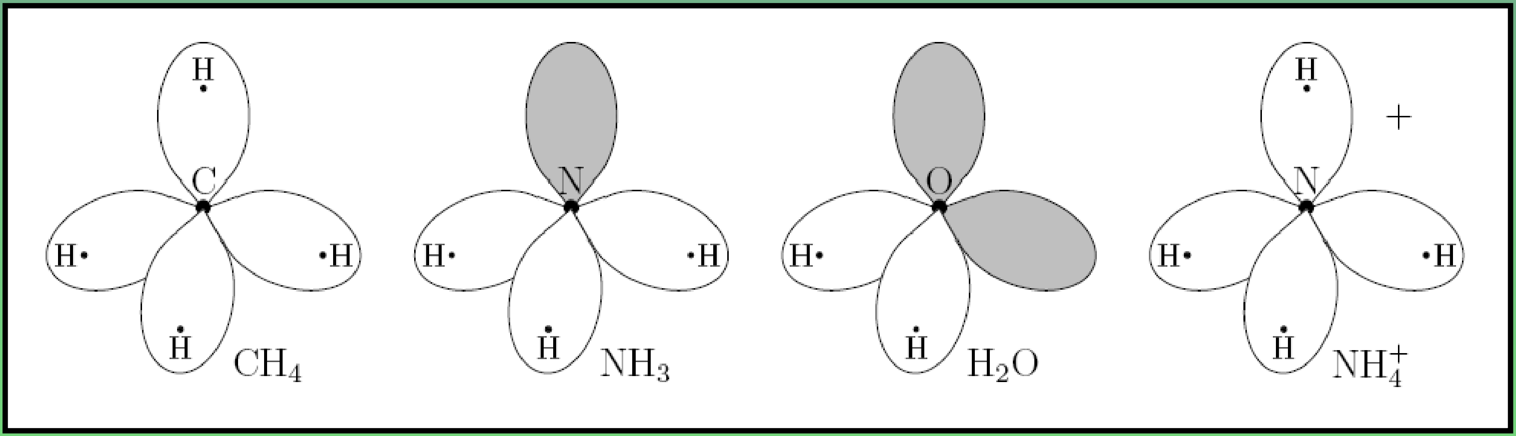
Basic Books in Science

Book 12

Quantum Mechanics of Many-Particle Systems: Atoms, Molecules – and More



Roy McWeeny

BASIC BOOKS IN SCIENCE

– a Series of books that start *at the beginning*

Book 12 Draft Version (10 May 2014) of all Chapters

Quantum mechanics of many-particle systems: atoms, molecules – and more

Roy McWeeny
Professore Emerito di Chimica Teorica, Università di Pisa, Pisa (Italy)

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BASIC BOOKS IN SCIENCE

Acknowledgements

In a world increasingly driven by information technology no educational experiment can hope to make a significant impact without effective bridges to the 'user community' – the students and their teachers.

In the case of "Basic Books in Science" (for brevity, "the Series"), these bridges have been provided as a result of the enthusiasm and good will of Dr. David Peat (The Pari Center for New Learning), who first offered to host the Series on his website, and of Dr. Jan Visser (The Learning Development Institute), who set up a parallel channel for further development of the project. The credit for setting up and maintaining the bridgeheads, and for promoting the project in general, must go entirely to them.

Education is a global enterprise with no boundaries and, as such, is sure to meet linguistic difficulties: these will be reduced by providing translations into some of the world's most widely used languages. Dr. Angel S. Sanz (Madrid) is preparing Spanish versions of the books and his initiative is most warmly appreciated. In 2014 it is our hope that translators will be found for French and Arabic versions.

We appreciate the interest shown by universities in Sub-Saharan Africa (e.g. University of the Western Cape and Kenyatta University), where trainee teachers are making use of the Series; and that shown by the Illinois Mathematics and Science Academy (IMSA) where material from the Series is being used in teaching groups of refugee children from many parts of the world.

All who have contributed to the Series in any way are warmly thanked: they have given freely of their time and energy 'for the love of Science'.

Pisa, 10 May 2014 Roy McWeeny (Series Editor)

BASIC BOOKS IN SCIENCE

About this book

This book, like the others in the Series[1], is written in simple English – the language most widely used in science and technology. It builds on the foundations laid in earlier Books, which have covered many areas of Mathematics and Physics.

The present book continues the story from Book 11, which laid the foundations of Quantum Mechanics and showed how it could account succesfully for the motion of a single particle in a given potential field. The almost perfect agreement between theory and experiment, at least for one electron moving in the field of a fixed positive charge, seemed to confirm that the principles were valid – to a high degree of accuracy. But what if we want to apply them to much more complicated systems, such as many-electron atoms and molecules, in order to get a general understanding of the structure and properties of matter? At first sight, remembering the mathematical difficulty of dealing with a *single* electron in the Hydrogen atom, we seem to be faced with an impossible task. The aim of Book 12 is to show how, guided by the work of the pioneers in the field, an astonishing amount of progress can be made. As in earlier books of the Series, the path to be followed will avoid a great deal of unnecessary detail (much of it being only of historical interest) in order to expose the logical development of the subject.

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[1] The aims of the Series are described elsewhere, e.g. in Book 1.

Looking ahead –

In Book 4, when you started on Physics, we said "Physics is a big subject and you'll need more than one book". Here is another one! Book 4 was mainly about **particles**, the ways they move when *forces* act on them, and how the same 'laws of motion' still hold good for all objects built up from particles – however big they may be. In Book 11 we moved from Classical Physics to Quantum Physics and again started with the study of a single moving particle and the laws that govern its behaviour. Now, in Book 12, we move on and begin to build up the 'mathematical machinery' for dealing with systems composed of *very many* particles – for example **atoms**, where up to about 100 electrons move in the electric field of one nucleus, or **molecules**, where the electrons move in the field provided by several nuclei.

- Chapter 1 reviews the priciples formulated in Book 11, along with the concepts of **vector space**, in which a **state vector** is associated with the state of motion of a particle, and in which an **operator** may be used to define a change of state. This chapter uses Schrödinger's form of quantum mechanics in which the state vectors are 'represented' by **wave functions** $\Psi = \Psi(x, y, z)$ (functions of the position of the particle in space) and the operators are typically differential operators. The chapter starts from the ideas of **'observables and measurement'**; and shows how measurement of a physical quantity can be described in terms of operations in a vector space. It follows with a brief reminder of the main way of calculating approximate wave functions, first for one electron, and then for more general systems.

- In Chapter 2 you take the first step by going from one electron to two: the Hamiltonian operator is then $\mathsf{H}(1,2) = \mathsf{h}(1) + \mathsf{h}(2) + \mathsf{g}(1,2)$, where only g – the 'interaction operator' – depends on the coordinates of *both* particles. With neglect of interaction the wave function can be taken as a *product* $Psi(1,2) = \psi_a(1)\psi_b(2)$, which indicates Particle 1 in state ψ_a and Particle 2 in state ψ_b. This is a first example of the **Independent Particle Model** and can give an *approximate* wave function for a 2-particle system. The calculation of the ground state electronic energy of the Helium atom is completed with an approximate wave function of product form (two electrons in an orbital of 1s type) and followed by a study of the excited states that result when one electron is 'promoted' into the 2s orbital. This raises interesting problems about the **symmetry** of the wave function. There are, it seems, two series of possible states: in one the function is unchanged if you swap the electrons (it is *symmetric*) but in the other it changes in sign (it is *antisymmetric*). Which must we choose for two electrons?

  At this point we note that **electron spin** has not yet been taken into account. The rest of the chapter brings in the spin functions $\alpha(s)$ and $\beta(s)$ to describe an electron in an 'up-spin' or a 'down-spin' state. When these spin factors are included in the wave functions an orbital $\phi(\mathbf{r})$ ($\mathbf{r}$ standing for the three spatial variables

x, y, z) is replaced by a **spin-orbital** $\psi(\mathbf{r}, s) = \phi(\mathbf{r})\alpha(s)$ (for an up-spin state) or $\psi(\mathbf{r}, s) = \phi(\mathbf{r})\beta(s)$ (for a down-spin state).

The Helium ground state is then found to be

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)[\alpha(s_1)\beta(s_2) - \alpha(s_1)\beta(s_2)],$$

where, from now on, a boldface letter ($\mathbf{x}$) will denote 'space-and-spin' variables. Interchanging Electron 1 and Electron 2 then shows that only *totally antisymmetric* wavefunctions can correctly predict the observed properties of the system. More generally, this is accepted as a fundamental property of **electronic systems**.

- Chapter 3 starts from the Antisymmetry Principle and shows how it can be included generally in the Independent Particle Model for an N-electron system. **Slater's rules** are derived as a basis for calculating the total energy of such a system in its 'ground state', where only the lowest-energy spin-orbitals are occupied by electrons. In this case, neglecting tiny spin-dependent effects, expressions for the ground-state energies of the first few many-electron atoms (He, Li, Be, ...) are easily derived.

- So far, we have not considered the analytical forms of the orbitals themselves, assuming that the atomic orbitals (AOs) for a 1-electron system (obtained in Book 11) will give a reasonable first approximation. In actual fact that is not so and the whole of this difficult Chapter 4 is devoted to the Hartree-Fock method of **optimizing orbital forms** in order to admit the effects of inter-electron repulsion. By defining two new *one*-electron operators, the **Coulomb operator** J and the **Exchange operator** K, it is possible to set up an *effective* 1-electron Hamiltonian F (the 'Fock operator') whose eigenfunctions will be 'best possible approximations' to the orbitals in an IPM wave function; and whose corresponding eigenvalues give a fairly realistic picture of the distribution of the total electronic energy E among the individual electrons. In fact, the eigenvalue ϵ_k represents the amount of energy 'belonging to' an electron in orbital ϕ_k; and this can be measured experimentally by observing how much energy is needed to knock the electron out. This gives a firm basis for the much-used energy-level diagrams. The rest of Chapter 4 deals with practical details, showing how the Hartree-Fock equation $\mathsf{F}\phi = \epsilon\phi$ can be written (by expanding ϕ in terms of a set of known functions) in the **finite basis form** $\mathbf{Fc} = \epsilon\mathbf{c}$, where $\mathbf{F}$ is a square *matrix* representing the Fock operator and $\mathbf{c}$ is a *column* of expansion coefficients.

- At last, in Chapter 5, we come to the first of the main themes of Book 12: "Atoms – the building blocks of matter". In all atoms, the electrons move in the field of a central nuclus, of charge Ze, and the **spherical symmetry** of the field allows us to use the theory of **angular momentum** (Chapter 5 of Book 11) in classifying the possible stationary states. By assigning the Z electrons to the 1-electron states (i.e. **orbitals**) of lowest energy we obtain the **electron configuration** of the electronic ground state; and by *coupling* the orbital angular momentum of individual electrons, in s, p, d, ... states with quantum numbers l = 0, 1, 2, ... it is possible to set up *many*-electron states with quantum numbers L = 0, 1, 2, ... These are called S, P, D, ... states and correspond to *total* angular momentum of 0, 1, 2, ... units: a state of given L is always **degenerate**, with $2L+1$ component states in which the angular momentum component (along a fixed z-axis) goes down in unit steps from $M = L$ to $M = -L$. Finally, the **spin** angular momentum must be included.

The next step is to calculate the total electronic energy of the various many-electron states in IPM approximation, using Slater's Rules. All this is done in detail, using worked examples, for the Carbon atom (Section 5.2). Once you have found wave functions for the **stationary states**, in which the expectation values of observables do not change in time, you'll want to know how to make an atom jump from one state to another. Remember from Book 10 that **radiation** consists of a rapidly varying electromagnetic field, carried by **photons** of energy $\epsilon = h\nu$, where h is Planck's constant and $\nu$is the radiation *frequency.* When radiation falls on an atom it produces a small oscillating 'perturbation' and if you add this to the free-atom Hamiltonian you can show that it may produce **transitions** between states of different energy. When this energy difference matches the photon energy $h\nu$ a photon will be absorbed by, or emitted from, the atom. And that is the basis of all kinds of **spectroscopy** – the main experimental 'tool' for investigating atomic structure.

The main *theoretical* tool for visualizing what goes on in atoms and molecules is provided by certain **electron density functions**, which give a 'classical' picture of how the electric charge, or the electron spin, is 'spread out' in space. These densities, which you first met in Chapter 4, are essentially components of the **density matrix**. The properties of atoms, as atomic number (i.e. nuclear charge, Z) increases, are usually displayed in a **Periodic Table**, which makes a clear connection between electronic and *chemical* properties of the elements. Here you find a brief description of the distribution of electrons among the AOs of the first 36 atoms.

This chapter ends with a brief look at the effects of small terms in the Hamiltonian, so far neglected, which arise from the **magnetic dipoles** associated with electron spins. The electronic states discussed so far are eignstates of the Hamiltonian H, the total angular momentum (squared) L^2, and one component L_z. But when spin is included we must also admit the *total spin* with operators S^2 and S_z, formed by coupling individual spins; the total angular momentum will then have components with operators $\mathsf{J}_x = \mathsf{L}_x + \mathsf{S}_x$ etc. The magnetic interactions between orbital and spin dipoles then lead to the **fine structure** of the energy levels found so far. The experimentally observed fine structure is fairly well accounted for, even with IPM wave functions.

- Atoms first started coming together, to form the simplest molecules, in the very early Universe. In Chapter 6 "Molecules: the first steps – " you go back to the

'Big Bang', when all the particles in the present Universe were contained in a small 'ball' which exploded – the interactions between them driving them apart to form the **Expanding Universe** we still have around us today. The first part of the chapter tells the story, as best we know it, from the time when there was nothing but an unbelievably hot 'sea' (nowadays called a **plasma**) of electrons, neutrons and protons, which began to come together in Hydrogen atoms (1 proton + 1 electron). Then, when another proton is added, you get a **hydrogen molecule ion** H_2^+ – and so it goes on!

In Section 6.2 you do a simple quantum mechanical calculation on H_2^+, combining two hydrogen-like atomic orbitals to form two approximate eigenfunctions for one electron in the field of two stationary protons. This is your first molecular orbital (MO) calculation, using 'linear combination of atomic orbitals' to obtain LCAO approximations to the first two MOs: the lower energy MO is a Bonding Orbital, the higher energy MO is Antibonding.

The next two sections deal with the *interpretation* of the chemical bond – where does it come from? There are two related interpretations and both can be generalized at once to the case of many-electon molecules. The first is based on an approximate calculation of the total electronic energy, which is strongly negative (describing the attraction of the electrons to the positive nuclei): this is balanced at a certain distance by the positive repulsive energy between the nuclei. When the total energy reaches a minimum value for some configuration of the nuclei we say the system is *bonded*. The second interpretation arises from an analysis of the *forces* acting on the nuclei: these can be calculated by calculating the energy *change* when a nucleus is displaced through an infinitesimal distance. The 'force-concept' interpretation is attractive because it gives a clear physical picture in terms of the **electron density function**: if the density is high between two nuclei it will exert forces bringing them together.

- Chapter 7 begins a systematic study of some important molecules formed mainly from the first 10 elements in the Periodic Table, using the Molecular Orbital approach which comes naturally out of the SCF method for calculating electronic wave functions. This may seem to be a very limited choice of topics but in reality it includes a vast range of molecules: think of the Oxygen (O_2) in the air we breath, the water (H_2O) in our oceans, the countless compounds of Hydrogen, Carbon, Oxygen that are present in all forms of plant and animal life.

  In Section 7.1 we begin the study of some simple diatomic molecules such as Lithium hydride (LiH) and Carbon monoxide (CO), introducing the idea of 'hybridization' in which AOs with the same principal quantum number are allowed to mix in using the variation method. Another key concept in understanding molecular electronic structure is that of the **Correlation Diagram**, developed in Section 7.2, which relates energy levels of the MOs in a molecule to those of the AOs of its constituent atoms. Figures 7.2 to 7.5 show simple examples for some diatomic molecules. The

AO energy levels you know something about already: the order of the MO levels depends on simple qualitative ideas about how the AOs *overlap* – which depends in turn on their sizes and shapes. So even without doing a big SCF calculation it is often possible to make progress using only pictorial arguments. Once you have an idea of the probable order of the MO energies, you can start filling them with the available valence electrons and when you've done that you can think about the resultant electron density! Very often a full SCF calculation serves only to confirm what you have already guessed.

In Section 7.3 we turn to some simple polyatomic molecules, extending the ideas used in dealing with diatomics to molecules whose experimentally known shapes suggest where **localized bonds** are likely to be found. Here the most important concept is that of **hybridization** – the mixing of s and p orbitals on the same centre, to produce hybrids that can point in any direction. It soon turns out that hybrids of given form can appear in sets of two, three, or four; and these are commonly found in linear molecules, trigonal molecules (three bonds in a plane, at 120° to each other) and tetrahedral molecules (four bonds pointing to the corners of a regular tetrahedron). Some systems of roughly tetrahdral form are shown in Figure 7.7.

It seems amazing that polyatomic molecules can often be well represented in terms of *localized MOs* similar to those found in diatomics. In Section 7.4 this mystery is resolved in a rigorous way by showing that the non-localized MOs that arise from a general SCF calculation can be mixed by making a unitary transformation – without changing the form of the total electron density in any way! This is another example of the fact that only the density itself (e.g. $|\psi|^2$, not ψ) can have a physical meaning.

Section 7.5 turns towards bigger molecules, particularly those important for Organic Chemistry and the Life Sciences, with fully worked examples. Many big molecules, often built largely from Carbon atoms, have properties connected with loosely bound electrons occupying π-type MOs that extend over the whole system.

Such molecules were a favourite target for calculations in the early days of Quantum Chemistry (before the 'computer age') because the π electrons could be considered by themselves, moving in the field of a 'framework', and the results could easily be compared with experiment. Many molecules of this kind belong to the class of *alternant* systems and show certain general properties. They are considered in Section 7.6, along with first attempts to discuss **chemical reactivity**.

To end this long chapter, Section 7.7 summarizes and extends the 'bridges' established between Theory and Experiment, emphasizing the pictorial value of density functions such as the electron density, the spin density, the current density and so on.

- Chapter 8 **Extended Systems: Polymers, Crystals and New Materials** concludes Book 12 with a study of applications to systems of great current interest and importance, for the Life Sciences, the Science of Materials and countless applications in Technology.

CONTENTS

Chapter 7 Molecules: Basic Molecular Orbital Theory

Chapter 8 Polymers, Crystals and New Materials

Chapter 1

The problem
– and how to deal with it

1.1 From one particle to many

Book 11, on the principles of quantum mechanics, laid the foundations on which we hope to build a rather complete theory of the structure and properties of all the matter around us; but how can we do it? So far, the most complicated system we have studied has been one atom of Hydrogen, in which a single electron moves in the central field of a heavy nucleus (considered to be at rest). And even that was mathematically difficult: the Schrödinger equation which determines the allowed **stationary states**, in which the energy does not change with time, took the form of a partial differential equation in three **position variables** x, y, z, of the electron, relative to the nucleus. If a second electron is added and its interaction with the first is included, the corresponding Schrödinger equation cannot be solved in 'closed form' (i.e. in terms of known mathematical functions). But Chemistry recognizes more than a 100 atoms, in which the nucleus has a positive charge Ze and is surrounded by Z electrons each with negative charge $-e$.

Furthermore, matter is not composed only of free atoms: most of the atoms 'stick together' in more elaborate structures called **molecules**, as will be remembered from Book 5. From a few atoms of the most common **chemical elements**, an enormous number of molecules may be constructed – including the 'molecules of life', which may contain many thousands of atoms arranged in a way that allows them to carry the 'genetic code' from one generation to the next (the subject of Book 9). At first sight it would seem impossible to achieve any understanding of the material world, at the level of the particles out of which it is composed. To make any progress at all, we have to stop looking for mathematically exact solutions of the Schrödinger equation and see how far we can get with good *approximate* wave functions, often starting from simplified *models* of the systems we are studying. The next few Sections will show how this can be done, without trying to be too complete (many whole books have been written in this field) and skipping proofs whenever the mathematics becomes too difficult.

The first three chapters of Book 11 introduced most of the essential ideas of Quantum Mechanics, together with the mathematical tools for getting you started on the further applications of the theory. You'll know, for example, that a single particle moving somewhere in 3-dimensional space may be described by a wave function $\Psi(x, y, z)$ (a function of the three coordinates of its position) and that this is just one special way of *representing* a **state vector**. If we want to talk about some observable property of the particle, such as its energy E or a momentum component p_x, which we'll denote here by X – whatever it may stand for – we first have to set up an associated **operator**[1] X. You'll also know that an operator like X works in an abstract **vector space**, simply by sending one vector into another. In Chapter 2 of Book 11 you first learnt how such operators could be defined and used to predict the average or 'expectation' value $\bar{X}$ that would be obtained from a large number of observations on a particle in a state described by the state vector Ψ.

In Schrödinger's form of quantum mechanics (Chapter 3) the 'vectors' are replaced by *functions* but we often use the same terminology: the 'scalar product' of two functions being defined (with Dirac's 'angle-bracket' notation) as $\langle\Psi_1|\Psi_2\rangle = \int \Psi_1^*(x, y, z)\Psi_2 \mathrm{d}x\mathrm{d}y\mathrm{d}z$ With this notation we often write the expectation value $\bar{X}$ as

$$\bar{X} = \langle X\rangle = \langle\Psi|\mathsf{X}\Psi\rangle, \tag{1.1}$$

which is a Hermitian scalar product of the 'bra-vector' $\langle\Psi|$ and the 'ket-vector' $|\mathsf{X}\Psi\rangle$ – obtained by letting the operator X work on the Ψ that stands on the right in the scalar product. Here it is assumed that the state vector is *normalized* to unity: $\langle\Psi|\Psi\rangle = 1$. Remember also that the same scalar product may be written with the *adjoint* operator, $\mathsf{X}^\dagger$, working on the left-hand Ψ. Thus

$$\bar{X} = \langle X\rangle = \langle\mathsf{X}^\dagger\Psi|\Psi\rangle. \tag{1.2}$$

This is the property of **Hermitian symmetry**. The operators associated with observables are *self*-adjoint, or 'Hermitian', so that $\mathsf{X}^\dagger = \mathsf{X}$.

In Schrödinger's form of quantum mechanics (Chapter 3 of Book 11) X is usually represented as a partial differential operator, built up from the coordinates x, y, z and the differential operators

$$\mathsf{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}, \quad \mathsf{p}_y = \frac{\hbar}{i}\frac{\partial}{\partial y}, \quad \mathsf{p}_z = \frac{\hbar}{i}\frac{\partial}{\partial z}, \tag{1.3}$$

which work on the wave *function* $\Psi(x, y, z)$.

1.2 The eigenvalue equation – as a variational condition

As we've given up on the idea of calculating wave functions and energy levels accurately, by directly solving Schrödinger's equation $\mathsf{H}\Psi = E\Psi$, we have to start thinking about

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[1] Remember that a special typeface has been used for operators, vectors and other non-numerical quantities.

possible ways of getting fair approximations. To this end, let's go back to first principles – as we did in the early chapters of Book 11

The expectation value given in (1.1) would be obtained experimentally by repeating the measurement of X a large number of times, always starting from the system in state Ψ, and recording the actual results $X_1, X_2, ...$ etc. – which may be found n_1 times, n_2 times, and so on, all scattered around their average value $\bar{X}$. The fraction n_i/N gives the **probability** p_i of getting the result X_i; and in terms of probabilities it follows that

$$\bar{X} = \langle X \rangle = p_1X_1 + p_2X_2 \,... + p_iX_i \,+\, ... + p_NX_N = \sum_i p_iX_i. \tag{1.4}$$

Now it's much easier to calculate an expectation value, using (1.1), than it is to solve an enormous partial differential equation; so we look for some kind of condition on Ψ, involving only an expectation value, that will be satisfied when Ψ is a solution of the equation $\mathsf{H}\Psi = E\Psi$.

The obvious choice is to take $\mathsf{X} = \mathsf{H} - E\mathsf{I}$, where I is the identity operator which leaves any operand unchanged, for in that case

$$\mathsf{X}\Psi = \mathsf{H}\Psi - E\Psi \tag{1.5}$$

and the state vector $\mathsf{X}\Psi$ is zero only when the Schrödinger equation is satisfied. The test for this is simply that the vector has zero length:

$$\langle \mathsf{X}\Psi | \mathsf{X}\Psi \rangle = 0. \tag{1.6}$$

In that case, Ψ may be one of the eigenvectors of H, e.g. Ψ_i with eigenvalue E_i, and the last equation gives $\mathsf{H}\Psi_i = E_i\Psi_i$. On taking the scalar product with Ψ_i, from the left, it follows that $\langle \Psi_i|\mathsf{H}|\Psi_i\rangle = E_i\langle\Psi_i|\Psi_i\rangle$ and for eigenvectors normalized to unity the energy expectation value coincides with the definite eigenvalue.

Let's move on to the case where Ψ is *not* an eigenvector of H but rather an arbitrary vector, which can be expressed as a mixture of a complete set of *all* the eigenvectors $\{\Psi_i\}$ (generally infinite), with numerical 'expansion coefficients' $c_1, c_2, ...c_i, ...$ Keeping Ψ (without subscript) to denote the arbitrary vector, we put

$$\Psi = c_1\Psi_1 + c_2\Psi_2 + \,... = \sum_i c_i\Psi_i \tag{1.7}$$

and use the general properties of eigenstates (Section 3.6 of Book 11) to obtain a general expression for the expectation value of the energy in state (1.7), which may be normalized so that $\langle\Psi|\Psi\rangle = 1$.

