\chi}^\dagger\psi_0 = \boldsymbol{\chi}'^\dagger\psi_0 = 0. \tag{147}$$

7. Construct the N-term polarizability pseudospectrum:

$$\alpha = 2\mathbf{N}_\psi^\dagger \mathbf{M}_\psi^{-1}\mathbf{N}_\psi = \sum_{i=1}^{N}\frac{2\mu_i^2}{\varepsilon_i} = \sum_{i=1}^{N}\alpha_i \implies \{\alpha_i, \varepsilon_i\} i = 1, 2, \cdots N. \tag{148}$$

Table 12.6.

Accurate values of isotropic C_6 dispersion coefficients $(E_h a_0^6)$ from best dipole monomer pseudospectra[1]

System	H	He	H_2^+	H_2
H	6.499			
He	2.820	1.460		
H_2^+	4.591	2.085	3.284	
H_2	8.502	3.898	6.096	11.32

[1] $H_2^+(^2\Sigma_g^+)$ at $R = 2a_0$, $H_2(^1\Sigma_g^+)$ at $R = 1.4a_0$.

Table 12.7.

Isotropic C_6 dispersion coefficients $(E_h a_0^6)$ from effective 2-term dipole monomer pseudospectra[1] compared with accurate results

System	H	He	H_2
H	6.453 (6.499) 99.3		
He	2.815 (2.820) 99.8	1.430 (1.460) 97.9	
H_2	8.733 (8.782) 99.4	3.985 (4.011) 99.3	12.02 (12.05) 99.7

[1] $H_2(^1\Sigma_g^+)$ at $R = 1.449a_0$.

8. Calculate London dispersion constants following equation (145).

A few examples of this technique are discussed below, while the $N = 2$ term calculation is detailed in Problems 11.7 and 12.5. Fairly accurate 4-term results for the C_6 dispersion coefficients for H_2–H_2 are discussed in Problem 11.6. Other techniques for evaluating dispersion coefficients for atoms can be found in Dalgarno and Davison (1966).

Accurate values of isotropic C_6 dispersion coefficients from best monomer dipole pseudospectra of the simplest one- and two-electron atomic and molecular systems are given in Table 12.6 (Magnasco and Ottonelli, 1999). The results are accurate to all figures given in Table 12.6.

The best dipole pseudospectra for static polarizabilities involve, respectively, $N = 2$ for $H(^2S)$, 15 for $H_2^+(^2\Sigma_g^+)$, 40 for $He(^1S)$, 34 for $H_2(^1\Sigma_g^+)$. Reduced N-term pseudospectra with $N = 2$ or 4 would be extremely useful in allowing a uniform tabulation of atomic or molecular data for the successive evaluation of C_6 dispersion coefficients between all different species. Effective 2-term dipole pseudospectra were evaluated by Spelsberg et al. (1993) for H, Li, Na, K, He, H^-, H_2, Li_2, Na_2, K_2 in their ground states. The resulting isotropic C_6 dispersion coefficients for all interactions involving H, He, H_2 are compared in Table 12.7 with accurate results (Ottonelli, 1998). The values resulting from the reduced

Table 12.8.

Dipole static polarizabilities α (a_0^3) and C_6 dispersion coefficients ($E_h a_0^6$) for a few atomic homodimers from reduced 2-term pseudospectra

Atom	α	Dimer	C_6
H	4.501	H–H	6.453
Li	163.7	Li–Li	1385
Na	162.2	Na–Na	1527
K	286.1	K–K	3637
He	1.388	He–He	1.430
H^-	210.99	H^-–H^-	10 001

spectra are always smaller than the correct ones, with a % error from 0.2 to 0.7 (average 0.5), but well 2.1 % for He_2. This means that 2-term pseudospectra are insufficient to give at least four figures accuracy in the results. 4-term pseudospectra, involving much the same number of terms as those resulting as best in a recently proposed interpolation technique on FDPs by Figari and Magnasco (2003), would probably do better, but are not disposable for the time being.

Even if the results are not expected to be particularly good, we give in Table 12.8 (taken from Spelsberg et al., 1993) the C_6 dispersion coefficients for a few atomic homodimers resulting from the 2-term dipole pseudospectra of the atoms.

12.6 THE VAN DER WAALS BOND

Weakly bound complexes with large-amplitude vibrational structure were called by Buckingham (1982) Van der Waals (VdW) molecules. Complexes of the heavier rare gases, such as Ar_2, Kr_2, Xe_2, or weak complexes between centrosymmetrical molecules like $(H_2)_2$ or $(N_2)_2$, fit well into this definition; but complexes between proton donor and proton acceptor molecules, like $(HF)_2$ or $(H_2O)_2$, which involve hydrogen bonding, are in the border-line between VdW molecules and "good" molecules. In the latter complexes, bonding is essentially electrostatic in nature. However, all complexes above are characterized by having closed-shell monomers[6] which are held together by *weak* forces, say with a binding energy comparable to $kT = 0.95 \times 10^{-3}\ E_h$ at $T = 300$ K.

The nature of the VdW bond has been discussed at different times by the author and his group (Magnasco and McWeeny, 1991; Magnasco et al., 1992; Magnasco, 2004a, Magnasco, 2004b). Attraction due to electrostatic, induction and dispersion energies offsets in long range the weak Pauli repulsion due to exchange-overlap of the closed-shells (see Section 12.5.2).

For spherical atoms in S states (ground state rare gases or H and Li dimers in excited ${}^3\Sigma_u^+$ states), only dispersion can offset, in second order, Pauli repulsion, leading to the typical R^{-6} attraction first postulated by London (1930).

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[6] With each monomer maintaining its original structure.

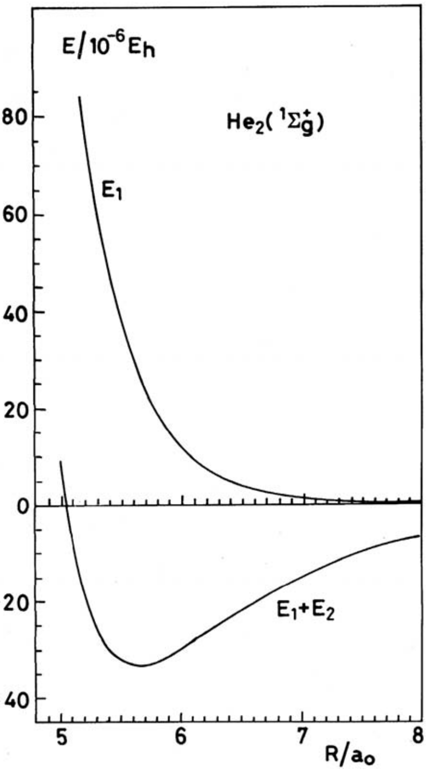

Figure 12.7 VdW bond in He_2 ($^1\Sigma_g^+$).

This is shown in Figure 12.7 for the He–He interaction in the VdW region, where the bottom curve, which results from adding to first-order E_1 (mostly exchange-overlap repulsion at these distances) second-order E_2 (mostly dispersion), fits well with accurate data from experiment (Feltgen et al., 1982). A weak VdW bond with $D_e = -33.4 \times 10^{-6}\, E_h$ is observed at the rather large interatomic distance $R_e = 5.6\, a_0$, at the bottom of the potential energy curve, as the result of the balance in long range of the weak repulsive E_1 with the weak attractive E_2.

The situation is quite different for the long-range interaction of two H_2O molecules (Figure 12.8), since now the dipolar monomers already attract each other in first order ($E_1 = E_1^{\text{es}} + E_1^{\text{exch-ov}}$) mostly with an R^{-3} interaction, and the resultant minimum is deepened by second-order induction and dispersion. The minimum is now much deeper (about $7 \times 10^{-3}\, E_h$ at $R = 5.50\, a_0$, roughly 200 times larger than that of He_2 at about the same distance), which means that the hydrogen bond is essentially electrostatic in nature.

The structures of VdW dimers are studied at low temperatures by far infrared spectra, high resolution rotational spectroscopy or molecular beams techniques. Distances R_e between centres-of-mass and bond strengths $|D_e|$ at the VdW minimum for some homodimers of atoms and molecules are given in Table 12.9. Notice that the energy units chosen

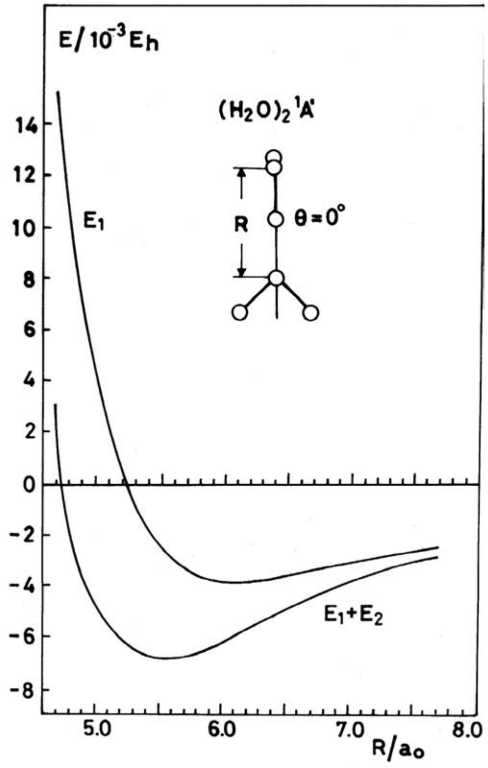

Figure 12.8 H-bond in $(H_2O)_2$ at $\theta = 0°$ (not the absolute minimum).

Table 12.9.

Bond distances R_e and bond strengths $|D_e|$ (atomic units) at the minimum of the potential energy surface for some homodimers of atoms and molecules

Atom	R_e/a_0	$D_e/10^{-6}\ E_h$	Molecule	R_e/a_0	$D_e/10^{-3}\ E_h$
$H_2(^3\Sigma_u^+)$	7.8	20.1	$(H_2)_2$	6.5	0.12
He_2	5.6	33.4	$(N_2)_2$	8.0	0.39
Ne_2	5.8	133	$(CH_4)_2$	7.3	0.69
Ar_2	7.1	449	$(NH_3)_2$	6.2	6.47
Kr_2	7.6	633	$(H_2O)_2$	5.4	10.3
Xe_2	8.2	894	$(HF)_2$	5.1	11.4
$Li_2(^3\Sigma_u^+)$	8.0	1332	$(BeH_2)_2$		52.2
Be_2	4.7	2964	$(LiH)_2$	4.0	75.8

for molecules (last column of Table 12.9) are $10^{-3}\ E_h$ while those chosen for atoms (third column) are $10^{-6}\ E_h$. Structures for molecular homodimers (Pople, 1982) as well as complete references can be found elsewhere (Magnasco, 2004b).

We may notice from Table 12.9 how large R_e and how small $|D_e|$ values characterize VdW dimers with respect to the values occurring for ordinary "chemically bonded" atoms.

Ending this Section, we notice that the distortion (induction) energy is zero for atoms, which do not have permanent moments, and mostly always smaller than the dispersion energy for molecules, with the exception of $(\mathrm{LiH})_2$, where the isotropic C_6 induction coefficient is 297 $E_h a_0^6$ compared to a C_6 dispersion coefficient of 125 $E_h a_0^6$ (Bendazzoli et al., 2000). This large value of the former coefficient ($C_6 = 2\alpha\mu^2$) is due to the combined large values of μ and α for $\mathrm{LiH}(^1\Sigma^+)$, $2.29\, ea_0$ and $28.3\, a_0^3$, respectively (Tunega and Noga, 1998).

Lastly, we must say that much before London work, Keesom (1921) pointed out that if two molecules possessing a permanent dipole moment undergo thermal motions, they will on the average assume orientations leading to attraction, with a T-dependent C_6 coefficient given by:

$$C_6(T) = \frac{2\mu_A^2\mu_B^2}{3kT}, \tag{149}$$

where μ_A, μ_B are the strengths of the dipoles, and k the Boltzmann constant. The corresponding attractive energies are the *isotropic* electrostatic contributions to the interaction energy and are temperature-dependent.

If $(\theta_A, \theta_B, \varphi) = \Omega$ are the angles describing the orientation of the dipoles μ_A and μ_B, the long-range (electrostatic) interaction between the dipoles at a distance R between their centres is given by (Coulson, 1958):

$$V(\Omega, R) = \frac{\mu_A\mu_B}{R^3} F(\Omega) \tag{150}$$

$$F(\Omega) = \sin\theta_A \sin\theta_B \cos\varphi - 2\cos\theta_A \cos\theta_B. \tag{151}$$

Averaged over all possible free orientations Ω assumed by the dipoles, $\langle V\rangle_\Omega = 0$ (the same being also true for all higher permanent multipole moments of the molecules), but its thermal average is not zero and leads to attraction. Averaging the quantity $V\exp(-V/kT)$ over all possible orientations Ω:

$$\langle V\exp(-V/kT)\rangle_\Omega = \frac{\mu_A\mu_B}{R^3}\frac{\int_\Omega d\Omega F(\Omega)\exp[aF(\Omega)]}{\int_\Omega d\Omega \exp[aF(\Omega)]} = \frac{\mu_A\mu_B}{R^3}\frac{d}{da}\ln K(a), \tag{152}$$

where:

$$a = -\frac{\mu_A\mu_B}{R^3kT} < 0 \tag{153}$$

is a dimensionless parameter depending on R, T, μ_A, μ_B, and the quantity:

$$K(a) = \int_\Omega d\Omega \exp[aF(\Omega)] \tag{154}$$

is called the Keesom integral.

Evaluation of the Keesom integral for *small* values of a is straightforward (Keesom, 1921), and gives:

$$K(a) \cong K_1(a) = 8\pi\left(1 + \frac{a^2}{3}\right), \tag{155}$$

which are the first two terms ($n = 0, 1$) in the expansion of the exponential in even powers of a:

$$L_1(a) = \frac{d\ln K_1(a)}{da} = \frac{2}{3}a\left(1 + \frac{a^2}{3}\right)^{-1} \cong \frac{2}{3}a \tag{156}$$

yielding the $C_6(T)$ Keesom coefficient of equation (149). Deviations occurring for *large* values of $|a|$ can be accounted by including higher terms in the expansion of the exponential. Recent work (Magnasco et al., 2006), where Keesom calculations were extended up to the R^{-10} term, shows that deviations of the Keesom approximation from the full series expansion are less important than consideration of the higher-order terms in the R^{-2n} expansion of the intermolecular potential. An asymptotic 2-term expansion in inverse powers of $(-a)$ for *very large* values of $|a|$ was recently derived by Battezzati and Magnasco (2004) in the simple form[7]:

$$K_\infty(a) \cong \frac{4\pi}{3}\frac{\exp(-2a)}{a^2}\left(1 - \frac{2}{3a}\right). \tag{157}$$

The three long-range C_6 isotropic coefficients for some homodimers at $T = 293$ K[8] are compared in Table 12.10. It is seen that Keesom $C_6(T)$ is negligible compared to

Table 12.10.

Comparison between isotropic dispersion and induction coefficients and Keesom $C_6(T)$ coefficients for some homodimers in the gas phase at $T = 293$ K

Molecule	μ/ea_0	α/a_0^3[a]	$C_6/E_h a_0^6$		
			Keesom	Dispersion[a]	Induction
CO	0.04	13.1	0.002	81.4	0.04
NO	0.06	11.5	0.009	69.8	0.08
N_2O	0.07	19.7	0.017	184.9	0.19
NH_3	0.58	14.6	81.30	89.1	9.82
HF	0.70	5.60	172.5	19.0	5.49
H_2O	0.73	9.64	204.0	45.4	10.3
LiH	2.29	28.3[b]	8436	125[c]	297

[a] Buckingham et al. (1988). [b] Tunega and Noga (1998). [c] Bendazzoli et al. (2000).

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[7] This formula works particularly well for the halides of alkaline metals.

[8] $kT = 9.28 \times 10^{-4} E_h$.

dispersion and induction only for the first three homodimers, while for $(NH_3)_2$, $(HF)_2$, $(H_2O)_2$ dipole orientation forces become increasingly dominant at room temperature, and cannot be neglected in assessing collective gas properties such as the equation of state for real gases and virial coefficients. For $(HF)_2$ and $(H_2O)_2$ small corrections over the original Keesom formula (149) are needed to avoid overestimation of $C_6(T)$, while $(LiH)_2$ is conveniently treated by the asymptotic formula (157).

12.7 PROBLEMS 12

12.1. Show that the exchange-overlap density matrix of molecule A vanishes when integrated over all space.

Answer:

$$\int d\mathbf{r}\, P_{\mathrm{ov}}^{A}(00|\mathbf{r};\mathbf{r}) = 0,$$

which shows that, even contributing to the first-order interaction energy, P_{ov}^{A} does not contribute to the integral of the total electron density, a property shared with the transition densities occurring in higher orders of perturbation theory.

Hint:
Use definitions (111) and (114) and interchange summation indices, remembering that the overlap matrix **S** is traceless.

12.2. Show that for a Hartree–Fock wavefunction of molecule A:

$$\int d\mathbf{r}\hat{F}^{A}(00|\mathbf{r})P_{\mathrm{ov}}^{A}(00|\mathbf{r};\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} = 0.$$

Hint:
Use the same suggestions of Problem 1 and notice that all diagonal elements of **S** are individually zero.

12.3. Verify expression (119) for the general transition matrix element $\langle A_i B_j|V|A_0 B_0\rangle$.

Hint:
Use the very properties of the Dirac δ-function given in Chapter 1.

12.4. Derive by elementary integration the integral transform (130).

Answer:
Evaluate the integral:

$$I = \int_0^\infty du \frac{1}{a^2+u^2}\cdot\frac{1}{b^2+u^2} = \frac{\pi}{2}\frac{1}{ab(a+b)}$$

with $a, b > 0$, where $a = \varepsilon_i$, $b = \varepsilon_j$.

Hint:
Use elementary integration techniques and change of the integration variable.

12.5. Evaluate the C_6 dispersion coefficient for the H–H interaction from the 2-term pseudospectrum of the dipole polarizability of H(1s).

Answer:

$$C_6 = \frac{363}{56}.$$

Hint:
Use the 2-term dipole pseudospectrum derived in Problem 11.7.

12.6. Evaluate the C_6 dispersion coefficients for the H_2–H_2 interaction.

Answer:
The dispersion constants are:

$$A = 2.683, \qquad B = C = 2.018, \qquad D = 1.522$$

giving:

(i) Isotropic dispersion coefficient

$$C_6 = 11.23$$

(ii) Anisotropic coefficients

$$\gamma_6^{020} = 0.098, \qquad \gamma_6^{220} = 0.030.$$

Hint:
Use the 4-term dipole pseudospectrum for $H_2(^1\Sigma_g^+)$ at $R = 1.4\,a_0$ found in Problem 11.9.