Thus, substitution of (1.7) gives

$$\bar{E} = \langle\Psi|\mathsf{H}|\Psi\rangle = \langle(\sum_i c_i\Psi_i)|\mathsf{H}|(\sum_j c_j\Psi_j)\rangle = \sum_{i,j} c_i^*c_j\langle\Psi_i|\mathsf{H}|\Psi_j\rangle$$

and since $\mathsf{H}\Psi_i = E_i\Psi_i$, while $\langle\Psi_i|\Psi_j\rangle = \delta_{ij}$ $(= 1,\ \text{for}\, i = j\,;\ = 0\ \text{for}\, i \neq j)$, this becomes

$$\bar{E}\langle\Psi|\mathsf{H}|\Psi\rangle = |c_1|^2 E_1 + |c_2|^2 E_2 + \ \ldots = \sum_i |c_i|^2 E_i. \tag{1.8}$$

Similarly, the squared length of the normalized Ψ becomes

$$\langle\Psi|\Psi\rangle = |c_1|^2 + |c_2|^2 + \ \ldots = \sum_i |c_i|^2 = 1. \tag{1.9}$$

Now suppose we are interested in the state of *lowest* energy, the 'ground' state, with E_1 less than any of the others. In that case it follows from the last two equations that

$$\begin{aligned} \langle\Psi|\mathsf{H}|\Psi\rangle - E_1 \quad &= \quad |c_1|^2 E_1 + |c_2|^2 E_2 + \ \ldots \\ &\quad\ -|c_1|^2 E_1 - |c_2|^2 E_1 + \ \ldots \\ &= \quad\quad 0 \quad\ + |c_2|^2(E_2 - E_1) + \ \ldots \quad . \end{aligned}$$

All the quantities on the right-hand side are essentially *positive*: $|c_i|^2 > 0$ for all i and $E_i - E_1 > 0$ because E_1 is the smallest of all the eigenvalues. It follows that

> Given an arbitrary state vector Ψ, which may be chosen so that $\langle\Psi|\Psi\rangle = 1$, the energy expectation value
>
> $$\bar{E} = \langle\Psi|\mathsf{H}|\Psi\rangle / \langle\Psi|\Psi\rangle$$
>
> must be greater than or equal to the lowest eigenvalue, E_1, of the Hamiltonian operator H

(1.10)

Here the normalization factor $\langle\Psi|\Psi\rangle$ has been left in the denominator of $\bar{E}$ and the result then remains valid even when Ψ is not normalized (check it!). This is a famous theorem and provides a basis for the **variation method** of calculating approximate eigenstates. In Schrödinger's formulation of quantum mechanics, where Ψ is represented by a wave function such as $\Psi(x, y, z)$, one can start from any 'trial' function that 'looks roughly right' and contains adjustable parameters. By calculating a 'variational energy' $\langle\Psi|\mathsf{H}|\Psi\rangle$ and varying the parameters until you can't find a lower value of this quantity you will know you have found the best approximation you can get to the ground-state energy E_1 and corresponding wave function. To do better you'll have to use a trial Ψ of different functional form.

As a first example of using the variation method we'll get an approximate wave function for the ground state of the hydrogen atom. In Book 11 (Section 6.2) we got the energy and wave function for the ground state of an electron in a hydrogen-like atom, with nuclear charge Ze, placed at the origin. They were, using atomic units,

$$E_{1s} = -\tfrac{1}{2}Z^2, \qquad \phi_{1s} = N_{1s}e^{-Zr},$$

where the normalizing factor is $N_{1s} = \pi^{-1/2}Z^{3/2}$.

We'll now try a gaussian approximation to the 1s orbital, calling it $\phi_{1s} = N \exp -\alpha r^2$, which correctly goes to zero for $r \to \infty$ and to N for $r = 0$; and we'll use this function (calling it ϕ for short) to get an approximation to the ground state energy $\bar{E} = \langle\phi|\mathsf{H}|\phi\rangle$. The first step is to evaluate the new normalizing factor and this gives a useful example of the mathematics needed:

Example 1.1 A gaussian approximation to the 1s orbital.

To get the normalizing factor N we must set $\langle\phi|\phi\rangle = 1$. Thus

$$\langle\phi|\phi\rangle = N^2 \int_0^\infty \exp(-2\alpha r^2)(4\pi r^2)\mathrm{d}r, \qquad \text{(A)}$$

the volume element being that of a spherical shell of thickness dr.

To do the integration we can use the formula (very useful whenever you see a gaussian!) given in Example 5.2 of Book 11:

$$\int_{-\infty}^{+\infty} \exp(-ps^2 - qs)\mathrm{d}s = \sqrt{\frac{\pi}{p}} \exp\left(\frac{q^2}{4p}\right),$$

which holds for any values (real or complex) of the constants p, q. Since the function we're integrating is symmetrical about $r = 0$ and is needed only for $q = 0$ we'll use the basic integral

$$I_0 = \int_0^\infty e^{-pr^2}\mathrm{d}r = \tfrac{1}{2}\sqrt{\pi}\, p^{-1/2}. \quad \text{(B)}$$

Now let's differentiate both sides of equation (B) with respect to the parameter p, just as if it were an ordinary variable (even though it is inside the integrand and really one should prove that this is OK). On the left we get (look back at Book 3 if you need to)

$$\frac{\mathrm{d}I_0}{\mathrm{d}p} = -\int_0^\infty r^2 e^{-pr^2}\mathrm{d}r = -I_1,$$

where we've called the new integral I_1 as we got it from I_0 by doing *one* differentiation. On differentiating the right-hand side of (B) we get

$$\frac{\mathrm{d}}{\mathrm{d}p}(\tfrac{1}{2}\sqrt{\pi}\, p^{-1/2}) = \tfrac{1}{2}\sqrt{\pi}(-\tfrac{1}{2}p^{-3/2}) = -\tfrac{1}{4}\sqrt{\pi}/p\sqrt{p}.$$

But the two results must be equal (if two functions of p are identically equal their slopes will be equal at all points) and therefore

$$I_1 = \int_0^\infty r^2 e^{-pr^2}\mathrm{d}r = \tfrac{1}{2}\sqrt{\pi}(\tfrac{1}{2}p^{-3/2}) = \tfrac{1}{4}\sqrt{\pi}/p\sqrt{p},$$

where the integral I_1 on the left is the one we need as it appears in (A) above. On using this result in (A) and remembering that $p = 2\alpha$ it follows that $N^2 = (p/\pi)^{3/2} = (2\alpha/\pi)^{3/2}$.

Example 1.1 has given the square of the normalizing factor,

$$N^2 = \left(\frac{2\alpha}{\pi}\right)^{3/2}, \tag{1.11}$$

which will appear in all matrix elements.

Now we turn to the expectation value of the energy $\bar{E} = \langle\phi|\mathsf{H}|\phi\rangle$. Here the Hamiltonian will be

$$\mathsf{H} = \mathsf{T} + \mathsf{V} = -\tfrac{1}{2}\nabla^2 - Z/r$$

and since ϕ is a function of only the radial distance r we can use the expression for ∇^2 obtained in Example 4.8 of Book 11, namely

$$\nabla^2 \equiv \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r} + \frac{\mathrm{d}^2}{\mathrm{d}r^2}.$$

On denoting the 1-electron Hamiltonian by h (we'll keep H for many-electron systems) we then find $\mathsf{h}\phi = -(Z/r)\phi - (1/r)(\mathrm{d}\phi/\mathrm{d}r) - \frac{1}{2}(\mathrm{d}^2\phi/\mathrm{d}r^2)$ and

$$\langle\phi|\mathsf{h}|\phi\rangle = -Z\langle\phi|(1/r)|\phi\rangle - \langle\phi|(1/r)(\mathrm{d}\phi/\mathrm{d}r)\rangle - \tfrac{1}{2}(\langle\phi|(\mathrm{d}^2\phi/\mathrm{d}r^2)\rangle. \tag{1.12}$$

We'll evaluate the three terms on the right in the next two Examples:

Example 1.2 Expectation value of the potential energy

We require $\langle\phi|\mathsf{V}|\phi\rangle = -Z\langle\phi|(1/r)|\phi\rangle$, where ϕ is the normalized function $\phi = Ne^{-\alpha r^2}$:

$$\langle\phi|\mathsf{V}|\phi\rangle = -ZN^2\int_0^\infty e^{-\alpha r^2}(1/r)e^{-\alpha r^2}(4\pi r^2)\mathrm{d}r,$$

which looks like the integral at "A" in Example 1.1 – except for the factor $(1/r)$. The new integral we need is $4\pi I_0'$, where

$$I_0' = \int_0^\infty r e^{-pr^2}\mathrm{d}r \quad (p = 2\alpha)$$

and the factor r spoils everything – we can no longer get I_0' from I_0 by differentiating, as in Example 1.1, for that would bring down a factor r^2. However, we can use another of the tricks you learnt in Chapter 4 of Book 3. (If you've forgotten all that you'd better read it again!) It comes from 'changing the variable' by putting $r^2 = u$ and expressing I_0' in terms of u. In that case we can use the formula you learnt long ago, namely $I_0' = \int_0^\infty (u^{1/2}e^{-pu})(\mathrm{d}r/\mathrm{d}u)\mathrm{d}u$.

To see how this works with $u = r^2$ we note that, since $r = u^{1/2}$, $\mathrm{d}r/\mathrm{d}u = \frac{1}{2}u^{-1/2}$; so in terms of u

$$I_0' = \int_0^\infty (u^{1/2}e^{-pu})(\tfrac{1}{2}u^{-1/2})\mathrm{d}u = \tfrac{1}{2}\textstyle\int_0^\infty e^{-pu}\mathrm{d}u.$$

The integral is a simple standard integral and when the limits are put in it gives (check it!) $I_0' = \frac{1}{2}[-e^{-pu}/p]_0^\infty = \frac{1}{2}(1/p)$.

From Example 1.2 it follows that

$$\langle\phi|\mathsf{V}|\phi\rangle = -4\pi Z N^2 \tfrac{1}{2}\left[-\tfrac{e^{-pu}}{p}\right]_0^\infty = -2\pi Z N^2/p. \qquad (1.13)$$

And now you know how to do the integrations you should be able to get the remaining terms in the expectation value of the Hamiltonian h. They come from the kinetic energy operator $\mathsf{T} = -\frac{1}{2}\nabla^2$, as in the next example.

Example 1.3 Expectation value of the kinetic energy

We require $\bar{T} = \langle\phi|\mathsf{T}|\phi\rangle$ and from (1.12) this is seen to be the sum of two terms. The first one involves the first derivative of ϕ, which becomes (on putting $-\alpha r^2 = u$ in $\phi = Ne^{-\alpha r^2}$)

$$(\mathrm{d}\phi/\mathrm{d}r) = (\mathrm{d}\phi/\mathrm{d}u)(\mathrm{d}u/\mathrm{d}r) = N(e^{-u})(-2r\alpha) = -2N\alpha r\, e^{-\alpha r^2}.$$

On using this result, multiplying by ϕ and integrating, it gives a contribution to $\bar{T}$ of

$$\bar{T}_1 = \langle\phi| - \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}|\phi\rangle = N^2 p\int_0^\infty \frac{1}{r} r e^{-pr^2}(4\pi r^2)\mathrm{d}r = 4\pi N^2 p\int_0^\infty e^{-pr^2}(r^2)\mathrm{d}r = 4\pi N^2 p I_1$$

– the integral containing a factor r^2 in the integrand (just like I_1 in Example 1.1).
The second term in $\bar{T}$ involves the second derivative of ϕ; and we already found the first derivative as $\mathrm{d}\phi/\mathrm{d}r = -Npr\, e^{-\alpha r^2}$ So differentiating once more (do it!) you should find

$$(\mathrm{d}^2\phi/\mathrm{d}r^2) = -Npe^{-\alpha r^2} - Npr(-pre^{-\alpha r^2}).$$

(check it by differentiating $-2N\alpha r e^{-\alpha r^2}$).
On using this result we obtain (again with $p = 2\alpha$)

$$\bar{T}_2 = \langle\phi| - \tfrac{1}{2}\tfrac{\mathrm{d}^2}{\mathrm{d}r^2}|\phi\rangle = -\tfrac{1}{2}N^2 4\pi p \textstyle\int_0^\infty r^2 e^{-pr^2}\mathrm{d}r + \tfrac{1}{2}N^2 4\pi p^2 \textstyle\int_0^\infty r^4 e^{-pr^2}\mathrm{d}r = 2\pi N^2(-p^2 I_2 + pI_1).$$

When the first-derivative term is added, namely $4\pi N^2 pI_1$, we obtain the expectation value of the kinetic energy as

$$4\pi N^2 pI_1 + 2\pi N^2(p^2 I_2 - pI_1) = 2\pi N^2(-p^2 I_2 + 3pI_1.)$$

The two terms in the final parentheses are

$$2\pi N^2 p^2 I_2 = 2\pi N^2 \frac{3}{8}\sqrt{\frac{\pi}{2\alpha}}, \qquad 2\pi N^2 pI_1 = 2\pi N^2 \frac{1}{4}\sqrt{\frac{\pi}{2\alpha}}$$

and remembering that $p = 2\alpha$ and that N^2 is given in (1.1), substitution gives the result $\bar{T} = \bar{T}_1 + \bar{T}_2 = 2\pi N^2(3/8)\sqrt{\pi/2\alpha}$.

The expectation value of the KE is thus, noting that $2\pi N^2 = 2p(p/\pi)^{1/2}$,

$$\langle\phi|\mathsf{T}|\phi\rangle = \frac{5}{8}\sqrt{\frac{\pi}{2\alpha}} \times 2\pi N^2 = \frac{3p}{4}. \qquad (1.14)$$

Finally, the expectation energy with a trial wave function of the form $\phi = Ne^{-\alpha r^2}$ becomes, on adding the PE term from (1.13), $-2\pi Z N^2(1/2\alpha)$

$$\bar{E} = \frac{3\alpha}{2} - 2Z\left(\frac{2}{\pi}\right)^{1/2}\alpha^{1/2}. \tag{1.15}$$

There is only one variable parameter α and to get the best approximate ground state function of Gaussian form we must adjust α until $\bar{E}$ reaches a minimum value. The value of $\bar{E}$ will be *stationary* (maximum, minimum, or turning point) when $\mathrm{d}\bar{E}/\mathrm{d}\alpha = 0$; so we must differentiate and set the result equal to zero.

Example 1.4 A first test of the variation method

Let's put $\sqrt{\alpha} = \mu$ and write (1.15) in the form

$$\bar{E} = A\mu^2 - B\mu \qquad (A = 3/2, \quad B = 2Z\sqrt{2/\pi})$$

which makes it look a bit simpler.

We can then vary μ, finding $\mathrm{d}\bar{E}/\mathrm{d}\mu = 2A\mu - B$, and this has a stationary value when $\mu = B/2A$. On substituting for μ in the energy expression, the stationary value is seen to be

$$\bar{E}_{\text{min}} = A(B^2/4A^2) - B(B/2A),$$

where the two terms are the kinetic energy $\bar{T} = \frac{1}{2}(B^2/2A)$ and the potential energy $\bar{V} = (B^2/2A)$. The total energy $\bar{E}$ at the stationary point is thus the sum KE + PE:

$$\bar{E} = \tfrac{1}{2}(B^2/2A) - (B^2/2A) = -\tfrac{1}{2}(B^2/2A) = -\bar{T}$$

and this is an energy *minimum*, because $\mathrm{d}^2\bar{E}/\mathrm{d}\mu^2 = 2A$ –which is positive.

The fact that the minimum energy is exactly $-1 \times$ the kinetic energy is no accident: it is a consequence of the **virial theorem**, about which you'll hear more later. For the moment, we note that for a hydrogen-like atom the 1-term gaussian wave function gives a best approximate energy $\bar{E}_{\text{min}} = -\frac{1}{2}(2Z\sqrt{2/\pi})^2/3 = -4Z^2/3\pi$.

Example 1.4 gives the result $-0.42442\,Z^2$, where all energies are in units of $\mathrm{e_H}$.

For the hydrogen atom, with $Z = 1$, the exact ground state energy is $-\frac{1}{2}\mathrm{e_H}$, as we know from Book 11. In summary then, the conclusion from the Example is that a gaussian function gives a very poor approximation to the hydrogen atom ground state, the estimate $-0.42442\,\mathrm{e_H}$ being in error by about 15%. The next Figure shows why:

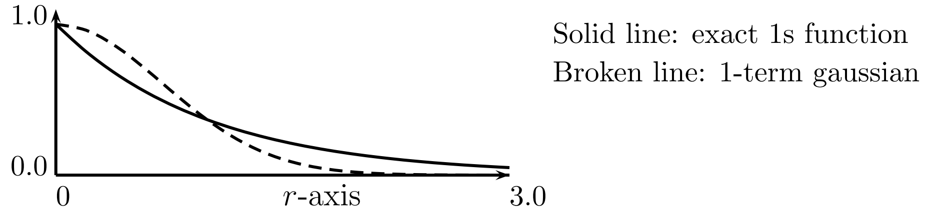

Figure 1.1 Comparison of exponential and gaussian functions

$\phi(r)$ fails to describe the sharp cusp when $r \to 0$ and also goes to zero much too rapidly when r is large.

Of course we could get the accurate energy $E_1 = -\frac{1}{2}\mathrm{e_H}$ and the corresponding wave function ϕ_1, by using a trial function of exponential form $\exp -ar$ and varying the parameter a until the approximate energy reaches a minimum value. But here we'll try another approach, taking a mixture of two gaussian functions, one falling rapidly to zero as r increases and the other falling more slowly: in that way we can hope to correct the main defects in the 1-term approximation.

Example 1.5 A 2-term gaussian approximation

With a trial function of the form $\phi = A\exp -ar^2 + B\exp -br^2$ there are *three* parameters that can be independently varied, a, b and the *ratio* $c = B/A$ – a fourth parameter not being necessary if we're looking for a normalized function (can you say why?). So we'll use instead a 2-term function $\phi = \exp -ar^2 + c\exp -br^2$.

From the previous Examples 1.1-1.3, it's clear how you can evaluate all the integrals you need in calculating $\langle\phi|\phi\rangle$ and the expectation values $\langle\phi|\mathsf{V}|\phi\rangle$, $\langle\phi|\mathsf{V}|\phi\rangle$; all you'll need to change will be the parameter values in the integrals.

Try to work through this by yourself, without doing the variation of all three values to find the minimum value of $\bar{E}$. (Until you've learnt to use a computer that's much too long a job! But you may like to know the result: the 'best' values of a, b, c are $a = 1.32965$, $b = 0.20146$, $c = 0.72542$ and the best approximation to E_{1s} then comes out as $\bar{E} = -0.4858Z^2\mathrm{e_H}$. This compares with the one-term approximation $\bar{E} = -0.4244Z^2\mathrm{e_H}$; the error is now reduced from about 15% to less than 3%.

The approximate wave function obtained in Example 1.5 is plotted in Figure 1.2 and again compared with the exact 1s function. (The functions are not normalized, being shifted vertically to show how well the cusp behaviour is corrected. Normalization improves the agreement in the middle range.)

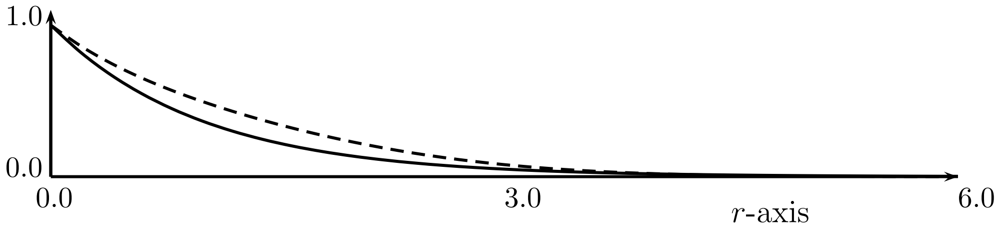

Figure 1.2 A 2-term gaussian approximation (broken line) to the hydrogen atom 1s function (solid line)

This Example suggests another form of the variation method, which is both easier to apply and much more powerful. We study it in the next Section, going back to the general case, where Ψ denotes any kind of wave function, expanded in terms of eigenfunctions Ψ_i.

1.3 The linear variation method

Instead of building a variational approximation to the wave function Ψ out of only two terms we may use as many as we please, taking in general

$$\Psi = c_1\Psi_1 + c_2\Psi_2 + \ ... \ + c_N\Psi_N, \tag{1.16}$$

where (with the usual notation) the functions $\{\Psi_i \ (i = 1, 2, \ ... \ N)\}$ are 'fixed' and we vary only the coefficients c_i in the linear combination: this is called a "linear variation function" and it lies at the root of nearly all methods of constructing atomic and molecular wave functions.

From the variation theorem (1.10) we need to calculate the expectation energy $\bar{E} = \langle\Psi|\mathsf{H}|\Psi\rangle/\langle\Psi|\Psi\rangle$, which we know will give an upper bound to the lowest exact eigenvalue E_1 of the operator H. We start by putting this expression in a convenient matrix form: you used matrices a lot in Book 11, 'representing' the operator H by a *square array* of numbers $\mathbf{H}$ with $H_{ij} = \langle\Psi_i|\mathsf{H}|\Psi_j\rangle$ (called a "matrix element") standing at the intersection of the ith row and jth column; and collecting the coefficients c_i in a single column $\mathbf{c}$. A matrix element H_{ij} with $j = i$ lies on the *diagonal* of the array and gives the expectation energy $\bar{E}_i$ when the system is in the particular state $\Psi = \Psi_i$. (Look back at Book 11 Chapter 7 if you need reminding of the rules for using matrices.)

In matrix notation the more general expectation energy becomes

$$\bar{E} = \frac{\mathbf{c}^\dagger\mathbf{H}\mathbf{c}}{\mathbf{c}^\dagger\mathbf{M}\mathbf{c}}, \tag{1.17}$$

where $\mathbf{c}^\dagger$ (the 'Hermitian transpose' of $\mathbf{c}$) denotes the *row* of coefficients $(c_1^* \, c_2^*, \ ... \ c_N^*)$ and $\mathbf{M}$ (the 'metric matrix') looks like $\mathbf{H}$ except that H_{ij} is replaced by $M_{ij} = \langle\Psi_i|\Psi_j\rangle$, the scalar product or 'overlap' of the two functions. This allows us to use sets of functions that are neither normalized to unity nor orthogonal – with no additional complication.

The best approximate state function (1.11) we can get is obtained by minimizing $\bar{E}$ to make it as close as possible to the (unknown!) ground state energy E_1, and to do this we look at the effect of a small variation $\mathbf{c} \to \mathbf{c} + \delta\mathbf{c}$: if we have reached the minimum, $\bar{E}$ will be *stationary*, with the corresponding change $\delta\bar{E} = 0$.

In the variation $\mathbf{c} \to \mathbf{c} + \delta\mathbf{c}$, $\bar{E}$ becomes

$$\bar{E} + \delta\bar{E} = \frac{\mathbf{c}^\dagger\mathbf{H}\mathbf{c} + \mathbf{c}^\dagger\mathbf{H}\delta\mathbf{c} + \delta\mathbf{c}^\dagger\mathbf{H}\mathbf{c} + \ ...}{\mathbf{c}^\dagger\mathbf{M}\mathbf{c} + \mathbf{c}^\dagger\mathbf{M}\delta\mathbf{c} + \delta\mathbf{c}^\dagger\mathbf{M}\mathbf{c} + \ ...},$$

where second-order terms that involve products of δ-quantities have been dropped (vanishing in the limit $\delta\mathbf{c} \to 0$).

The denominator in this expression can be re-written, since $\mathbf{c}^\dagger\mathbf{M}\mathbf{c}$ is just a number, as

$$\mathbf{c}^\dagger\mathbf{M}\mathbf{c}[1 + (\mathbf{c}^\dagger\mathbf{M}\mathbf{c})^{-1}(\mathbf{c}^\dagger\mathbf{M}\delta\mathbf{c} + \delta\mathbf{c}^\dagger\mathbf{M}\mathbf{c})]$$

and the part in square brackets has an inverse (to first order in small quantities)

$$1 - (\mathbf{c}^\dagger\mathbf{M}\mathbf{c})^{-1}(\mathbf{c}^\dagger\mathbf{M}\delta\mathbf{c} + \delta\mathbf{c}^\dagger\mathbf{M}\mathbf{c}).$$

On putting this result in the expression for $\bar{E} + \delta\bar{E}$ and re-arranging a bit (do it!) you'll find

$$\bar{E} + \delta\bar{E} = \bar{E} + \mathbf{c}^\dagger\mathbf{M}\mathbf{c})^{-1}[(\mathbf{c}^\dagger\mathbf{H}\delta\mathbf{c} + \delta\mathbf{c}^\dagger\mathbf{H}\mathbf{c}) - \bar{E}(\mathbf{c}^\dagger\mathbf{M}\delta\mathbf{c} + \delta\mathbf{c}^\dagger\mathbf{M}\mathbf{c})].$$

It follows that the first-order variation is given by

$$\delta\bar{E} = \mathbf{c}^\dagger\mathbf{M}\mathbf{c})^{-1}[(\mathbf{c}^\dagger\mathbf{H} - \bar{E}\mathbf{c}^\dagger\mathbf{M})\delta\mathbf{c} + \delta\mathbf{c}^\dagger(\mathbf{H}\mathbf{c} - \bar{E}\mathbf{M}\mathbf{c})]. \tag{1.18}$$

The two terms in (1.18) are complex conjugate, giving a real result which will vanish only when each is zero.

The condition for a stationary value thus reduces to a *matrix* eigenvalue equation

$$\mathbf{H}\mathbf{c} = \bar{E}\mathbf{M}\mathbf{c}. \tag{1.19}$$

To get the *minimum* value of $\bar{E}$ we therefore take the lowest eigenvalue; and the corresponding 'best approximation' to the wave function $\Psi \approx \Psi_1$ will follow on solving the simultaneous equations equivalent to (1.19), namely

$$\sum_j H_{ij}c_j = \bar{E}\sum_j M_{ij}c_j \quad (\text{all}\, i). \tag{1.20}$$

This is essentially what we did in Example 1.2, where the linear coefficients c_1, c_2 gave a best approximation when they satisfied the two simultaneous equations

$$\begin{aligned}(H_{11} - \bar{E}M_{11})c_1 + (H_{12} - \bar{E}M_{12})c_2 &= 0,\\ (H_{21} - \bar{E}M_{21})c_1 + (H_{22} - \bar{E}M_{22})c_2 &= 0,\end{aligned}$$

the other parameters bing fixed. Now we want to do the same thing generally, using a large basis of N expansion functions $\{\Psi_i\}$, and to make the calculation easier it's best to use an orthonormal set. For the case $N = 2$, $M_{11} = M_{22} = 1$ and $M_{12} = M_{21} = 0$, the equations then become

$$\begin{aligned}(H_{11} - \bar{E})c_1 &= -H_{12}c_2,\\ H_{21}c_1 &= -(H_{22} - \bar{E})c_2.\end{aligned}$$

Here there are three unknowns, $\bar{E}, c_1, c_2$. However, by dividing each side of the first equation by the corresponding side of the second, we can eliminate two of them, leaving only

$$\frac{(H_{11} - \bar{E})}{H_{21}} = \frac{H_{12}}{(H_{22} - \bar{E})}.$$

This is quadratic in $\bar{E}$ and has two possible solutions. On 'cross-multiplying' it follows that $(H_{11} - \bar{E})(H_{22} - \bar{E}) = H_{12}H_{21}$ and on solving we get lower and upper values $\bar{E}_1$

and $\bar{E}_2$. After substituting either value back in the original equations, we can solve to get the *ratio* of the expansion coefficients. Normalization to make $c_1^2 + c_2^2 = 1$ then results in approximations to the first two wave functions, Ψ_1 (the ground state) and Ψ_2 (a state of higher energy).

Generalization

Suppose we want a really good approximation and use a basis containing hundreds of functions Ψ_i. The set of simultaneous equations to be solved will then be enormous; but we can see how to continue by looking at the case $N = 3$, where they become

$$\begin{aligned}
(H_{11} - \bar{E}M_{11})c_1 + (H_{12} - \bar{E}M_{12})c_2 + (H_{13} - \bar{E}M_{13})c_3 &= 0,\\
(H_{21} - \bar{E}M_{21})c_1 + (H_{22} - \bar{E}M_{22})c_2 + (H_{23} - \bar{E}M_{23})c_3 &= 0,\\
(H_{31} - \bar{E}M_{31})c_1 + (H_{32} - \bar{E}M_{32})c_2 + (H_{33} - \bar{E}M_{33})c_3 &= 0.
\end{aligned}$$

We'll again take an orthonormal set, to simplify things. In that case the equations reduce to (in matrix form)

$$\begin{pmatrix} H_{11} - \bar{E} & H_{12} & H_{13} \\ H_{21} & H_{22} - \bar{E} & H_{23} \\ H_{31} & H_{32} & H_{33} - \bar{E} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}.$$

When there were only two expansion functions we had similar equations, but with only two rows and columns in the matrices:

$$\begin{pmatrix} H_{11} - \bar{E} & H_{12} \\ H_{21} & H_{22} - \bar{E} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}.$$

And we got a solution by 'cross-multiplying' in the square matrix, which gave

$$(H_{11} - \bar{E})(H_{22} - \bar{E}) - H_{21}H_{12} = 0.$$

This is called a **compatibility condition**: it determines the only values of $\bar{E}$ for which the equations are *compatible* (i.e. can both be solved at the same time).

In the general case, there are N simultaneous equations and the condition involves the **determinant** of the square array: thus for $N = 3$ it becomes

$$\begin{vmatrix} H_{11} - \bar{E} & H_{12} & H_{13} \\ H_{21} & H_{22} - \bar{E} & H_{23} \\ H_{31} & H_{32} & H_{33} - \bar{E} \end{vmatrix} = 0. \qquad (1.21)$$

There are many books on algebra, where you can find whole chapters on the theory of determinants, but nowadays equations like (1.16) can be solved easily with the help of a small computer. All the 'theory' you really need, was explained long ago in Book 2 (Section 6.12). So here a reminder should be enough:

Given a square matrix $\mathbf{A}$, with three rows and columns, its determinant can be evaluated as follows. You can start from the 11-element A_{11} and then get the determnant of the 2×2 matrix that is left when you take away the first row and first column:

$$\begin{vmatrix} A_{22} & A_{23} \\ A_{32} & A_{33} \end{vmatrix} = A_{22}A_{33} - A_{32}A_{23}.$$

– as follows from what you did just before (1.16). What you have evaluated is called the 'co-factor' of A_{11} and is denoted by $A^{(11)}$.

Then move to the next element in the first row, namely A_{12}, and do the same sort of thing: take away the first row and *second* column and then get the determinant of the 2×2 matrix that is left. This would seem to be the co-factor of A_{12}; but in fact, whenever you move from one element in the row to the next, you have to attach a minus sign; so what you have found is $-A^{(12)}$.

When you've finished the row you can put together the three contributions to get

$$|\mathbf{A}| = A_{11}A^{(11)} - A_{12}A^{(12)} + A_{13}A^{(13)}$$

and you've evaluated the 3×3 determinant!

The only reason for reminding you of all that (since a small computer can do such things much better than we can) was to show that the determinant in (1.21) will give you a polynomial of degree 3 in the energy $\bar{E}$. (That is clear if you take $\mathbf{A} = \mathbf{H} - \bar{E}\mathbf{1}$, make the expansion, and look at the terms that arise from the product of elements on the 'principal diagonal', namely $(H_{11} - \bar{E}) \times (H_{22} - \bar{E}) \times (H_{33} - \bar{E})$. These include $-\bar{E}^3$.) Generally, as you can see, the expansion of a determinant like (1.16), but with N rows and columns, will contain a term of highest degree in $\bar{E}$ of the form $(-1)^N\bar{E}^N$. This leads to conclusions of very great importance – as you're just about to see.

1.4 Going all the way! Is there a limit?

The first time you learnt anything about **eigenfunctions** and how they could be used was in Book 3 (Section 6.3). Before starting the present Section 1.4 of Book 12, you should read again what was done there. You were studying a simple differential equation, the one that describes standing waves on a vibrating string, and the solutions were sine functions (very much like the eigenfunctions coming from Schrödinger's equation for a 'particle in a box', discussed in Book 11). By putting together a large number of such functions, corresponding to increasing values of the vibration frequency, you were able to get approximations to the instantaneous shape of the string for *any* kind of vibration. That was a first example of an **eigenfunction expansion**. Here we're going to use such expansions in constructing approximate wave functions for atoms and molecules; and we've taken the first steps by starting from linear variation functions. What we must do now is to ask how a function of the form (1.16) can approach more and more closely an exact eigenfunction of the Hamiltonian H as N is increased.

In Section 1.3 it was shown that an N-term variation function (1.16) could give an optimum approximation to the ground state wave function Ψ_1, provided the expansion coefficients c_i were chosen so as to satisfy a set of linear equations: for $N = 3$ these took the form

$$\begin{aligned}(H_{11}-\bar{E}M_{11})c_1+(H_{12}-\bar{E}M_{12})c_2+(H_{13}-\bar{E}M_{13})c_3 &= 0,\\ (H_{21}-\bar{E}M_{21})c_1+(H_{22}-\bar{E}M_{22})c_2+(H_{23}-\bar{E}M_{23})c_3 &= 0,\\ (H_{31}-\bar{E}M_{31})c_1+(H_{32}-\bar{E}M_{32})c_2+(H_{33}-\bar{E}M_{33})c_3 &= 0.\end{aligned}$$

and were compatible only when the variational energy $\bar{E}$ satisfied the condition (1.16). There are only *three* values of $\bar{E}$ which do so. We know that $\bar{E}_1$ is an upper bound to the accurate lowest-energy eigenvalue E_1 but what about the other two?

In general, equations of this kind are called **secular equations** and a condition like (1.16) is called a **secular determinant**. If we plot the value, Δ say, of the determinant (having worked it out for any chosen value of $\bar{E}$) against $\bar{E}$, we'll get a curve something like the one in Figure 1.3; and whenever the curve crosses the horizontal axis we'll have $\Delta = 0$, the compatibility condition will be satisfied and that value of $\bar{E}$ will allow you to solve the secular equations. For *other* values you just can't do it!

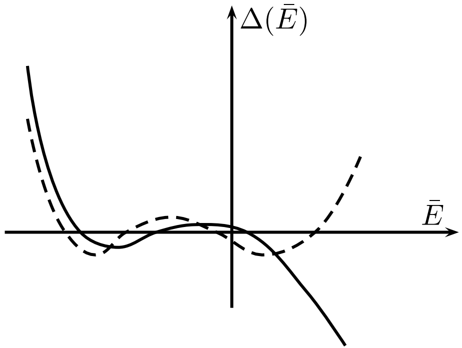

Figure 1.3 Secular determinant
Solid line: for $N = 3$
Broken line: for $N = 4$

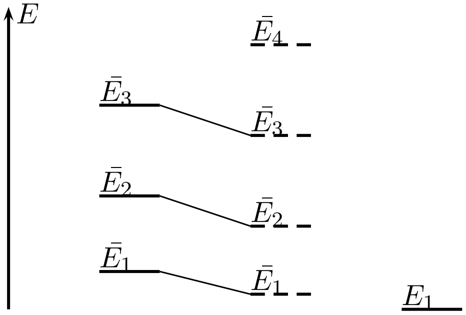

Figure 1.4 Energy levels
Solid lines: for $N = 3$
Broken lines: for $N = 4$

On the far left in Fig.1.3, Δ will become indefinitely large and positive because its expansion is a polynomial dominated by the term $-\bar{E}^3$ and $\bar{E}$ is negative. On the other side, where $\bar{E}$ is positive, the curve on the far right will go off to large *negative* values. In between there will be three crossing points, showing the acceptable energy values.

Now let's look at the effect of increasing the number of basis functions by adding another, Ψ_4. The value of the secular determinant then changes and, since expansion gives a polynomial of degree 4, it will go towards $+\infty$ for large values of $\bar{E}$. Figure 1.3 shows that there are now *four* crossing points on the x-axis and therefore four acceptable solutions of the secular equations. The corresponding energy levels for $N = 3$ and $N = 4$ are compared in Figure 1.4, where the first three are seen to go down, while one new level ($\bar{E}_4$) appears at higher energy. The levels for $N = 4$ fall in between the levels above and below for $N = 3$ and this result is often called the "separation theorem": it can be proved properly by studying the values of the determinant $\Delta_N(\bar{E})$ for values of $\bar{E}$ at the crossing points of $\Delta_{N-1}(\bar{E})$.

The conclusion is that, as more and more basis functions are added, the roots of the secular determinant go steadily (or 'monotonically') *down* and will therefore approach limiting values. The first of these, E_1, is known to be an upper bound to the exact lowest eigenvalue of H (i.e. the groundstate of the system) and it now appears that the higher roots will give upper bounds to the higher 'excited' states. For this conclusion to be true it is necessary that the chosen basis functions form a **complete set**.

1.5 Complete set expansions

So far, in the last section, we've been thinking of linear variation functions in general, without saying much about the forms of the expansion functions and how they can be constructed; but for atoms and molecules they may be functions of many variables (e.g. coordinates $x_1, y_1, z_1, x_2, y_2, z_2, x_3, \dots z_N$ for N particles – even without including spins!). From now on we'll be dealing mainly with wave functions built up from one-particle functions, which from now on we'll denote by lower-case letters $\{\phi_k(\mathbf{r}_i)\}$ with the index i labelling 'Particle i' and $\mathbf{r}_i$ standing for all three variables needed to indicate its position in space (spin will be put in later); as usual the subscript on the function will just indicate which one of the whole set ($k = 1, 2, \dots n$) we mean. (It's a pity so many labels are needed, and that sometimes we have to change their names, but by now you must be getting used to the fact that you're playing a difficult game – once you're clear about what the symbols stand for the rest will be easy!)

Let's start by thinking again of the simplest case; one particle, moving in one dimension, so the particle label i is not needed and $\mathbf{r}$ can be replaced by just one variable, x. Instead of $\phi_k(\mathbf{r}_i)$ we can then use $\phi_k(x)$. We want to represent *any* function $f(x)$ as a linear combination of these basis functions and we'll write

$$f^{(n)}(x) = c_1\phi_1(x) + c_2\phi_2(x) + \ \dots \ + c_n\phi_n(x) \tag{1.22}$$

as the 'n-term approximation' to $f(x)$.

Our first job will be to choose the coefficients so as to get a *best* approximation to $f(x)$ over the whole range of x-values (not just at one point). And by "the whole range" we'll mean for all x in the interval, (a, b) say, outside which the function has values that can be neglected: the range may be very small (think of the delta-function you met in Book 11) or very large (think of the interval $(-\infty, +\infty)$ for a particle moving in free space). (When we need to show the limits of the interval we'll just use $x = a$ and $x = b$.)

Generally, the curves we get on plotting $f(x)$ and $f^{(n)}(x)$ will differ and their difference can be measured by $\Delta(x) = f(x) - f^{(n)}(x)$ at all points in the range. But $\Delta(x)$ will sometimes be positive and sometimes negative. So it's no good adding these differences for all points on the curve (which will mean integrating $\Delta(x)$) to get a measure of how poor the approximation is; for cancellations could lead to zero even when the curves were very different. It's really the *magnitude* of $\Delta(x)$ that matters, or its *square* – which is always positive.

So instead let's measure the difference by $|f(x) - f^{(n)}(x)|^2$, at any point, and the 'total difference' by

$$D = \int_a^b \Delta(x)^2 dx = \int_a^b |f(x) - f^{(n)}(x)|^2 dx. \tag{1.23}$$

The integral gives the sum of the areas of all the strips between $x = a$ and $x = b$ of height Δ^2 and width $\mathrm{d}x$. This quantity will measure the *error* when the whole curve is approximated by $f^{(n)}(x)$ and we'll only get a really good fit, over the whole range of x, when D is close to zero.

The coefficients c_k should be chosen to give D its lowest possible value and you know how to do that: for a function of one variable you find a minimum value by first seeking a 'turning point' where $(\mathrm{d}f/\mathrm{d}x) = 0$; and then check that it really *is* a minimum, by verifying that $(\mathrm{d}^2 f/\mathrm{d}x^2)$ is positive. It's just the same here, except that we look at the variables *one at a time, keeping the others constant.* Remember too that it's the coefficients c_k that we're going to vary, not x.

Now let's put (1.17) into (1.18) and try to evaluate D. You first get (dropping the usual variable x and the limits a, b when they are obvious)

$$D = \int |f - f^{(n)}|^2 \mathrm{d}x = \int f^2 \mathrm{d}x + \int (f^{(n)})^2 \mathrm{d}x - 2 \int f f^{(n)} \mathrm{d}x. \tag{1.24}$$

So there are three terms to differentiate – only the last two really, because the first doesn't contain any c_k and so will disappear when you start differentiating. These two terms are very easy to deal with if you make use of the supposed orthonormality of the expansion functions: for real functions $\int \phi_k^2 \mathrm{d}x = 1$, $\int \phi_k \phi_l \mathrm{d}x = 0$ $(k \neq l)$. Using these two properties, we can go back to (1.19) and differentiate the last two terms, with respect to each c_k (one at a time, holding the others fixed): the first of the two terms leads to

$$\frac{\partial}{\partial c_k} \int (f^{(n)})^2 \mathrm{d}x = \frac{\partial}{\partial c_k} c_k^2 \int \phi_k(x)^2 \mathrm{d}x = 2c_k;$$

while the second one gives

$$-2\frac{\partial}{\partial c_k} \int f f^{(n)} \mathrm{d}x = -2\frac{\partial}{\partial c_k} c_k \int f(x)\phi_k(x) \mathrm{d}x = -2\langle f|\phi_k\rangle,$$

where Dirac notation (see Chapter 9 of Book 11) has been used for the integral $\int f(x)\phi_k(x)\mathrm{d}x$, which is the **scalar product** of the two functions $f(x)$ and $\phi_k(x)$:

$$\langle f|\phi_k\rangle = \int f(x)\phi_k(x)\mathrm{d}x.$$

We can now do the differentiation of the whole difference function D in (1.18). The result is

$$\frac{\partial D}{\partial c_k} = 2c_k - 2\langle f|\phi_k\rangle$$

and this tells us immediately how to choose the coefficients in the n-term approximation (1.17) so as to get the best possible fit to the given function $f(x)$: setting all the derivatives equal to zero gives

$$c_k = \langle f|\phi_k\rangle \quad \text{(for all } k). \tag{1.25}$$

So it's really very simple: you just have to evaluate one integral to get any coefficient you want. And once you've got it, there's never any need to change it in getting a better approximation. You can make the expansion as long as you like by adding more terms, but the coefficients of the ones you've already done are *final*. Moreover, the results are quite general: if you use basis functions that are no longer real you only need change the definition of the scalar product, taking instead the *Hermitian* scalar product as in (1.1).

Generalizations

In studying atoms and molecules we'll have to deal with functions of very many variables, not just one. But some of the examples we met in Book 11 suggest possible ways of proceeding. Thus, in going from the harmonic oscillator in one dimension (Example 4.3), with eigenfunctions $\Psi_k(x)$, to the 3-dimensional oscillator (Example 4.4) it was possible to find eigenfunctions of *product form*, each of the three factors being of 1-dimensional form. The same was true for a particle in a rectangular box; and also for a free particle.

To explore such possibilities more generally we first ask if a function of two variables, x and x', defined for x in the interval (a,b) and x' in (a',b'), can be expanded in products of the form $\phi_i(x)\phi'_j(x')$. Suppose we write (hopefully!)

$$f(x,x') = \sum_{i,j} c_{ij}\phi_i(x)\phi'_j(x') \tag{1.26}$$

where the set $\{\phi_i(x)\}$ is complete for functions of x defined in (a,b), while $\{\phi'_i(x')\}$ is complete for functions of x' defined in (a',b'). Can we justify (1.26)? A simple argument suggests that we can.

For any given value of the variable x' we may safely take (if $\{\phi_i(x)\}$ is indeed complete)

$$f(x,x') = c_1\phi_1(x) + c_2\phi_2(x) \, + \, ... \, c_i\phi_i(x) \, + \, ...$$

where the coefficients must depend on the chosen value of x'. But then, because $\{\phi'_i(x')\}$ is also supposed to be complete, for functions of x' in the interval (a',b'), we may express the general coefficient c_i in the previous expansion as

$$c_i = c_{i1}\phi'_1(x') + c_{i2}\phi'_2(x') + ...c_{ij}\phi_j(x') + ...$$

On putting this expression for c_i in the first expansion we get the double summation postulated in (1.26) (as you should verify!). If the variables x, x' are interpreted as Cartesian coordinates the expansion may be expected to hold good within the rectangle bounded by the summation limits.

Of course, this argument would not satisfy any pure mathematician; but the further generalizations it suggests have been found satisfactory in a wide range of applications in

Applied Mathematics and Physics. In the quantum mechanics of many-electron systems, for example, where the different particles are physically identical and may be described in terms of a single complete set, the many-electron wave function is commonly expanded in terms of products of 1-electron functions (or 'orbitals').

Thus, one might expect to find 2-electron wave functions constructed in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i,j} c_{i,j}\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2),$$

where the same set of orbitals $\{\phi_i\}$ is used for each of the identical particles, the two factors in the product being functions of the different particle variables $\mathbf{r}_1, \mathbf{r}_2$. Here a boldface letter $\mathbf{r}$ stands for the set of three variables (e.g. Cartesian coordinates) defining the position of a particle at point r. The labels i and j run over all the orbitals of the (in principle) complete set, or (in practice) over all values $1, 2, 3, \ldots . n,$ in the finite set used in constructing an approximate wave function.

In Chapter 2 you will find applications to 2-electron atoms and molecules where the wave functions are built up from one-centre orbitals of the kind studied in Book 11. (You can find pictures of atomic orbitals there, in Chapter 3.)

Chapter 2

Some two-electron systems

2.1 Going from one particle to two

For two electrons moving in the field provided by one or more positively charged nuclei (supposedly fixed in space), the Hamiltonian takes the form

$$\mathsf{H}(1,2) = \mathsf{h}(1) + \mathsf{h}(2) + \mathsf{g}(1,2) \tag{2.1}$$

where $\mathsf{H}(1,2)$ operates on the variables of both particles, while $\mathsf{h}(i)$ operates on those of Particle i alone. (Don't get mixed up with names of the indices – here $i = 1,2$ label the two electrons.) The one-electron Hamiltonian $\mathsf{h}(i)$ has the usual form (see Book 11)

$$\mathsf{h}(i) = -\tfrac{1}{2}\nabla^2(i) + V(i), \tag{2.2}$$

the first term being the kinetic energy (KE) operator and the second being the potential energy (PE) of Electron i in the given field. The operator $\mathsf{g}(1,2)$ in (2.1) is simply the *interaction* potential, $e^2/\kappa_0 r_{ij}$, expressed in 'atomic units' (see Book 11) [1] So in (2.1) we take

$$\mathsf{g}(1,2) = g(1,2) = \frac{1}{r_{12}}, \tag{2.3}$$

r_{12} being the inter-electron distance. To get a very rough estimate of the total energy E, we may neglect this term altogether and use an approximate Hamiltonian

$$\mathsf{H}_0(1,2) = \mathsf{h}(1) + \mathsf{h}(2), \tag{2.4}$$

which describes an **Independent Particle 'Model'** of the system. The resultant IPM approximation is fundamental to all that will be done in Book 12.

---

[1] A fully consistent set of units on an 'atomic' scale is obtained by taking the **mass** and **charge** of the electron (m, e) to have unit values, along with the **action** $\hbar = h/2\pi$. Other units are $\kappa_0 = 4\pi\epsilon_0$ (ϵ_0 being the "**electric permittivity** of free space"); **length** $a_0 = \hbar^2\kappa_0/me^2$ and **energy** $e_{\rm H} = me^4/\kappa_0^2\hbar^2$. These quantities may be set equal to unity wherever they appear, leading to a great simplification of all equations. If the result of an *energy* calculation is the *number* x this just means that $E = xe_{\rm H}$; similarly a distance calculation would give $L = xa_0$.

With a Hamiltonian of this IPM form we can look for a solution of *product* form and use the 'separation method' (as in Chapter 4 of Book 11). We therefore look for a wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_m(\mathbf{r}_1)\phi_n(\mathbf{r}_2)$. Here each factor is a function of the position variables of only one of the two electrons, indicated by $\mathbf{r}_1$ or $\mathbf{r}_2$, and (to be general!) Electron 1 is described by a wave function ϕ_m while Electron 2 is described by ϕ_n.

On substituting this product in the eigenvalue equation $\mathsf{H}_0\Psi = E\Psi$ and dividing throughout by Ψ you get (do it!)

$$\frac{\mathsf{h}_(1)\phi_m(\mathbf{r}_1)}{\phi_m(\mathbf{r}_1)} + \frac{\mathsf{h}(2)\phi_n(\mathbf{r}_2)}{\phi_n(\mathbf{r}_2)} = E.$$

Now the two terms on the left-hand side are quite independent, involving different sets of variables, and their sum can be a constant E, only if each term is separately a constant. Calling the two constants ϵ_m and ϵ_n, the product $\Psi_{mn}(\mathbf{r}_1, \mathbf{r}_2) = \phi_m(\mathbf{r}_1)\phi_n(\mathbf{r}_2)$ will satisfy the eigenvalue equation provided

$$\begin{aligned} \mathsf{h}(1)\phi_m(\mathbf{r}_1) &= \epsilon_m\phi_m(\mathbf{r}_1), \\ \mathsf{h}(2)\phi_n(\mathbf{r}_2) &= \epsilon_n\phi_n(\mathbf{r}_2). \end{aligned}$$

The total energy will then be

$$E = \epsilon_m + \epsilon_n. \tag{2.5}$$

This means that the **orbital product** is an eigenfunction of the IPM Hamiltonian provided ϕ_m and ϕ_n are *any* solutions of the **one-electron** eigenvalue equation

$$\mathsf{h}\phi(\mathbf{r}) = \epsilon\phi(\mathbf{r}). \tag{2.6}$$

Note especially that the names given to the electrons, and to the corresponding variables $\mathbf{r}_1$ and $\mathbf{r}_2$, don't matter at all. The same equation applies to each electron and $\phi = \phi(\mathbf{r})$ is a function of position for whichever electron we're thinking of: that's why the labels 1 and 2 have been dropped in the *one-electron* equation (2.6). Each electron has 'its own' **orbital energy**, depending on which solution we choose to describe it, and since H_0 in (2.4) does not contain any interaction energy it is not surprising that their sum gives the total energy E. We often say that the electron "is in" or "occupies" the orbital chosen to describe it. If Electron 1 is in ϕ_m and Electron 2 is in ϕ_n, then the two-electron function

$$\Psi_{mn}(\mathbf{r}_1, \mathbf{r}_2) = \phi_m(\mathbf{r}_1)\phi_n(\mathbf{r}_2)$$

will be an exact eigenfunction of the IPM Hamiltonian (2.4), with eigenvalue (2.5).