12.8 SOLVED PROBLEMS

12.1. Recall that the metric matrix $\mathbf{M}$ of the non-orthogonal basis $\boldsymbol{\phi}$ of occupied MOs is:

$$\mathbf{M} = \mathbf{1} + \mathbf{S}$$

so that its inverse can be written as:

$$\mathbf{M}^{-1} = (\mathbf{1}+\mathbf{S})^{-1} = \mathbf{1} - \mathbf{S}(\mathbf{1}+\mathbf{S})^{-1} = \mathbf{1} + \boldsymbol{\Delta},$$

where the overlap matrix **S** is traceless and has each diagonal element individually zero. Using definitions (111) and (114) we find that:

$$\begin{aligned}\int d\mathbf{r} P^A_{\text{ov}}(00|\mathbf{r};\mathbf{r}) &= 2\sum_i^{(A)}\sum_p^{\text{all}} \Delta_{ip}(\mathbf{1}+\mathbf{S})_{pi}\\ &= -2\sum_i^{(A)}\sum_p^{\text{all}}\sum_q^{\text{all}} S_{iq}(\mathbf{1}+\mathbf{S})^{-1}_{qp}(\mathbf{1}+\mathbf{S})_{pi}\\ &= -2\sum_i^{(A)}\sum_q^{\text{all}} S_{iq}\left(\sum_p^{\text{all}}(\mathbf{1}+\mathbf{S})^{-1}_{qp}(\mathbf{1}+\mathbf{S})_{pi}\right)\\ &= -2\sum_i^{(A)}\sum_q^{\text{all}} S_{iq}\delta_{qi} = -2\sum_i^{(A)} S_{ii} = 0.\end{aligned}$$

12.2. Much in the same way as in Problem 12.1:

$$\begin{aligned}\int d\mathbf{r}\hat{F}^A(00|\mathbf{r})P^A_{\text{ov}}(00|\mathbf{r};\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}} &= 2\sum_i^{(A)}\sum_p^{\text{all}}\Delta_{ip}\int d\mathbf{r}\phi_p^*(\mathbf{r})\hat{F}^A(00|\mathbf{r})\phi_i(\mathbf{r})\\ &= -2\sum_i^{(A)}\sum_p^{\text{all}}\Delta_{ip}\varepsilon_i(\mathbf{1}+\mathbf{S})_{pi}\\ &= -2\sum_i^{(A)}\varepsilon_i\sum_p^{\text{all}}\sum_q^{\text{all}} S_{iq}(\mathbf{1}+\mathbf{S})^{-1}_{qp}(\mathbf{1}+\mathbf{S})_{pi}\\ &= -2\sum_i^{(A)}\varepsilon_i\sum_q^{\text{all}} S_{iq}\delta_{qi} = -2\sum_i^{(A)}\varepsilon_i S_{ii} = 0.\end{aligned}$$

12.3. We recall from Chapter 1 the very property of the Dirac δ-function:

$$\int dx'\delta(x-x')f(x') = f(x).$$

Then:

$$U^B(00|\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{\gamma^B(00|\mathbf{r}_2)}{r_{12}}$$

$$= \int d\mathbf{r}_2 \frac{\sum_\beta Z_\beta \delta(\mathbf{r}_2 - \mathbf{r}_\beta) - P^B(00|\mathbf{r}_2;\mathbf{r}_2)}{r_{12}}$$

$$= \sum_\beta Z_\beta \frac{1}{r_{1\beta}} - \int d\mathbf{r}_2 \frac{P^B(00|\mathbf{r}_2;\mathbf{r}_2)}{r_{12}},$$

so that we can write for E_1^{es}:

$$\begin{aligned}
E_1^{\text{es}} &= \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\gamma^A(00|\mathbf{r}_1)\gamma^B(00|\mathbf{r}_2)}{r_{12}} \\
&= \int d\mathbf{r}_1 \left[\int d\mathbf{r}_2 \frac{\gamma^B(00|\mathbf{r}_2)}{r_{12}}\right] \gamma^A(00|\mathbf{r}_1) \\
&= \int d\mathbf{r}_1 \left[\sum_\beta \frac{Z_\beta}{r_{1\beta}} - \int d\mathbf{r}_2 \frac{P^B(00|\mathbf{r}_2;\mathbf{r}_2)}{r_{12}}\right] \\
&\quad \times \left[\sum_\alpha Z_\alpha \delta(\mathbf{r}_1 - \mathbf{r}_\alpha) - P^A(00|\mathbf{r}_1;\mathbf{r}_1)\right] \\
&= \sum_\alpha \sum_\beta \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \\
&\quad - \sum_\beta Z_\beta \int d\mathbf{r}_1 \frac{P^A(00|\mathbf{r}_1;\mathbf{r}_1)}{r_{1\beta}} - \sum_\alpha Z_\alpha \int d\mathbf{r}_2 \frac{P^B(00|\mathbf{r}_2;\mathbf{r}_2)}{r_{2\alpha}} \\
&\quad + \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{P^A(00|\mathbf{r}_1;\mathbf{r}_1) P^B(00|\mathbf{r}_2;\mathbf{r}_2)}{r_{12}}
\end{aligned}$$

which is the expression given in (121). The same can be done for the transition density matrices of equation (117), which are only electronic, since first, second and last term of equation (119) disappear for $i, j \neq 0$.

12.4. In the integral:

$$I = \int_0^\infty du \frac{1}{a^2+u^2} \cdot \frac{1}{b^2+u^2} \qquad a, b > 0$$

we can decompose the product in the integrand according to:

$$\frac{A}{a^2+u^2} + \frac{B}{b^2+u^2} = \frac{A(b^2+u^2) + B(a^2+u^2)}{(a^2+u^2)(b^2+u^2)}$$

with the condition that:

$$A(b^2+u^2) + B(a^2+u^2) = 1$$

$$(Ab^2 + Ba^2) + (A + B)u^2 = 1$$

giving:

$$A + B = 0 \qquad B = -A$$

$$Ab^2 + Ba^2 = 1 \qquad A(b^2 - a^2) = 1.$$

We therefore obtain:

$$A = (b^2 - a^2)^{-1}, \qquad B = -(b^2 - a^2)^{-1}$$

$$\frac{1}{(a^2 + u^2)(b^2 + u^2)} = (b^2 - a^2)^{-1}\left(\frac{1}{a^2 + u^2} - \frac{1}{b^2 + u^2}\right).$$

For the first of the two resulting integrals we have:

$$\int_0^\infty du \frac{1}{a^2 + u^2} = \frac{1}{a^2}\int_0^\infty du \frac{1}{1 + \left(\frac{u}{a}\right)^2} = \frac{1}{a}\int_0^\infty dx \frac{1}{1 + x^2}$$
$$= \frac{1}{a}\tan^{-1} x\Big|_0^\infty = \frac{\pi}{2a},$$

where we have posed $u/a = x$, $du = adx$, the integration limits being unchanged. Proceeding similarly with the remaining integral, we finally obtain:

$$\begin{aligned} I &= \int_0^\infty du \frac{1}{a^2 + u^2} \cdot \frac{1}{a^2 + b^2} \\ &= (b^2 - a^2)^{-1}\int_0^\infty du \left(\frac{1}{a^2 + u^2} - \frac{1}{b^2 + u^2}\right) \\ &= (b^2 - a^2)^{-1}\left(\frac{\pi}{2a} - \frac{\pi}{2b}\right) \\ &= (b^2 - a^2)^{-1}\frac{\pi}{2}\frac{b - a}{ab} = \frac{\pi}{2}\frac{1}{ab(a + b)} \end{aligned}$$

which is the required value. Hence, we get the integral transform:

$$\frac{1}{a + b} = \frac{2}{\pi}\int_0^\infty du \frac{a}{a^2 + u^2} \cdot \frac{b}{b^2 + u^2} \qquad a, b > 0.$$

12.5. C_6 dispersion coefficient for H(1*s*)–H(1*s*) from the 2-term dipole polarizability pseudospectrum of H(1*s*).

We evaluate first the dipole dispersion constant:

$$C_{11} = \frac{1}{4}\sum_{i=1}^{2}\sum_{j=1}^{2}\alpha_i\alpha_j\frac{\varepsilon_i\varepsilon_j}{\varepsilon_i+\varepsilon_j}$$

$$= \frac{1}{8}\alpha_1^2\varepsilon_1 + \frac{1}{2}\alpha_1\alpha_2\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2} + \frac{1}{8}\alpha_2^2\varepsilon_2.$$

Then the pseudospectrum of Problem 11.7 gives:

$$C_{11} = \frac{1}{8}\cdot\frac{4}{36}\cdot 1 + \frac{1}{2}\cdot\frac{50}{36}\cdot\frac{2}{5}\cdot\frac{5}{7} + \frac{1}{8}\cdot\frac{625}{36}\cdot\frac{2}{5} = \frac{1}{72} + \frac{25}{126} + \frac{125}{144} = \frac{121}{112},$$

and the C_6 dispersion coefficient will be:

$$C_6 = 6\,C_{11} = \frac{363}{56} = 6.482\,142\,857\,142\,86\cdots$$

The C_6 dispersion coefficient is obtained as a fraction of simple not divisible integers.

Using a non-variational technique in momentum space, Koga and Matsumoto (1985; see also Koga and Ujiie, 1986) gave the 3-term C_6 for H–H as the ratio of not divisible integers as:

$$C_6 = \frac{12529}{1928} = 6.498\,443\,983\,402\,49\cdots$$

and, for the 4-term:

$$C_6 = \frac{6313807}{971504} = 6.499\,002\,577\,446\,93\cdots$$

The last value is accurate to four decimal figures, the best C_6 value, accurate to fifteen decimal figures, being (Ottonelli, 1998, $N = 25$; Magnasco et al., 1998):

$$C_6 = 6.499\,026\,705\,405\,839\cdots$$

12.6. C_6 dispersion coefficients for H_2–H_2.

An accurate evaluation of C_6 dispersion coefficients for H_2–H_2, based on the pseudostate decomposition of Kołos and Wolniewicz (1967) static dipole polarizabilities for ground state H_2, can be found in a paper by Magnasco and Ottonelli (1996). We shall be content here with a less accurate evaluation based on the 4-term dipole pseudospectra of $H_2(^1\Sigma_g^+)$ at $R = 1.4\,a_0$ described in Problem 11.9.

We first calculate the three independent dipole-dipole dispersion constants A, $B = C$, D of equations (136)–(139), which in London form are:

$$A = \frac{1}{4}\sum_i\sum_j\alpha_i^{\parallel}\alpha_j^{\parallel}\frac{\varepsilon_i^{\parallel}\varepsilon_j^{\parallel}}{\varepsilon_i^{\parallel}+\varepsilon_j^{\parallel}}$$

Table 12.11.

4-term numerical values for the $L_A L_B M$-components of the C_6 dispersion coefficients for H_2–H_2 ($R = 1.4a_0$)

L_A	L_B	M	$C_6^{L_A L_B M}/E_h a_0^6$
0	0	0	11.23
0	2	0	1.105
2	0	0	1.105
2	2	0	0.338
2	2	1	−0.075
2	2	2	0.009

$$B = C = \frac{1}{4}\sum_i \sum_j \alpha_i^{\parallel} \alpha_j^{\perp} \frac{\varepsilon_i^{\parallel} \varepsilon_j^{\perp}}{\varepsilon_i^{\parallel} + \varepsilon_j^{\perp}} \quad \text{for the homodimer}$$

$$D = \frac{1}{4}\sum_i \sum_j \alpha_i^{\perp} \alpha_j^{\perp} \frac{\varepsilon_i^{\perp} \varepsilon_j^{\perp}}{\varepsilon_i^{\perp} + \varepsilon_j^{\perp}}.$$

The 4-term pseudospectrum gives:

$$\text{Dispersion constant} = \frac{1}{4}\sum_{i=1}^{4} \sum_{j=1}^{4} \alpha_i \alpha_j \frac{\varepsilon_i \varepsilon_j}{\varepsilon_i + \varepsilon_j}.$$

Using the 4-term values of Problem 11.9, we obtain for H_2–H_2 the following numerical results:

$$A = \underset{\text{diagonal}}{1.422} + \underset{\text{cross-term}}{1.261} = 2.683 \quad 99.8\% \text{ of } 2.689$$

$$B = C = \underset{i=j}{0.969} + \underset{i<j}{0.629} + \underset{i>j}{0.420} = \underset{\text{diagonal}}{0.969} + \underset{\text{cross-term}}{1.049} = \underset{99.3\% \text{ of } 2.032}{2.018}$$

$$D = \underset{\text{diagonal}}{0.677} + \underset{\text{cross-term}}{0.845} = 1.522 \quad 98.7\% \text{ of } 1.542.$$

The results for the three dispersion constants are excellent, all being within 99% of the accurate values (1996) or more.

Using the results of Table 12.5, we finally obtain for the $L_A L_B M$-components of the C_6 dispersion coefficients for H_2–H_2 ($R = 1.4a_0$) the numerical results collected in Table 12.11.

The 4-term results of Table 12.11 compare favourably with the results of the accurate calculations (Magnasco and Ottonelli, 1996; Ottonelli, 1998) reported in Table 12.6 of the main text:

(i) The isotropic dispersion coefficient, $C_6^{000} = C_6 = 11.23$, is within 99.2% of the accurate value 11.32;

(ii) The anisotropy coefficients, defined as:

$$\gamma_6^{L_A L_B M} = \frac{C_6^{L_A L_B M}}{C_6}$$

are also in good agreement with the accurate data:

$$\gamma_6^{020} = 0.098 \quad \text{instead of } 0.096$$

$$\gamma_6^{220} = 0.030 \quad \text{instead of } 0.029.$$

– 13 –

Evaluation of Molecular Integrals over STOs

13.1 INTRODUCTION

We introduced in Chapter 4 some 1-centre 1-electron integrals over STOs or GTOs. In this last Chapter, we shall take into consideration also 2-electron integrals, mostly 2-centre integrals over STOs. From a mathematical standpoint the 2-electron integrals are multiple integrals over six variables, the position coordinates in space of the two interacting electrons. They are best dealt with by finding first the electrostatic potential due to one charge distribution, say that of the second electron, followed by integration of the resulting potential with the charge distribution of the first. In this way, all 2-electron integrals can be reduced to just 1-electron integrals in three variables. The molecular 2-electron integrals[1] may be classified into 1-, 2-, 3-, and 4-centre integrals, according to the number of nuclei to which the AOs are referred. The difficulty in their analytical evaluation increases greatly with the number of centres involved, 3- and 4-centre integrals being necessarily evaluated by numerical techniques. In the context of some particularly refined molecular energy calculations, which involve the interelectronic distance r_{12} directly into the wavefunction (Kutzelnigg and Klopper, 1991; see Chapter 7), still more difficult 3- and 4-electron many-centre integrals may occur.

In this Chapter, we shall mostly consider an elementary approach to the evaluation of some 1- and 2-centre 2-electron integrals over STOs when the integrand is expressed in spherical or spheroidal coordinates, respectively. In particular, we shall derive in Section 13.7 the explicit expressions for all 2-centre molecular integrals over 1s STOs occurring in the study of the H_2 molecule, while Section 13.8 illustrates two different strategies for the evaluation of 2-centre integrals over general STOs. A short outline of a possible way of evaluating multicentre integrals over 1s STOs is then given in Section 13.9, while problems and solved problems conclude the Chapter as usual.

13.2 THE BASIC INTEGRALS

13.2.1 The Indefinite Integral

The basic indefinite integral occurring in all atomic or molecular calculations involving STOs with exponential decay is (Gradshteyn and Ryzhik, 1980):

$$\int dx \exp(ax)x^n = \exp(ax)\sum_{k=0}^{n}(-1)^k \frac{n!}{(n-k)!}\frac{x^{n-k}}{a^{k+1}} \tag{1}$$

with $n =$ non-negative integer and $a =$ real, a result that can be obtained by repeated integration by parts. The case of interest in molecular quantum mechanics is:

$$a = -\rho \qquad Re(\rho) > 0 \tag{2}$$

$$\begin{aligned}\int dx \exp(-\rho x)x^n &\\ &= \exp(-\rho x)\sum_{k=0}^{n}(-1)^k \frac{n!}{(n-k)!}\frac{x^{n-k}}{(-\rho)^{k+1}}\\ &= -\frac{n!}{\rho^{n+1}}\exp(-\rho x)\left\{\frac{(\rho x)^n}{n!}+\frac{(\rho x)^{n-1}}{(n-1)!}+\cdots+\frac{(\rho x)^2}{2!}+\rho x+1\right\}\end{aligned}$$

---

[1] 1-electron integrals involve at most three centres.

$$= -\frac{n!}{\rho^{n+1}}\exp(-\rho x)\sum_{k=0}^{n}\frac{(\rho x)^k}{k!} = \mathcal{F}_n(x), \tag{3}$$

where $\mathcal{F}_n(x)$ is the primitive function. This result can be checked by taking the first derivative of $\mathcal{F}_n(x)$. Then:

$$\begin{aligned}
\frac{d\mathcal{F}_n}{dx} &= -\frac{n!}{\rho^{n+1}}\exp(-\rho x)\left\{\rho\left[1+\frac{2(\rho x)}{2!}+\frac{3(\rho x)^2}{3!}+\cdots+\frac{n(\rho x)^{n-1}}{n!}\right]\right.\\
&\qquad\left.-\rho\left[1+\rho x+\frac{(\rho x)^2}{2!}+\cdots+\frac{(\rho x)^n}{n!}\right]\right\}\\
&= -\frac{n!}{\rho^{n}}\exp(-\rho x)\left\{\left[1+\rho x+\frac{(\rho x)^2}{2!}+\cdots+\frac{(\rho x)^{n-1}}{(n-1)!}\right]\right.\\
&\qquad\left.-\left[1+\rho x+\frac{(\rho x)^2}{2!}+\cdots+\frac{(\rho x)^{n-1}}{(n-1)!}+\frac{(\rho x)^n}{n!}\right]\right\}\\
&= -\frac{n!}{\rho^{n}}\exp(-\rho x)\left[-\frac{(\rho x)^n}{n!}\right] = \exp(-\rho x)x^n.
\end{aligned} \tag{4}$$

There is a term by term cancellation with the exception of the last term in the second sum. We now turn to the definite integrals of interest to us.

13.2.2 Definite Integrals and Auxiliary Functions

For *atomic* (1-centre) problems:

$$\int_0^\infty dx\,\exp(-\rho x)x^n = \frac{n!}{\rho^{n+1}} \tag{5}$$

$$\int_0^u dx\,\exp(-\rho x)x^n = \frac{n!}{\rho^{n+1}}\left\{1-\exp(-\rho u)\sum_{k=0}^{n}\frac{(\rho u)^k}{k!}\right\} \tag{6}$$

$$\int_u^\infty dx\,\exp(-\rho x)x^n = \frac{n!}{\rho^{n+1}}\exp(-\rho u)\sum_{k=0}^{n}\frac{(\rho u)^k}{k!}. \tag{7}$$

Adding (6) to (7) gives (5).

For *molecular* (2-centre) problems:

$$\int_1^\infty dx\,\exp(-\rho x)x^n = \frac{n!}{\rho^{n+1}}\exp(-\rho)\sum_{k=0}^{n}\frac{\rho^k}{k!} = A_n(\rho) \tag{8}$$

$$\int_1^u dx\,\exp(-\rho x)x^n = A_n(\rho) - \frac{n!}{\rho^{n+1}}\exp(-\rho u)\sum_{k=0}^{n}\frac{(\rho u)^k}{k!} \tag{9}$$

$$\int_u^\infty dx \exp(-\rho x)x^n = \frac{n!}{\rho^{n+1}} \exp(-\rho u) \sum_{k=0}^{n} \frac{(\rho u)^k}{k!} \tag{10}$$

$$\int_{-1}^{1} dx \exp(-\rho x)x^n = B_n(\rho) = (-1)^{n+1} A_n(-\rho) - A_n(\rho). \tag{11}$$

Adding (9) to (10) gives (8).

In the calculation of 2-centre molecular integrals, the two integrals (8) and (11) are known as *auxiliary functions* (Rosen, 1931 and Roothaan, 1951b). It should be noted that:

$$B_n(-\rho) = (-1)^n B_n(\rho) \tag{12}$$

$$B_n(0) = \frac{2}{n+1}\delta_{en} \quad e = \text{even}. \tag{13}$$

The explicit form for the first few auxiliary functions is:

$$A_0(\rho) = \frac{\exp(-\rho)}{\rho}$$

$$A_1(\rho) = \frac{\exp(-\rho)}{\rho^2}(1+\rho) \tag{14}$$

$$A_2(\rho) = \frac{2\exp(-\rho)}{\rho^3}\left(1+\rho+\frac{\rho^2}{2}\right)$$

$$\begin{aligned} A_3(\rho) &= \frac{6\exp(-\rho)}{\rho^4}\left(1+\rho+\frac{\rho^2}{2}+\frac{\rho^3}{6}\right) \\ A_4(\rho) &= \frac{24\exp(-\rho)}{\rho^5}\left(1+\rho+\frac{\rho^2}{2}+\frac{\rho^3}{6}+\frac{\rho^4}{24}\right) \end{aligned} \tag{15}$$

$$B_0(\rho) = \frac{\exp(\rho)}{\rho} - \frac{\exp(-\rho)}{\rho} = \frac{\exp(\rho)}{\rho}[1-\exp(-2\rho)] \tag{16}$$

$$\begin{aligned} B_1(\rho) &= \frac{\exp(\rho)}{\rho^2}(1-\rho) - \frac{\exp(-\rho)}{\rho^2}(1+\rho) \\ &= \frac{\exp(\rho)}{\rho^2}[(1-\rho)-\exp(-2\rho)(1+\rho)] \end{aligned} \tag{17}$$

$$B_2(\rho) = \frac{2\exp(\rho)}{\rho^3}\left[\left(1-\rho+\frac{\rho^2}{2}\right)-\exp(-2\rho)\left(1+\rho+\frac{\rho^2}{2}\right)\right] \tag{18}$$

$$B_3(\rho) = \frac{6\exp(\rho)}{\rho^4}\left[\left(1-\rho+\frac{\rho^2}{2}-\frac{\rho^3}{6}\right)-\exp(-2\rho)\left(1+\rho+\frac{\rho^2}{2}+\frac{\rho^3}{6}\right)\right] \tag{19}$$

$$\begin{aligned} B_4(\rho) = \frac{24\exp(\rho)}{\rho^5}\Bigg[&\left(1-\rho+\frac{\rho^2}{2}-\frac{\rho^3}{6}+\frac{\rho^4}{24}\right) \\ &-\exp(-2\rho)\left(1+\rho+\frac{\rho^2}{2}+\frac{\rho^3}{6}+\frac{\rho^4}{24}\right)\Bigg]. \end{aligned} \tag{20}$$

Recurrence relations are often used in numerical calculations. We give as an example those for $A_n(\rho)$. From the definition (8) it follows:

$$A_{n-1}(\rho) = \frac{(n-1)!}{\rho^n}\exp(-\rho)\sum_{k=0}^{n-1}\frac{\rho^k}{k!}. \tag{21}$$

Hence follows the recurrence relation:

$$\begin{aligned} A_n(\rho) &= \frac{n!}{\rho^{n+1}}\exp(-\rho)\sum_{k=0}^{n-1}\frac{\rho^k}{k!} + \frac{n!}{\rho^{n+1}}\exp(-\rho)\frac{\rho^n}{n!} \\ &= \frac{n}{\rho}\left[\frac{(n-1)!}{\rho^n}\exp(-\rho)\sum_{k=0}^{n-1}\frac{\rho^k}{k!}\right] + \frac{\exp(-\rho)}{\rho} \\ &= \frac{1}{\rho}[nA_{n-1}(\rho)+\rho A_0(\rho)]. \end{aligned} \tag{22}$$

13.3 1-CENTRE INTEGRALS

13.3.1 1-Electron Integrals

Non-orthogonality, Coulomb, and Laplacian integrals are calculated directly in spherical coordinates starting from the general definition of STO orbitals in real form, equation (116) of Chapter 4. We obtain the following.

(i) Non-orthogonality.

$$\begin{aligned} S_{n'l'm',nlm} &= \langle n'l'm'|nlm\rangle \\ &= \delta_{ll'}\delta_{mm'}\frac{(n+n')!}{\sqrt{(2n)!(2n')!}}\left(\frac{c}{c'}\right)^{\frac{n-n'}{2}}\left(\frac{2(cc')^{1/2}}{c+c'}\right)^{n+n'+1}. \end{aligned} \tag{23}$$

Since the spherical harmonics are orthonormal, it will be sufficient to integrate over the radial part:

$$\begin{aligned}\langle R_{n'}(r)|R_n(r)\rangle &= N_n N_{n'} \int_0^\infty dr\, r^{n+n'} \exp[-(c+c')r] \\ &= \left(\frac{(2c)^{2n+1}(2c')^{2n'+1}}{(2n)!(2n')!}\right)^{1/2} \frac{(n+n')!}{(c+c')^{n+n'+1}} \\ &= \frac{(n+n')!}{\sqrt{(2n)!(2n')!}}\left(\frac{c}{c'}\right)^{\frac{n-n'}{2}} \left(\frac{2(cc')^{1/2}}{c+c'}\right)^{n+n'+1} \qquad (24)\end{aligned}$$

as can be easily verified. In fact:

$$(2^{2n+1+2n'+1})^{1/2} = 2^{\frac{2n+2n'+2}{2}} = 2^{n+n'+1}$$

$$(c^{n-n'+n+n'+1} \cdot c'^{n'-n+n+n'+1})^{1/2} = (c^{2n+1} \cdot c'^{2n'+1})^{1/2}$$

as it must be.

In the following, we put for short $R = R_n$, $Y = Y_{lm}$, $R' = R_{n'}$, $Y' = Y_{l'm'}$.

(ii) Coulomb.

$$\begin{aligned}\langle n'l'm'|r^{-1}|nlm\rangle &= \langle R'Y'|r^{-1}|RY\rangle \\ &= \delta_{ll'}\delta_{mm'}\langle R'|r^{-1}|R\rangle \\ &= \delta_{ll'}\delta_{mm'} N_n N_{n'} \int_0^\infty dr\, r^{n+n'-1} \exp[-(c+c')r] \\ &= \delta_{ll'}\delta_{mm'} N_n N_{n'} \frac{(n+n'-1)!}{(c+c')^{n+n'}} \\ &= \left(\delta_{ll'}\delta_{mm'} N_n N_{n'} \frac{(n+n')!}{(c+c')^{n+n'+1}}\right) \frac{c+c'}{n+n'} \\ &= \frac{c+c'}{n+n'} S_{n'l'm',nlm}. \qquad (25)\end{aligned}$$

So, the 1-centre Coulomb integral over STOs is proportional to the non-orthogonality integral S, and vanishes for orthogonal STOs. The nuclear attraction integral is obtained by multiplying (25) by minus the nuclear charge Z.

(iii) Laplacian.

$$\langle n'l'm'|\nabla^2|nlm\rangle = \left\langle R'Y' \middle| \nabla_r^2 - \frac{\hat{L}^2}{r^2} \middle| RY \right\rangle \qquad (26)$$

but:

$$\hat{L}^2 Y_{lm} = l(l+1) Y_{lm} \qquad \langle Y_{l'm'} | Y_{lm} \rangle = \delta_{ll'} \delta_{mm'}$$

$$\nabla_r^2 = \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \qquad R(r) = r^{n-1} \exp(-cr)$$

$$\frac{dR}{dr} = \exp(-cr)\{(n-1)r^{n-2} - cr^{n-1}\} \tag{27}$$

$$\frac{d^2R}{dr^2} = \exp(-cr)\{(n-1)(n-2)r^{n-3} - 2c(n-1)r^{n-2} + c^2 r^{n-1}\}$$

$$\nabla_r^2 R = \exp(-cr)\{n(n-1)r^{n-3} - 2ncr^{n-2} + c^2 r^{n-1}\}$$

so that:

$$\begin{aligned} \nabla^2(RY) &= Y\big(\nabla_r^2 R\big) - l(l+1) r^{-2} (RY) \\ &= Y \exp(-cr)\{[n(n-1) - l(l+1)] r^{n-3} - 2ncr^{n-2} + c^2 r^{n-1}\} \end{aligned} \tag{28}$$

$$\begin{aligned} \langle R'Y' | \nabla^2 | RY \rangle &= \delta_{ll'} \delta_{mm'} N_n N_{n'} \int_0^\infty dr\, r^{n'+1} \exp[-(c+c')r] \\ &\quad \times \{[n(n-1) - l(l+1)] r^{n-3} - 2ncr^{n-2} + c^2 r^{n-1}\} \\ &= \delta_{ll'} \delta_{mm'} N_n N_{n'} \left\{ [n(n-1) - l(l+1)] \frac{(n+n'-2)!}{(c+c')^{n+n'-1}} \right. \\ &\quad \left. - 2nc \frac{(n+n'-1)!}{(c+c')^{n+n'}} + c^2 \frac{(n+n')!}{(c+c')^{n+n'+1}} \right\} \\ &= \delta_{ll'} \delta_{mm'} N_n N_{n'} \frac{(n+n')!}{(c+c')^{n+n'+1}} \left\{ \frac{n(n-1) - l(l+1)}{(n+n')(n+n'-1)} \right. \\ &\quad \left. \times (c+c')^2 - \frac{2nc}{n+n'}(c+c') + c^2 \right\} \\ &= S_{n'l'm',nlm} \left\{ \frac{n(n-1) - l(l+1)}{(n+n')(n+n'-1)} (c+c')^2 \right. \\ &\quad \left. - \frac{2nc}{n+n'}(c+c') + c^2 \right\} \end{aligned} \tag{29}$$

so that even the off-diagonal matrix element of the 1-centre Laplacian operator over STOs is proportional to the non-orthogonality integral S. This is not true for GTOs.

For the diagonal element we have:

$$n' = n, \qquad l' = l, \qquad m' = m, \qquad c' = c, \qquad S = 1$$
$$\langle nlm|\nabla^2|nlm\rangle = -\frac{n + 2l(l+1)}{n(2n-1)}c^2. \tag{30}$$

13.3.2 2-Electron Integrals

Putting $|a\rangle = |nlm\rangle$, we recall the two equivalent notations:

$$\underbrace{\left\langle \overset{1}{a'}\overset{2}{a'''} \middle| \frac{1}{r_{12}} \middle| \overset{1}{a}\overset{2}{a''} \right\rangle}_{\text{Dirac}} = \underbrace{\left(\overset{1}{aa'} \middle| \overset{2}{a''a'''} \right)}_{\text{Charge density}}. \tag{31}$$

The charge density notation is most used in molecular calculations. The general 2-electron repulsion integral (31) is reduced to a 1-electron integral by evaluating first the electrostatic potential $J_{a''a'''}$ at point $\mathbf{r}_1$ due to electron 2 of density $\{a''(\mathbf{r}_2)a'''(\mathbf{r}_2)\}$:

$$J_{a''a'''}(\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{\{a''(\mathbf{r}_2)a'''(\mathbf{r}_2)\}}{r_{12}}. \tag{32}$$

Hence:

$$(aa'|a''a''') = \int d\mathbf{r}_1 J_{a''a'''}(\mathbf{r}_1)\{a(\mathbf{r}_1)a'(\mathbf{r}_1)\}, \tag{33}$$

where either the potential or the final integral are evaluated in spherical coordinates. We take as simple examples the evaluation of the potential J_{1s} due to a spherical $\{1s^2\}$ charge distribution, and the two-electron repulsion integral $(1s^2|1s^2)$.

13.4 EVALUATION OF THE ELECTROSTATIC POTENTIAL J_{1s}

13.4.1 Spherical Coordinates

With reference to Figure 13.1, $[1s(\mathbf{r}_2)]^2 d\mathbf{r}_2$ is the element of electronic charge (in atomic units) at $d\mathbf{r}_2$ due to electron 2 in state $1s$. Then (electric potential = charge/distance):

$$\frac{[1s(\mathbf{r}_2)]^2 d\mathbf{r}_2}{r_{12}}$$

is the element of electrostatic potential at space point $\mathbf{r}_1$ due to the electron charge at $\mathbf{r}_2$;

$$J_{1s}(\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{[1s(\mathbf{r}_2)]^2}{r_{12}} \tag{34}$$

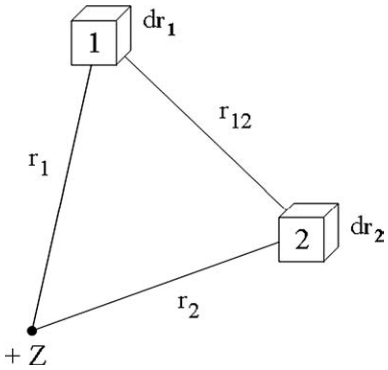

Figure 13.1 Infinitesimal volume elements for electrostatic potential calculation.

the resultant of all elementary electrostatic potential contributions at $\mathbf{r}_1$ due to the continuously varying charge distribution of electron 2, that is the electrostatic potential at point $\mathbf{r}_1$.

To evaluate the electrostatic potential (34) in a general way, it is convenient to use the one-centre Neumann expansion (Eyring et al., 1944) for the inverse of the interelectronic distance r_{12}:

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} \sum_{m=-l}^{l} Y_{lm}(\Omega_1) Y_{lm}(\Omega_2), \tag{35}$$

where:

$$\begin{aligned} r_< &= \min(r_1, r_2) \\ r_> &= \max(r_1, r_2) \end{aligned} \tag{36}$$

and Y_{lm} are spherical harmonics in *real* form, having the properties:

$$\int d\Omega\, Y_{lm}(\Omega) Y_{l'm'}(\Omega) = \delta_{ll'} \delta_{mm'}. \tag{37}$$

Here Ω stands for the angular variables θ, φ.

Taking into account integrals (6) and (7), we can easily evaluate the electrostatic potential $J_{1s}(\mathbf{r}_1)$ in spherical coordinates. The interval of variation of r_2 must be *divided* into the two regions of Figure 13.2.

It is convenient to choose $1s$ AOs separately normalized in the form:

$$1s(\mathbf{r}) = (4c^3)^{1/2} \exp(-cr) Y_{00} \quad Y_{00} = \frac{1}{\sqrt{4\pi}}. \tag{38}$$

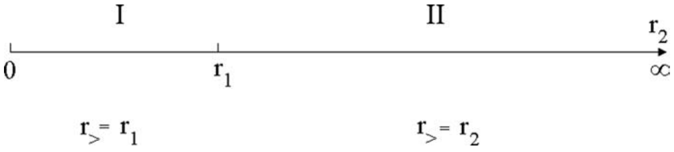

Figure 13.2 The two regions occurring in the integration over r_2.

Introducing the Neumann expansion into the expression for the potential gives:

$$\begin{aligned}
J_{1s}(\mathbf{r}_1) &= \int dr_2\, r_2^2 d\Omega_2\, 4c^3 \exp(-2cr_2)(Y_{00})^2 \\
&\quad \times \sum_l \sum_m \frac{4\pi}{2l+1} Y_{lm}(\Omega_1) Y_{lm}(\Omega_2) \frac{r_<^l}{r_>^{l+1}} \\
&= \sum_l \sum_m 4c^3 \frac{4\pi}{2l+1} Y_{lm}(\Omega_1) Y_{00}(\Omega_1) \int d\Omega_2\, Y_{lm}(\Omega_2) Y_{00}(\Omega_2) \\
&\quad \times \left\{ \frac{1}{r_1^{l+1}} \int_0^{r_1} dr_2\, r_2^2 \exp(-2cr_2) r_2^l + r_1^l \int_{r_1}^{\infty} dr_2\, r_2^2 \exp(-2cr_2) \frac{1}{r_2^{l+1}} \right\} \\
&= 4c^3 \cdot 4\pi \left(\frac{1}{\sqrt{4\pi}} \right)^2 \left\{ \frac{1}{r_1} \int_0^{r_1} dr_2 \exp(-2cr_2) r_2^2 \right. \\
&\qquad \left. + \int_{r_1}^{\infty} dr_2 \exp(-2cr_2) r_2 \right\} \qquad (39)
\end{aligned}$$

since only the term $l = m = 0$ survives in the expansion because of the spherical symmetry of $1s^2$. Evaluating the integrals over r_2 with the aid of (6) and (7) gives:

$$\begin{aligned}
J_{1s}(\mathbf{r}_1) &= 4c^3 \left\{ \frac{1}{r_1} \left[\frac{2!}{(2c)^3} \left(1 - \exp(-2cr_1) \left(1 + 2cr_1 + \frac{(2cr_1)^2}{2!} \right) \right) \right] \right. \\
&\qquad \left. + \frac{\exp(-2cr_1)}{(2c)^2} (1 + 2cr_1) \right\} \\
&= \frac{1}{r_1} - \frac{\exp(-2cr_1)}{r_1} (1 + cr_1) = J(r_1) \qquad (40)
\end{aligned}$$

showing that the potential J_{1s} due to the spherical density $1s^2$ has only a *radial* dependence on the distance r_1 of the electron from the nucleus.

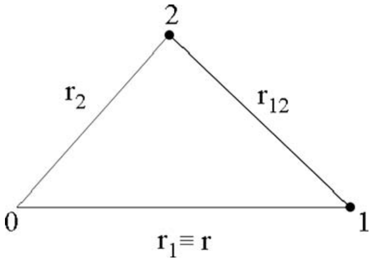

Figure 13.3 A confocal spheroidal coordinate system for the evaluation of J_{1s}.