For example, putting both electrons in the lowest energy orbital, ϕ_1 say, gives a wave function $\Psi_{11}(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2)$ corresponding to total energy $E = 2\epsilon_1$. This is the (strictly!) IPM description of the **ground state** of the system. To improve on this approximation, which is very crude, we must allow for electron interaction: the next approximation is to use the full Hamiltonian (2.1) to calculate the energy expectation value for the IPM function (no longer an *eigen*-function of H). Thus

$$\Psi_{11}(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2). \tag{2.7}$$

and this gives

$$\bar{E} = \langle\Psi_{11}|\mathsf{h}(1) + \mathsf{h}(2) + \mathsf{g}(1,2)|\Psi_{11}\rangle = 2\langle\phi_1|\mathsf{h}|\phi_1\rangle + \langle\phi_1\phi_1|g|\phi_1\phi_1\rangle, \tag{2.8}$$

where the first term on the right is simply twice the energy of one electron in orbital ϕ_1, namely $2\epsilon_1$. The second term involves the *two*-electron operator given in (2.3) and has explicit form

$$\langle\phi_1\phi_1|g|\phi_1\phi_1\rangle = \int \phi_1^*(\mathbf{r}_1)\phi_1^*(\mathbf{r}_2)\frac{1}{r_{12}}\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2, \tag{2.9}$$

Here the variables in the bra and the ket will always be labelled in the order 1,2 and the volume element $\mathrm{d}\mathbf{r}_1$, for example, will refer to integration over all particle variables (e.g. in Cartesian coordinates it is $\mathrm{d}x_1\mathrm{d}y_1\mathrm{d}z_1$). (Remember also that, in bra-ket notation, the functions that come from the bra should in general carry the star (complex conjugate); and even when the functions are real it is useful to keep the star.)

To evaluate the integral we need to know the form of the 1-electron wave function ϕ_1, but the expression (2.9) is a valid first approximation to the electron repulsion energy in the ground state of any 2-electron system.

Let's start with the Helium atom, with just two electrons moving in the field of a nucleus of charge $Z = 2$.

2.2 The Helium atom

The function (2.7) is clearly normalized when, as we suppose, the orbitals themselves (which are now **atomic orbitals**) are normalized; for

$$\langle\phi_1\phi_1|\phi_1\phi_1\rangle = \int \phi_1^*(\mathbf{r}_1)\phi_1^*(\mathbf{r}_2)\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 = \langle\phi_1|\phi_1\rangle\,\langle\phi_1|\phi_1\rangle = 1 \times 1.$$

The approximate energy (2.8) is then

$$\bar{E} = 2\epsilon_1 + \langle\phi_1\phi_1|g|\phi_1\phi_1\rangle = 2\epsilon_1 + J_{11}, \tag{2.10}$$

Here ϵ_1 is the *orbital energy* of an electron, by itself, in orbital ϕ_1 in the field of the nucleus; the 2-electron term J_{11} is often called a 'Coulomb integral' because it corresponds to the Coulombic repulsion energy (see Book 10) of two distributions of electric charge, each of density $|\phi_1(\mathbf{r})|^2$ per unit volume. For a hydrogen-like atom, with atomic number Z, we know that $\epsilon_1 = -\frac{1}{2}Z^2\mathrm{e_H}$. When the Coulomb integral is evaluated it turns out to be $J_{11} = (5/8)Z\mathrm{e_H}$ and the approximate energy thus becomes $\bar{E} = -Z^2 + (5/8)Z$ in 'atomic' units of $\mathrm{e_H}$. With $Z = 2$ this gives a first estimate of the electronic energy of the Helium atom in its ground state: $\bar{E} = -2.75\,\mathrm{e_H}$, compared with an experimental value $-2.90374\,\mathrm{e_H}$.

To improve the ground state wave function we may use the variation method as in Section 1.2 by choosing a new function $\phi_1' = N'e^{-Z'r}$, where Z' takes the place of the actual nuclear charge and is to be treated as an adjustable parameter. This allows the electron to 'feel' an 'effective nuclear charge' a bit different from the actual $Z = 2$. The corresponding normalizing factor N' will have to be chosen so that

$$\langle\phi_1'|\phi_1'\rangle = N'^2 \int \exp(-2Z'r)(4\pi r^2)\mathrm{d}r = 1$$

and this gives (prove it!) $N'^2 = Z'^3/\pi$.

The energy expectation value still has the form (2.8) and the terms can be evaluated separately

Example 2.1 Evaluation of the one-electron term

The first 1-electron operator has an expectation value $\langle\Psi_{11}|\mathsf{h}(1)|\Psi_{11}\rangle = \langle\phi_1'|\mathsf{h}|\phi_1'\rangle\langle\phi_1'|\phi_1'\rangle$, a matrix element of the operator h times the scalar product $\langle\phi_1'|\phi_1'\rangle$. In full, this is

$$\langle\Psi_{11}|\mathsf{h}(1)|\Psi_{11}\rangle = N'^2\int_0^\infty e^{-Z'r}\mathsf{h}e^{-Z'r}4\pi r^2\mathrm{d}r \times N'^2\int_0^\infty e^{-Z'r}e^{-Z'r}4\pi r^2\mathrm{d}r,$$

where h working on a function of r alone is equivalent to $(-\frac{1}{2}\nabla^2 - Z/r)$ – h containing the *actual* charge (Z).

We can spare ourselves some work by noting that if we put $Z = Z'$ the function $\phi_1' = N'e^{-Z'r}$ becomes an eigenfunction of $(-\frac{1}{2}\nabla^2 - Z'/r)$ with eigenvalue $\epsilon' = -\frac{1}{2}Z'^2$ (Z' being a 'pretend' value of Z. So

$$\mathsf{h} = -\tfrac{1}{2}\nabla^2 - Z/r = (-\tfrac{1}{2}\nabla^2 - Z'/r) + (Z' - Z)/r,$$

where the operator in parentheses is easy to handle: when it works on ϕ_1' it simply multiplies it by the eigenvalue $-\frac{1}{2}Z'^2$. Thus, the operator h, *working on the function* $N'e^{-Z'r}$ gives

$$\mathsf{h}(N'e^{-Z'r}) = \left(-\tfrac{1}{2}Z'^2 + \tfrac{Z'-Z}{r}\right)N'e^{-Z'r}.$$

The one-electron part of (2.8) can now be written as (two equal terms – say why!) $2\langle\Psi_{11}|\mathsf{h}(1)|\Psi_{11}\rangle$ where

$$\begin{aligned}
\langle\Psi_{11}|\mathsf{h}(1)|\Psi_{11}\rangle &= \langle\phi_1'|\mathsf{h}|\phi_1'\rangle\langle\phi_1'|\phi_1'\rangle \\
&= N'^2\int_0^\infty e^{-Z'r}\mathsf{h}e^{-Z'r}4\pi r^2\mathrm{d}r \times N'^2\int_0^\infty e^{-2Z'r}4\pi r^2\mathrm{d}r \\
&= N'^2\int_0^\infty e^{-Z'r}\left(-\tfrac{1}{2}Z'^2 + \tfrac{Z'-Z}{r}\right)e^{-Z'r}4\pi r^2\mathrm{d}r.
\end{aligned}$$

Here the last integral on the second line is unity (normalization) and leaves only the one before it. This remaining integration gives (check it out!) $\langle\Psi_{11}|\mathsf{h}(1)|\Psi_{11}\rangle = -\frac{1}{2}Z'^2 + 4\pi(Z' - Z)N'^2\int_0^\infty(re^{-2Z'r})\mathrm{d}r$ and from the simple definite integral $\int_0^\infty xe^{-ax}\mathrm{d}x = (1/a^2)$ it follows that

$$\langle\Psi_{11}|\mathsf{h}(1)|\Psi_{11}\rangle = -\tfrac{1}{2}Z'^2 + 4\pi(Z' - Z)N'^2(1/2Z')$$

and since $N'^2 = Z'^3/\pi$ the final result is

$$\langle\Psi_{11}|\mathsf{h}(1)|\Psi_{11}\rangle = -\tfrac{1}{2}Z'^2 + Z'(Z' - Z).$$

Example 2.1 has given the expectation value of the $\mathsf{h}(1)$ term in (2.8), but $\mathsf{h}(2)$ must give an identical result since the only difference is a change of electron label from 1 to 2; and the third term must have the value $J'_{11} = (5/8)Z'$ since the nuclear charge Z has been given the varied value Z' only in the orbital exponent (nothing else being changed).

On putting these results together, the energy expectation value after variation of the orbital exponent will be

$$\bar{E} = -Z'^2 + 2Z'(Z' - Z) + (5/8)Z' \tag{2.11}$$

– all, as usual, in energy units of $\mathrm{e_H}$.

The variational calculation can now be completed: $\bar{E}$ will be stationary when

$$\frac{\mathrm{d}\bar{E}}{\mathrm{d}Z'} = -2Z' + 4Z' - 2Z + (5/8) = 0$$

and this means that the best estimate of the total electronic energy will be found on reducing the orbital exponent from its value $Z = 2$ for one electron *by itself* to the value $Z' = 2 - (5/16)$ in the presence of the second electron. In other words, the central field is effectively reduced or 'screened' when it holds another electron: the **screening constant** (5/16) is quite large and the ground state orbital expands appreciably as a result of the screening.

The corresponding estimate of the ground state energy is

$$\bar{E} = -(27/16)^2 = -2.84765\,\mathrm{e_H} \tag{2.12}$$

– a value which compares with $-2.75\,\mathrm{e_H}$ before the variation of Z and is much closer to the 'exact' value of $-2.90374\,\mathrm{e_H}$ obtained using a very elaborate variation function.

Before moving on, we should make sure that the value used for the Coulomb integral $J = (5/8)Z\mathrm{e_H}$ is correct[2]. This is our first example of a 2-electron integral: for two electrons in the same orbital ϕ it has the form (2.9), namely (dropping the orbital label '1')

$$J = \int \phi^*(\mathbf{r}_1)\phi^*(\mathbf{r}_2)\frac{1}{r_{12}}\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2.$$

To evaluate it, we start from Born's interpretation of the wave function $|\phi(\mathbf{r})|^2 = \phi^*(\mathbf{r})\phi(\mathbf{r})$ (the star allowing the function to be *complex*) as a **probability density**. It is the probability *per unit volume* of finding the electron in a small element of volume $\mathrm{d}\mathbf{r}$ at Point $\mathbf{r}$ and will be denoted by $\rho(\mathbf{r}) = \phi^*(\mathbf{r})\phi(\mathbf{r})$. As you know from Book 11, this interpretation is justified by countless experimental observations.

We now go a step further: the average value of any quantity $f(\mathbf{r})$ that depends only on the instantaneous *position* of the moving electron will be given by $\bar{f} = \int f(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r}$ where, as usual, the integration is over all space (i.e. all values of the electronic variables). Now the electron carries a charge $-e$ and produces a potential field $V_{\mathbf{r}'}$ at any chosen 'field point' $\mathbf{r}'$.

---

[2] If you find the proof too difficult, just take the result on trust and keep moving!

It's convenient to use $\mathbf{r}_1$ for the position of the electron (instead of $\mathbf{r}$) and to use $\mathbf{r}_2$ for the second point, at which we want to get the potential $V_{\mathbf{r}_2}$. This will have the value $V_{\mathbf{r}_2} = -e/\kappa_0|\mathbf{r}_{21}|$, where $|\mathbf{r}_{21}| = |\mathbf{r}_{12}| = r_{12}$ is the *distance* between the electron at $\mathbf{r}_1$ and the field point $\mathbf{r}_2$.

When the electron moves around, its position being described by the probability density $\rho(\mathbf{r}_1)$, the electric potential it produces at any point $\mathbf{r}'$ will then have an average value

$$\bar{V}(\mathbf{r}_2) = \frac{-e}{\kappa_0}\int \frac{1}{|\mathbf{r}_{21}|}\mathrm{d}\rho(\mathbf{r}_1)\mathbf{r}_1.$$

In words, this means that

> The average electric field at point $\mathbf{r}_2$, produced by an electron at point $\mathbf{r}_1$ with probability density $\rho(\mathbf{r}_1)$, can then be calculated just as if the 'point' electron were 'smeared out' in space, with a charge density $-e\rho(\mathbf{r}_1)$.

(2.13)

The statement (2.13) provides the **charge cloud** picture of the probability density. It allows us to visualize very clearly, as will be seen later, the origin of many properties of atoms and molecules. As a first application let's look at the Coulomb integral J.

Example 2.2 Interpretation of the electron interaction.

The integral J can now be viewed as the interaction energy of two distributions of electric charge, both of density $-e\rho(\mathbf{r})$ and of spherical form (one on top of the other). (If that seems like nonsense remember this is only a mathematical interpretation!)

The two densities are in this case $\rho_1(\mathbf{r}_1) = N^2 \exp -2Zr_1^2$ and $\rho_2(\mathbf{r}_2) = N^2 \exp -2Zr_2^2$; and the integral we need follows on putting the interaction potential $V(\mathbf{r}_1, \mathbf{r}_2) = 1/r_{12}$ between the two and integrating over all positions of both points. Thus, giving e and κ_0 their unit values, J becomes the double integral

$$J = ZN^4 \int\int \exp -2Zr_1^2 \,\frac{1}{r_{12}} \exp -2Zr_2^2 \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2,$$

where $(1/r_{12})$ is simply the inverse distance between the two integration points. On the other hand, $\mathrm{d}\mathbf{r}_1$ and $\mathrm{d}\mathbf{r}_2$ are 3-dimensional elements of volume; and when the charge distributions are spherically symmetrical functions of distance (r_1, r_2) from the origin (the nucleus), they may be divided into spherical *shells* of charge. The density is then constant within each shell, of thickness $\mathrm{d}r$; and each holds a total charge $4\pi r^2 \mathrm{d}r \times \rho(r)$, the density being a function of radial distance (r) alone.

Now comes a nice connection with Electrostatics, which you should read about again in Book 10, Section 1.4. Before going on you should pause and study Figure 2.2, to have a clear picture of what we must do next.

Example 2.2 perhaps gave you an idea of how difficult it can be to deal with 2-electron integrals. The diagram below will be helpful if you want to actually evaluate J, the simplest one we've come across.

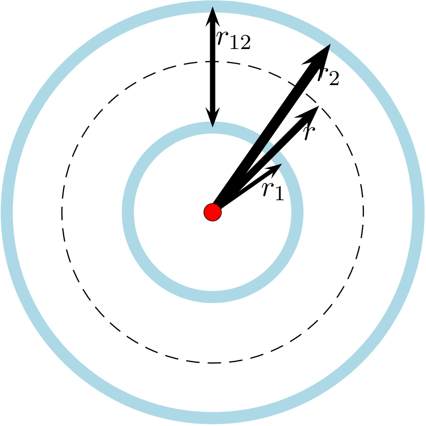

Figure 2.2 Spherical shells of electron density (blue)

The integral J gives the electrostatic potential energy of two spherical charge distributions. Each could be built up from spherical 'shells' (like an onion): these are shown in blue, one for Electron 1 having radius r_1 and another for Electron 2 with radius r_2. The distance between the two shells is shown with label r_{12} and this determines their potential energy as the product of the total charges they contain ($4\pi r_1^2 \mathrm{d}r_1$ and $4\pi r_2^2 \mathrm{d}r_2$) times the inverse distance (r_{12}^{-1}). The total potential energy is obtained by summing (integrating) over all shells – but you need a trick! at any distance r from the nucleus, the potential due to an *inner* shell ($r_1 < r$) is constant until r_1 reaches r and changes form; so the first integration breaks into two parts, giving a result which depends only on where you put r (indicated by the broken line).

Example 2.3 Evaluation of the electron interaction integral, J

To summarize, J arises as the interaction energy of all pairs of spherical shells of charge, shown (blue) in Figure 2.2, and this will come from integration over all shells. We take one pair at a time.

You know from Book 10 that the electrostatic potential at distance r from the origin (call it $V(r)$) due to a spherical shell of charge, of radius r_1, is given by

$$\begin{aligned} V(r) &= Q_{r_1} \times \frac{1}{r_1} \quad \text{for } r < r_1, \\ &= Q_{r_1} \times \frac{1}{r} \quad \text{for } r > r_1, \end{aligned}$$

where $Q_{r_1} = 4\pi r_1^2 \mathrm{d}r_1 \times \rho(r_1)$ is the total charge contained in the shell of radius r_1 and thickness $\mathrm{d}r_1$. The potential is thus constant *within* the first shell; but *outside* has a value corresponding to all the charge being put *at the origin.*

We can now do the integration over the variable r_1 as it goes from 0 to ∞. For $r_1 < r$ the sum of the contributions to J from the shells within a sphere of radius r will be

$$(1/r)\int_0^r \exp(-2Zr_1^2) 4\pi r_1^2 \mathrm{d}r_1, \qquad (A)$$

while for $r_1 > r$ the rest of the r_1 integration will give the sum of contributions from shells of radius greater than r, namely

$$\int_r^\infty \exp(-2Zr_1^2)(1/r_1)4\pi r_1^2 \mathrm{d}r_1. \qquad (B)$$

You've met integrals a bit like these in Chapter 1, so you know how to do them and can show (do it!) that the sum of A and B is the potential function

$$V(r) = \frac{4\pi}{r}[2 - e^{-r}(2 + r)].$$

This is a function of r alone, the radius of the imaginary sphere that we used to separate the integration over r_1 into two parts, so now we can put $r = r_2$ and multiply by $(4\pi r_2^2 \mathrm{d}r_2)Ne^{-r_2}$ to obtain the energy of one shell of the second charge distribution in the field generated by the first.

After that it's all plain sailing: the integration over all the outer shells (r_2) now goes from 0 to ∞ – and you're home and dry! Integration over r_2, for all shells from $r_2 = 0$ to ∞, will then give (check it out!)

$$J = \frac{Z}{2}\int_0^\infty [2 - e^{-r_2}(2 + r_2)]e^{-r_2} r_2 \mathrm{d}r_2 = (5/8)Z.$$

Example 2.3 gave you a small taste of how difficult it can be to actually evaluate the 2-electron integrals that are needed in describing electron interactions.

Now you know how to get a decent wave function for two electrons moving in the field of a single nucleus – the helium atom – and how the approximation can be improved as much as you wish by using the variation method with more elaborate trial functions. But following that path leads into difficult mathematics; so instead let's move on and take a quick look at some excited states.

First excited states of He

In Book 11 we studied central-field systems, including many-electron atoms, in order to illustrate the general principles of quantum mechanics. In particular, we looked for sets of commuting operators associated with observable quantities such as angular momentum, finding that the angular momentum operators for motion in a central field commuted with the Hamiltonian H (see Chapter 6 of Book 11) and could therefore take simultaneously definite eigenvalues, along with the energy. For such a system, the energy eigenstates could be grouped into series, according to values of the angular momentum quantum numbers L and M which determine the angular momentum and *one* of its three components.

But here we are dealing with systems of at most two electrons and the general theory is not needed: a 2-electron wave function is represented approximately as a product of 1-electron **orbitals**. And for the Helium atom we are dealing with spherically symmetrical wave functions, which involve only 's-type' orbitals, with zero angular momentum.

As a first example of an excited state we suppose one of the two electrons in the ground state, with wave function $\Psi_{11}(\mathsf{r}_1, \mathsf{r}_2) = \phi_1(\mathsf{r}_1)\phi_2(\mathsf{r}_2)$, is 'promoted' into the next higher orbital ϕ_2 of the s series. According to equation (6.10) of Book 11 Chapter 6, this AO corresponds to energy $E_2 = -\frac{1}{2}(Z^2/4)$, the whole series being depicted in Figure 13.

Example 2.4 Excited state wave functions and energies

When one of the two electrons is promoted from the lowest-energy AO ϕ_1 into the next one, ϕ_2, there are clearly two distinct ways of representing the state by an IPM function: it could be either

$$\Psi_{12}(\mathbf{r}_1,\mathbf{r}_2) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2),$$

in which Electron 2 has been promoted, or

$$\Psi_{21}(\mathbf{r}_1,\mathbf{r}_2) = \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2),$$

in which Electron 1 (with coordinates $\mathbf{r}_1$) has been put into ϕ_2, the second electron staying in ϕ_1. And at this point *three* product functions are available for constructing 2-electron wave functions – those we have called Ψ_{11}, the IPM ground state, and Ψ_{12}, Ψ_{21}, in which one of the electrons has been promoted. We could of course set up other products Ψ_{lm}, with both electrons promoted to higher-energy AOs, and suppose these may be used in the first few terms of a **complete set** expansion of the 2-electron wave function. The products corresponding to any particular choice of the orbitals e.g. ϕ_1, ϕ_2 are said to belong to the same **electron configuration**.

Here, to simplify things, we'll use a single-subscript notation to denote the first three products: $\Psi_1 = \phi_1\phi_1,\ \Psi_2 = \phi_1\phi_2,\ \Psi_3 = \phi_2\phi_1$, We can then use the linear variation method (Section 1.3) to get improved approximations to the three lowest-energy wave functions in the form

$$\Psi = c_1\Psi_1 + c_2\Psi_2 + c_3\Psi_3.$$

This involves setting up the **secular equations**

$$\begin{aligned}(H_{11} - \bar{E}M_{11})c_1 + (H_{12} - \bar{E}M_{12})c_2 + (H_{13} - \bar{E}M_{13})c_3 = 0,\\ (H_{21} - \bar{E}M_{21})c_1 + (H_{22} - \bar{E}M_{22})c_2 + (H_{23} - \bar{E}M_{23})c_3 = 0,\\ (H_{31} - \bar{E}M_{31})c_1 + (H_{32} - \bar{E}M_{32})c_2 + (H_{33} - \bar{E}M_{33})c_3 = 0,\end{aligned}$$

where, as usual, $H_{ij} = \langle\Psi_i|\mathsf{H}|\Psi_j\rangle$ and $M_{ij} = \langle\Psi_i|\Psi_j\rangle$. On solving them we obtain, along with the optimized mixtures, improved approximations to the energies E_1, E_2, E_3 of the first three electronic states. (Read Section 1.3 again if you need to.)

Here, the approximate ground-state function Ψ_1 has a very small overlap with Ψ_2 and Ψ_3; for example

$$M_{12} = \langle\Psi_1|\Psi_2\rangle = \langle\phi_1\phi_1|\phi_1\phi_2\rangle = \langle\phi_1|\phi_1\rangle\langle\phi_1|\phi_2\rangle \approx 0,$$

because $\langle\phi_1|\phi_1\rangle = 1$ and $\langle\phi_1|\phi_2\rangle \approx 0$ – the 1s and 2s AOs being normalized and lying mainly in different regions of space. For similar reasons, other off-diagonal terms such as H_{12}, H_{13}, which connect the IPM ground state Ψ_1 with the higher-energy functions Ψ_2, Ψ_3 are usually small enough to be neglected.

With such approximations (check them out!) the secular equations may be written

$$\begin{aligned}(H_{11} - \bar{E})c_1 &= 0,\\ (H_{22} - \bar{E})c_2 &= -H_{23}c_3,\\ H_{32}c_2 &= -(H_{33} - \bar{E})c_3.\end{aligned}$$

The first equation says that $\bar{E} \approx H_{11}$ is still an approximation to the ground-state energy E_1. The other equations allow us to eliminate the expansion coefficients and to determine approximate eigenvalues for two excited states. Thus (you've done it all before in Section 1.3!), on dividing each side of the second equation by the corresponding side of the third, the coefficients cancel and leave you with

$$\frac{(H_{22} - \bar{E})}{H_{32}} = \frac{H_{23}}{(H_{33} - \bar{E})}.$$

Now we know that $H_{22} = H_{33}$ (say why!) and $H_{32} = H_{23}$ (real matrix elements) and if we call these quantities α and β the equation becomes $(\alpha - \bar{E})^2 = \beta^2$. The two roots are $(\alpha - \bar{E}) = \pm\beta$ and give two approximate excited-state energies: $\bar{E}^{(+)} = \alpha + \beta$ and $\bar{E}^{(-)} = \alpha - \beta$.

To end this example let's get the energies of these states, just as we did for the ground state, where we found $\bar{E} = 2\epsilon_1 + J_{11}$ in terms of orbital energy ϵ_1 and Coulomb interaction J_{11}. (You should read again, from equation (2.7) to equation (2.8), to remind yourself of how we did it.)