13.4.2 Spheroidal Coordinates

We can evaluate the potential J_{1s} in spheroidal coordinates as well. Since the distance of electron 1 from the nucleus is *fixed* during the evaluation of the potential, we may use a system of spheroidal coordinates in the form (Figure 13.3):

$$\begin{aligned}
&\mu = \frac{r_2 + r_{12}}{r}, \qquad \nu = \frac{r_2 - r_{12}}{r}, \qquad \varphi \\
&r_2 = \frac{r}{2}(\mu + \nu), \qquad r_{12} = \frac{r}{2}(\mu - \nu) \\
&d\mathbf{r_2} = \left(\frac{r}{2}\right)^3 (\mu^2 - \nu^2) d\mu\, d\nu\, d\varphi.
\end{aligned} \tag{41}$$

By posing $\rho = cr$, we find ($r_1 = r$):

$$\begin{aligned}
J_{1s}(\mathbf{r}_1) &= \int d\mathbf{r}_2 \frac{\{1s(\mathbf{r}_2)\}^2}{r_{12}} = \frac{c^3}{\pi} \int d\mathbf{r}_2 \frac{\exp(-2cr_2)}{r_{12}} \\
&= \frac{c^3}{\pi}\left(\frac{r}{2}\right)^3 \int_0^{2\pi} d\varphi \int_{-1}^{1} d\nu \int_1^\infty d\mu\, (\mu^2 - \nu^2) \frac{\exp[-\rho(\mu + \nu)]}{\frac{r}{2}(\mu - \nu)} \\
&= \frac{2\pi}{\pi}\left(\frac{\rho}{2}\right)^3 \left(\frac{2}{r}\right) \left\{ \int_{-1}^{1} d\nu \exp(-\rho\nu) \int_1^\infty d\mu \exp(-\rho\mu)\mu \right. \\
&\quad \left. + \int_{-1}^{1} d\nu \exp(-\rho\nu)\nu \int_1^\infty d\mu \exp(-\rho\mu) \right\} \\
&= 2c\left(\frac{\rho}{2}\right)^2 \{A_1(\rho)B_0(\rho) + A_0(\rho)B_1(\rho)\}
\end{aligned}$$

$$
\begin{aligned}
&= 2c\left(\frac{\rho}{2}\right)^2\left\{\frac{\exp(-\rho)}{\rho^2}(1+\rho)\frac{\exp(\rho)}{\rho}[1-\exp(-2\rho)]\right.\\
&\quad\left.+\frac{\exp(-\rho)}{\rho}\frac{\exp(\rho)}{\rho^2}[(1-\rho)-\exp(-2\rho)(1+\rho)]\right\}\\
&= \frac{c}{2\rho}\{2-2\exp(-2\rho)(1+\rho)\} = \frac{1}{r}-\frac{\exp(-2cr)}{r}(1+cr) \qquad (42)
\end{aligned}
$$

which is the result (40) found previously.

13.5 THE $(1s^2|1s^2)$ ELECTRON REPULSION INTEGRAL

13.5.1 Same Orbital Exponent

The 2-electron integral $(1s^2|1s^2)$ in charge density notation can then be written as:

$$
\begin{aligned}
(1s^2|1s^2) &= \iint d\mathbf{r}_1\, d\mathbf{r}_2 \frac{[1s(\mathbf{r}_2)]^2}{r_{12}}[1s(\mathbf{r}_1)]^2\\
&= \int d\mathbf{r}_1 J_{1s}(\mathbf{r}_1)[1s(\mathbf{r}_1)]^2. \qquad (43)
\end{aligned}
$$

The integral is easily calculated using the expression just found for the potential $J_{1s}(\mathbf{r}_1)$. We obtain immediately:

$$
\begin{aligned}
(1s^2|1s^2) &= \frac{c^3}{\pi}\cdot 4\pi\int_0^\infty dr r^2\left[\frac{1}{r}-\frac{\exp(-2cr)}{r}(1+cr)\right]\exp(-2cr)\\
&= 4c^3\left[\int_0^\infty dr\exp(-2cr)r - \int_0^\infty dr\exp(-4cr)(r+cr^2)\right]\\
&= 4c^3\left[\frac{1}{(2c)^2}-\frac{1}{(4c)^2}-\frac{2c}{(4c)^3}\right] = \frac{5}{8}c. \qquad (44)
\end{aligned}
$$

13.5.2 Different Orbital Exponents

Write the 2-electron integral as $(\overset{1}{\varphi_1\varphi_1} \mid \overset{2}{\varphi_2\varphi_2})$, where $\varphi_1 = 1s_1$ (orbital exponent c_1) and $\varphi_2 = 1s_2$ (orbital exponent c_2). The electrostatic potential due to electron 2 is now ($\mathbf{r}_1 = \mathbf{r}$, $r_1 = r$):

$$
J_{\varphi_2\varphi_2} = \int d\mathbf{r}_2 \frac{[\varphi_2(\mathbf{r}_2)]^2}{r_{12}} = \frac{1}{r}-\frac{\exp(-2c_2r)}{r}(1+c_2r) \qquad (45)
$$

giving for the 2-electron integral:

$$
\begin{aligned}
(\varphi_1^2|\varphi_2^2) &= \int d\mathbf{r} J_{\varphi_2\varphi_2}(r)[\varphi_1(\mathbf{r})]^2 \\
&= 4c_1^3 \int_0^\infty dr \exp(-2c_1 r)\{r - \exp(-2c_2 r)(r + c_2 r^2)\} \\
&= 4c_1^3 \left\{ \frac{1}{(2c_1)^2} - \frac{1}{(2c_1+2c_2)^2} - \frac{2c_2}{(2c_1+2c_2)^3} \right\} \\
&= c_1^3 \left\{ \frac{c_1^2 + c_2^2 + 2c_1c_2 - c_1^2}{c_1^2(c_1+c_2)^2} - \frac{c_2}{(c_1+c_2)^3} \right\} \\
&= \frac{c_1c_2^2 + 2c_1^2c_2}{(c_1+c_2)^2} - \frac{c_1^3c_2}{(c_1+c_2)^3} = \frac{c_1c_2}{c_1+c_2}\left\{ \frac{2c_1+c_2}{c_1+c_2} - \frac{c_1^2}{(c_1+c_2)^2} \right\} \\
&= \frac{c_1c_2}{c_1+c_2}\left\{ 1 + \frac{c_1c_2}{(c_1+c_2)^2} \right\}. \qquad (46)
\end{aligned}
$$

For $c_1 = c_2 = c$, we recover our previous expression (44).

13.6 GENERAL FORMULA FOR 1-CENTRE 2-ELECTRON INTEGRALS

The product of two STOs onto the same centre originates a density, say $\{a(\mathbf{r})a'(\mathbf{r})\}$, that can be reduced to a finite linear combination of elementary (or *basic*) charge distributions $D_{NLM}(\mathbf{r})$ (Roothaan, 1951b):

$$D_{NLM}(\mathbf{r}) = \sqrt{\frac{2L+1}{4\pi}} R_{NL}(r) Y_{LM}(\theta, \varphi) \qquad (47)$$

$$R_{NL}(r) = \frac{2^L (2\zeta)^{N+2}}{(N+L+1)!} r^{N-1} \exp(-2\zeta r), \qquad (48)$$

where:

$$\zeta = \frac{c_a + c_{a'}}{2} \qquad (49)$$

$$N = n_a + n_{a'} - 1 \qquad (50)$$

$$|l_a - l_{a'}| \le L \le l_a + l_{a'} \quad (L + l_a + l_{a'} = \text{even}). \qquad (51)$$

$D_{NLM}(\mathbf{r})$ behaves as a single STO of quantum numbers (NLM) and orbital exponent 2ζ, acting at large distances as a multipole of order 2^L and magnitude ζ^{-L}. The complete expression of $\{a(\mathbf{r})a'(\mathbf{r})\}$ in terms of the D_{NLM}s involves the Clebsch–Gordan vector coupling coefficients (Brink and Satchler, 1993) arising from the coupling of the angular momenta of the individual AOs (Guidotti et al., 1962; Figari et al., 1990). A compact general formula for the 2-electron integral between any two of such basic charge distributions was given by Gianinetti et al. (1959) as:

$$\begin{aligned}\left(\overset{1}{D}_{NLM} \mid \overset{2}{D}_{N'L'M'}\right) &= \delta_{LL'}\delta_{MM'}\frac{(\zeta_1\zeta_2)^{L+1}2^{2L+1}}{(\zeta_1+\zeta_2)^{N+N'+1}} \\ &\quad\times\left\{\frac{(N-L)!\zeta_2^{N+N'-2L}}{(N+L+1)!}\sum_{k=0}^{N-L-1}\binom{N+N'+1}{k}\left(\frac{\zeta_1}{\zeta_2}\right)^k\right. \\ &\quad+\frac{(N'-L)!\zeta_1^{N+N'-2L}}{(N'+L+1)!}\sum_{k=0}^{N'-L-1}\binom{N+N'+1}{k}\left(\frac{\zeta_2}{\zeta_1}\right)^k \\ &\quad\left.+\frac{(N+N'+1)!\zeta_1^{N-L}\zeta_2^{N'-L}}{(N+L+1)!(N'+L+1)!}\right\}. \qquad (52)\end{aligned}$$

The 2-electron integrals $(aa'|a''a''')$ are then easily obtained once the decomposition of the densities $\{a(\mathbf{r}_1)a'(\mathbf{r}_1)\}$ and $\{a''(\mathbf{r}_2)a'''(\mathbf{r}_2)\}$ in terms of the D_{NLM}s is known. Gianinetti et al. (1959) gave Tables containing the explicit coefficients for all expansions of s, p, d Slater AOs in terms of such fundamental charge distributions.

13.7 2-CENTRE INTEGRALS OVER 1*s* STOS

These are the integrals occurring in the elementary MO and HL theories for the H_2 molecule. They can be evaluated using the system of spheroidal coordinates described in Chapter 1 (Figure 13.4) and the auxiliary functions A_n and B_n of Section 2 of this Chapter. For the sake of simplicity, we shall take identical orbital exponents ($c' = c$) onto the two

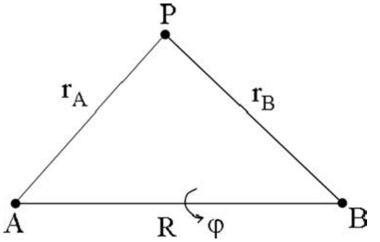

Figure 13.4 The system of confocal spheroidal coordinates for the evaluation of 2-centre integrals.

centres. We have:

$$\begin{aligned}
&\mu=\frac{r_A+r_B}{R}, \qquad \nu=\frac{r_A-r_B}{R}, \qquad \varphi \\
&r_A=\frac{R}{2}(\mu+\nu), \qquad r_B=\frac{R}{2}(\mu-\nu) \\
&d\mathbf{r}=\left(\frac{R}{2}\right)^3(\mu^2-\nu^2)d\mu\,d\nu\,d\varphi.
\end{aligned} \tag{53}$$

13.7.1 1-Electron Integrals

(i) Overlap.

$$\begin{aligned}
S_{ba}&=\langle b|a\rangle=(ab|1)=\frac{c^3}{\pi}\int d\mathbf{r}\exp[-c(r_A+r_B)] \qquad \rho=cR \\
&=\frac{c^3}{\pi}\left(\frac{R}{2}\right)^3\int_0^{2\pi}d\varphi\int_{-1}^{1}d\nu\int_1^\infty d\mu(\mu^2-\nu^2)\exp(-\rho\mu) \\
&=2\left(\frac{\rho}{2}\right)^3\left\{\int_{-1}^{1}d\nu\int_1^\infty d\mu\exp(-\rho\mu)\mu^2\right. \\
&\qquad\left.-\int_{-1}^{1}d\nu\nu^2\int_1^\infty d\mu\exp(-\rho\mu)\right\} \\
&=2\left(\frac{\rho}{2}\right)^3\left\{2A_2(\rho)-\frac{2}{3}A_0(\rho)\right\}=\frac{4}{3}\left(\frac{\rho}{2}\right)^3(3A_2-A_0) \\
&=\frac{4}{3}\left(\frac{\rho}{2}\right)^3\frac{\exp(-\rho)}{\rho^3}(6+6\rho+3\rho^2-\rho^2) \\
&=\exp(-\rho)\left(1+\rho+\frac{\rho^2}{3}\right).
\end{aligned} \tag{54}$$

(ii) Exchange.

$$\begin{aligned}
\left(ab\middle|r_B^{-1}\right)&=\int d\mathbf{r}\frac{a(\mathbf{r})b(\mathbf{r})}{r_B}=\frac{c^3}{\pi}\int d\mathbf{r}\frac{1}{r_B}\exp[-c(r_A+r_B)] \\
&=\frac{c^3}{\pi}\left(\frac{R}{2}\right)^3 2\pi\int_{-1}^{1}d\nu\int_1^\infty d\mu\frac{\mu^2-\nu^2}{\frac{R}{2}(\mu-\nu)}\exp(-\rho\mu) \\
&=2c\left(\frac{\rho}{2}\right)^2\left\{\int_{-1}^{1}d\nu\int_1^\infty d\mu\exp(-\rho\mu)\mu\right.
\end{aligned}$$

$$+\int_{-1}^{1} d\nu\,\nu \int_{1}^{\infty} d\mu \exp(-\rho\mu)\Big\}$$

$$= 2c\left(\frac{\rho}{2}\right)^2 \{2A_1(\rho)\} = c\exp(-\rho)(1+\rho). \tag{55}$$

(iii) Coulomb.

This integral was already calculated in Section 13.4 of this Chapter, equation (42), if we take $r_2 = r_A$, $r_{12} = r_B$, $r_1 = R$. The result is:

$$\left(a^2 \middle| r_B^{-1}\right) = \frac{c}{\rho}\{1 - \exp(-2\rho)(1+\rho)\}. \tag{56}$$

(iv) Laplacian.

$$(\nabla^2)_{ba} = \langle b|\nabla^2|a\rangle = (ab|\nabla^2) \tag{57}$$

$$a = \left(\frac{c^3}{\pi}\right)^{1/2} \exp\left[-\frac{\rho}{2}(\mu+\nu)\right] \qquad b = \left(\frac{c^3}{\pi}\right)^{1/2} \exp\left[-\frac{\rho}{2}(\mu-\nu)\right] \tag{58}$$

$$\nabla^2 = \frac{c^2}{\frac{\rho^2}{4}(\mu^2-\nu^2)}\left\{\nabla_\mu^2 + \nabla_\nu^2 + \frac{\mu^2-\nu^2}{(\mu^2-1)(1-\nu^2)}\frac{\partial^2}{\partial\varphi^2}\right\} \tag{59}$$

$$\nabla_\mu^2 = (\mu^2-1)\frac{\partial^2}{\partial\mu^2} + 2\mu\frac{\partial}{\partial\mu}, \qquad \nabla_\nu^2 = (1-\nu^2)\frac{\partial^2}{\partial\nu^2} - 2\nu\frac{\partial}{\partial\nu}, \tag{60}$$

where the last factor involving $\frac{\partial^2}{\partial\varphi^2}$ can be omitted for spherical AOs. Evaluating the derivatives gives:

$$\nabla_\mu^2 \exp\left(-\frac{\rho}{2}\mu\right) = \left(\frac{\rho^2}{4}\mu^2 - \rho\mu - \frac{\rho^2}{4}\right)\exp\left(-\frac{\rho}{2}\mu\right) \tag{61}$$

$$\nabla_\nu^2 \exp\left(-\frac{\rho}{2}\nu\right) = \left(-\frac{\rho^2}{4}\nu^2 + \rho\nu + \frac{\rho^2}{4}\right)\exp\left(-\frac{\rho}{2}\nu\right) \tag{62}$$

$$\nabla^2 \exp\left[-\frac{\rho}{2}(\mu+\nu)\right] = \frac{c^2\exp[-\frac{\rho}{2}(\mu+\nu)]}{\frac{\rho^2}{4}(\mu^2-\nu^2)}\left\{\frac{\rho^2}{4}(\mu^2-\nu^2) - \rho(\mu-\nu)\right\}. \tag{63}$$

Hence:

$$\langle b|\nabla^2|a\rangle = \frac{c^3}{\pi}\left(\frac{R}{2}\right)^3 2\pi \int_{-1}^{1} d\nu \int_{1}^{\infty} d\mu \frac{c^2(\mu^2-\nu^2)}{\frac{\rho^2}{4}(\mu^2-\nu^2)}$$

$$\begin{aligned}
&\quad\times\left\{\frac{\rho^2}{4}(\mu^2-\nu^2)-\rho(\mu-\nu)\right\}\exp(-\rho\mu)\\
&=c^2\rho\left\{\frac{\rho^2}{4}\left[\int_{-1}^{1}d\nu\int_{1}^{\infty}d\mu\exp(-\rho\mu)\mu^2\right.\right.\\
&\quad\left.\left.-\int_{-1}^{1}d\nu\nu^2\int_{1}^{\infty}d\mu\exp(-\rho\mu)\right]-\rho\int_{-1}^{1}d\nu\int_{1}^{\infty}d\mu\,\mu\exp(-\rho\mu)\right\}\\
&=c^2\rho\left\{\frac{\rho^2}{4}\left(2A_2-\frac{2}{3}A_0\right)-2\rho A_1\right\}\\
&=\frac{1}{6}c^2\rho\left\{\rho^2(3A_2-A_0)-12\rho A_1\right\}.
\end{aligned}\tag{64}$$

Evaluating the terms in brackets gives:

$$\begin{aligned}
&\rho^2(3A_2-A_0)-12\rho A_1\\
&\quad=\rho^2\frac{\exp(-\rho)}{\rho^3}(6+6\rho+3\rho^2-\rho^2)-12\rho\frac{\exp(-\rho)}{\rho^2}(1+\rho)\\
&\quad=6\frac{\exp(-\rho)}{\rho}\left(-1-\rho+\frac{\rho^2}{3}\right),
\end{aligned}\tag{65}$$

so that the integral results:

$$\langle b|\nabla^2|a\rangle=c^2\exp(-\rho)\left(-1-\rho+\frac{\rho^2}{3}\right)\tag{66}$$

which coincides with the result given by Roothaan (1951b).

13.7.2 2-Electron Integrals

The integrals are evaluated in spheroidals by finding first the potential due to the charge distribution of one electron, say electron 2.

(i) Coulomb.

$$(a^2|b^2)=\int d\mathbf{r}_1\,J_B(\mathbf{r}_1)a^2(\mathbf{r}_1)\tag{67}$$

$$\begin{aligned}
J_B(\mathbf{r}_1)&=\int d\mathbf{r}_2\frac{b^2(\mathbf{r}_2)}{r_{12}}=\frac{1}{r_{B1}}\{1-(1+cr_{B1})\exp(-2cr_{B1})\}\\
&=\frac{c}{\frac{\rho}{2}(\mu-\nu)}\left\{1-\left(1+\frac{\rho}{2}(\mu-\nu)\right)\exp[-\rho(\mu-\nu)]\right\}
\end{aligned}\tag{68}$$

so that:

$$
\begin{aligned}
(a^2|b^2) &= \frac{c^3}{\pi}\left(\frac{R}{2}\right)^3 2\pi \int_{-1}^{1} d\nu \int_{1}^{\infty} d\mu \frac{c(\mu^2-\nu^2)}{\frac{\rho}{2}(\mu-\nu)} \\
&\quad \times \left\{1-\left(1+\frac{\rho}{2}(\mu-\nu)\right)\exp[-\rho(\mu-\nu)]\right\}\exp[-\rho(\mu+\nu)] \\
&= 2c\left(\frac{\rho}{2}\right)^2 \int_{-1}^{1} d\nu \int_{1}^{\infty} d\mu(\mu+\nu) \\
&\quad \times \left\{\exp[-\rho(\mu+\nu)]-\exp(-2\rho\mu)-\frac{\rho}{2}(\mu-\nu)\exp(-2\rho\mu)\right\} \\
&= 2c\left(\frac{\rho}{2}\right)^2 \left\{[A_1(\rho)B_0(\rho)+A_0(\rho)B_1(\rho)]\right. \\
&\qquad \left. -\left[2A_1(2\rho)+\rho A_2(2\rho)-\frac{1}{3}\rho A_0(2\rho)\right]\right\}.
\end{aligned}
\tag{69}
$$

Evaluating the terms in brackets gives:

$$
\begin{aligned}
&A_1(\rho)B_0(\rho)+A_0(\rho)B_1(\rho) \\
&\quad = \frac{\exp(-\rho)}{\rho^2}(1+\rho)\frac{\exp(\rho)}{\rho}[1-\exp(-2\rho)] \\
&\qquad + \frac{\exp(-\rho)}{\rho}\frac{\exp(\rho)}{\rho^2}[(1-\rho)-\exp(-2\rho)(1+\rho)] \\
&\quad = \frac{1}{\rho^3}\left\{\begin{pmatrix} 1+\rho \\ 1-\rho \end{pmatrix} - \exp(-2\rho)\begin{pmatrix} 1+\rho \\ 1+\rho \end{pmatrix}\right\} = \frac{2}{\rho^3}\{1-\exp(-2\rho)(1+\rho)\}
\end{aligned}
$$

$$
\begin{aligned}
&2A_1(2\rho)+\rho A_2(2\rho)-\frac{1}{3}\rho A_0(2\rho) \\
&\quad = \frac{1}{3}\{6A_1(2\rho)+3\rho A_2(2\rho)-\rho A_0(2\rho)\} \\
&\quad = \frac{1}{3}\left\{6\frac{\exp(-2\rho)}{(2\rho)^2}(1+2\rho)+3\frac{2\rho}{2}\frac{2\exp(-2\rho)}{(2\rho)^3}(1+2\rho+2\rho^2)\right. \\
&\qquad \left. -\rho\frac{\exp(-2\rho)}{(2\rho)^2}(2\rho)\right\} \\
&\quad = \frac{1}{3}\frac{\exp(-2\rho)}{(2\rho)^2}\begin{pmatrix} 6+12\rho \\ +3+\ \ 6\rho+6\rho^2 \\ -2\rho^2 \end{pmatrix} = \frac{3}{4}\frac{\exp(-2\rho)}{\rho^2}\left(1+2\rho+\frac{4}{9}\rho^2\right)
\end{aligned}
$$

so that:

$$\{\cdots\} = \frac{2}{\rho^3} - \frac{\exp(-2\rho)}{\rho^3}\begin{pmatrix} 2 + \ 2\rho \\ \quad + \frac{3}{4}\rho + \frac{3}{2}\rho^2 + \frac{1}{3}\rho^3 \end{pmatrix}$$

$$= \frac{2}{\rho^3} - \frac{\exp(-2\rho)}{\rho^3}\left(2 + \frac{11}{4}\rho + \frac{3}{2}\rho^2 + \frac{1}{3}\rho^3\right)$$

finally giving:

$$(a^2|b^2) = \frac{c}{\rho}\left\{1 - \exp(-2\rho)\left(1 + \frac{11}{8}\rho + \frac{3}{4}\rho^2 + \frac{1}{6}\rho^3\right)\right\}. \tag{70}$$

For $c = 1$, $\rho = R$:

$$(a^2|b^2) = \underbrace{\frac{1}{R}}_{\substack{\text{Coulomb}\\\text{part}}} - \underbrace{\frac{\exp(-2R)}{R}\left(1 + \frac{11}{8}R + \frac{3}{4}R^2 + \frac{1}{6}R^3\right)}_{\text{Charge–overlap part}}. \tag{71}$$

(ii) Hybrid (or ionic)

$$\begin{aligned}(ab|b^2) &= \int d\mathbf{r}_1 J_B(\mathbf{r}_1)\{a(\mathbf{r}_1)b(\mathbf{r}_1)\} \\ &= \frac{c^3}{\pi}\left(\frac{R}{2}\right)^3 2\pi \int_{-1}^{1} d\nu \int_1^\infty d\mu \frac{c(\mu^2 - \nu^2)}{\frac{\rho}{2}(\mu - \nu)} \\ &\quad \times \left\{1 - \left(1 + \frac{\rho}{2}(\mu - \nu)\right)\exp[-\rho(\mu - \nu)]\right\}\exp(-\rho\mu) \\ &= 2c\left(\frac{\rho}{2}\right)^2 \int_{-1}^{1} d\nu \int_1^\infty d\mu(\mu + \nu) \\ &\quad \times \left\{\exp(-\rho\mu) - \exp(-2\rho\mu)\exp(\rho\nu) \right. \\ &\qquad \left. - \frac{\rho}{2}(\mu - \nu)\exp(-2\rho\mu)\exp(\rho\nu)\right\} \\ &= 2c\left(\frac{\rho}{2}\right)^2 \left\{[2A_1(\rho) - A_1(2\rho)B_0(-\rho) - A_0(2\rho)B_1(-\rho)] \right. \\ &\qquad \left. - \frac{\rho}{2}[A_2(2\rho)B_0(-\rho) - A_0(2\rho)B_2(-\rho)]\right\}. \end{aligned} \tag{72}$$

Taking into account the parity (12) of the auxiliary functions $B_n(\rho)$, evaluating the terms in brackets gives:

$$
\begin{aligned}
&2\frac{\exp(-\rho)}{\rho^2}(1+\rho)\\
&\quad-\frac{\exp(-2\rho)}{(2\rho)^2}(1+2\rho)\frac{\exp(\rho)}{\rho}[1-\exp(-2\rho)]\\
&\quad+\frac{\exp(-2\rho)}{2\rho}\frac{\exp(\rho)}{\rho^2}[(1-\rho)-\exp(-2\rho)(1+\rho)]\\
&\quad-\frac{\rho}{2}\frac{2\exp(-2\rho)}{(2\rho)^3}(1+2\rho+2\rho^2)\frac{\exp(\rho)}{\rho}[1-\exp(-2\rho)]\\
&\quad+\frac{\rho}{2}\frac{\exp(-2\rho)}{2\rho}\frac{2\exp(\rho)}{\rho^3}\left[\left(1-\rho+\frac{\rho^2}{2}\right)-\exp(-2\rho)\left(1+\rho+\frac{\rho^2}{2}\right)\right]\\
&=\frac{\exp(-\rho)}{\rho^3}\begin{pmatrix} \hfill 2\rho+\ 2\rho^2 \\ -\frac{1}{4}-\frac{1}{2}\rho \hfill \\ +\frac{1}{2}-\frac{1}{2}\rho \hfill \\ -\frac{1}{8}-\frac{1}{4}\rho-\frac{1}{4}\rho^2 \\ +\frac{1}{2}-\frac{1}{2}\rho+\frac{1}{4}\rho^2 \end{pmatrix}+\frac{\exp(-3\rho)}{\rho^3}\begin{pmatrix} \frac{1}{4}+\frac{1}{2}\rho \hfill \\ -\frac{1}{2}-\frac{1}{2}\rho \hfill \\ +\frac{1}{8}+\frac{1}{4}\rho+\frac{1}{4}\rho^2 \\ -\frac{1}{2}-\frac{1}{2}\rho-\frac{1}{4}\rho^2 \end{pmatrix}\\
&=\frac{\exp(-\rho)}{\rho^3}\left(\frac{5}{8}+\frac{1}{4}\rho+2\rho^2\right)+\frac{\exp(-3\rho)}{\rho^3}\left(-\frac{5}{8}-\frac{1}{4}\rho\right)
\end{aligned}
$$

so that we finally obtain:

$$
(ab|b^2)=\frac{c}{\rho}\left\{\exp(-\rho)\left(\frac{5}{16}+\frac{1}{8}\rho+\rho^2\right)-\exp(-3\rho)\left(\frac{5}{16}+\frac{1}{8}\rho\right)\right\}. \tag{73}
$$

For $c=1$, $\rho=R$:

$$
(ab|b^2)=\frac{\exp(-R)}{R}\left(\frac{5}{16}+\frac{1}{8}R+R^2\right)-\frac{\exp(-3R)}{R}\left(\frac{5}{16}+\frac{1}{8}R\right). \tag{74}
$$

The hybrid integral over $1s$ STOs is a pure charge-overlap term.

(iii) Exchange.

This rather difficult integral can be evaluated in two steps: (i) by finding first the 2-centre *exchange* potential at $\mathbf{r}_1$ due to the density $\{a(\mathbf{r}_2)b(\mathbf{r}_2)\}$, which requires calculation of three characteristic parametric integrals depending on the variable μ (Tauber, 1958), (ii) then followed by a repeated partial integration over this variable to get the final result. Therefore:

$$(\overset{1}{ab} \mid \overset{2}{ab}) = \int d\mathbf{r}_1 K_{ab}(\mathbf{r}_1)\{a(\mathbf{r}_1)b(\mathbf{r}_1)\} \tag{75}$$

$$K_{ab}(\mathbf{r}_1) = \int d\mathbf{r}_2 \frac{a(\mathbf{r}_2)b(\mathbf{r}_2)}{r_{12}} \quad \text{2-centre exchange potential at } \mathbf{r}_1. \tag{76}$$

Expanding $1/r_{12}$ in spheroidal coordinates (*real* form) according to Neumann (1887) gives:

$$\frac{1}{r_{12}} = \frac{2}{R}\sum_{l=0}^{\infty}\sum_{m=0}^{l} D_{lm} Q_l^m(\mu_>) P_l^m(\mu_<) P_l^m(\nu_1) P_l^m(\nu_2) \cos m(\varphi_1 - \varphi_2) \tag{77}$$

$$D_{lm} = (-1)^m 2(2l+1)\left\{\frac{(l-m)!}{(l+m)!}\right\}^2 \quad m > 0, \qquad D_{l0} = 2l+1 \quad m = 0, \tag{78}$$

where P_l^m, Q_l^m are associated Legendre functions of first and second kind (Hobson, 1965), respectively. For spherical 1*s* AOs with *equal* orbital exponent, only the terms $l = 0, 2$ survive upon integration over φ_2 (that gives 2π for $m = 0$, zero otherwise), so that after integration over ν_2 the series truncates to:

$$\begin{aligned} K_{ab}(\mathbf{r}_1) = \frac{4}{R}\left(\frac{\rho}{2}\right)^3 \Bigg\{ & \int_1^{\infty} d\mu_2 \exp(-\rho\mu_2)\left(2\mu_2^2 - \frac{2}{3}\right) Q_0(\mu_>) \\ & - \frac{4}{3} P_2(\nu_1) \int_1^{\infty} d\mu_2 \exp(-\rho\mu_2) Q_2(\mu_>) P_2(\mu_<) \Bigg\}, \end{aligned} \tag{79}$$

where:

$$Q_0(x) = \frac{1}{2}\ln\frac{x+1}{x-1}, \qquad Q_2(x) = P_2(x)Q_0(x) - \frac{3}{2}P_1(x) \tag{80}$$

$$P_1(x) = x, \qquad P_2(x) = \frac{3x^2 - 1}{2}. \tag{81}$$

Splitting the integration range over μ_2 in two regions (Figure 13.5):

Figure 13.5 The two regions occurring in the integration over μ_2.

the exchange potential (which has cylindrical symmetry) can be written as ($\mu_1 = \mu$, $\nu_1 = \nu$):

$$K_{ab}(\mu, \nu) = \frac{16}{3R}\left(\frac{\rho}{2}\right)^3 [A(\mu) - P_2(\nu)B(\mu)], \tag{82}$$

where:

$$A(\mu) = Q_0(\mu)I_2(\mu) + K_2(\mu) \tag{83}$$

$$B(\mu) = Q_2(\mu)I_2(\mu) + P_2(\mu)K_2(\mu) - \frac{3}{2}J_1(\mu)P_2(\mu) \tag{84}$$

having defined (Tauber, 1958):

$$I_n(\mu) = \int_1^{\mu} dx \exp(-\rho x) P_n(x) \tag{85}$$

$$J_n(x) = \int_{\mu}^{\infty} dx \exp(-\rho x) P_n(x) \tag{86}$$

$$K_n(x) = \int_{\mu}^{\infty} dx \exp(-\rho x) P_n(x) Q_0(x). \tag{87}$$

Integration by parts gives for the integrals of interest:

$$I_2(\mu) = -\frac{\exp(-\rho\mu)}{\rho}\left(\frac{3}{\rho^2} + \frac{3}{\rho}\mu + \frac{3\mu^2 - 1}{2}\right) + \frac{3}{\rho^3}S \tag{88}$$

$$J_1(\mu) = \frac{\exp(-\rho\mu)}{\rho}\left(\frac{1}{\rho} + \mu\right) \tag{89}$$

$$\begin{aligned} K_2(\mu) = {} & -\frac{3}{2\rho^2}\exp(-\rho\mu) - \frac{3}{2\rho^3}S' Ei[-\rho(\mu+1)] + \frac{3}{2\rho^3} S Ei[-\rho(\mu-1)] \\ & + \frac{\exp(-\rho\mu)}{\rho} Q_0(\mu)\left(\frac{3}{\rho^2} + \frac{3}{\rho}\mu + \frac{3\mu^2 - 1}{2}\right), \end{aligned} \tag{90}$$

where:

$$\begin{aligned} S &= S(\rho) = \exp(-\rho)\left(1 + \rho + \frac{\rho^2}{3}\right), \\ S' &= S(-\rho) = \exp(\rho)\left(1 - \rho + \frac{\rho^2}{3}\right) \end{aligned} \tag{91}$$

$$Ei(-x) = -\int_x^{\infty} dt \frac{\exp(-t)}{t} = -E_1(x) \qquad \frac{dEi(-x)}{dx} = \frac{\exp(-x)}{x} \tag{92}$$

the exponential integral function (Abramowitz and Stegun, 1965):

$$\gamma = \lim_{x \to 0} \{-\ln x + Ei(-x)\} = 0.577\,215\,665 \cdots \quad \text{Euler's constant.}$$

Introducing the expression for the exchange potential in the exchange integral (75) we obtain, upon integration over angle φ and noting that $\int_{-1}^{1} d\nu P_2(\nu) = 0$:

$$\begin{aligned}
(ab|ab) &= \frac{c^3}{\pi}\left(\frac{R}{2}\right)^3 2\pi \frac{16}{3R}\left(\frac{\rho}{2}\right)^3 \int_{-1}^{1} d\nu \int_{1}^{\infty} d\mu (\mu^2 - \nu^2) \\
&\quad \times [A(\mu) - P_2(\nu) B(\mu)] \exp(-\rho\mu) \\
&= \frac{\rho^6}{6R}\left\{ \int_{-1}^{1} d\nu \int_{1}^{\infty} d\mu \exp(-\rho\mu) \mu^2 A(\mu) \right. \\
&\quad - \int_{-1}^{1} d\nu \nu^2 \int_{1}^{\infty} d\mu \exp(-\rho\mu) A(\mu) \\
&\quad - \int_{-1}^{1} d\nu P_2(\nu) \int_{1}^{\infty} d\mu \exp(-\rho\mu) \mu^2 B(\mu) \\
&\quad \left. + \int_{-1}^{1} d\nu P_2(\nu) \nu^2 \int_{1}^{\infty} d\mu \exp(-\rho\mu) B(\mu) \right\} \\
&= \frac{\rho^6}{6R}\left\{ 2 \int_{1}^{\infty} d\mu \exp(-\rho\mu) \left(\mu^2 - \frac{1}{3}\right) A(\mu) \right. \\
&\quad \left. + \int_{-1}^{1} d\nu P_2(\nu) \left[\frac{2}{3} P_2(\nu) + \frac{1}{3} P_0(\nu)\right] \int_{1}^{\infty} d\mu \exp(-\rho\mu) B(\mu) \right\} \\
&= \frac{\rho^6}{3R}\left\{ \int_{1}^{\infty} d\mu \exp(-\rho\mu) \frac{2}{3} P_2(\mu) A(\mu) + \frac{1}{3} \cdot \frac{2}{5} \int_{1}^{\infty} d\mu \exp(-\rho\mu) B(\mu) \right\} \\
&= \frac{2}{45} \frac{\rho^6}{R} \int_{1}^{\infty} d\mu \exp(-\rho\mu) \{5 P_2(\mu) A(\mu) + B(\mu)\} \\
&= \frac{2}{45} \frac{\rho^6}{R} \int_{1}^{\infty} d\mu \exp(-\rho\mu) \left\{ 6 P_2 (K_2 + I_2 Q_0) - \frac{3}{2} (P_1 I_2 + J_1 P_2) \right\}. \qquad (93)
\end{aligned}$$

Repeated integration by parts then gives:

$$\int_1^\infty d\mu \exp(-\rho\mu)(P_1 I_2 + J_1 P_2) \qquad \text{factor } -\frac{3}{2}$$
$$= \frac{\exp(-2\rho)}{\rho^5}\left(\frac{15}{8} + \frac{15}{4}\rho + 3\rho^2 + \rho^3\right)$$

$$\int_1^\infty d\mu \exp(-\rho\mu) P_2(K_2 + I_2 Q_0) \qquad \text{factor } +6 \tag{94}$$
$$= \frac{\exp(-2\rho)}{\rho^5}\left(\frac{45}{16} - \frac{27}{8}\rho - \frac{3}{2}\rho^2\right)$$
$$+ \frac{9}{2\rho^6}\left\{S^2(\gamma + \ln\rho) + S'^2 Ei(-4\rho) - 2SS' Ei(-2\rho)\right\}. \qquad \text{logarithmic part}$$

Collecting all terms altogether we finally obtain:

$$(ab|ab) = \frac{c}{5}\left\{\exp(-2\rho)\left(\frac{25}{8} - \frac{23}{4}\rho - 3\rho^2 - \frac{1}{3}\rho^3\right) + \frac{6}{\rho}\left[S^2(\gamma + \ln\rho) + S'^2 Ei(-4\rho) - 2SS' Ei(-2\rho)\right]\right\} \tag{95}$$

which, for $c = 1$, $\rho = R$, coincides with the result first given by Sugiura (1927).

An alternative, more general, way of evaluating the exchange integral was suggested by Rosen (1931) in terms of the generalized double integral:

$$H_l(m, n, \rho) = H_l(n, m, \rho)$$
$$= \int_1^\infty d\mu_1 \int_1^\infty d\mu_2 \exp[-\rho(\mu_1 + \mu_2)]\mu_1^m \mu_2^n Q_l(\mu_>) P_l(\mu_<). \tag{96}$$

This method can be easily extended to calculations involving James–Coolidge or Kołos–Wolniewicz wavefunctions and is suitable for implementation on electronic computers. A further generalization is due to Ruedenberg (1951), and will be recalled later on in Section 13.8.