The excited states are linear combinations of the functions Ψ_2, Ψ_3, which belong to the configuration 1s2s. Thus $\Psi_2^{(+)}$ for the 'plus combination', with energy $\bar{E}_2^{(+)}$, is obtained by putting $\bar{E}_2^{(+)} = \alpha + \beta$ back into the second equation, which shows that $c_3 = c_2$. This state therefore has the (normalized) form $\Psi_2^{(+)} = (\Psi_2 + \Psi_3)/\sqrt{2}$ and $\Psi_2^{(-)}$ will be similar, with the plus changed to a minus.

The energy expectation value in state $\Psi_2^{(+)}$ will be $\langle\Psi_2^{(+)}|\mathsf{H}|\langle\Psi_2^{(+)}\rangle = \frac{1}{2}[H_{22} + H_{33} + 2H_{23}]$, where $H_{22} = H_{33} = \langle\Psi_2|\mathsf{H}|\Psi_2\rangle$ and $H_{23} = \langle\Psi_2|\mathsf{H}|\Psi_3\rangle$. Now $\Psi_2 = \phi_1\phi_2$ and $\Psi_3 = \phi_2\phi_1$, so it follows (check it, remembering that the order of the variables in an orbital product is always $\mathbf{r}_1, \mathbf{r}_2$) that

$$H_{22} = H_{33} = \langle\Psi_2|\mathsf{H}|\langle\Psi_2\rangle = \epsilon_1 + \epsilon_2 + J_{12} \text{ and } H_{23} = \langle\Psi_2|\mathsf{H}|\Psi_3\rangle = K_{12}.$$

Finally, then, the energy expectation value in state $\Psi_2^{(+)}$ will be

$$E_2^{(+)} = \langle\Psi_2^{(+)}|\mathsf{H}|\langle\Psi_2^{(+)}\rangle = [\epsilon_1 + \epsilon_2 + J_{12}] + K_{12},$$

while $E_2^{(-)}$ will follow on changing the sign of the K-term.

(Note that the J and K terms are quite different:

$$J_{12} = \langle\Psi_2|\mathsf{g}|\Psi_2\rangle = \langle\phi_1\phi_2|g(1,2)|\phi_1\phi_2\rangle, \qquad K_{12} = \langle\Psi_2|\mathsf{g}|\Psi_3\rangle = \langle\phi_1\phi_2|g(1,2)|\phi_2\phi_1\rangle,$$

– the 'ket' part of the matrix element $\langle\Psi_2|\mathsf{g}|\Psi_3\rangle$ containing the orbitals *after* exchange of the electron labels. It's no surprise that K_{12} is called an "exchange integral"!)

Example 2.4 was tough, but was done in detail because it leads us to tremendously important conclusions, as you'll see presently. (If you didn't manage to get through it yourself, don't worry – you can move on and come back to it later.) What matters here is mainly the way the two wave functions $\Psi_2^{(+)}$ and $\Psi_2^{(-)}$ behave under *symmetry operations* that make no apparent change to the system. The two terms in $\Psi_2^{(+)}$ differ only by an interchange of electronic variables $\mathbf{r}_1, \mathbf{r}_2$ (as you can check from the definitions) and their *sum* does not change at all under such an operation: we say the wave function $\Psi_2^{(+)}$ is **symmetric under exchange of the electrons**. On the other hand the other state, with energy $\bar{E}_2^{(-)} = \alpha - \beta$, has a wave function $\Psi_2^{(-)} = (\Phi_2 - \Phi_3)/\sqrt{2}$, which changes sign on exchanging the electrons and is said to be **antisymmetric**.

2.3 But what happened to the spin?

We started Book 11, on the basic principles of quantum mechanics, by talking about the Stern-Gerlach experiment – which showed a moving electron was not fully described by giving its *position* variables x, y, z, it needed also a **spin variable** s with only two observable values. But it seems as if we've completely forgotten about spin, using wave functions that depend only on position of the electron in space. The reason is simple: the spin (identified in Book 11 as some kind of *internal* angular momentum) has such a small effect on energy levels that it's hardly observable! You can solve the Schrödinger equation, and get meaningful results, because the usual Hamiltonian operator contains no spin operators and acts only on the position variables in the wave function. But in dealing with many-particle systems it's absolutely essential to label states according to their spin properties: as you will see presently, without spin you and I would not exist – there would be no Chemistry!

It's easy to put the spin back into our equations: just as the product function $\Psi_{mn}(\mathbf{r}_1, \mathbf{r}_2) = \phi_m(\mathbf{r}_1)\phi_n(\mathbf{r}_2)$ was used to describe two independent particles, in states ϕ_m and ϕ_n, so can we use a product $\phi(\mathbf{r})\theta(s)$ to describe a particle in orbital state ϕ and in spin state θ. If ϕ is an eigenstate of the *spinless* operator h (with eigenvalue ϵ) and θ is an eigenstate of S_z (with spin component $s = S_z$ along the z-axis), then the product is a simultaneous eigenstate of both operators:

$$\mathsf{h}[\phi\theta] = (\mathsf{h}\phi)\theta = (\epsilon\phi)\theta = \epsilon[\phi\theta]$$

since the operator h doesn't touch the θ-factor; and similarly

$$\mathsf{S}_z[\phi\theta] = \phi(\mathsf{S}_z\theta) = \phi(S_z\theta) = S_z[\phi\theta]$$

– since the operator S_z doesn't touch the ϕ-factor.

Now the 'spin-space' is only two-dimensional, with basis vectors denoted by α and β corresponding to $s = +\frac{1}{2}$ and $s = -\frac{1}{2}$ (in units of $\hbar$), respectively. So for any given orbital state ϕ there will be two alternative possibilities $\phi\alpha$ and $\phi\beta$ when spin is taken into account. Products of this kind are called **spin-orbitals**. From now on let's agree to use Greek letters (ψ, Ψ) for states with the spin description included, leaving ϕ, Φ for 'orbital' states (as used so far) which don't contain any spin factors. The lower-case (small) letters will be used for *one*-electron states, upper-case (capital) letters for *many*-electron states.

As long as we deal only with a *two*-electron system, the state vector (or corresponding wave function) can be expressed as a product of space and spin factors: $\Psi(1,2) = \Phi(1,2)\Theta(1,2)$, where the electron labels are used to indicate spatial or spin variables for electrons 1 and 2. When we want to be more explicit we'll use a fuller notation, as below.

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \Phi(\mathbf{r}_1, \mathbf{r}_2)\Theta(s_1, s_2). \tag{2.14}$$

Here $\mathbf{x}$ stands for both space and spin variables together, so $\mathbf{x} \equiv \mathbf{r}, s$. This is a neat way of saying that $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ in (2.14) really means $\Phi(x_1, y_1, z_1, x_2, y_2, z_2)\Theta(s_1, s_2)$!

In the following Example we shall be looking for a simultaneous eigenstate of all commuting operators, which will normally include H, S^2, S_z. We suppose $\Phi(1,2)$ is an eigenstate (exact or approximate) of the usual spinless Hamiltonian $\mathsf{H}(1,2)$ and take $\Theta(1,2)$ as an eigenstate of *total spin* of the two particles i.e. of the operators S^2, S_z.

Before continuing you should turn back to Section 2.2 of Book 11 and make sure you understand the properties of the total spin operators $\mathsf{S}_x = \mathsf{S}_x(1) + \mathsf{S}_x(2)$, $\mathsf{S}_y = \mathsf{S}_y(1) + \mathsf{S}_y(2)$, $\mathsf{S}_z = \mathsf{S}_z(1) + \mathsf{S}_z(2)$.

Remember, they follow the same commutation rules as for a single particle and that you can define step-up and step-down operators $\mathsf{S}^{\pm} = (\mathsf{S}_x \pm i\mathsf{S}_y)$ in the same way; from them you can set up the operator S^2 and show that it has eigenvalues of the form $S(S+1)$ (in units of $\hbar^2$), where $S = 1$ ('parallel-coupled' spins) or $S = 0$ ('paired' spins). Study especially Example 2.2, which gives the spin eigenstates for a 2-electron system.

Example 2.7 Symmetry properties of the spin eigenstates

In Example 2.2 of Book 11 it was shown that, for two spin-coupled electrons, the eigenstates of S^2 and S_z with quantum numbers $S = 0, \pm 1$ were as follows:

- (1,1) $\Theta_{1,1} = \alpha(1)\alpha(2)$
- (1,0) $\Theta_{1,0} = \beta(1)\alpha(2) + \alpha(1)\beta(2)$
- (0,0) $\Theta_{0,0} = \beta(1)\alpha(2) - \alpha(1)\beta(2)$
- (1,-1) $\Theta_{1,-1} = \beta(1)\beta(2)$

(Here the S- and M- quantum numbers are shown in parentheses and the state symbol Θ has been used to denote a two-electron spin state)

It's important to know how these eigenstates change under a **symmetry operation** which has no observable effect on the system. In this case, all electrons are identical – we can't tell one from another – so exchanging the labels '1' and '2' (call it P_{12}) should be a symmetry operation ($\mathsf{P}_{12}\alpha(1)\beta(2) = \alpha(2)\beta(1)$ means that Electron '1' goes into the 'down-spin' state, previously occupied by Electron '2', while Electron '2' goes into an 'up-spin' state – but the change is not observable).

If you examine all the spin states listed above you'll see at once that all the states with $S = 1$ are unchanged, they are *symmetric* under the exchange; but the single state with $S = 0$ *changes sign* – it is *antisymmetric* under exchange, being multiplied by -1.

We're now ready to go back and look again at the excited states of the Helium atom, but *with spin included.* The complete wave function will now be a 'space-spin' product of the form $\Psi(1,2) = \Phi(1,2)\Theta(1,2)$, where the two factors are now re-named as agreed in the run-up to (2.16). Possible choices for the orbital factor are then Φ_1, for the ground state, with both electrons in the first (lowest-energy) AO ϕ_1; and $\Phi_2^{(+)}$ or $\Phi_2^{(-)}$, for the excited states with one electron in the AO ϕ_1 and the other is in the next AO ϕ_2 – with a 'plus' combination or a 'minus' combination of Φ_2, Φ_3. The available energy states for the two-electron atom, without spin, would seem to be:

- Ground state. Energy = E_1, wave function Φ_1
- 1st excited state. Energy = $E_2^{(-)}$, wave function $(\Phi_2 - \Phi_3)/\sqrt{2}$ (normalized 'minus' combination),
- 2nd excited state. Energy = $E_2^{(+)}$, wave function $(\phi_2 + \Phi_3)/\sqrt{2}$ (normalized'plus' combination).

What happens when spin is taken into account? When the two electrons are interchanged, both space and spin variables change:

$$\mathbf{r}_1, \mathbf{r}_2 \rightarrow \mathbf{r}_2, \mathbf{r}_1 \quad \text{and} \quad s_1, s_2 \rightarrow s_2, s_1.$$

But the energy levels are determined essentially by the Φ factor; so let's take the states as listed above and ask what symmetry each state will have when spin is included.

The space-spin product function $\Psi = \Phi\Theta$ for the ground state will have $\Phi = \Phi_1$ which is symmetric under electron exchange, but may take possible spin factors:

$$\Theta = \Theta_{1,1}, \quad \text{or} \quad \Theta_{1,0}, \quad \text{or} \quad \Theta_{1,-1},$$

which are all symmetric under spin exchange. So three possible Ψ products can be found; all are 'totally' symmetric and correspond to the same energy – suggesting a 'three-fold degenerate triplet' ground state.

On the other hand, Φ_1 might have been combined with $\Theta_{0,0} = \beta(1)\alpha(2) - \alpha(1)\beta(2)$ and that would have given a totally *antisymmetric* space-spin product – a 'non-degenerate singlet' ground state.

The results we're going to get can be summarized very easily in a diagram showing the first few energy levels you might expect to find for any two-electron system. The alternatives we've just found for the ground state correspond to the lowest levels in (a) and (b) of Figure 2.7:

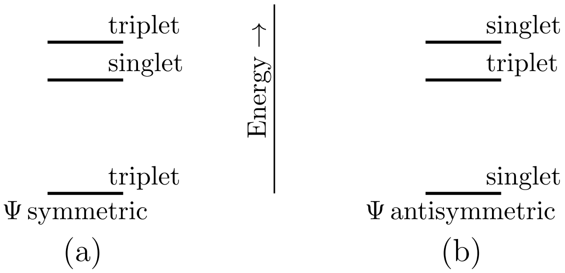

Figure 2.7 Some electronic states of the He atom

Lowest level (ground state) for configuration $1s^2$, upper levels (excited states) for configuration 1s2s. Multiplicities of the calculated states are shown in (a) for *symmetric* Ψ and (b) for *antisymmetric* Ψ.

What about the excited state with energy $E_2^{(-)}$? The antisymmetric space factor $\Phi_2^{(-)}$ could be associated with any of the three symmmetric spin factors, to give three antisymmetric space-spin products. But it could equally well be attached to the antisymmetric spin factor $\Theta_{0,0} = \beta(1)\alpha(2) - \alpha(1)\beta(2)$ to give a single totally symmetric Ψ-product.

Finally, the excited state with energy $E_2^{(+)}$ and symmetric space factor $\Phi_2^{(+)}$ could be associated with the antisymmetric spin factor $\Theta_{0,0}$ to give an antisymmetric space-spin Ψ-product; or equally well combined with any one of the three symmetric spin factors $\Theta_{1,1}$, $\Theta_{1,0}$, $\Theta_{1,-1}$, to give a three-fold degenerate Ψ, all products being totally antisymmetric.

That was quite a lot of work, but the results indicated in Figure 2.7 are rather general and apply to any two-electron system. As long as there are no spin operators in the Hamiltonian, the electronic energy depends only on the spatial wave function Φ. But the nature of any state – whether it is degenerate or non-degenerate and whether or not it corresponds to definite values of the total spin – depends on the overall *symmetry* of the space-spin function Ψ. Remember that a state of total spin S has $2S + 1$ degenerate components (labelled by the quantum number M_S) and that this is the **multiplicity** of the state.

The remarkable fact is that the experimentally observed states correspond only to those shown in Figure 2.7(b), where the ground state is a singlet and the first excited state is a triplet. But wait a minute! How can we be sure the state we're calling the "first excited state" really *is* the lowest excited state? If you look back at Example 2.4 you'll see that the first excited state, going up in energy, was taken to be the one with wave function $\Phi_2^{(-)}$, namely the 'minus' combination of Φ_2 and Φ_3; and that is the one with energy

$$E_2^{(-)} = [\epsilon_1 + \epsilon_2 + J_{12}] - K_{12}.$$

On the other hand, the 'plus' combination gave an energy

$$E_2^{(+)} = [\epsilon_1 + \epsilon_2 + J_{12}] + K_{12}$$

and since K_{12} is an essentially *positive* quantity this energy lies *above* that of the "first excited state". So we got it right! The energy levels on the right-hand side in Figure 2.6 are in complete agreement with experiment, while those on the left simply do not appear!

Overall antisymmetry of an electronic wave function seems to be an intrinsic property of the electrons themselves – or of the 'wave field' Ψ with which they are described. In fact this conclusion is perfectly general: it applies not just to two-electron systems but to all the electrons in the universe! – and it is confirmed by countless experiments.

2.4 The antisymmetry principle

This brings us to the last general principle of quantum mechanics that we're going to need in Book 12. It wasn't included in Book 11 because in formulating the basic principles we were thinking mainly of *one*-particle systems; but the antisymmetry of many-electron wave functions is just as important as anything we've discovered so far. So let's state the **antisymmetry principle** in the general form which applies to systems of any number of electrons:

The wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$ describing any state of an N-electron system is *antisymmetric* for any permutation P of the electrons:

$$\mathrm{P}\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \epsilon_{\mathsf{P}}\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N),$$

where $\epsilon_{\mathsf{P}} = \pm 1$ for permutations of even or odd parity, respectively.

(2.15)

Here P is a general **permutation**, which acts on the numbered electronic variables $\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N$ and changes them into $\mathbf{x}_{1'}, \mathbf{x}_{2'}, ..., \mathbf{x}_{N'}$, where the new numbers $1', 2', ..., N'$ are the old ones written in a different order. This permutation can be achieved by making a series of **transpositions** $(1, 1')(2, 2')...(N, N')$, where each (i, i') interchanges one pair of numbers, one 'old' and one 'new': thus (1,3)(4,2) will send 1 2 3 4 into 3 4 1 2. Any permutation is equivalent to a number of transpositions: when the number is odd the **parity** of the permutation is said to be "odd'; when it is even, the parity is "even". (Note that, in counting, (i, i) (where a number is interchanged with itself) is not included – not being a true transposition.)

Section 2.4 opened with the amazing claim that "without spin you and I would not exist – there would be no Chemistry!" To end this chapter we must ask how this can be so – and how does the Antisymmetry Principle come into the picture?

During the early development of quantum theory, before Schrödinger's introduction of the wave function, the electrons in an atom were assigned to 'states' on a basis of experimental evidence. Atomic spectroscopy had shown that the emission and absorption of light could be associated with 'quantum jumps' of single electrons between energy levels with characteristic 'quantum numbers'. (See Book 11 for spectral series and energy level diagrams.) A key postulate in accounting for the electronic structures of atoms, was **Pauli's Exclusion Principle**, which stated that no two electrons could be in states with the same set of quantum numbers.

The Antisymmetry Principle is simply the modern and more general form of Pauli's Exclusion Principle[3] To see how antisymmetry of the wave function contains the idea of 'exclusion' it's enough to go one step beyond the two-electron systems studied in the present chapter. In an IPM description the first two spin-orbitals might be $\psi_1 = \phi_1\alpha, \psi_2 = \phi_1\beta$, with both electrons in the same orbital ϕ_1, but with opposite spins. The corresponding antisymmetric 2-electron state, found in Section 2.4, is then seen to be (before normalization) $\psi_1\psi_2 - \psi_2\psi_1$, which is called an "antisymmetrized spin-orbital product". It can

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[3] Over the years, starting from Pauli himself, there has been much argument about the fundamental status of the two principles, but that can be found in books on the philosophy of quantum mechanics – when you're ready!

be derived from the leading term, a 'parent product', $\psi_1\psi_2$, by subtracting the product obtained after making an electron interchange. The operator $\mathsf{A} = (1/2)(\mathsf{I} - \mathsf{P}_{12})$ (I being the usual identity operator and P_{12} being the interchange of variables for electrons 1 and 2) is called an **anti-symmetrizer**. There is a more general form of this operator, which we'll need in Chapter 3, namely

$$\mathsf{A} = \frac{1}{N!}\sum_{\mathsf{P}} \epsilon_{\mathsf{P}}\mathsf{P} \tag{2.16}$$

which acts on a product of N spin-orbitals to produce an antisymmetric N-electron wave function. Here the summation runs over all $N!$ permutations and the parity factor ϵ_{P} was defined after (2.15); the extra factor $1/N!$ is included simply for convenience (you can apply the operator a second time without making any difference i.e. $\mathsf{AA} = \mathsf{A}$)

Now let's try to get a wave function for a three-electron system, by adding another electron to orbital ϕ_1. There are only two possible choices of spin factor and the third electron can therefore occupy only $\psi_3 = \phi_1\alpha$ or $\psi_3 = \phi_1\beta$. The parent product will then be $\psi_1\psi_2\psi_3$ and we want to find a function that changes sign under *any* permutation of electronic variables. To do it we use (2.16) with $N = 3$, noting that two spin-orbitals are identical: for example, $\psi_3 = \psi_1$. In that case, the permutations P will act on the parent product $\psi_1\psi_2\psi_1$, which can also be replaced by $\psi_1\psi_1\psi_2$ (it can't matter *which* product we antisymmetrize).

Thus

$$\mathsf{A}[\psi_1\psi_1\psi_2] = \frac{1}{N!}\sum_{\mathsf{P}} \epsilon_{\mathsf{P}}\mathsf{P}[\psi_1\psi_1\psi_2].$$

But now think about the effect of the 'first' permutation (the order doesn't matter as the sum is over *all* $N!$ permutations), taking it to be one that interchanges the first two spin variables. This will leave the product unchanged, and as the parity factor for a single interchange is -1 the resultant term in the sum will be $-[\psi_1\psi_1\psi_2]$. But the identity permutation, included in the summation, leaves the parent product unchanged and the net result is thus exactly zero! In fact, what we have shown for three electrons is true for any number (think about it, noting that if P_{12} leaves the parent function unchanged, then any permutation can be expressed as $\mathsf{P} = \mathsf{P}'\mathsf{P}_{12}$ where P' acts on all the variables *except* $\mathbf{x}_1, \mathbf{x}_2$).

To summarize,

> The antisymmetrized product function
> $\mathsf{A}\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \mathsf{A}\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) \dots \psi_N(\mathbf{x}_N)$,
> representing an IPM approximation to the state of an N-electron system, can contain no repetitions of any given spin-orbital: every electron must have its own distinct spin-orbital. A given *spatial orbital* can hold not more than two electrons, one with spin factor α, the other with β.

(2.17)

This is the quantum mechanical equivalent of Pauli's Exclusion Principle: it *excludes* the possibility of finding more than two electrons in the same spatial orbital; and when two are present they must have opposite spins $\pm\frac{1}{2}$. It is less general than the Antisymmetry Principle, because it applies only to approximate wave functions of particular form: but is very simple to apply and leads directly to conclusions that provide the basis for all modern theories of the electronic structure of atoms and molecules. The example with which we introduced it explains at once why the 3-electron Lithium atom does not have all three electrons in the lowest-energy 1s orbital: because the Helium-like configuration $(1s)^2$ is already 'full' and a third electron must then 'overflow' into the higher-energy 2s orbital, giving the configuration Li$[(1s)^2(2s)]$. Thus, there are two electrons in an **inner shell**, tightly localized around the nucleus, and one electron by itself, in a more diffuse 2s orbital. And that is the beginning of Chemistry, and of Life in all forms! Without antisymmetry and the exclusion property to which it leads, all matter would collapse – every nucleus would take all the electrons it could hold, becoming an uncharged and unreactive system, like no atom in the world we know.

Chapter 3

Electronic structure: the independent particle model

3.1 The basic antisymmetric spin-orbital products

By the end of Chapter 2 it was already clear that a general antisymmetric wave function could be built up from products of spin-orbitals $\psi_i(\mathbf{x}) = \phi_i(\mathbf{r})\theta(s)$, where $\phi_i(\mathbf{r})$ is a particular **orbital factor** and $\theta(s)$ is a **spin factor** (α or β) indicating the spin state of the electron ('up-spin' or 'down-spin', respectively); and that this could be a difficult matter. Only for a 2-electron system was it possible to factorize an eigenfunction Ψ, corresponding to a state of definite energy and spin, into a product $\Phi \times \Theta$. However, as Example xxx showed, a space-spin function could be expressed in terms of *antisymmetrized* spin-orbital products. This discovery, by the physicist J.C.Slater (1929), provided a basis for nearly all electronic structure calculations in the years that followed.

From now on, we'll be dealing with *many*-electron systems: so we need to generalize what was done in Section 2.1, starting from the definition of the Hamiltonian operator. Instead of (2.1) we'll use

$$\mathsf{H} = \sum_i \mathsf{h}(i) + \tfrac{1}{2}\textstyle\sum'_{i,j} \mathsf{g}(i,j), \tag{3.1}$$

where $\mathsf{h}(i)$ is the 1-electron Hamiltonian of (3.1), in which the nuclei are treated as if fixed in space and simply determine the potential field in which the electrons move (the 'clamped nucleus' approximation); and $\mathsf{g}(i,j)$ is the 2-electron operator of (2.3), which simply multiplies the wave function by the (classical) interaction energy $1/r_{ij}$ between electrons i and j separated by a distance r_{ij} (remember we normally use 'atomic units'). The prime on the summation sign indicates that there is no term when $i = j$; and the $\frac{1}{2}$ is put in to avoid counting every interaction twice (which would happen in summing over both i and j. As in the case of two electrons, leaving out the electron interaction leads to an IPM approximation in which the wave function is represented as a single spin-orbital product. (Read the rest of Section 2.2 if you need to.)

From the general principle (2.15) we must be sure that any approximate wave function we may construct is properly **antisymmetric**. And we already know how this can be done by making use of the 'antisymmetrizer' (2.16). So we start with this operator, already used in Section 2, and show its basic property.

The name of the permutation P is not important when we're going to sum over *all* permutations of the N variables, so (2.16) can be written in two equivalent ways:

$$\mathsf{A} = \frac{1}{N!}\sum_{\mathsf{P}} \epsilon_{\mathsf{P}}\mathsf{P} = \frac{1}{N!}\sum_{\mathsf{Q}} \epsilon_{\mathsf{Q}}\mathsf{Q}$$

where there are $N!$ terms in each sum. The product of the two operators is thus

$$\left(\frac{1}{N!}\right)^2 \sum_{\mathsf{PQ}} \epsilon_{\mathsf{P}}\epsilon_{\mathsf{Q}}\mathsf{PQ}.$$

But $\mathsf{PQ} = \mathsf{R}$, which is just another permutation that's been given a different name, and the last result can thus be written

$$\mathsf{A}^2 = \mathsf{AA} = \left(\frac{1}{N!}\right)\sum_{\mathsf{R}} \epsilon_{\mathsf{R}}\mathsf{R},$$

where for each choice of one permutation (Q say) there are the same $N!$ product permutations $\mathsf{R} = \mathsf{PQ}$, appearing in some different order. And this fact has let us cancel one factor $(1/N!)$ in the previous expression. The remarkable result then is that

$$\mathsf{A}^2 = \mathsf{AA} = \frac{1}{N!}\sum_{\mathsf{R}} \epsilon_{\mathsf{R}}\mathsf{R} = \mathsf{A}. \qquad (3.2)$$

Operators with this property are said to be **idempotent** – and you first met them long ago in Book 1 (Chapter 6)! (The word comes from Latin and means "the same power" – all powers of A are the same.) You met such operators also in Geometry (Chapter 7 of Book 2), where they applied to the **projection** of a vector on some axis in space (if you do it twice you get the same result as doing it once!).

An immediate result is that A applied to a product of N orthogonal spin-orbitals gives a wave function which, besides being antisymmetric, can easily be normalized. Let's call the basic spin-orbital product

$$\pi(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N) = \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\ldots\psi_N(\mathbf{x}_N), \qquad (3.3)$$

where all the spin-orbital factors are **orthonormal** (i.e. individually normalized and mutually orthogonal) and go ahead as follows.

Example 3.1 How to normalize an antisymmetrized spin-orbital product

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We can get a normalized function easily from the antisymmetric function formed from the product (3.3), namely

$$F(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N) = \sum_{\mathsf{P}} \epsilon_{\mathsf{P}} \mathsf{P} \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) \dots \psi_N(\mathbf{x}_N).$$

Thinking about how the normalization integral arises is a good exercise. To make it easier we'll use $1, 2, 3, \dots .N$ to stand for the variables $\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N$

To get $\langle F|F\rangle$ you have to integrate, over all space-spin variables, the product of two sums, each containing $N!$ spin-orbital products. Typical terms are

$\epsilon_{\mathsf{P}} \mathsf{P}[\psi_1(1)\psi_2(2) \dots \psi_N(N)]$, from the 'bra', and

$\epsilon_{\mathsf{Q}} \mathsf{Q}[\psi_1(1)\psi_2(2) \dots \psi_N(N)]$ from the 'ket'.

After making the permutations P and Q, which put the variables in a different order, you may find P has sent the 'bra' product into

$\psi_1(1')\psi_2(2') \dots \psi_N(N')$,

while Q has sent the 'ket' product into

$\psi_1(1'')\psi_2(2'') \dots \psi_N(N'')$.

And then you have to do the integrations – which seems like an impossible task! (Even for the Carbon atom, with only six electrons, $6! = 720$ and gives you 518400 distinct pairs of products to look at – before doing anything else.) But in fact the whole thing is very easy because the spin-orbitals are orthonormal. This means that in every pair of products the variables must be in exactly the same order ($i'' = i' = i$) for all i – and the integration will always give unity ($\langle \psi_i|\psi_i\rangle = 1$). So you've done – for all matching pairs of products the result will be unity, and there are $N!$ of them. Thus the normalization integral $\langle F|F\rangle = N!$ and to normalize F you only have to divide it by $\sqrt{N!}$.

Example 3.1 has shown how we can produce a *normalized* wave function from the spin-orbital product in (3.3): the result is

$$\begin{aligned} \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N) &= \frac{1}{\sqrt{N!}} \sum_{\mathsf{P}} \epsilon_{\mathsf{P}} \mathsf{P} \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) \dots \psi_N(\mathbf{x}_N) \\ &= \sqrt{N!}\mathsf{A}[\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) \dots \psi_N(\mathbf{x}_N)], \end{aligned} \tag{3.4}$$

where the second form introduces the antisymmetrizer A defined in (2.16).

The next step will be to evaluate the expectation values, in the state with wave function (3.4), of the 1- and 2-electron operators, $\mathsf{h}(i), \mathsf{g}(i,j)$, that make up the full Hamiltonian (3.1). But first we should be sure about what the permutations are actually doing. We're thinking about numbered variables $\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N$; and swapping electrons '1' and '2' means putting Electron 1 where Electron 2 was and vice versa (the other way round). In other words, *in our equations*, we replace $\mathbf{x}_1$ by the 'new position' $\mathbf{x}_2$ and $\mathbf{x}_2$ by $\mathbf{x}_1$: that is the simple 'transposition' denoted by (1,2). But what if there are *many* electrons? There's a general way of describing any P, already used in Example 3.1, in which we simply list the integers $1, 2, \dots N$, before the permutation, and the integers $1', 2', \dots N'$ after putting them in a different order. Thus

$$\mathsf{P} = \begin{pmatrix} 1 & 2 & . & . & . & N \\ 1' & 2' & . & . & . & N' \end{pmatrix}. \tag{3.5}$$

Let's take first the 1-electron sum $\sum_j \mathsf{h}(j)$ and focus on $\langle\Psi|\sum_j \mathsf{h}(j)|\Psi\rangle$, getting it in the next example in much the same way as we got the normalization integral. As everything is symmetrical in the electrons, their 'names' don't matter and we can make things look easier by taking $j = 1$ and writing the corresponding operator $\mathsf{h}(1) = \mathsf{h}_1$ so as not to mix it up with the other labels. The expectation value for the operator sum will then be N times that for the single term.

Example 3.2 Getting a 1-electron expectation value

To evaluate $\langle\Psi|\sum_j \mathsf{h}_1|\Psi\rangle$, with Ψ defined in (3.4), we note that a typical term will be the 'bra-ket' with h_1 between two spin-orbital products:

$$\frac{1}{N!}\langle\psi_1(1')\psi_2(2')\,...\,\psi_N(N')|\mathsf{h}_1|\psi_1(1'')\psi_2(2'')\,...\,\psi_N(N'')\rangle,$$

where the primed variables result from permutation P and the double-primed from permutation Q. Now, as in Example 3.1, every such term will be zero unless $i' = i''$, because otherwise the two spin-orbital products, $\psi_1(1')\psi_2(2')\,...\,\psi_N(N')$ and $\psi_1(1'')\psi_2(2'')\,...\,\psi_N(N'')$, would lead to zero overlap factors, $\langle\psi_i(i')|\psi_i(i'')\rangle = 0$ for $i'' \neq i'$.

The variables in the N spin-orbitals must therefore match exactly and the only non-zero terms in the last expression will be of the form

$$\frac{1}{N!}\langle\psi_1(1')\psi_2(2')\,...\,\psi_N(N')|\mathsf{h}_1|\psi_1(1')\psi_2(2')\,...\,\psi_N(N')\rangle.$$

Note that only the i' ('integer-primed') variables are involved in the permutations and that h_1 works only on the factor with $i' = 1$, namely ψ_i – in *position* i where the integer 1 has 'landed' after the permutation. You can see that from the list of permuted products: $\psi_1(1')\psi_2(2')\psi_3(3')\,...$. (e.g. if $3'$, after a permutation, has been replaced by 1 it still refers to spin-orbital ψ_3.) Putting $i' = 1$ fixes one non-zero factor as $\langle\psi_i|\mathsf{h}_1|\psi_i\rangle$, but this will result from all permutations of the remaining $N-1$ variables. So there are N ways of choosing $i = 1$ and $(N-1)!$ ways of choosing the other matching pairs of overlap integrals. That's all for one term $\mathsf{h}_1 = \mathsf{h}(1)$ in the sum $\mathsf{h}(1) + \mathsf{h}(2) + \,...\, \mathsf{h}(N)$ and every term will appear $N \times (N-1)! = N!$ times. Thus the sum of all the 1-electron operators will have an expectation value $\langle\Psi|\sum_j \mathsf{h}(j)|\Psi\rangle = \sum_j \langle\psi_j|\mathsf{h}(j)|\psi_j\rangle$, where the normalizing factor $1/N!$ is conveniently cancelled.

In case you didn't follow the argument in Example 3.2, run through it with just 3 electrons instead of N. With electrons 1,2,3 in spin-orbitals ψ_1, ψ_2, ψ_3, the basic spin-orbital product will then be $\pi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\psi_3(\mathbf{x}_3)$ or, for short, $\pi(1,2,3) = \psi_1(1)\psi_2(2)\psi_3(3)$, where again the integer i will stand for the variable $\mathbf{x}_i$.

To antisymmetrize the products we need to apply the permutation operators, which give $\mathsf{P}\pi(1,2,3) = \psi_1(1')\psi_2(2')\psi_3(3')$ and $\mathsf{Q}\pi(1,2,3) = \psi_1(1'')\psi_2(2'')\psi_3(3'')$, and then put the results together with parity factors ± 1, remembering that $i'' = i'$ for all $i\,(= 1,2,3)$.

The six permuted variables are (1 2 3), (1 3 2), (2 1 3), (2 3 1), (3 1 2), (3 2 1) and the expectation value contributions are thus, on putting these indices in place of $1'\ 2'\ 3'$ and choosing a typical operator $\mathsf{h}_1 = \mathsf{h}(j)$ with $j = 1$:

$$\langle 1\,2\,3\,|\mathsf{h}_1|\,1\,2\,3\rangle = \langle\psi_1|\mathsf{h}_1|\psi_1\rangle\langle\psi_2|\psi_2\rangle\langle\psi_3|\psi_3\rangle = h_{11},$$

$$\langle 1\,3\,2\,|\mathsf{h}_1|\,1\,3\,2\rangle = \langle\psi_1|\mathsf{h}_1|\psi_1\rangle\langle\psi_2|\psi_2\rangle\langle\psi_3|\psi_3\rangle = h_{11},$$

$$\langle 2\,1\,3\,|\mathsf{h}_1|\,2\,1\,3\rangle = \langle\psi_1|\psi_1\rangle\langle\psi_2|\mathsf{h}_1|\psi_2\rangle\langle\psi_3|\psi_3\rangle = h_{22},$$

$$\langle 2\,3\,1\,|\mathsf{h}_1|\,2\,3\,1\rangle = \langle\psi_1|\psi_1\rangle\langle\psi_2|\psi_2\rangle\langle\psi_3|\mathsf{h}_1|\psi_3\rangle = h_{33},$$

$$\langle 3\,1\,2\,|\mathsf{h}_1|\,3\,1\,2\rangle = \langle\psi_1|\psi_1\rangle\langle\psi_2|\mathsf{h}_1|\psi_2\rangle\langle\psi_2|\psi_2\rangle = h_{22},$$

$$\langle 3\,2\,1\,|\mathsf{h}_1|\,3\,2\,1\rangle = \langle\psi_1|\psi_1\rangle\langle\psi_2|\psi_2\rangle\langle\psi_3|\mathsf{h}_1|\psi_3\rangle = h_{33},$$

Note especially that the labelled ψ-factors do not change their positions: only their arguments (the electronic variables, not shown) are affected by the permutations. For example, the third permutation puts $2' = 1$ in the second position, showing that h_1 operates on ψ_2.

To summarize the conclusion from Example 3.2, in a strictly IPM approximation the expectation value of the total energy is simply the sum of the individual orbital energies, derived using the 1-electron operator h (which no longer carries the label '1'). Thus

$$\bar{E}_{\text{IPM}} = \sum_i \epsilon_i, \qquad (\epsilon_i = \langle\psi_i|\mathsf{h}|\psi_i\rangle). \tag{3.6}$$

The orbital energy ϵ_i is that for an electron occupying spin-orbital ψ_i.

The next step will be to allow for the electron *interaction energy*, represented in the $N-$electron Hamiltonian (3.1) by the term $\sum_{(i,j)} \mathsf{g}(i,j)$ given in (2.3) for the case of only two electrons. Again we focus on a typical term in the sum, calling it $\mathsf{g}(j,k)$ (i is getting overworked!), and proceed as we did in the last Example.

Example 3.3 Getting a 2-electron expectation value

To evaluate $\langle\Psi|\sum'_{j,k}\mathsf{g}(j,k)|\Psi\rangle$, with Ψ defined in (3.4), we note that the expectation value will be

$$\frac{1}{N!}\langle\psi_1(1')\psi_2(2')\ldots\psi_N(N')|\mathsf{g}(j,k)|\psi_1(1'')\psi_2(2'')\ldots\psi_N(N'')\rangle,$$

where the primed variables result from permutation P and the double-primed from permutation Q. (The prime on the summation symbol is used to indicate that terms with $j = k$ will be excluded – they would refer to only *one* electron and there is no *self*-interaction!)

As in Example 3.2, we first suppose the variables in the two spin-orbital products must match exactly ($i' = i''$ for all $i \neq j, k$) to avoid zero overlap factors. In that case, the only *non-zero* terms in the last expression will be of the form

$$\frac{1}{N!}\langle\psi_1(1')\psi_2(2')\ldots\psi_N(N')|\mathsf{g}(j,k)|\psi_1(1')\psi_2(2')\ldots\psi_N(N')\rangle.$$

Note that only the i' ('integer-primed') variables are involved in the permutations and that $\mathsf{g}(j,k)$ works on the factors with $i' = j$ or $i' = k$, namely ψ_j, ψ_k – the j-th and k-th spin-orbitals in the standard order $1, 2, \ldots N$.

On making this choice, the contribution to the expectation value will contain the 2-electron integral $\langle\psi_j\psi_k|\mathsf{g}(j,k)|\psi_j\psi_k\rangle$, multiplied by $N-2$ unit overlap factors, coming from all other matching pairs of spin-orbitals. And the same result will be obtained on making all permutations of the remaining $N-2$ variables. So there are N ways of choosing $i'=j$, $N-1$ ways of choosing *another* $i'=k$ and $(N-2)!$ ways of choosing the remaining matching pairs of overlap integrals. That's all for one term $\mathsf{g}(j,k)$ in the sum $\sum'_{j,k}\mathsf{g}(j,k)$ and every term will thus appear $N\times(N-1)\times(N-2)! = N!$ times.

The sum of all the 2-electron interactions will therefore have an expectation value, after cancelling the normalizing factor $1/N!$, $\langle\Psi|\frac{1}{2}\sum'_{j,k}\mathsf{g}(j,k)|\Psi\rangle = \frac{1}{2}\sum'_{j,k}\langle\psi_j\psi_k|\mathsf{g}(j,k)|\psi_j\psi_k\rangle$. This is the quantity we met in Section 2.2 (Example 2.4) and called a **Coulomb integral** because it represents the Coulomb interaction of two distributions of electric charge, of density $|\psi_j|^2$ and $|\psi_k|^2$ respectively. (Look back at (3.1) if you don't see where the factor $\frac{1}{2}$ comes from.)

That all seems fine – but have we included everything? We started by saying that the permutations P in the 'bra' and Q in the 'ket' must put the variables in matching order, as any mis-match would lead to zero overlap integrals. But with 2-electron operators like $\mathsf{g}(j,k)$ it is clear that non-zero contributions to the expectation value *can* arise as long as the $N-2$ 'matching pairs' (for $i'\neq j,k$) are not changed by the permutations. So after getting all the non-zero contributions $\langle\psi_j\psi_k|\mathsf{g}(j,k)|\psi_j\psi_k\rangle$ we must still allow new permutations, which differ from those already made by a transposition of the indices j,k. When two indices are swapped, the term just found will be accompanied by another, $\langle\psi_j\psi_k|\mathsf{g}(j,k)|\psi_k\psi_j\rangle$, which is called an **exchange integral**. But, in summing over all permutations, those which lead to an exchange term are of different *parity* from those that lead to the corresponding Coulomb term; and when they are included they must be given a minus sign. Consequently, the expectation value of the 2-electron energy term, namely $\langle\Psi|\frac{1}{2}\sum'_{j,k}\mathsf{g}(j,k)|\Psi\rangle$, must now include *'exchange terms'*, becoming

$$\tfrac{1}{2}\textstyle\sum'_{j,k}[\langle\psi_j\psi_k|\mathsf{g}(j,k)|\psi_j\psi_k\rangle - \langle\psi_j\psi_k|\mathsf{g}(j,k)|\psi_k\psi_j\rangle].$$

If you still have difficulty with such a long and abstract argument, try repeating it with just three electrons (1,2,3) in spin-orbitals ψ_1,ψ_2,ψ_3, as we did after Example 3.2, but replacing h_1 by the 2-electron operator $\mathsf{g}_{12}=\mathsf{g}(1,2)$. Note that g_{12} acts on *two* spin-orbitals; thus, for example,

$$\langle 2\,1\,3\,|\mathsf{g}_{12}|\,2\,1\,3\rangle = \langle\psi_1\psi_2|\mathsf{g}_{12}|\psi_1\psi_2\rangle\langle\psi_3|\psi_3\rangle = \langle\psi_1\psi_2|\mathsf{g}|\psi_1\psi_2\rangle.$$

We can now summarize the conclusions from Examples 3.2 and 3.3 for a state Ψ, represented by a single antisymmetrized spin-orbital product and normalized to unity in (3.4):

Given $\Psi(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N) = (1/N!)^{1/2}\sum_{\mathsf{P}}\epsilon_{\mathsf{P}}\mathsf{P}\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\,...\,\psi_N(\mathbf{x}_N)$, the 1- and 2-electron contributions to $\bar{E}=\langle\Psi|\mathsf{H}|\Psi\rangle$ are:

$$\langle\Psi|\textstyle\sum_i\mathsf{h}(i)|\Psi\rangle = \sum_i\langle\psi_i|\mathsf{h}|\psi_i\rangle$$

and

$$\langle\Psi|\tfrac{1}{2}\textstyle\sum'_{i,j}\mathsf{g}(i,j)|\Psi\rangle = \tfrac{1}{2}\sum'_{i,j}[\langle\psi_i\psi_j|\mathsf{g}|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\mathsf{g}|\psi_j\psi_i\rangle].$$

(3.7)

These results, 'Slater's rules', will be used throughout the rest of Book 12, r so if you had trouble in getting them just take them on trust – applying them is much easier! (Note that the summation indices in the 2-electron sum have been changed back to i, j, as used originally in (3.1), now there's no longer any risk of confusion.)

3.2 Getting the total energy

Now that we know how to get the expectation energy for a wave function of the form (3.4) we'll be wanting to get the best possible approximation of this kind. In Chapter 2 this was done by the **variation method**, in which the forms of the *orbitals* were varied until $\bar{E}$ reached a stationary minimum value.

For a many-electron ground state we can go ahead in the same way; but the details will be a bit more complicated. Apart from the fact that we now have to use *spin*-orbitals, N of them for an N-electron system, the orbital factors may not be simple functions, containing a few adjustable parameters; they may be complicated functions of electronic positions (r_i) and we'll be looking for a 1-electron *eigenvalue equation* to determine the orbitals and corresponding orbital energies. That's the problem we face in the next section: here we have to start by getting an expression for the total electronic energy of the system.

First of all, as long as there are no spin operators in the *Hamiltonian* – and this first approximation is the one usually accepted – we can get rid of all the spin factors (α, β) and spin variables s by doing the spin integrations before anything else in evaluating the expectation value $\bar{E}$. Remember that in general, where $\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N)$ and $\bar{E} = \langle\Psi|\mathsf{H}|\Psi\rangle$, this involves integrating over *all* variables in the wave function.

Let's start from the single antisymmetrized spin-orbital product in (3.7) and do the spin integrations to get a 'spin-free' expression for $\bar{E} = \langle E\rangle$. In terms of spin-orbitals, we already know

$$\langle E\rangle = \langle\Psi|\mathsf{H}|\Psi\rangle = \sum_i \langle\psi_i|\mathsf{h}|\psi_i\rangle + \tfrac{1}{2}\textstyle\sum'_{i,j}[\langle\psi_i\psi_j|\mathsf{g}|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\mathsf{g}|\psi_j\psi_i\rangle], \qquad (3.8)$$

so now we only have to substitute $\psi_i(\mathbf{x}) = \phi_i(\mathbf{r})\alpha(s)$, or $\phi_i(\mathbf{r})\beta(s)$ in this expression and complete the spin integrations.

Example 3.4 Getting rid of the spins!

In Chapter 2 we found that quantum mechanics was not complete until we allowed for particles with *spin*: otherwise it was not possible to describe the fact that electrons are *identical particles* of a very special kind – their wave functions must be **antisymmetric** under exchange of any two particles (an operation that can make no observable difference to the system). So why should we want to 'get rid of spin'? The simple reason is that the observable effects of spin (e.g. on the energy levels of a system) are tiny and, in good approximation, can often be neglected. That being so, it's a nuisance to keep them in the theory for any longer than necessary.

The 1-electron part of the energy in (3.8) depends on the spin-orbitals only through the term $\langle\psi_i|\mathsf{h}|\psi_i\rangle = \int \psi_i^*(\mathbf{x}_1)\mathsf{h}(1)\psi_i(\mathbf{x}_1)\mathrm{d}\mathbf{x}_1$, in which ψ_i is occupied by the electron we're calling '1', with space-spin coordinates $\mathbf{x}_1$, and $\mathrm{d}\mathbf{x}_1 = \mathrm{d}\mathbf{r}_1\mathrm{d}s_1$. When the Hamiltonian $\mathsf{h}(1)$ does not contain spin operators, it works on a spin-orbital $\psi_i(\mathbf{x}_1) = \phi_i(\mathbf{r}_1)\alpha(s_1)$ to give $[\mathsf{h}(1)\phi_i(\mathbf{r}_1)]\alpha(s_1)$, without touching the spin factor $\alpha(s_1)$. Thus

$$\begin{aligned}\int \psi_i^*(\mathbf{x}_1)\mathsf{h}(1)\psi_i(\mathbf{x}_1)\mathrm{d}\mathbf{x}_1 &= \int \alpha^*(s_1)\alpha(s_1)\mathrm{d}s_1 \int \phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}_1)[\mathsf{h}(1)\phi_i(\mathbf{r}_1)]\mathrm{d}\mathbf{r}_1 \\ &= \langle\alpha|\alpha\rangle\langle\phi_i|\mathsf{h}|\phi_i\rangle = \langle\phi_i|\mathsf{h}|\phi_i\rangle.\end{aligned}$$

The spin integration just takes away the spin factors, leaving $\langle\phi_i|\mathsf{h}|\phi_i\rangle$ in place of $\langle\psi_i|\mathsf{h}|\psi_i\rangle$, and this will clearly be true also for a spin-orbital with a β spin factor. (Integration limits not shown when obvious.)

What about the 2-electron term in (3.8)? This is $\frac{1}{2}\sum'_{i,j}[\langle\psi_i\psi_j|\mathsf{g}|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\mathsf{g}|\psi_j\psi_i\rangle]$ and is a bit more difficult, so let's take the Coulomb and exchange parts separately. If we take $\psi_i(\mathbf{x}_1) = \phi_i(\mathbf{r}_1)\alpha(s_1)$ and $\psi_j(\mathbf{x}_2) = \phi_j(\mathbf{r}_2)\alpha(s_2)$, then a single Coulomb term becomes

$$\begin{aligned}\langle\psi_i\psi_j|\mathsf{g}|\psi_i\psi_j\rangle &= \int \psi_i^*(\mathbf{x}_1)\int \psi_j^*(\mathbf{x}_2)\mathsf{g}(1,2)\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2 \\ &= \int \phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\mathsf{g}(1,2)\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \\ &= \langle\phi_i\phi_j|\mathsf{g}|\phi_i\phi_j\rangle.\end{aligned}$$

– spin factors matching and each giving $\langle\alpha|\alpha\rangle = 1$.

The corresponding exchange term reduces in the same way;

$$\begin{aligned}\langle\psi_i\psi_j|\mathsf{g}|\psi_j\psi_i\rangle &= \int \psi_i^*(\mathbf{x}_1)\int \psi_j^*(\mathbf{x}_2)\mathsf{g}(1,2)\psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2 \\ &= \int \phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\mathsf{g}(1,2)\phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \\ &= \langle\phi_i\phi_j|\mathsf{g}|\phi_j\phi_i\rangle.\end{aligned}$$

and could be obtained from the Coulomb term simply by exchanging the two orbitals (no spins!) in the 'ket'.

(Note that you don't always have to show everything in such detail, with the variables and integral signs. A shorter way is to write the spin-orbitals $\psi_i = \phi_i\alpha$, $\psi_j = \phi_j\alpha$, so

$$\langle(\phi_i\alpha)(\phi_j\alpha)|\mathsf{g}|(\phi_j\alpha)(\phi_i\alpha)\rangle = \langle\alpha|\alpha\rangle_1\langle\alpha|\alpha\rangle_2\langle\phi_i\phi_j|\mathsf{g}|\phi_j\phi_i\rangle,$$

where the first spin scalar product comes from the first spin-orbital and the next one from the second (it's enough just to keep the order). As the spin states are normalized both factors are 1 and the 'short cut' gives the same result: $\langle\psi_i\psi_j|\mathsf{g}|\psi_j\psi_i\rangle = \langle\phi_i\phi_j|\mathsf{g}|\phi_j\phi_i\rangle$.)

Now suppose that ψ_i and ψ_j have *different* spins: $\psi_i = \phi_i\alpha$, $\psi_j = \phi_j\beta$. In this case we get, using the 'short cut', an exchange term $\langle(\phi_i\alpha)(\phi_j\beta)|\mathsf{g}|(\phi_j\beta)(\phi_i\alpha)\rangle = \langle\alpha|\beta\rangle_1\langle\beta|\alpha\rangle_2\langle\phi_i\phi_j|\mathsf{g}|\phi_j\phi_i\rangle$. Here, because the different spin states are orthogonal, there are two factors of 0 and the exchange term is $\langle\psi_i\psi_j|\mathsf{g}|\psi_j\psi_i\rangle = 0 \times \langle\phi_i\phi_j|\mathsf{g}|\phi_j\phi_i\rangle$.) The Coulomb term, on the other hand, again reduces to $\langle\phi_i\phi_j|\mathsf{g}|\phi_i\phi_j\rangle$, because the spin factors are both 1 (check it out!).