13.7.3 Limiting Values of 2-Centre Integrals

All 2-centre integrals for H_2 we saw so far go to zero as $\rho \to \infty$. In the limit of the united atom ($\rho \to 0$), we shall give for completeness the coefficients of the non-vanishing terms going to zero as ρ^2. We shall use the small ρ-expansions for exponential and exponential integral functions (Abramowitz and Stegun, 1965):

$$\exp(-x) \approx 1 - x + \frac{1}{2}x^2 - \frac{1}{6}x^3 + \frac{1}{24}x^4 \tag{97}$$

$$Ei(-x) \approx (\gamma + \ln x) + \left(-x + \frac{1}{4}x^2 - \frac{1}{18}x^3 + \frac{1}{96}x^4\right). \tag{98}$$

To illustrate how the calculation must be organized, we shall give the example of the 2-electron Coulomb integral $(a^2|b^2)$, while the more difficult 2-electron exchange integral $(ab|ab)$ will be treated in detail.

In the first case, we have the multiplication table:

$$\begin{array}{rrrrrl}
1- & 2\rho+ & 2\rho^2- & \frac{4}{3}\rho^3+ & \frac{2}{3}\rho^4 & \qquad \exp(-2\rho) \\
1+ & \frac{11}{8}\rho+ & \frac{3}{4}\rho^2+ & \frac{1}{6}\rho^3 & & \\
\hline
1- & 2\rho+ & 2\rho^2- & \frac{4}{3}\rho^3+ & \frac{2}{3}\rho^4 & \\
 & +\frac{11}{8}\rho- & \frac{11}{4}\rho^2+ & \frac{11}{4}\rho^3- & \frac{11}{6}\rho^4 & \\
 & & +\ \frac{3}{4}\rho^2- & \frac{3}{2}\rho^3+ & \frac{3}{2}\rho^4 & \\
 & & & +\ \frac{1}{6}\rho^3- & \frac{1}{3}\rho^4 & \\
\hline
1- & \frac{5}{8}\rho & \cdot & +\frac{1}{12}\rho^3 & \cdot &
\end{array} \tag{99}$$

We then have:

$$\begin{aligned}
&1 - \exp(-2\rho)\left(1 + \frac{11}{8}\rho + \frac{3}{4}\rho^2 + \frac{1}{6}\rho^3\right) \\
&\quad \approx 1 - \left(1 - \frac{5}{8}\rho + \frac{1}{12}\rho^3\right) = \rho\left(\frac{5}{8} - \frac{1}{12}\rho^2\right)
\end{aligned} \tag{100}$$

finally giving:

$$(a^2|b^2) \approx \frac{c}{\rho} \cdot \rho\left(\frac{5}{8} - \frac{1}{12}\rho^2\right) = c\left(\frac{5}{8} - \frac{1}{12}\rho^2\right), \tag{101}$$

where the Coulomb singularity was cancelled by the expansion.

For the 2-electron exchange integral, we have similarly:

$$\begin{array}{rrrrrl}
1- & 2\rho+ & 2\rho^2- & \frac{4}{3}\rho^3+ & \frac{2}{3}\rho^4 & \qquad \exp(-2\rho)\\
\frac{25}{8}- & \frac{23}{4}\rho- & 3\rho^2- & \frac{1}{3}\rho^3 & & \\
\cline{1-5}
\frac{25}{8}- & \frac{25}{4}\rho+ & \frac{25}{4}\rho^2- & \frac{25}{6}\rho^3+ & \frac{25}{12}\rho^4 & \\
- & \frac{23}{4}\rho+ & \frac{23}{2}\rho^2- & \frac{23}{2}\rho^3+ & \frac{23}{3}\rho^4 & \\
 & - & 3\rho^2+ & 6\rho^3- & 6\rho^4 & \\
 & & - & \frac{1}{3}\rho^3+ & \frac{2}{3}\rho^4 & \\
\cline{1-5}
\frac{25}{8} & -\;12\rho+ & \frac{59}{4}\rho^2- & 10\rho^3+ & \frac{53}{12}\rho^4 &
\end{array} \tag{102}$$

as the expansion for the first analytic term of equation (95).

For the logarithmic part (non-analytic at $R = 0$), we now expand each individual term inside the square bracket of (95). We give below only the expansion for S^2, which is seen to be equal to the expansions for S'^2 and SS':

$$\begin{array}{rrrrrl}
1-2\rho+ & 2\rho^2- & \frac{4}{3}\rho^3+ & \frac{2}{3}\rho^4 & & \qquad \exp(-2\rho)\\
1+2\rho+ & \frac{5}{3}\rho^2+ & \frac{2}{3}\rho^3+ & \frac{1}{9}\rho^4 & & \\
\cline{1-4}
1-2\rho+ & 2\rho^2- & \frac{4}{3}\rho^3+ & \frac{2}{3}\rho^4 & & \\
+2\rho- & 4\rho^2+ & 4\rho^3- & \frac{8}{3}\rho^4 & & \\
+ & \frac{5}{3}\rho^2- & \frac{10}{3}\rho^3+ & \frac{10}{3}\rho^4 & & \\
 & + & \frac{2}{3}\rho^3- & \frac{4}{3}\rho^4 & & \\
 & & + & \frac{1}{9}\rho^4 & & \\
\cline{1-4}
1\quad\cdot\quad- & \frac{1}{3}\rho^2 & \cdot\quad + & \frac{1}{9}\rho^4 & \multicolumn{2}{l}{\approx S^2 = S'^2 = SS'.}
\end{array} \tag{103}$$

Next, using expansion (98) for the exponential integral functions:

$$Ei(-2\rho) \approx (\gamma + \ln 2\rho) + \left(-2\rho + \rho^2 - \frac{4}{9}\rho^3 + \frac{1}{6}\rho^4\right)$$

$$Ei(-4\rho) \approx (\gamma + \ln 4\rho) + \left(-4\rho + 4\rho^2 - \frac{32}{9}\rho^3 + \frac{8}{3}\rho^4\right)$$

we obtain:

$$S^2(\gamma + \ln \rho) \approx (\gamma + \ln \rho)\left(1 - \frac{1}{3}\rho^2 + \frac{1}{9}\rho^4\right)$$

$$\begin{aligned} S'^2 Ei(-4\rho) &\approx (\gamma + \ln 4\rho)\left(1 - \frac{1}{3}\rho^2 + \frac{1}{9}\rho^4\right) + \left(-4\rho + 4\rho^2 - \frac{20}{9}\rho^3 + \frac{4}{3}\rho^4\right) \\ &- 2SS'Ei(-2\rho) \approx (\gamma + \ln 2\rho)\left(-2 + \frac{2}{3}\rho^2 - \frac{2}{9}\rho^4\right) \\ &+ \left(4\rho - 2\rho^2 - \frac{4}{9}\rho^3 + \frac{2}{3}\rho^4\right). \end{aligned} \tag{104}$$

By adding all such terms we see that the logarithmic parts cancel altogether:

$$\begin{aligned} &S^2(\gamma + \ln \rho) + S'^2 Ei(-4\rho) - 2SS'Ei(-2\rho) \\ &\quad \approx (\gamma + \ln \rho) + (\gamma + \ln \rho + \ln 4) - 2(\gamma + \ln \rho + \ln 2) \\ &\quad + \left(2\rho^2 - \frac{8}{3}\rho^3 + 2\rho^4\right) = 2\rho^2\left(1 - \frac{4}{3}\rho + \rho^2\right), \end{aligned}$$

so that we obtain for the terms in brackets in (95):

$$\begin{aligned} \{\cdots\} &\approx \left(\frac{25}{8} - 12\rho + \frac{59}{4}\rho^2 - 10\rho^3 + \frac{53}{12}\rho^4\right) + 12\rho\left(1 - \frac{4}{3}\rho + \rho^2\right) \\ &= \frac{25}{8} - \frac{5}{4}\rho^2 + 2\rho^3, \end{aligned} \tag{105}$$

finally giving as limiting value for the 2-electron exchange integral:

$$(ab|ab) \approx c\left(\frac{5}{8} - \frac{1}{4}\rho^2\right). \tag{106}$$

The limiting values of the remaining integrals are:

$$
\begin{aligned}
&S(\rho)=S(-\rho)\approx 1-\frac{1}{6}\rho^2\\
&\left(ab|r_B^{-1}\right)\approx c\left(1-\frac{1}{2}\rho^2\right)\\
&\left(a^2|r_B^{-1}\right)\approx c\left(1-\frac{2}{3}\rho^2\right)\\
&(ab|\nabla^2)\approx -c^2\left(1-\frac{5}{6}\rho^2\right)\\
&(ab|b^2)\approx c\left(\frac{5}{8}-\frac{7}{48}\rho^2\right).
\end{aligned}
\tag{107}
$$

13.8 ON THE GENERAL FORMULAE FOR 2-CENTRE INTEGRALS

General formulae for 1- and 2-electron 2-centre integrals over STOs were obtained by us by generalizing the techniques described in the previous Sections. All expressions were tested (i) with the similar results by Roothaan (1951b), and (ii) by numerical computations based on use of the Mathematica software or by the QCPE program DERIC[2].

Figure 13.6 gives the coordinate systems used by us (Roothaan) and by DERIC (James-Coolidge). Roothaan uses *two* Cartesian coordinate systems, one right-handed centred at A, the other left-handed centred at B, while DERIC uses a *unique* reference system centred at A (James and Coolidge, 1933). Great care is needed in choosing the correct sign resulting for integrals involving $2p\sigma$ functions when comparing results from different sources.

13.8.1 Spheroidal Coordinates

Compact analytical formulae for 1- and 2-electron 2-centre integrals over *complex* STOs were recently derived by our group (Casanova, 1997; Magnasco et al., 1998) after expressing in spheroidals the charge distributions on the two centres (see Wahl et al., 1964). 1-electron integrals can all be expressed in terms of the auxiliary functions T_{jm} and G_{jm}, while Coulomb, hybrid and exchange 2-electron integrals are described by a unified formula containing the two functions B_{lj}^{m} and H_{lmpq} introduced by Ruedenberg (1951). The accuracy in the value of these integrals depends on the accuracy with which such auxiliary functions are calculated.

The *generalized auxiliary functions* are defined as:

$$
T_{jm}(\rho)=\int_1^\infty dx\,x^j(x^2-1)^m\exp(-\rho x)
\tag{108}
$$

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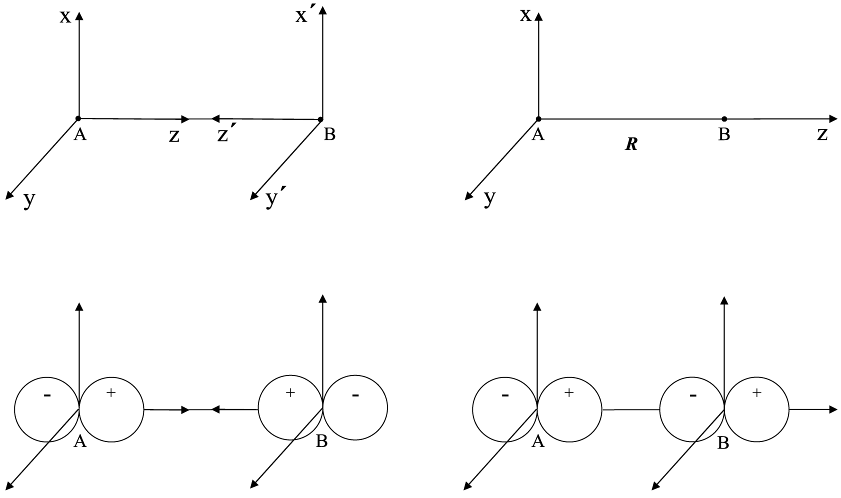
[2] DERIC (Diatomic Electron Repulsion Integral Code), N. 252 of the Quantum Chemistry Program Exchange (QCPE) of the Indiana University (Hagstrom, 1974). The program evaluates 1-electron integrals as well.



Roothaan

James-Coolidge

Figure 13.6 Reference systems for the calculation of 2-centre molecular integrals.

$$G_{jm}(\rho) = \int_{-1}^{1} dx\, x^j (1 - x^2)^m \exp(-\rho x) \tag{109}$$

$$B_{lj}^m(\rho) = \int_{-1}^{1} dx\, x^j (1 - x^2)^m \mathcal{P}_l^m(x) \exp(-\rho x) \tag{110}$$

$$\begin{aligned} H_{lmpq}(\rho_1, \rho_2) = \int_1^\infty dx \int_1^\infty & dy\, x^p y^q [(x^2 - 1)(y^2 - 1)]^{m/2} \\ & \times \mathcal{Q}_l^m(x_>) \mathcal{P}_l^m(x_<) \exp(-\rho_1 x) \exp(-\rho_2 y), \end{aligned} \tag{111}$$

where j, l, m, p, q are non-negative integers, $Re(\rho) > 0$, and $\mathcal{P}_l^m$, $\mathcal{Q}_l^m$ *normalized* associated Legendre functions of first and second kind (Hobson, 1965), respectively. T_{jm} and G_{jm} are generalizations of the elementary auxiliary functions $A_j(\rho)$ and $B_j(\rho)$, defined in equations (8) and (11), while (110) and (111) are defined by Ruedenberg (1951), (111) being a generalization of integral (96) to include order m and different values for ρ_1 and ρ_2. It is easily seen that (108) and (109) can be written as *finite* sums involving A_n and B_n functions:

$$T_{jm}(\rho) = \sum_{k=0}^{m} (-1)^{m+k} \binom{m}{k} A_{j+2k}(\rho) \tag{112}$$

$$G_{jm}(\rho) = \sum_{k=0}^{m} (-1)^k \binom{m}{k} B_{j+2k}(\rho). \tag{113}$$

While evaluation of T_{jm} by equation (112) is straightforward through use of recurrence relations, for some values of the indices j, m G_{jm} is affected by strong numerical instabilities due to cancellation of numbers of similar magnitude. Stability in the calculation of G_{jm} with high numerical accuracy (up to 14–15 figures) is obtained by use of a series expansion of the exponential in (109).

Similar problems were met with the evaluation of (110), and again stable numerical consistency to about 14–15 figures for all values of the indices was achieved by the series expansion of the exponential. The functions H_{lmpq} represent the main time-consuming factor in the calculation of the 2-centre integrals, owing to the considerable difficulty of their accurate evaluation.

We shall not give the final formulae for the 2-centre integrals, full details being found in the original paper[3]. We simply outline here that exchange (resonance) and Laplacian 1-electron integrals are all expressed in terms of suitably scaled overlap integrals, while using the *complex* form of the Neumann expansion (Neumann, 1887) for $\frac{1}{r_{12}}$:

$$\begin{aligned}\frac{1}{r_{12}} = \frac{4}{R} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (-1)^m \frac{(l-m)!}{(l+m)!} \\ \times \mathcal{Q}_l^m(\mu_>) \mathcal{P}_l^m(\mu_<) \mathcal{P}_l^m(\nu_1) \mathcal{P}_l^m(\nu_2) \exp[im(\varphi_1 - \varphi_2)]\end{aligned} \tag{114}$$

a *unified* formula was derived for the general 2-electron integral. Similar formulae for *real* STOs were derived by Yasui and Saika (1982) and Guseinov and Yassen (1995). As a simple example, we give in Problem 13.4 the calculation of the overlap integral (54) from the general formula.

13.8.2 Spherical Coordinates

If a STO on centre B is expressed in spherical coordinates (r, θ, φ) referred to centre A (taken as origin of the coordinate system), one–centre integration over these variables would be straigthforward either for 1-electron or 2-electron integrals. This can be done by an *exact* translation of the regular solid harmonic part of the orbital (Barnett and Coulson, 1951; Löwdin, 1956) followed by the series expansion of the residual spherical part in powers of the radial variable. Using *complex* STOs with their angular part expressed in terms of normalized Racah spherical harmonics with Condon–Shortley phase, this method was successfully tested in high accuracy calculations of overlap (Rapallo, 1997; Magnasco et al., 1999) and 2-centre 2-electron molecular integrals (Magnasco and Rapallo, 2000). Good rate of convergence in the expansion and great numerical stability under wide changes in the molecular parameters (orbital exponents and internuclear distances) was obtained in both cases. The calculation of Coulomb and hybrid integrals is carried out by

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[3] We regret that the CPL (1998) Letter is full of typographical misprints.

means of suitable 1-centre 1-electron potentials, while the exchange integral requires translation of *two* spherical residues, related to *two* displaced orbitals referred to the different electrons, and use of *two* serie expansions. At variance with what we did for H_2 following Tauber, 1-electron potentials were not used in this last case.

Angular coefficients, unique for all 2-centre 2-electron integrals, arise from integration over angular variables, and are expressed in terms of Gaunt coefficients related in turn to Clebsch–Gordan coupling coefficients (see Chapter 9; Brink and Satchler, 1993). They can be stored and re-used during the integral evaluation.

Radial coefficients arise from integration over the radial variable, and are particularly involved for the exchange integral. They need calculation of further auxiliary functions and of E_n, the generalized exponential integral function of order n (Abramowitz and Stegun, 1965):

$$E_n(\rho) = \int_1^\infty dx \exp(-\rho x) x^{-n} \tag{115}$$

with n a non-negative integer and $Re(\rho) > 0$.

High accuracy (10–12 digits) in the final numerical results is achieved through multiple precision arithmetic calculations using recurrence relations and accurate Gaussian integration techniques (Ralston, 1965) to get reliable values for the starting terms of the recursion. This spherical approach seems quite promising for its possible extension to the calculation of multicentre integrals. An alternative way involving spheroidal coordinates is shortly examined in the next Section for $1s$ STOs.

13.9 A SHORT NOTE ON MULTICENTRE INTEGRALS

Multicentre integrals over STOs are very difficult to evaluate for more than two centres. They are the 3-centre 1-electron $(ab|r_C^{-1})$ Coulomb integral, the 3-centre 2-electron Coulomb $(bc|a^2)$ and exchange $(ab|ac)$ integrals, and the 4-centre 2-electron $(ab|cd)$ integral. They are still today the bottleneck of any ab-initio calculation in terms of accurate functions showing correct cusp behaviour and exponential decay. Rather than giving a general survey of the subject, that in recent years enjoyed increased popularity among quantum chemists, we shall treat briefly here in some detail the evaluation of the 3-centre 1-electron integral $(ab|r_C^{-1})$ and of the 4-centre 2-electron integral $(ab|cd)$ when a, b, c, d are $1s$ STOs centred at different nuclei in the molecule. These integrals were evaluated in the early sixties by the pioneering work of the author's group (Magnasco and Dellepiane, 1963, 1964; Musso and Magnasco, 1971) using 3-dimensional numerical integration techniques in spheroidal coordinates following previous work by Magnusson and Zauli (1961). This avoids any convergence problem in the series expansions over the radial variables which are typical of all approaches involving 1-centre expansions in spherical coordinates.

13.9.1 3-Centre 1-Electron Integral over $1s$ STOs

With reference to the right-handed Cartesian system centred at the midpoint of AB (Figure 13.7), centre C is always chosen in the zx-plane, with its position specified by the two

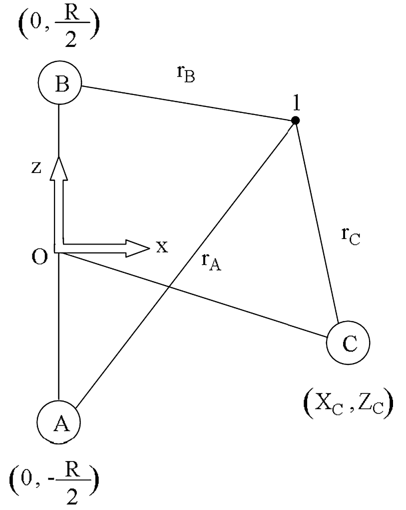

Figure 13.7 Coordinate system for the evaluation of the 3-centre 1-electron integral.

coordinates X_C, Z_C. In the system of confocal spheroidal coordinates μ, ν, φ with foci in A, B, the 3-centre 1-electron integral for two STOs with different orbital exponents c_a and c_b can be written as:

$$\begin{aligned}\left(ab|r_C^{-1}\right) = \frac{(c_a c_b)^{3/2}}{\pi}\left(\frac{R}{2}\right)^2 \int_1^\infty d\mu \int_{-1}^1 d\nu\,(\mu^2-\nu^2) \\ \times \exp\left[-\frac{R}{2}(c_a+c_b)\mu - \frac{R}{2}(c_a-c_b)\nu\right] \\ \times \int_0^{2\pi} d\varphi\big[X_C^2+Z_C^2-1+\mu^2+\nu^2 \\ -2Z_C\mu\nu - 2X_C(\mu^2-1)^{1/2}(1-\nu^2)^{1/2}\cos\varphi\big]^{-1/2}. \qquad (116)\end{aligned}$$

Since the integration variables are not separable, a 3-dimensional integration by the Gauss–Legendre method (Kopal, 1961) was used to get the numerical value of the integral by conveniently choosing the integration points in those regions where the integrand is larger. This allows for a reduction of the number of integration points. Since 3-dimensional integration is today standard with the Mathematica software (Wolfram, 1996), this technique seems quite interesting even today.

13.9.2 4-Centre 2-Electron Integral over 1*s* STOs

With reference to the right-handed Cartesian system centred at the midpoint of AB (Figure 13.8), centre C was chosen in the *zx*-plane, the geometry of the system being

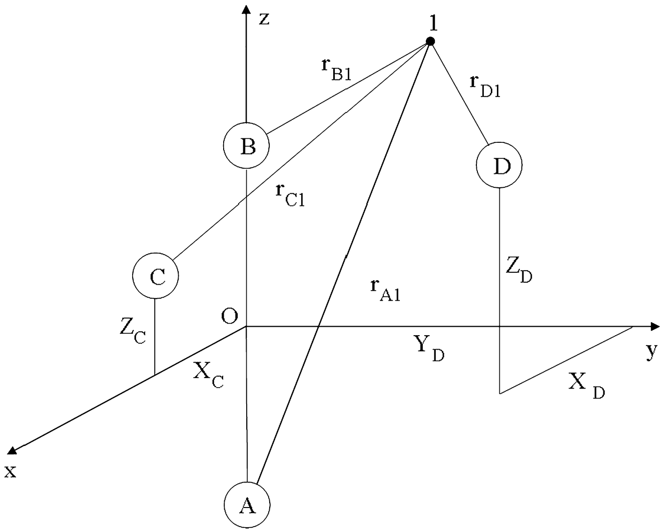

Figure 13.8 Coordinate system for the evaluation of the 4-centre 2-electron integral.

completely specified by giving (in atomic units) the distance R between centres A and B, and the coordinates (units of $R/2$) X_C, Z_C of centre C, and X_D, Y_D, Z_D of centre D. The 4-centre 2-electron integral between $1s$ STOs is then given by:

$$(ab|cd) = \int d\mathbf{r}_2 K_{ab}(\mathbf{r}_2)\{c(\mathbf{r}_2)d(\mathbf{r}_2)\}, \tag{117}$$

where $K_{ab}(\mathbf{r}_2)$ is the 2-centre potential at $\mathbf{r}_2$:

$$K_{ab}(\mathbf{r}_2) = \int d\mathbf{r}_1 \frac{a(\mathbf{r}_1)b(\mathbf{r}_1)}{r_{12}}. \tag{118}$$

When the orbital exponents on centres A and B are the *same* ($c_b = c_a$), this 2-centre potential was already calculated in the case of the 2-centre exchange integral $(ab|ab)$ using Tauber method in equations (79)–(90) of Section 13.7. We thereby obtain for the 4-centre integral:

$$(ab|cd) = (c_c c_d)^{3/2}\frac{R^3}{8\pi}\int_1^\infty d\mu \int_{-1}^1 d\nu\,(\mu^2-\nu^2)K_{ab}(\mu,\nu)$$

$$\times \int_0^{2\pi} d\varphi \exp\left\{-\frac{R}{2}c_c\big[X_C^2 + Z_C^2 - 1 + \mu^2 + \nu^2 - 2Z_C\mu\nu\right.$$

$$\left. - 2X_C(\mu^2-1)^{1/2}(1-\nu^2)^{1/2}\cos\varphi\big]^{1/2}\right.$$

$$
\begin{aligned}
&-\frac{R}{2}c_d\big[X_D^2+Y_D^2+Z_D^2-1+\mu^2+\nu^2-2Z_D\mu\nu \\
&-2(\mu^2-1)^{1/2}(1-\nu^2)^{1/2}(X_D\cos\varphi+Y_D\sin\varphi)\big]^{1/2}\bigg\}. \qquad (119)
\end{aligned}
$$

This integral is again evaluated using 3-dimensional Gauss–Legendre numerical integration, and is obviously more time consuming than integral (116).

When the orbital exponents on A and B are *different* ($c_b \neq c_a$), Tauber method originates for K_{ab} an infinite series expansion in terms of associated Legendre functions of the first and second kind (Hobson, 1965) multiplied by suitable coefficients. In this last case, the 4-centre integral was fully evaluated by Musso and Magnasco (1971) using appropriate recursion formulae for the auxiliary functions. The evaluation of the integral implies now a 4-dimensional numerical integration (a 3-dimensional integration for each term of the series). The convergence of the series was found to be satisfactory as far as accuracy and computing time were concerned. Examples and further details can be found in the original paper.

13.10 PROBLEMS 13

13.1. Give an alternative way of evaluating 2-centre Laplacian integrals over STOs.

Answer:
The result is the same as that obtained by direct use of the Laplacian operator in spheroidals.

Hint:
Use matrix elements of the hydrogenic Hamiltonian and the fact that $1s$ and $2p\sigma$ are eigenfunctions when $Z = c$ and $Z = 2c$, respectively.

13.2. Apply the same technique to the evaluation of the 2-centre Laplacian integral over s STOs.

Answer:

$$
(s_A s_B|\nabla^2) = c^2(s_A s_B|1) - 4c\big(s_A s_B\big|r_A^{-1}\big) + \frac{2\sqrt{3}}{3}c\big(1s_A s_B\big|r_A^{-1}\big) \quad \text{for } c' \neq c.
$$

Hint:
Use a suitable linear combination of s_A and $1s_A$ (*same* orbital exponent c) which is eigenfunction of the hydrogenic Hamiltonian with $Z = 2c$ and eigenvalue $-c^2/2$.

13.3. Evaluate by direct calculation in spheroidals the integral $(2p\sigma_A 2p\sigma'_A|r_B^{-1})$.

Answer:
$c' \neq c$

$$\begin{aligned}
&\big(\underset{c}{2p\sigma_A}\,\underset{c'}{2p\sigma'_A}\,|r_B^{-1}\big)\\
&\quad=\frac{3}{2}(c+c')\left(\frac{2(cc')^{1/2}}{c+c'}\right)^5\frac{1}{\sigma^3}\left\{\left(1+\frac{1}{3}\sigma^2\right)\right.\\
&\qquad\left.-\exp(-2\sigma)\left(1+2\sigma+\frac{7}{3}\sigma^2+\frac{11}{6}\sigma^3+\sigma^4+\frac{1}{3}\sigma^5\right)\right\}
\end{aligned}$$

$c' = c$

$$\begin{aligned}
&\big(2p\sigma_A^2|r_B^{-1}\big)\\
&\quad=3c\frac{1}{\rho^3}\left\{\left(1+\frac{1}{3}\rho^2\right)-\exp(-2\rho)\left(1+2\rho+\frac{7}{3}\rho^2+\frac{11}{6}\rho^3+\rho^4+\frac{1}{3}\rho^5\right)\right\},
\end{aligned}$$

where:

$$\sigma=\frac{c+c'}{2}R, \qquad \rho=cR.$$

Hint:
Express the integrand in spheroidals and use the definitions of the auxiliary functions A_n and B_n.

13.4. Calculate the overlap integral $(1s_A 1s_B|1)$ for $c' = c$ from the general formula given in Magnasco et al. (1998).

Answer:
The same as in equation (54).

Hint:
Identify all necessary parameters, finding the explicit expressions for coefficients, summation limits and integrals $T_{jm}(\rho)$ and $G_{jm}(0)$ for $1s$ STOs as given in Appendix B of that paper.

13.11 SOLVED PROBLEMS

13.1. An alternative way of evaluating 2-centre Laplacian integrals.

An interesting simple way of calculating 2-centre Laplacian integrals over STOs, alternative to the direct calculation of the Laplacian operator in spheroidals, uses the matrix element of the hydrogenic Hamiltonian between AOs which are eigenfunctions of this Hamiltonian with the appropriate nuclear charge Z, say $1s$ and $2p\sigma$ STOs with $Z = c$ and $Z = 2c$, respectively. As the simplest example, let us take the integral:

$$(\underset{c}{1s_A}\,\underset{c'}{1s_B}\,|\nabla^2).$$

We start from the matrix element:

$$\left\langle 1s_B \left| -\frac{1}{2}\nabla^2 - \frac{Z}{r_A} \right| 1s_A \right\rangle$$

and use the fact that $1s_A$ is an *eigenfunction* of the hydrogenic Hamiltonian having $Z = c$ with *eigenvalue* $-c^2/2$:

$$\begin{aligned}\left\langle 1s_B \left| -\frac{1}{2}\nabla^2 - \frac{Z}{r_A} \right| 1s_A \right\rangle &= \left\langle 1s_B \left| \left(-\frac{1}{2}\nabla^2 - \frac{c}{r_A}\right) + (c-Z)\frac{1}{r_A} \right| 1s_A \right\rangle \\ &= -\frac{c^2}{2}(1s_A 1s_B|1) + (c-Z)\big(1s_A 1s_B\big|r_A^{-1}\big)\end{aligned}$$

giving, after simplification and multiplication by -2:

$$\big(1s_A 1s_B\big|\nabla^2\big) = c^2(1s_A 1s_B|1) - 2c\big(1s_A 1s_B\big|r_A^{-1}\big).$$

The Laplacian integral is hence expressible in terms of the overlap and the Coulomb integrals involving the same density $\{1s_A(\mathbf{r})1s_B(\mathbf{r})\}$.

If $c' = c$:

$$(1s_A 1s_B|1) = \exp(-\rho)\left(1 + \rho + \frac{1}{3}\rho^2\right)$$

$$\big(1s_A 1s_B\big|r_A^{-1}\big) = c\exp(-\rho)(1+\rho)$$

giving:

$$\begin{aligned}\big(\underset{c}{1s_A}\,\underset{c'}{1s_B}\,\big|\nabla^2\big) &= c^2\exp(-\rho)\begin{pmatrix} 1 + \;\rho + \frac{1}{3}\rho^2 \\ -2 - 2\rho \end{pmatrix} \\ &= c^2\exp(-\rho)\left(-1 - \rho + \frac{1}{3}\rho^2\right)\end{aligned}$$

which coincides with our previous result (66).

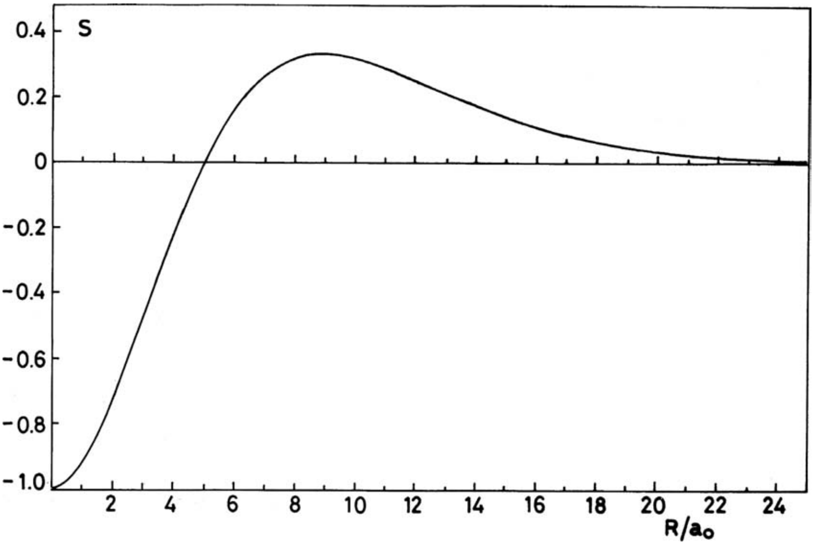

Figure 13.9 Plot of $(2p\sigma_A 2p\sigma_B|1)$ vs R for $c = 0.5$.

The same can be easily done for the integral $(2p\sigma_A 2p\sigma_B|\nabla^2)$, obtaining the result:

$$c' \neq c$$

$$\left(2p\sigma_A 2p\sigma_B\middle|\nabla^2\right) = c^2(2p\sigma_A 2p\sigma_B|1) - 4c\left(2p\sigma_A 2p\sigma_B\middle|r_A^{-1}\right)$$

$$c' = c$$

$$(2p\sigma_A 2p\sigma_B|1) = -\exp(-\rho)\left(1 + \rho + \frac{1}{5}\rho^2 - \frac{2}{15}\rho^3 - \frac{1}{15}\rho^4\right)$$

$$(2p\sigma_A 2p\sigma_B|r_A^{-1}) = -\frac{c}{2}\exp(-\rho)\left(1 + \rho - \frac{1}{3}\rho^3\right)$$

giving:

$$(2p\sigma_A 2p\sigma_B|\nabla^2) = c^2\exp(-\rho)\left(1 + \rho - \frac{1}{5}\rho^2 - \frac{8}{15}\rho^3 + \frac{1}{15}\rho^4\right).$$

The overlap integral $(2p\sigma_A 2p\sigma_B|1)$ is plotted vs R in Figure 13.9 for $c = 0.5$. It is seen that S is negative up to $R \approx 5a_0$, then becomes positive with a maximum at about $R = 9a_0$, then goes asymptotically to zero from above.

13.2. Evaluation of $(s_A s_B|\nabla^2)$ by the alternative method.

The same method cannot be applied directly to the integral:

$$(\underset{c}{s_A}\,\underset{c'}{s_B}\,|\nabla^2)$$

since the $2s$ STO s_A is *not* an eigenfunction of the appropriate hydrogenic Hamiltonian. We notice however that the normalized linear combination (*same* orbital exponent c):

$$2s_A = 1s_A - \sqrt{3}s_A$$

is an eigenfunction of the hydrogenic Hamiltonian with $Z = 2c$ and eigenvalue $-c^2/2$. In fact (same c, $S = \sqrt{3}/2$):

$$\begin{aligned}
h_{2s2s} &= \left\langle 1s - \sqrt{3}s \left| -\frac{1}{2}\nabla^2 - \frac{Z}{r} \right| 1s - \sqrt{3}s \right\rangle = h_{1s1s} + 3h_{ss} - 2\sqrt{3}h_{s1s} \\
&= \left(\frac{c^2}{2} - Zc\right) + 3\left(\frac{c^2}{6} - \frac{1}{2}Zc\right) - \frac{2\sqrt{3}}{3}S\left[2c(c-Z) - \frac{3}{2}c^2\right] \\
&= \frac{1}{2}(c^2 - Zc)
\end{aligned}$$

which, for $Z = 2c$, gives:

$$h_{2s2s} = \frac{1}{2}(c^2 - 2c^2) = -\frac{c^2}{2}.$$

Therefore, we can express the STO s_A through the *inverse* transformation:

$$s_A = \frac{1}{\sqrt{3}}(1s_A - 2s_A)$$

as a linear combination of *two* eigenfunctions of the hydrogenic Hamiltonian. We then have:

$$\begin{aligned}
\left\langle \underset{c'}{s_B} \left| -\frac{1}{2}\nabla^2 - \frac{Z}{r_A} \right| \underset{c}{s_A} \right\rangle &= \left\langle s_B \left| -\frac{1}{2}\nabla^2 - \frac{Z}{r_A} \right| \frac{1s_A - 2s_A}{\sqrt{3}} \right\rangle \\
&= \frac{1}{\sqrt{3}} \left\{ \left\langle s_B \left| \left(-\frac{1}{2}\nabla^2 - \frac{c}{r_A}\right) + (c - Z)\frac{1}{r_A} \right| 1s_A \right\rangle \right. \\
&\quad \left. - \left\langle s_B \left| \left(-\frac{1}{2}\nabla^2 - \frac{2c}{r_A}\right) + (2c - Z)\frac{1}{r_A} \right| 2s_A \right\rangle \right\} \\
&= \frac{1}{\sqrt{3}} \left\{ -\frac{c^2}{2}(1s_A s_B|1) + (c - Z)\big(1s_A s_B\big|r_A^{-1}\big) \right. \\
&\quad \left. - \left[-\frac{c^2}{2}(2s_A s_B|1) + (2c - Z)\big(2s_A s_B\big|r_A^{-1}\big) \right] \right\}.
\end{aligned}$$

The last term can be rearranged to:

$$\frac{c^2}{2}\left[(1s_As_B|1)-\sqrt{3}(s_As_B|1)\right]-(2c-Z)\left[\left(1s_As_B\middle|r_A^{-1}\right)-\sqrt{3}\left(s_As_B\middle|r_A^{-1}\right)\right]$$

giving, upon substitution and simplification:

$$\begin{aligned}\left\langle s_B\middle|-\frac{1}{2}\nabla^2-\frac{Z}{r_A}\middle|s_A\right\rangle &= -\frac{c^2}{2}(s_As_B|1)+(2c-Z)\left(s_As_B\middle|r_A^{-1}\right)\\ &\quad -\frac{\sqrt{3}}{3}c\left(1s_As_B\middle|r_A^{-1}\right)\end{aligned}$$

from which it follows:

$$\left(s_As_B|-\frac{1}{2}\nabla^2\right)=-\frac{c^2}{2}(s_As_B|1)+2c\left(s_As_B\middle|r_A^{-1}\right)-\frac{\sqrt{3}}{3}c\left(1s_As_B\middle|r_A^{-1}\right).$$

Hence we finally obtain:

$$(\underset{c}{s_A}\,\underset{c'}{s_B}\,|\nabla^2)=c^2(s_As_B|1)-4c\left(s_As_B\middle|r_A^{-1}\right)+\frac{2\sqrt{3}}{3}c\left(1s_As_B\middle|r_A^{-1}\right).$$

For $c'=c$:

$$(s_As_B|1)=\exp(-\rho)\left(1+\rho+\frac{4}{9}\rho^2+\frac{1}{9}\rho^3+\frac{1}{45}\rho^4\right)$$

$$\left(s_As_B\middle|r_A^{-1}\right)=\frac{c}{2}\exp(-\rho)\left(1+\rho+\frac{4}{9}\rho^2+\frac{1}{9}\rho^3\right)$$

$$\left(1s_As_B\middle|r_A^{-1}\right)=\frac{\sqrt{3}}{3}c\exp(-\rho)\left(1+\rho+\frac{2}{3}\rho^2\right)$$

and, adding the three terms altogether:

$$\begin{aligned}(s_As_B|\nabla^2)&=\frac{1}{3}c^2\exp(-\rho)\begin{pmatrix} \quad 3+3\rho+\frac{4}{3}\rho^2+\frac{1}{3}\rho^3+\frac{1}{15}\rho^4\\ -6-6\rho-\frac{8}{3}\rho^2-\frac{2}{3}\rho^3\\ +2+2\rho+\frac{4}{3}\rho^2\end{pmatrix}\\ &=\frac{1}{3}c^2\exp(-\rho)\left(-1-\rho-\frac{1}{3}\rho^3+\frac{1}{15}\rho^4\right)\end{aligned}$$

which is the result given by Roothaan (1951b).