In summary, Example 3.4 showed how a system whose Hamiltonian contains no spin operators can be dealt with in terms of *orbitals* alone, without the spin factors α and β:

Given $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \sqrt{N!}\mathsf{A}\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) \ldots \psi_N(\mathbf{x}_N)$, the 1- and 2-electron energy terms reduce as follows.

When $\psi_i = \phi_i\alpha : \quad \langle\psi_i|\mathsf{h}|\psi_i\rangle \to \langle\phi_i|\mathsf{h}|\phi_i\rangle$

and when $\psi_i = \phi_i\alpha, \ \psi_j = \phi_j\alpha :$

$$[\langle\psi_i\psi_j|\mathsf{g}|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\mathsf{g}|\psi_j\psi_i\rangle] \to [\langle\phi_i\phi_j|\mathsf{g}|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|\mathsf{g}|\phi_j\phi_i\rangle].$$

But when $\psi_i = \phi_i\alpha, \ \psi_j = \phi_j\beta$ there is no exchange term:

$$\langle\psi_i\psi_j|\mathsf{g}|\psi_i\psi_j\rangle \to \langle\phi_i\phi_j|\mathsf{g}|\phi_i\phi_j\rangle.$$

(3.9)

Of course, there are similar results if you interchange α and β throughout. The Coulomb integrals in terms of ψ_i, ψ_j give results of the same form in terms of the orbital factors ϕ_i, ϕ_j when both spins are the same (α, α or β, β), or different (α, β or β, α): but this is so for the exchange integrals *only when both spins are the same*, the exchange integrals reducing to zero when the spins are different.

The results listed in (3.7) and (3.9) may be used to obtain energy expectation values, in IPM approximation, for any kind of many-electron system. They apply equally to atoms, where the occupied orbitals are AOs (centered on a single nucleus), and to molecules, where the molecular orbitals (MOs) extend over several nuclei.

Here we start by thinking about **atoms**, whose AOs have been studied in detail in Chapter 6 of Book 11. You'll remember something about atoms from Book 5 (Sections 1.1 and 1.2, which you might like to read again). In particular, the **atomic number** Z gives the number of electrons in the electrically neutral atom and allows us to list all the known 'chemical elements' in increasing order of atomic mass and electronic complexity. The first 10 (lightest) atoms in the list are of special importance: they are Hydrogen (H), Helium (He), Lithium (Li), Beryllium (Be), Boron (B), Carbon (C), Nitrogen (N), Oxygen (O), Fluorine (F) and Neon (Ne). Together they make up most of the world we live in, including the water of the oceans, the main gases of the Earth's atmosphere and even about 99% of our human bodies – so no wonder they are important! In Book 12 we'll be tryng to understand some of the properties of these few atoms and the ways they can be put together to form molecules and other structures. The main 'tool' for doing this is provided by quantum mechanics; and by now you know enough about this to get started.

In the next two examples we'll get approximate energy expressions for the atoms of Lithium ($Z = 3$) and Beryllium ($Z = 4$) in their lowest-energy ground states.

Example 3.5 Energy expression for the Lithium atom

Suppose the electrons are added, one at a time, to the bare nucleus with charge $Z = 3$ (atomic units). In IPM approximation the first two go into the AO ϕ_{1s}, one in $\phi_{1s}\alpha$ and the other in $\phi_{1s}\beta$, giving the 'helium-like' **electron configuration** (1s)^2. The third electron is excluded from this **closed shell** and must go into the next higher-energy AO ϕ_{2s}, with 'up-spin' or 'down-spin'. Taking the up-spin state we have the three spin-orbitals

$$\psi_1 = \phi_{1s}\alpha \qquad \psi_2 = \phi_{1s}\beta \qquad \psi_3 = \phi_{2s}\alpha \qquad \text{(A)}$$

from which we can evaluate the 1- and 2-electron sums in (3.8). To make things easier, we can rewrite the 2-electron summation as $\sum_{i<j}$ (which takes away the $\frac{1}{2}$ and includes only distinct terms) and denote $[\langle\psi_i\psi_j|\mathsf{g}|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\mathsf{g}|\psi_j\psi_i\rangle]$ by $\langle\psi_i\psi_j||\psi_i\psi_j\rangle$. Thus

$$\langle E\rangle = \langle\Psi|\mathsf{H}|\Psi\rangle = \sum_i \langle\psi_i|\mathsf{h}|\psi_i\rangle + \sum_{i<j}\langle\psi_i\psi_j||\psi_i\psi_j\rangle.$$

The 1-electron sum (call it Σ_1) then becomes

$$\Sigma_1 = \langle\psi_1|\mathsf{h}|\psi_1\rangle + \langle\psi_2|\mathsf{h}|\psi_2\rangle + \langle\psi_3|\mathsf{h}|\psi_3\rangle,$$

and similarly

$$\Sigma_2 = \langle\psi_1\psi_2||\psi_1\psi_2\rangle + \langle\psi_1\psi_3||\psi_1\psi_3\rangle + \langle\psi_2\psi_3||\psi_2\psi_3\rangle.$$

With the spin-orbitals listed above in (A), Σ_1 becomes (making use of (3.9))

$$\Sigma_1 = 2\langle\phi_{1s}|\mathsf{h}|\phi_{1s}\rangle + \langle\phi_{2s}|\mathsf{h}|\phi_{2s}\rangle;$$

and similarly

$$\Sigma_2 = \langle\phi_{1s}\phi_{1s}||\phi_{1s}\phi_{1s}\rangle + \langle\phi_{1s}\phi_{2s}||\phi_{1s}\phi_{2s}\rangle + \langle\phi_{1s}\phi_{2s}||\phi_{1s}\phi_{2s}\rangle',$$

where the terms that have been given a 'prime' are the ones that come from spin-orbitals of different spin – and therefore include no exchange term. On using the letters J and K to denote Coulomb and exchange integrals (as in Example 2.4 on a 2-electron system), the last result reduces to (do it!) $\Sigma_2 = J_{1s,1s} + 2J_{1s,2s} - K_{1s,2s}$

Finally, then, using ϵ_{1s} and ϵ_{2s} for the 1s and 2s orbital energies, the expectation value of the total energy in IPM approximation will be $\bar{E} = 2\epsilon_{1s} + \epsilon_{2s} + J_{1s,1s} + 2J_{1s,2s} - K_{1s,2s}$.

Example 3.5 has given the expression

$$\bar{E} = 2\epsilon_{1s} + \epsilon_{2s} + J_{1s,1s} + 2J_{1s,2s} - K_{1s,2s} \qquad (3.10)$$

for the expectation energy, in the ground state, of a 3-electron system (the Lithium atom), in terms of the orbital energies

$$\epsilon_{1s} = \langle\phi_{1s}|\mathsf{h}|\phi_{1s}\rangle, \quad \epsilon_{2s} = \langle\phi_{2s}|\mathsf{h}|\phi_{2s}\rangle,$$

the Coulomb integrals

$$J_{1s,1s} = \langle\phi_{1s}\phi_{1s}|\mathsf{g}|\phi_{1s}\phi_{1s}\rangle,\ J_{1s,2s} = \langle\phi_{1s}\phi_{2s}|\mathsf{g}|\phi_{1s}\phi_{2s}\rangle,$$

and the exchange integral $K_{1s,2s} = \langle\phi_{1s}\phi_{2s}|\mathsf{g}|\phi_{2s}\phi_{1s}\rangle$.

All the terms in (3.10) have a clear physical meaning: ϵ_{1s} is the energy of one electron, by itself, in the lowest-energy (1s) orbital; ϵ_{2s} is that of one electron in the 2s orbital; $J_{1s,1s}$ is the Coulomb repulsion energy between the two electrons in the 1s orbital, while $J_{1s,2s}$ is that between the single 2s electron and one of the the two 1s electrons; the final term $K_{1s,2s}$ is the exchange part of the interaction between the 2s electron and the 1s electron of the same spin (there is no term when the spins are different). The 'charge density' interpretation of $J_{1s,1s}$ was given in Example 2.2, but more generally

$$J_{\phi_1,\phi_2} = \int \phi_1^*(\mathbf{r}_1)\phi_2^*(\mathbf{r}_2)\mathbf{g}\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 = \int \rho_1(\mathbf{r}_1)\rho_2(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2,$$

where $\rho_1(\mathbf{r}_1) = \phi_1^*(\mathbf{r}_1)\phi_1(\mathbf{r}_1)$ is a *real* quantity and so is $\rho_2(\mathbf{r}_2)$. This interaction integral, between real charge densities, is often denoted by $(\phi_1\phi_1, \phi_2\phi_2)$ and has a purely classical interpretation; $J_{\phi_1,\phi_2} = (\phi_1\phi_1, \phi_2\phi_2)$. The corresponding exchange integral does not have a classical interpretation: it is $K(\phi_1, \phi_2) = (\phi_1^*\phi_2, \phi_2^*\phi_1)$ where the 'charge densities' are, in general, complex quantities and have their origin in the region of *overlap* of the two orbitals.

The next atom Be, with $Z = 4$, will contain *two* doubly occupied orbitals, giving it the electron configuration $(1s)^2(2s)^2$. It is the model for all atoms that contain n 'closed shells' of doubly occupied orbitals and leads to an important generalization.

Example 3.6 Energy expression for the Beryllium atom

Again suppose the electrons are added, one at a time, to the bare nucleus – now with charge $Z = 4$ (atomic units). The first two go into the AO ϕ_{1s} and the other two into ϕ_{2s}, giving the electron configuration $(1s)^2(2s)^2$ in which both orbitals are doubly occupied and can accept no more electrons. The atom has a **closed-shell ground state** in which the singly occupied *spin*-orbitals are

$$\psi_1 = \phi_{1s}\alpha \qquad \psi_2 = \phi_{1s}\beta \qquad \psi_3 = \phi_{2s}\alpha \qquad \psi_4 = \phi_{2s}\beta \qquad\qquad (\mathrm{A})$$

from which we can evaluate the 1- and 2-electron sums in (3.8).

With the notation used in Example 3.5, the energy expectation value is given by

$$\langle E\rangle = \langle\Psi|\mathsf{H}|\Psi\rangle = \sum_i \langle\psi_i|\mathsf{h}|\psi_i\rangle + \sum_{i<j}\langle\psi_i\psi_j||\psi_i\psi_j\rangle,$$

in which the 1-electron sum (Σ_1) becomes

$$\Sigma_1 = \langle\psi_1|\mathsf{h}|\psi_1\rangle + \langle\psi_2|\mathsf{h}|\psi_2\rangle + \langle\psi_3|\mathsf{h}|\psi_3\rangle + \langle\psi_4|\mathsf{h}|\psi_4\rangle,$$

and similarly

$$\begin{aligned}\Sigma_2 &= \langle\psi_1\psi_2||\psi_1\psi_2\rangle + \langle\psi_1\psi_3||\psi_1\psi_3\rangle + \langle\psi_1\psi_4||\psi_1\psi_4\rangle \\ &+ \langle\psi_2\psi_3||\psi_2\psi_3\rangle + \langle\psi_2\psi_4||\psi_2\psi_4\rangle + \langle\psi_3\psi_4||\psi_3\psi_4\rangle.\end{aligned}$$

With the spin-orbitals listed above in (A), Σ_1 becomes (making use of (3.9))

$$\Sigma_1 = 2\langle\phi_{1s}|\mathsf{h}|\phi_{1s}\rangle + 2\langle\phi_{2s}|\mathsf{h}|\phi_{2s}\rangle$$

and similarly

$$\begin{aligned}\Sigma_2 &= \langle\phi_{1s}\phi_{1s}||\phi_{1s}\phi_{1s}\rangle' + \langle\phi_{1s}\phi_{2s}||\phi_{1s}\phi_{2s}\rangle + \langle\phi_{1s}\phi_{2s}||\phi_{1s}\phi_{2s}\rangle' \\ &+ \langle\phi_{1s}\phi_{2s}||\phi_{1s}\phi_{2s}\rangle' + \langle\phi_{1s}\phi_{2s}||\phi_{1s}\phi_{2s}\rangle + \langle\phi_{2s}\phi_{2s}||\phi_{2s}\phi_{2s}\rangle'.\end{aligned}$$

Again the terms that have been given a 'prime' are the ones that come from spin-orbitals of different spin – and therefore include no exchange term.

On using the J and K notation for the Coulomb and exchange integrals, the last result becomes (showing the terms in the same order) $\Sigma_2 = J_{1s,1s} + (J_{1s,2s} - K_{1s,2s}) + (J_{1s,2s}) + (J_{1s,2s}) + (J_{1s,2s} - K_{1s,2s}) + (J_{2s,2s})$. Thus $\Sigma_2 = J_{1s,1s} + J_{2s,2s} + 4J_{1s,2s} - 2K_{1s,2s}$, where the first two terms give the Coulomb repulsion energy within the two doubly occupied AOs while the remainder give the four Coulomb repulsions between the two electron pairs, (1s^2) and (2s^2), together with the two exchange terms from the electrons with the same spin.

The total electronic energy of the Beryllium atom, in IPM approximation, thus has the expectation value

$$\bar{E} = 2\epsilon_{1s} + 2\epsilon_{2s} + J_{1s,1s} + J_{2s,2s} + 4J_{1s,2s} - 2K_{1s,2s}.$$

Example 3.6 has given an expression for the total energy of a system consisting of two doubly occupied AOs, namely

$$\bar{E} = 2\epsilon_{1s} + 2\epsilon_{2s} + J_{1s,1s} + J_{2s,2s} + 4J_{1s,2s} - 2K_{1s,2s}. \tag{3.11}$$

The beauty of this result is that it can be generalized (with no more work!) and will then hold good for *any atom* for which the IPM provides a decent approximate wave function. It was derived for two doubly occupied AOs, ϕ_{1s} and ϕ_{2s}, but for a system with n such orbitals – which we can call simply $\phi_1, \phi_2, \dots \phi_i, \dots \phi_n$ – the derivation will be just the same (think about it!). The n orbitals can hold $N = 2n$ electrons and the general energy expression will be (summation limits, not shown, are normally $i = 1, n$)

$$\bar{E} = 2\sum_i \epsilon_i + \sum_i J_{i,i} + 4\sum_{i<j} J_{i,j} - 2\sum_{i<j} K_{i,j}, \tag{3.12}$$

where the indices now label the *orbitals* in ascending energy order. The terms being summed have the same meaning as for only two orbitals: the first is the energy of two electrons in orbital ϕ_i; the next is their Coulomb repulsion energy; and then there is the repulsion between each electron of the pair in ϕ_i and each in ϕ_j; the last is the exchange energy between the two pairs that have the same spin.

At this point we begin to think about how the orbitals might be improved; for we know that using the AOs obtained for one electron alone, moving in the field of the nucleus, will give a very poor approximate wave function. Even with only the two electrons of the Helium atom (Example 2.1) the exponential factor in the 1s orbital is changed quite a lot by the presence of a second electron: instead of corresponding to nuclear charge $Z = 2$ a more realistic value turned out to be $Z_{\text{eff}} = Z - (5/8)$. This is an 'effective nuclear charge', reduced by the **screening constant** (5/8) which allows for some of the *repulsion* between the electrons.

Clearly, the 2s AO in the Lithium atom would be much better represented by giving it an exponent closer to 1 instead of the actual value $Z = 3$, , to allow for the fact that the $1s^2$ inner shell holds two charges of $-e$ close to the nucleus. Of course we can find a better value of the effective nuclear charge, which determines the sizes of the outer AOs, by minimizing the expectation value $\bar{E}$; but we really want to find the best possible IPM wave function and that means allowing the AOs to take *arbitrary* – not just hydrogen-like – forms. That's a much more difficult job.

Chapter 4

The Hartree-Fock method

4.1 Getting the best possible orbitals: Step 1

Note to the reader The next sections contain difficult material and you may need to be reminded about summations. You've been summing numbered terms ever since Book 1: if there are n of them, $t_1, t_2, \dots t_n$ say, you may write their sum as $T = \sum_{i=1}^{i=n} t_i$ or, when the limits are clear, just as $\sum_i t_i$; but if the terms are labeled by *two* indices, i, j you may need to add *conditions* e.g. $i \neq j$ or $i < j$ to exclude some of the terms. Thus, with $n = 3$, $\sum_{i<j} t_{i,j}$ will give you $T = t_{1,2} + t_{1,3} + t_{2,3}$; and if you want to sum over one index only you can use parentheses to exclude the one you don't want to sum over, using for example $\sum_{i(\neq 2)}$ to keep $j = 2$ fixed. Think carefully about what you want to do!

When the IPM approximation was first introduced in Chapter 2, it was taken for granted that the 'best' 1-electron wave functions would describe accurately a single electron moving in some kind of 'effective field'. That means they would be eigenfunctions of an eigenvalue equation $\mathsf{h}_{\text{eff}}\psi = \epsilon\psi$, with $\mathsf{h}_{\text{eff}} = \mathsf{h} + \mathsf{V}$. Here we'll suppose the spin variables have been eliminated, as in Examples 3.5 and 3.6, and start from the energy expression (3.12), namely

$$\bar{E} = 2\sum_i \epsilon_i + \sum_i J_{ii} + 4\sum_{i<j} J_{ij} - 2\sum_{i<j} K_{ij}.$$

where, with the usual notation, $\epsilon_i = \langle\phi_i|\mathsf{h}|\phi_i\rangle, \quad J_{ij} = \langle\phi_i\phi_j|\mathsf{g}|\phi_i\phi_j\rangle, \quad K_{ij} = \langle\phi_i\phi_j|\mathsf{g}|\phi_j\phi_i\rangle$. To find the stationary value of the energy we can rewrite $\bar{E}$ as

$$\bar{E} = 2\sum_i \epsilon_i + 2\sum_{i,j} J_{ij} - \sum_{i,j} K_{ij}. \tag{4.1}$$

(checking that the summations come out right!) and then vary the orbitals one at a time. Suppose then that $\phi_k \to \phi_k + \delta\phi_k$, where k is any chosen ('fixed') index, for the orbital we're going to vary. The corresponding small change in the 1-electron part of $\bar{E}$ will be easy, since $\epsilon_i = \langle\phi_i|\mathsf{h}|\phi_i\rangle$ and changes only when we take the term with $i = k$ in the 'bra' or in the 'ket'. The change in the sum is thus $\langle\delta\phi_k|\mathsf{h}|\phi_k\rangle + (c.c)$ where $(c.c.)$ stands for the complex conjugate of the term before it. But the interaction terms are more difficult: we'll deal with them in the next two examples.

Example 4.1 The Coulomb operator

It would be nice to write the J- and K-terms as expectation values of 1-electron operators, for then we could deal with them in the same way as ϵ_i. A single Coulomb integral is

$$J_{ij} = \langle\phi_i\phi_j|\mathsf{g}|\phi_i\phi_j\rangle = \int(1/r_{12})\phi_i^*(\mathbf{r}_1))\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2,$$

since g is just a multiplying factor and can be put anywhere in the integrand. We'd like to get one integration out of the way first, the one that involves the $\mathbf{r}_2$ variable, and we can do it by defining an operator

$$\mathsf{J}_j(1) = \int(1/r_{12})\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_2)\mathrm{d}\mathbf{r}_2$$

that works on any function of $\mathbf{r}_1$, multiplying it by the factor that comes from the integration and obviously depends on orbital ϕ_j.

With Born's interpretation of the wave function (see Example 2.3), $\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_2) = P_j(\mathbf{r}_2)$ is the probability density of finding an electron in orbital ϕ_j at point $\mathbf{r}_2$. And the integral $\int(1/r_{12})P_j(\mathbf{r}_2)\mathrm{d}\mathbf{r}_2$ is the electric potential at point $\mathbf{r}_1$ due to an electron in orbital ϕ_j, treating P_j as the density (in electrons/unit volume) of a 'smeared out' distribution of charge.

Example 4.1 has given the expression (putting the volume element $\mathrm{d}\mathbf{r}_2$ just after the integration sign that goes with it, so as not to get mixed up)

$$\mathsf{J}_j(1) = \int \mathrm{d}\mathbf{r}_2(1/r_{12})\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2) \tag{4.2}$$

for the **Coulomb operator** associated with an electron in orbital ϕ_j, being the electrostatic potential at point $\mathbf{r}_1$ arising from its 'charge cloud'.

And with this definition we can write the Coulomb term as the double integral

$$\begin{aligned} J_{ij} &= \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2(1/r_{12})\phi_i^*(\mathbf{r}_1))\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \\ &= \int \mathrm{d}\mathbf{r}_1\phi_i^*(\mathbf{r}_1))\,(\mathsf{J}_j(1))\,\phi_i(\mathbf{r}_1) = \langle\phi_i|\mathsf{J}_j(1)|\phi_i\rangle, \end{aligned} \tag{4.3}$$

which is an expectation value, just as we wished, of the 1-electron operator $\mathsf{J}_j(1)$ that gives the 'effective field' provided by an electron in orbital ϕ_j. Now we want to do something similar for the exchange term K_{ij}.

Example 4.2 The exchange operator

The exchange integral is

$$K_{ij} = \langle\phi_i\phi_j|\mathsf{g}|\phi_j\phi_i\rangle = \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2(1/r_{12})\phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2\phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2),$$

and the interchange of labels in the 'ket' spoils everything. We'll have to invent a new operator!

If you compare the expression for K_{ij} with that for J_{ij} in (5.3) you'll see where they disagree. Since the order of the factors doesn't matter, we can keep the variables in the standard order – swapping the labels instead. The J_{ij} integral is

$$J_{ij} = \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 (1/r_{12})\phi_i^*(\mathbf{r}_1))\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2),$$

while K_{ij}, with its interchange of labels in the 'ket', is

$$K_{ij} = \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 (1/r_{12})\phi_i^*(\mathbf{r}_1))\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2).$$

The Coulomb operator (4.2) could be defined that way (as a multiplier) because the integration over $\mathbf{r}_2$ could be completed first, leaving behind a function of $\mathbf{r}_1$, before doing the final integration over $\mathbf{r}_1$ to get J_{ij} as the expectation value in (5.3). We'd like to do something similar for the exchange integral K_{ij}, but the best we can do is to introduce $\mathsf{K}_j(1)$, whose effect on *any* function ϕ of $\mathbf{r}_1$ will be to give

$$\mathsf{K}_j(1)\phi(\mathbf{r}_1) = \int \mathrm{d}\mathbf{r}_2 (1/r_{12})\phi_j(\mathbf{r}_1))\phi_j^*(\mathbf{r}_2)\phi(\mathbf{r}_2).$$

This looks very strange, because operating on $\phi(\mathbf{r}_1)$, it first has to change the variable to $\mathbf{r}_2$ and then do an integration which finally leaves behind a new function of $\mathbf{r}_1$. To put that in symbols we could say

$$\mathsf{K}_j(1)\phi(\mathbf{r}_1) = \int \mathrm{d}\mathbf{r}_2 (1/r_{12})\phi_j(\mathbf{r}_1))\phi_j^*(\mathbf{r}_2)\,(\mathbf{r}_1 \rightarrow \mathbf{r}_2)\phi_i(\mathbf{r}_1),$$

where the operator $(\mathbf{r}_1 \rightarrow \mathbf{r}_2)$ means "replace $\mathbf{r}_1$ by $\mathbf{r}_2$ in any function that follows it".

Let's test it on the function $\phi_i(\mathbf{r}_1)$ by writing the final factor in the expression for K_{ij} as $(\mathbf{r}_1 \rightarrow \mathbf{r}_2)\phi_i(\mathbf{r}_1)$ and noting that the integration over $\mathbf{r}_2$ is already present. We then find

$$K_{ij} = \int \mathrm{d}\mathbf{r}_1 \phi_i^*(\mathbf{r}_1)\left[\int \mathrm{d}\mathbf{r}_2 (1/r_{12})\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\,(\mathbf{r}_1 \rightarrow \mathbf{r}_2)\phi_i(\mathbf{r}_1)\right] = \int \mathrm{d}\mathbf{r}_1 \phi_i^*(\mathbf{r}_1)\mathsf{K}_j(1)\phi_i(\mathbf{r}_1),$$

which is conventionally written in the same form as (5.3): $K_{ij} = \langle\phi_i|\mathsf{K}_j(1)|\phi_i\rangle$, so the exchange integral $\langle\phi_i\phi_j|\mathsf{g}|\phi_j\phi_i\rangle$ can also be expressed as the expectation value of an **exchange operator**.

Example 3.8 has given an expression for the exchange integral $\langle\phi_i\phi_j|\mathsf{g}|\phi_j\phi_i\rangle$, similar to that in (5.3) but with the **exchange operator**

$$\mathsf{K}_j(1) = \int \mathrm{d}\mathbf{r}_2 (1/r_{12})\phi_j(\mathbf{r}_1))\phi_j^*(\mathbf{r}_2)(\mathbf{r}_1 \rightarrow \mathbf{r}_2). \qquad (4.4)$$

in place of the Coulomb operator. Both operators describe the effect on Electron '1', in any orbital ϕ, of another electron ('2') in orbital ϕ_j, but while the Coulomb operator has a simple classical interpretation (giving the energy of '1' in the field produced by the smeared-out charge density associated with '2') the exchange operator is more mysterious.