13.3. Direct evaluation of $(2p\sigma_A 2p\sigma'_A|r_B^{-1})$.

There is no difficulty in evaluating this integral in spheroidals, but it is of some interest to see how to organize the computations in such a rather heavy case.

$$
\begin{aligned}
&\big(\underset{c}{2p\sigma_A}\,\underset{c'}{2p\sigma'_A}\,|r_B^{-1}\big)\\
&= \frac{(cc')^{5/2}}{\pi}\int d\mathbf{r}\frac{1}{r_B}\cdot z_A\exp(-cr_A)\cdot z_A\exp(-c'r_A)\\
&= \frac{(cc')^{5/2}}{\pi}\left(\frac{R}{2}\right)^3 2\pi\int_{-1}^{1}d\nu\int_{1}^{\infty}d\mu\frac{\mu^2-\nu^2}{\frac{R}{2}(\mu-\nu)}\cdot\frac{R}{2}(1+\mu\nu)\\
&\quad\times\exp\left[-c\frac{R}{2}(\mu+\nu)\right]\frac{R}{2}(1+\mu\nu)\exp\left[-c'\frac{R}{2}(\mu+\nu)\right]\\
&= 2(cc')^{5/2}\left(\frac{R}{2}\right)^4\int_{-1}^{1}d\nu\int_{1}^{\infty}d\mu(1+\mu\nu)^2(\mu+\nu)\exp(-\sigma\mu)\exp(-\sigma\nu)\\
&= 2(cc')^{5/2}\left(\frac{R}{2}\right)^4\int_{-1}^{1}d\nu\int_{1}^{\infty}d\mu\{\nu+\mu(1+2\nu^2)+\mu^2(2\nu+\nu^3)+\mu^3\nu^2\}\\
&\quad\times\exp(-\sigma\mu)\exp(-\sigma\nu)\\
&= 2(cc')^{5/2}\left(\frac{R}{2}\right)^4\{A_0(\sigma)B_1(\sigma)+A_1(B_0+2B_2)+A_2(2B_1+B_3)+A_3B_2\}\\
&= 48(cc')^{5/2}\left(\frac{R}{2}\right)^4\frac{1}{\sigma^7}\left\{\left(1+\frac{1}{3}\sigma^2\right)\right.\\
&\quad\left.-\exp(-2\sigma)\left(1+2\sigma+\frac{7}{3}\sigma^2+\frac{11}{6}\sigma^3+\sigma^4+\frac{1}{3}\sigma^5\right)\right\}\\
&= \frac{3}{2}(c+c')\left(\frac{2(cc')^{1/2}}{c+c'}\right)^5\\
&\quad\times\frac{1}{\sigma^3}\left\{\left(1+\frac{1}{3}\sigma^2\right)-\exp(-2\sigma)\left(1+2\sigma+\frac{7}{3}\sigma^2+\frac{11}{6}\sigma^3+\sigma^4+\frac{1}{3}\sigma^5\right)\right\}
\end{aligned}
$$

since:

$$
\sigma=\frac{c+c'}{2}R,\qquad \frac{R}{2}=\frac{\sigma}{c+c'}
$$

$$
\left(\frac{R}{2}\right)^4=\frac{\sigma^4}{(c+c')^4}=(c+c')\frac{\sigma^4}{(c+c')^5}
$$

$$
48(cc')^{5/2}\left(\frac{R}{2}\right)^4=\frac{3}{2}(c+c')\left(\frac{2(cc')^{1/2}}{c+c'}\right)^5\sigma^4.
$$

The calculation of the different contributions arising from the auxiliary functions can be organized as follows. First we evaluate the contributions of the B-functions:

$$\begin{aligned}
2B_2 + B_0 &= \frac{2\exp(\sigma)}{\sigma^3}[(2 - 2\sigma + \sigma^2) - \exp(-2\sigma)(2 + 2\sigma + \sigma^2)] \\
&\quad + \frac{2\exp(\sigma)}{\sigma^3}\left(\frac{1}{2}\sigma^2 - \exp(-2\sigma)\frac{1}{2}\sigma^2\right) \\
&= \frac{2\exp(\sigma)}{\sigma^3}\left\{\begin{pmatrix} 2 - 2\sigma + & \sigma^2 \\ & +\dfrac{1}{2}\sigma^2 \end{pmatrix} - \exp(-2\sigma)\begin{pmatrix} 2 + 2\sigma + & \sigma^2 \\ & +\dfrac{1}{2}\sigma^2 \end{pmatrix}\right\} \\
&= \frac{2\exp(\sigma)}{\sigma^3}\left\{\left(2 - 2\sigma + \frac{3}{2}\sigma^2\right) - \exp(-2\sigma)\left(2 + 2\sigma + \frac{3}{2}\sigma^2\right)\right\}
\end{aligned}$$

$$\begin{aligned}
B_3 + 2B_1 &= \frac{2\exp(\sigma)}{\sigma^4}\left\{\begin{pmatrix} 3 - 3\sigma + & \dfrac{3}{2}\sigma^2 - & \dfrac{1}{2}\sigma^3 \\ + & \sigma^2 - & \sigma^3 \end{pmatrix}\right. \\
&\qquad\qquad \left. - \exp(-2\sigma)\begin{pmatrix} 3 + 3\sigma + & \dfrac{3}{2}\sigma^2 + & \dfrac{1}{2}\sigma^3 \\ + & \sigma^2 + & \sigma^3 \end{pmatrix}\right\} \\
&= \frac{2\exp(\sigma)}{\sigma^4}\left\{\left(3 - 3\sigma + \frac{5}{2}\sigma^2 - \frac{3}{2}\sigma^3\right)\right. \\
&\qquad\qquad \left. - \exp(-2\sigma)\left(3 + 3\sigma + \frac{5}{2}\sigma^2 + \frac{3}{2}\sigma^3\right)\right\}.
\end{aligned}$$

Then we include the products with the A-functions:

$$\begin{aligned}
A_3B_2 &= \frac{6\exp(-\sigma)}{\sigma^4}\left(1 + \sigma + \frac{1}{2}\sigma^2 + \frac{1}{6}\sigma^3\right) \\
&\quad \times \frac{2\exp(\sigma)}{\sigma^3}\left[\left(1 - \sigma + \frac{1}{2}\sigma^2\right) - \exp(-2\sigma)\left(1 + \sigma + \frac{1}{2}\sigma^2\right)\right] \\
&= \frac{2}{\sigma^7}(6 + 6\sigma + 3\sigma^2 + \sigma^3)\left[\left(1 - \sigma + \frac{1}{2}\sigma^2\right)\right. \\
&\qquad\qquad \left. - \exp(-2\sigma)\left(1 + \sigma + \frac{1}{2}\sigma^2\right)\right]
\end{aligned}$$

$$
\begin{aligned}
&= \frac{2}{\sigma^7}\left\{\left(\begin{array}{l} 6+6\sigma+3\sigma^2+\sigma^3 \\ \quad -6\sigma-6\sigma^2-3\sigma^3-\sigma^4 \\ \qquad +3\sigma^2+3\sigma^3+\frac{3}{2}\sigma^4+\frac{1}{2}\sigma^5 \end{array}\right)\right. \\
&\qquad \left. -\exp(-2\sigma)\left(\begin{array}{l} 6+6\sigma+3\sigma^2+\sigma^3 \\ \quad +6\sigma+6\sigma^2+3\sigma^3+\sigma^4 \\ \qquad +3\sigma^2+3\sigma^3+\frac{3}{2}\sigma^4+\frac{1}{2}\sigma^5 \end{array}\right)\right\} \\
&= \frac{2}{\sigma^7}\left\{\left(6+\sigma^3+\frac{1}{2}\sigma^4+\frac{1}{2}\sigma^5\right)\right. \\
&\qquad \left. -\exp(-2\sigma)\left(6+12\sigma+12\sigma^2+7\sigma^3+\frac{5}{2}\sigma^4+\frac{1}{2}\sigma^5\right)\right\}
\end{aligned}
$$

$$
\begin{aligned}
A_1(2B_2+B_0) &= \frac{\exp(-\sigma)}{\sigma^2}(1+\sigma) \\
&\quad \times \frac{2\exp(\sigma)}{\sigma^3}\left[\left(2-2\sigma+\frac{3}{2}\sigma^2\right)-\exp(-2\sigma)\left(2+2\sigma+\frac{3}{2}\sigma^2\right)\right] \\
&= \frac{2}{\sigma^5}\left\{\left(\begin{array}{l} 2-2\sigma+\frac{3}{2}\sigma^2 \\ \quad +2\sigma-2\sigma^2+\frac{3}{2}\sigma^3 \end{array}\right)-\exp(-2\sigma)\left(\begin{array}{l} 2+2\sigma+\frac{3}{2}\sigma^2 \\ \quad +2\sigma+2\sigma^2+\frac{3}{2}\sigma^3 \end{array}\right)\right\} \\
&= \frac{2}{\sigma^5}\left\{\left(2-\frac{1}{2}\sigma^2+\frac{3}{2}\sigma^3\right)-\exp(-2\sigma)\left(2+4\sigma+\frac{7}{2}\sigma^2+\frac{3}{2}\sigma^3\right)\right\} \\
&= \frac{2}{\sigma^7}\left\{\left(2\sigma^2-\frac{1}{2}\sigma^4+\frac{3}{2}\sigma^5\right)-\exp(-2\sigma)\left(2\sigma^2+4\sigma^3+\frac{7}{2}\sigma^4+\frac{3}{2}\sigma^5\right)\right\}
\end{aligned}
$$

$$
\begin{aligned}
&A_2(B_3+2B_1) \\
&= \frac{2\exp(-\sigma)}{\sigma^3}\left(1+\sigma+\frac{1}{2}\sigma^2\right) \\
&\quad \times \frac{2\exp(\sigma)}{\sigma^4}\left[\left(3-3\sigma+\frac{5}{2}\sigma^2-\frac{3}{2}\sigma^3\right)\right. \\
&\qquad \left. -\exp(-2\sigma)\left(3+3\sigma+\frac{5}{2}\sigma^2+\frac{3}{2}\sigma^3\right)\right]
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{2}{\sigma^7}\left\{\left(\begin{array}{l} 6 - 6\sigma + 5\sigma^2 - 3\sigma^3 \\ \quad + 6\sigma - 6\sigma^2 + 5\sigma^3 - 3\sigma^4 \\ \qquad + 3\sigma^2 - 3\sigma^3 + \frac{5}{2}\sigma^4 - \frac{3}{2}\sigma^5 \end{array}\right)\right. \\
&\qquad \left. - \exp(-2\sigma)\left(\begin{array}{l} 6 + 6\sigma + 5\sigma^2 + 3\sigma^3 \\ \quad + 6\sigma + 6\sigma^2 + 5\sigma^3 + 3\sigma^4 \\ \qquad + 3\sigma^2 + 3\sigma^3 + \frac{5}{2}\sigma^4 + \frac{3}{2}\sigma^5 \end{array}\right)\right\} \\
&= \frac{2}{\sigma^7}\left\{\left(6 + 2\sigma^2 - \sigma^3 - \frac{1}{2}\sigma^4 - \frac{3}{2}\sigma^5\right)\right. \\
&\qquad \left. - \exp(-2\sigma)\left(6 + 12\sigma + 14\sigma^2 + 11\sigma^3 + \frac{11}{2}\sigma^4 + \frac{3}{2}\sigma^5\right)\right\}
\end{aligned}
$$

$$
\begin{aligned}
A_0 B_1 &= \frac{\exp(-\sigma)}{\sigma}\frac{\exp(\sigma)}{\sigma^2}[(1-\sigma) - \exp(-2\sigma)(1+\sigma)] \\
&= \frac{1}{\sigma^3}[(1-\sigma) - \exp(-2\sigma)(1+\sigma)] \\
&= \frac{2}{\sigma^7}\left[\left(\frac{1}{2}\sigma^4 - \frac{1}{2}\sigma^5\right) - \exp(-2\sigma)\left(\frac{1}{2}\sigma^4 + \frac{1}{2}\sigma^5\right)\right].
\end{aligned}
$$

By adding all contributions altogether, we finally obtain:

$$
\begin{aligned}
&A_3 B_2 + A_2(B_3 + 2B_1) + A_1(2B_2 + B_0) + A_0 B_1 \\
&= \frac{2}{\sigma^7}\left\{\left(\begin{array}{l} 6 \qquad\quad + \sigma^3 + \frac{1}{2}\sigma^4 + \frac{1}{2}\sigma^5 \\ 6 \;+ 2\sigma^2 - \sigma^3 - \frac{1}{2}\sigma^4 - \frac{3}{2}\sigma^5 \\ \quad\; + 2\sigma^2 \qquad - \frac{1}{2}\sigma^4 + \frac{3}{2}\sigma^5 \\ \qquad\qquad\qquad + \frac{1}{2}\sigma^4 - \frac{1}{2}\sigma^5 \end{array}\right)\right. \\
&\qquad \left. - \exp(-2\sigma)\left(\begin{array}{l} 6 + 12\sigma + 12\sigma^2 + 7\sigma^3 + \frac{5}{2}\sigma^4 + \frac{1}{2}\sigma^5 \\ 6 + 12\sigma + 14\sigma^2 + 11\sigma^3 + \frac{11}{2}\sigma^4 + \frac{3}{2}\sigma^5 \\ \qquad\qquad + 2\sigma^2 + 4\sigma^3 + \frac{7}{2}\sigma^4 + \frac{3}{2}\sigma^5 \\ \qquad\qquad\qquad\qquad + \frac{1}{2}\sigma^4 + \frac{1}{2}\sigma^5 \end{array}\right)\right\}
\end{aligned}
$$

$$= \frac{2}{\sigma^7}\{(12+4\sigma^2) - \exp(-2\sigma)(12+24\sigma+28\sigma^2+22\sigma^3+12\sigma^4+4\sigma^5)\}$$

$$= \frac{24}{\sigma^7}\left\{\left(1+\frac{1}{3}\sigma^2\right) - \exp(-2\sigma)\left(1+2\sigma+\frac{7}{3}\sigma^2+\frac{11}{6}\sigma^3+\sigma^4+\frac{1}{3}\sigma^5\right)\right\}$$

which is the result given by Roothaan (1951b).

The result for $c' = c$ follows immediately by taking $\sigma = cR = \rho$.

13.4. Calculation of the overlap $(1s_A 1s_B|1)$ from the general formulae.

According to Magnasco et al. (1998) the general 2-centre overlap integral between STOs is given by:

$$S_{ba} = (n_a l_a m_a, n_b l_b m_b|1) = \delta_{m_a m_b}\left(\frac{R}{2}\right)^{N+1} N_{n_a} N_{n_b} a_{l_a}^{m_a} a_{l_b}^{m_b}$$

$$\times \sum_p \sum_j a_{pj}^{ab} G_{jm}(\tau_{ab}) T_{N-L-2p-j,m}(\sigma_{ab}),$$

where:

$$N = n_a + n_b, \qquad L = l_a + l_b$$

$$N_n = \left[\frac{(2c)^{2n+1}}{(2n)!}\right]^{1/2}$$

$$a_l^m = \left[\frac{2l+1}{2}\frac{(l-m)!}{(l+m)!}\right]^{1/2} \qquad m = |m| = m_a + m_b$$

$$\sigma_{ab} = \frac{R}{2}(c_a + c_b), \qquad \tau_{ab} = \frac{R}{2}(c_a - c_b)$$

and explicit expressions for the coefficients a_{pj}^{ab} and the summation limits are given in Appendix B of that paper. For $1s$ STOs:

$$n_a = n_b = 1, \qquad l_a = l_b = m_a = m_b = m = 0, \qquad N = 2, \qquad L = 0$$

$$N_a = N_b = (4c^3)^{1/2}, \qquad a_0^0 = \left(\frac{1}{2}\right)^{1/2}$$

$$p \in [0, L - M] = 0$$

$$j \in [\max(0,0,0), \min(2,2,2)] = [0,2] = 0,1,2$$

and we obtain, for $c_a = c_b = c$, $cR = \rho$:

$$S_{ba} = (100,100|1) = \left(\frac{R}{2}\right)^3 (N_a)^2 \big(a_0^0\big)^2 \sum_{j=0}^{2} a_{0j}^{ab} G_{j0}(0) T_{2-j,0}(\rho)$$

$$= \frac{\rho^3}{4}\big[a_{00}^{ab} G_{00}(0) T_{20}(\rho) + a_{01}^{ab} G_{01}(0) T_{10}(\rho) + a_{02}^{ab} G_{20}(0) T_{00}(\rho)\big]$$

Coefficients and integrals are seen to be:

j	a_{0j}^{ab}	G integrals		T integrals	
0	1	G_{00}	2	T_{00}	$\exp(-\rho)/\rho$
1	0	G_{10}	0	T_{10}	$\exp(-\rho)\rho^{-2}(1+\rho)$
2	-1	G_{20}	$\frac{2}{3}$	T_{20}	$\exp(-\rho)\rho^{-3}(2+2\rho+\rho^2)$

so that we finally obtain:

$$S_{ba} = (100,100|1) = \langle 1s_A | 1s_B \rangle$$

$$= \frac{\rho^3}{4}\left\{2\frac{\exp(-\rho)}{\rho^3}(2+2\rho+\rho^2) - \frac{2}{3}\frac{\exp(-\rho)}{\rho}\right\}$$

$$= \frac{\rho^3}{4}\frac{\exp(-\rho)}{\rho^3}\begin{pmatrix} 4+4\rho+\ 2\rho^2 \\ \qquad -\frac{2}{3}\rho^2 \end{pmatrix}$$

$$= \frac{\exp(-\rho)}{4}\left(4+4\rho+\frac{4}{3}\rho^2\right)$$

$$= \exp(-\rho)\left(1+\rho+\frac{1}{3}\rho^2\right)$$

as it must be.

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