There is, however, another way of describing an operator like $\mathsf{K}_j(1)$. An operator in a function space is simply a 'recipe' for going from one function to another e.g from $f(x)$ to $g(x)$. You've used *differential* operators a lot, but another way of getting from $f(x)$ to $g(x)$ is to use an **integral operator**, k say, defined by means of a 'kernel' $k(x, x')$ which includes a second variable x': the kernel determines the effect of the operator and $\mathsf{k}f(x) = \int k(x,x')f(x')\mathrm{d}x'$ becomes a new function $g(x) = \mathsf{k}f(x)$. Clearly, $\mathsf{K}_j(1)$ in (4.4) is an operator of this kind: it contains two electronic variables, $\mathbf{r}_1, \mathbf{r}_2$, and an integration over the second one ($\mathbf{r}_2$).

Here we'll define the **kernel** of the operator K_j as the *function of two variables*

$$K_j(\mathbf{r}_1,\mathbf{r}_2) = (1/r_{12})\phi_j(\mathbf{r}_1))\phi_j^*(\mathbf{r}_2). \tag{4.5}$$

It then becomes clear that (4.4) can also be written as

$$\mathsf{K}_j(1)\phi_i(\mathbf{r}_1) = \int \mathrm{d}\mathbf{r}_2 K_j(\mathbf{r}_1,\mathbf{r}_2)\phi_i(\mathbf{r}_2). \tag{4.6}$$

(**Note:** From now on we'll no longer indicate that the 1-electron operators act on functions of $\mathbf{r}_1$, by writing $\mathsf{h}(1)$ etc – as that will always be clear from the function they act on.)

The relationship between the operator and its kernel is usually written $\mathsf{K}_j \rightarrow K_j(\mathbf{r}_1,\mathbf{r}_2)$. Notice that the operator J_j, defined in (4.2) has a similar integrand, except that the variable $\mathbf{r}_1$ has been replaced by $\mathbf{r}_2$ and the integration $\int \mathrm{d}\mathbf{r}_2$ has been completed before going on to get (5.3).

We're now nearly ready to go back to (4.1), writing the Coulomb and exchange integrals in terms of the newly defined operators J_j and K_j, given in (4.2) and (4.6). Remember that $\epsilon_i = \langle\phi_i|\mathsf{h}|\phi_i\rangle$ in terms of the 1-electron Hamiltonian h; and we now know how to express $J_{ij} = \langle\phi_i\phi_j|\mathsf{g}|\phi_i\phi_j\rangle$ and $K_{ij} = \langle\phi_i\phi_j|\mathsf{g}|\phi_j\phi_i\rangle$ in similar form.

Thus, (4.1) becomes

$$\begin{aligned}\bar{E} &= 2\sum_i \epsilon_i + 2\sum_{j,i} J_{ij} - \sum_{j,i} K_{ij} \\ &= 2\sum_i \langle\phi_i|\mathsf{h}|\phi_i\rangle + 2\sum_{j,i} J_{ij} - \sum_{j,i} K_{ij}.\end{aligned}$$

The 1-electron energy (called ϵ_i only with complete neglect of electron interaction) has now been written explicitly as the expectation value of the 'bare nuclear' Hamiltonian h.

The summations over j can now be done, after putting $J_{ij} = \langle\phi_i|\mathsf{J}_j|\phi_i\rangle$, $K_{ij} = \langle\phi_i|\mathsf{K}_j|\phi_i\rangle$ and defining *total* Coulomb and exchange operators as $\mathsf{J} = 2\sum_j \mathsf{J}_j,\ \mathsf{K} = 2\sum_j \mathsf{K}_j$. (Remember that J_j and K_j are operators for *one* electron in orbital ϕ_j, but here we have doubly-occupied orbitals.) Thus, on putting $\mathsf{J} - \frac{1}{2}\mathsf{K} = \mathsf{G}$, we find

$$\begin{aligned}\bar{E} &= 2\sum_i \langle\phi_i|\mathsf{h}|\phi_i\rangle + \sum_i \langle\phi_i|\mathsf{J}|\phi_i\rangle - \tfrac{1}{2}\textstyle\sum_i \langle\phi_i|\mathsf{K}|\phi_i\rangle \\ &= 2\sum_i \langle\phi_i|(\mathsf{h} + \tfrac{1}{2}\mathsf{G})|\phi_i\rangle \quad (\mathsf{G} = \mathsf{J} - \tfrac{1}{2}\mathsf{K})\end{aligned} \tag{4.7}$$

Having found a neat expression for the expectation value of the total energy, the next step will be to find its variation when the orbitals are changed.

4.2 Getting the best possible orbitals: Step 2

To find the stationary value of the energy we vary the orbitals one at a time, supposing $\phi_k \to \phi_k + \delta\phi_k$ and working to the first order of small quantities. The part of $\bar{E}$, given in (4.7), that depends on the single orbital ϕ_k – the one which is going to be varied – is

$$\begin{aligned} \bar{E}^{(k)} &= 2\epsilon_k + J_{kk} + \sum_{j(\neq k)} J_{kj} - \tfrac{1}{2}\sum_{j(\neq k)} K_{kj} \\ &= 2\langle\phi_k|\mathsf{h}|\phi_k\rangle + \sum_j J_{kj} - \tfrac{1}{2}\sum_j K_{kj}. \end{aligned} \qquad (4.8)$$

Here the 1-electron energy (called ϵ_k only with complete neglect of electron interaction) has again been written explicitly as the expectation value of the 'bare nuclear' Hamiltonian h.

On making the change $\phi_k \to \phi_k + \delta\phi_k$, the corresponding first-order change in (4.8) is

$$\begin{aligned} \delta\bar{E}^{(k)} &= 2\langle\delta\phi_k|\mathsf{h}|\phi_k\rangle + (c.c.) + \\ &\left(\sum_j \langle\delta\phi_k\phi_j|\mathsf{g}|\phi_k\phi_j\rangle + \sum_i \langle\phi_i\delta\phi_k|\mathsf{g}|\phi_i\phi_k\rangle\right) + (c.c.) \\ &-\tfrac{1}{2}\left(\sum_j \langle\delta\phi_k\phi_j|\mathsf{g}|\phi_k\phi_j\rangle + \sum_i \langle\phi_i\delta\phi_k|\mathsf{g}|\phi_k\phi_i\rangle\right) + (c.c.), \end{aligned}$$

where each (c.c.) is the complex conjugate of the term before it.

(Note that the two sums in the parentheses are identical because, for example, the term $\langle\phi_i\phi_j|\mathsf{g}|\phi_i\phi_j\rangle$ in the expression for $E^{(k)}$ could just as well have been written $\langle\phi_j\phi_i|\mathsf{g}|\phi_j\phi_i\rangle$ and then, calling the *second* factor ϕ_k, the change $\phi_k \to \phi_k + \delta\phi_k$ would have made the second sum into $\sum_j\langle\phi_j\delta\phi_k|\mathsf{g}|\phi_j\phi_k\rangle$) – the same as the first sum if you interchange the summation indices i, j.)

Thus, noting that the same argument applies on the last line of the equation above, the first-order change in energy becomes

$$\delta\bar{E}^{(k)} = \left(2\langle\delta\phi_k|\mathsf{h}|\phi_k\rangle + 2\sum_j\langle\delta\phi_k\phi_j|\mathsf{g}|\phi_k\phi_j\rangle - \sum_j\langle\delta\phi_k\phi_j|\mathsf{g}|\phi_j\phi_k\rangle\right) + (c.c.).$$

But $\langle\delta\phi_k\phi_j|\mathsf{g}|\phi_k\phi_j\rangle = \langle\delta\phi_k|\mathsf{J}_j|\phi_k\rangle$ and $\langle\delta\phi_k\phi_j|\mathsf{g}|\phi_j\phi_k\rangle = \langle\delta\phi_k|\mathsf{K}_j|\phi_k\rangle$; and the last expression can therefore be written (doing the summations over j)

$$\begin{aligned} \delta\bar{E}^{(k)} &= (2\langle\delta\phi_k|\mathsf{h}|\phi_k\rangle + 2\langle\delta\phi_k|\mathsf{J}|\phi_k\rangle - \langle\delta\phi_k|\mathsf{K}|\phi_k\rangle) + (c.c.) \\ &= 2\langle\delta\phi_k|[\mathsf{h} + \mathsf{J} - \tfrac{1}{2}\mathsf{K}]|\phi_k\rangle + (c.c.). \end{aligned} \qquad (4.9)$$

The *total* first-order energy variation, $\delta\bar{E}$, will be simply the sum of such changes over all values of index k. Here, however, we are interested in minimizing the IPM energy approximation against infinitesimal variation of any orbital ϕ_k, subject to the usual **normalization condition**. Since this variation is otherwise *arbitrary*, it follows (see Section 1.2 of Chapter 1) that a solution is obtained when $[\mathsf{h} + \mathsf{J} - \frac{1}{2}\mathsf{K}]\phi_k$ is a multiple of ϕ_k. The operator in square brackets is often denoted by F and called the **Fock operator**, after the Russian physicist who first used it. The condition for finding the best orbital ϕ_k is therefore that it be an eigenfunction of F:

$$\mathsf{F}\phi_k = \epsilon_k\phi_k \qquad (\mathsf{F} = \mathsf{h} + \mathsf{J} - \tfrac{1}{2}\mathsf{K} = \mathsf{h} + \mathsf{G}), \tag{4.10}$$

where ϵ_k, the corresponding eigenvalue, is the **orbital energy**.

What have we done? Starting from a 1-electron system, with orbitals determined from a simple 3-dimensional eigenvalue equation $\mathsf{h}\phi = \epsilon\phi$, we've moved on to a *many*-electron system, with an enormous eigenvalue equation $\mathsf{H}\Phi = E\Phi$ (there may be *thousands* of electrons), and found that in IPM approximation it can be quite well described in terms of orbitals that satisfy an 'effective' eigenvalue equation $\mathsf{F}\phi = \epsilon\phi$. The 'effective' 1-electron operator that replaces the original h is the Fock operator in (4.10), $\mathsf{F} = \mathsf{h}+\mathsf{G}$. The presence of all other electrons in the system is 'taken care of' by using this effective Hamiltonian and dealing with a *one*-electron problem. That's a gigantic step forward!

4.3 The self-consistent field

There's no simple way of solving the eigenvalue equation found in the last section, because the Fock operator depends on the forms of all the occupied orbitals – which determine the electron density and consequently the **effective field** in which all the electrons move! The best that can be done is to go step by step, using a very rough first approximation to the orbitals to estimate the J- and K-operators and then using them to set up, and solve, a revised eigenvalue equation. The new orbitals which come out will usually be a bit different from those that went in but will hopefully give an improved estimate of the Fock operator. This allows us to go ahead by **iteration** until, after several cycles, no further improvement is needed: at that stage the effective field stops changing and the 'output' orbitals agree with the ones used in setting up the eigenvalue equation. This is the **self-consistent field method**, invented by Hartree (without the exchange operator) and Fock (including exchange). It has been employed, in one form or another, ever since the 1930s in calculations on atoms, molecules and more extended systems, and will serve us well in the rest of Book 12.

The first thing we need to do is to relate the J- and K-operators to the electron density functions and we already know how to do that. From (5.3) it follows that the total Coulomb operator, for the whole system with two electrons in every orbital, is

$$\mathsf{J} = 2\sum_j \mathsf{J}_j = 2\int \mathrm{d}\mathbf{r}_2(1/r_{12})\sum_j[\phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2)],$$

while the total exchange operator is K with kernel

$$K(\mathbf{r}_1, \mathbf{r}_2) = 2\sum_j K_j(\mathbf{r}_1, \mathbf{r}_2) = 2(1/r_{12})\sum_j [\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)]$$

Now the sum of all orbital contributions to the electron density at point $\mathbf{r}_2$ is $P(\mathbf{r}_2) = 2\sum_j \phi_j(\mathbf{r}_2)\phi_j^*(\mathbf{r}_2)$, and this determines the Coulomb interaction between an electron at $\mathbf{r}_1$ and the whole electron distribution. The exchange interaction is similar, but depends on the same density function *evaluated at two points* – for which we use the notation $P(\mathbf{r}_1; \mathbf{r}_2)$. The usual density function $P(\mathbf{r}_1)$ then arises on putting $\mathbf{r}_2 = \mathbf{r}_1$: $P(\mathbf{r}_1) = P(\mathbf{r}_1; \mathbf{r}_1)$.

To summarize, the effect of J and K on any function ϕ of $\mathbf{r}_1$ is given as follows:

The Coulomb and exchange operators for any closed-shell system are defined by their effect on any 1-electron function $\phi(\mathbf{r}_1)$:

$$\mathrm{J}\phi(\mathbf{r}_1) = \left[\int \mathrm{d}\mathbf{r}_2 (1/r_{12}) P(\mathbf{r}_2; \mathbf{r}_2)\right] \times \phi(\mathbf{r}_1),$$

$$\mathrm{K}\phi(\mathbf{r}_1) = \left[\int \mathrm{d}\mathbf{r}_2 (1/r_{12}) P(\mathbf{r}_1; \mathbf{r}_2) \times \phi(\mathbf{r}_2)\right],$$

where $\quad P(\mathbf{r}_1; \mathbf{r}_2) = 2\sum_j [\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)$

is a 2-variable generalization of the electron density function $P(\mathbf{r}_1)$.

(4.11)

To show how the Fock operator depends on $\mathsf{G} = \mathsf{J} - \frac{1}{2}\mathsf{K}$, and therefore on the density function $P(\mathbf{r}_1; \mathbf{r}_2)$, we write

$$\mathsf{F}\phi_k = \epsilon_k \phi_k \qquad (\mathsf{F} = \mathsf{h} + \mathsf{G}(P)). \tag{4.12}$$

It is important to note that F is a **Hermitian operator** and that its eigenfunctions may therefore be taken as forming an *orthogonal set* – as we supposed in Section 3.1; but this is not the case unless the exchange operator is included.

All very well, you might say, but if the Hartree-Fock equations are so difficult to handle why do we spend so much time on them? And if we do manage to get rough approximations to orbitals and orbital energies, do they really 'exist' and allow us to get useful information? The true answer is that orbitals and their energies 'exist' only in our *minds*, as solutions to the mathematical equations we have formulated. In the rare cases where accurate solutions can be found, they are much more complicated than the simple approximate functions set up in Chapter 2. Nevertheless, by going ahead we can usually find simple *concepts* that help us to understand the relationships among the quantities we can observe and measure. In Chapter 6 of Book 11 you saw how the idea of orbital energies allowed us to interpret the selective absorption of radiation of different colours in terms of 'quantum jumps' between energy levels. The Hartree-Fock method provides a tool for extending that interpretation from a one-electron system to a *many*-electron system, simply by using an 'effective' 1-electron Hamiltonian $\mathsf{F} = \mathsf{h} + \mathsf{G}$, in which G 'takes care' of all the electron interactions.

One very striking example of the value of the orbital energy concept is provided by **photo-electron spectroscopy**, an experimental method of directly observing quantum jumps in an atom adsorbed on a solid surface. In this example, the atom usually belongs to a molecule embedded in the surface; and when radiation falls on the surface it is struck by photons of energy $h\nu$.

(You should read again Section 6.5 of Book 10, where the **electromagnetic spectrum** is related to the frequency ν and wavelength λ of the radiation. There we were using the 'classical' picture of radiation in terms of electromagnetic *waves*; but here we use the 'quantum' description in which the energy is carried by 'wave packets', behaving like particles called *photons*. This wave-particle 'duality' is dealt with more fully in Book 11.)

The energy of an X-ray photon is big enough to knock an electron out of an atomic inner shell, leaving behind an ion with an inner-shell 'hole'. The ejected electron has a kinetic energy which can be measured and related to the energy of the orbital from which it came. The whole process can be pictured as in Figure 4.1, which shows the various energy levels.

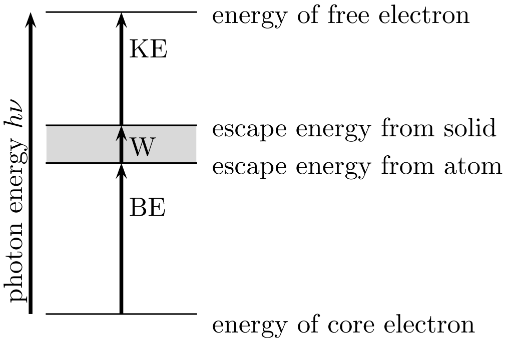


Figure 4.1 Energy diagram for X-PS (see text)

The name "X-PS" stands for "X-ray Photoelectron Spectroscopy". The lengths of the upward-pointing arrows in the Figure correspond to (i) the X-ray photon energy (left) and (ii) the excitations that lead to the ionization of the system. 'BE' stands for the Binding Energy of an electron in an atomic core orbital, ϕ_k say, and for a free atom this would have the value $I = -\epsilon_k$ in IPM approximation. But when the atom is part of a molecule attached to a solid surface I will be the 'escape energy' for getting the electron out of the molecule and into the solid. A large system like a solid normally has a continuum of closely-spaced electron energy levels and if the escaping electron has enough energy it can reach the level labelled "escape energy from solid"(W) and pass out into space as a **free electron** with any remaining kinetic energy (KE) it may have. The general energy-conservation principle (which you've been using ever since Book 4) then allows you to write

$$h\nu = \mathrm{BE} + \mathrm{W} + \mathrm{KE}.$$

In this approximation the binding energy 'BE' $= -\epsilon_k$ when the electron comes from orbital ϕ_k (ϵ_k being negative for bound states), while 'W' (called the "work function") is the extra work that has to be done to get the electron from the level labelled "escape energy from atom" to the one labelled "escape energy from solid". At that point the electron really is *free* to travel through empty space until it reaches a 'collector', in which its KE can be measured. (Experiments like this are always made in high vacuum, so the electron released has nothing to collide with.) The work function 'W' can also be measured, by doing the experiment with a clean surface (no adsorbed atoms or molecules) and a much smaller photon energy, so the electron collected can only have come from the energy levels in the solid.

The last equation can now be rearranged to give an experimental value of 'BE' $= -\epsilon_k$ in terms of the observed 'KE' of the electron reaching the collector:

$$-\epsilon_k = h\nu - \mathrm{W} - \mathrm{KE}.$$

So even if orbitals don't really exist you can measure experimentally the energies of the electrons they describe! Similar experiments can be done with lower photon energies: if you use ultraviolet radiation instead of X-rays you'll be using "Ultraviolet Photoelectron Spectroscopy" ("U-PS") and will be able to get information about the upper energy levels of the adsorbed atoms and molecules. Nowadays, such techniques are widely used not only to find what atoms are present in any given sample (their inner-shell orbital energies being their 'footprints') but also to find how many of them there are in each adsorbed molecule. For this reason 'X-PS' is often known as "Electron Spectroscopy for Chemical Analysis" ("ESCA").

It's now time to ask how the Hartree-Fock equations can be solved with enough accuracy to allow us to make meaningful comparisons between theory and experiment.

4.4 Finite-basis approximations

In earlier sections we've often built up approximate 1-electron wave functions as linear combinations of some given set of functions. This is one form of the more general procedure for building 1-electron wave functions from a **finite basis** of functions which, from now on, we'll denote by

$$\chi_1,\ \chi_2,\ \cdots \chi_r,\ \cdots \chi_m.$$

Here we suppose there are m linearly independent functions, labelled by a general index r, out of which we're going to construct the n occupied orbitals. Usually the functions will be supposed **orthonormal**, with Hermitian scalar products $\langle\chi_r|\chi_s\rangle = 1\,\mathrm{for}\,r =$

s; = 0 (otherwise). Very often the scalar product will be denoted by S_{rs} and called an "overlap integral". The basis functions are normally set out in a *row*, as a 'row matrix', and denoted by $\boldsymbol{\chi}$. With this convention, a linear combination of basis functions can be written

$$\phi = c_1\chi_1 + c_2\chi_2 + \ ...\ + c_r\chi_r + \ ...\ + c_m\chi_m \tag{4.13}$$

or, in matrix form, as the row-column product

$$\phi = (\chi_1\,\chi_2\,...\,\chi_m)\begin{pmatrix} c_1 \\ c_2 \\ .. \\ .. \\ c_m \end{pmatrix} = \boldsymbol{\chi}\mathbf{c}, \tag{4.14}$$

where $\mathbf{c}$ stands for the whole *column* of expansion coefficients and $\boldsymbol{\chi}$ for the *row* of basis functions. Sometimes it is useful to write such equations with the summation conventions, so that $\phi = \sum_r c_r\chi_r$. (Look back at Section 3.1, or further back to Chapter 7 of Book 11, if you need reminding of the rules for using matrices.)

In dealing with molecules, (4.14) is used to express a molecular orbital (MO) as a linear combination of atomic orbitals (AOs) and forms the basis of the **LCAO method**. The Hartree-Fock equation $\mathsf{F}\phi = \epsilon\phi$ is easily put in finite-basis form by noting that $\mathsf{F}\phi = \sum_s c_s\mathsf{F}\chi_s$ and, on taking a scalar product from the left with χ_r, the r-component of the new vector $\mathsf{F}\phi$ becomes

$$\langle\chi_r|\mathsf{F}|\phi\rangle = \sum_s \langle\chi_r|\mathsf{F}|\chi_s\rangle c_s.$$

The quantity $\langle\chi_r|\mathsf{F}|\chi_s\rangle$ is the rs-element of the square matrix $\mathbf{F}$ which *'represents'* the operator F in the χ-basis. The next example will remind you of what you need to know before going on.

Example 4.3 Matrix representations

When an operator A acts on a function ϕ, expressed as in (4.14), it produces a new function ϕ' with a new set of expansion coefficients, c'_r say. Thus $\phi' = \sum_s \chi_s c'_s$ and to find the r-component of the new function we form the scalar product $\langle\chi_r|\phi'\rangle$, getting (with an orthonormal basis)

$$c'_r = \langle\chi_r|\phi'\rangle = \langle\chi_r|\mathsf{A}\phi\rangle = \langle\chi_r|\mathsf{A}|\left(\sum_s \chi_s\rangle c_s\right) = \sum_s \langle\chi_r|\mathsf{A}|\chi_s\rangle c_s.$$

This is just a sum of products of ordinary numbers:

$$c'_r = \sum_s \langle\chi_r|\mathsf{A}|\chi_s\rangle c_s.$$

So the operator equation $\phi' = \mathsf{A}\phi$ is 'echoed' in the algebraic equation $c'_r = \sum_s A_{rs}c_s$ and this in turn can be written as a simple *matrix* equation $\mathbf{c}' = \mathbf{A}\mathbf{c}$. (Remember the typeface convention: A ('sans serif') stands for an *operator*; $\mathbf{A}$ ('boldface') for a *matrix* representing it; and A_{rs} (lightface italic) for a single number, such as a matrix element.)

In the same way, you can show (do it!) that when a second operator B works on $\mathsf{A}\phi$, giving $\phi'' = \mathsf{BA}\phi = \mathsf{C}\phi$, the product of operators $\mathsf{C} = \mathsf{BA}$ is represented by the *matrix* product $\mathbf{C} = \mathbf{BA}$.

To summarize: When a basis set $\boldsymbol{\chi}$ is defined, along with linear combinations of the basis functions of the type (4.13), or (4.14) in matrix form, the operator equality $\phi' = \mathsf{A}\phi$ allows us to say $\mathbf{c}' = \mathbf{Ac}$. In this case we write

$$\phi' = \mathsf{A}\phi \ \rightarrow \ \mathbf{c}' = \mathbf{Ac}$$

and say the equality on the left "implies" the one on the right. But this doesn't have to be true the other way round! Each implies the other only when the basis set is **complete** (see Section 3.1) and in that case we write

$$\phi' = \mathsf{A}\phi \ \leftrightarrow \ \mathbf{c}' = \mathbf{Ac}.$$

In both cases we speak of a **matrix representation** of the operator equation, but only in the second case can we call it **"faithful"** (or "one-to-one"). In the same way, the product of two operators applied in succession ($\mathsf{C} = \mathsf{BA}$) is represented by the matrix product $\mathbf{BA}$ and we write $\mathsf{BA} \leftrightarrow \mathbf{BA}$; but the 'double-headed' arrow applies only when the basis is complete. (Examples can be found in Book 11.)

It's important to remember that the representations used in the applications of quantum mechanics are hardly ever faithful. That's why we usually have to settle for *approximate* solutions of eigenvalue equations.

When the eigenvalue equation $\mathsf{F}\phi = \epsilon\phi$ is written in matrix form it becomes $\mathbf{Fc} = \epsilon\mathbf{c}$, the equality holding only in the limit where the basis is complete and the matrices are infinite. With only three basis functions, for example, the matrix eigenvalue equation is

$$\begin{pmatrix} F_{11} & F_{12} & F_{13} \\ F_{21} & F_{22} & F_{23} \\ F_{31} & F_{32} & F_{13} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \epsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} \tag{4.15}$$

To find the full matrix $\mathbf{F}$ associated with the operator given in (**??**) we need to look at the separate terms $\mathsf{h}, \mathsf{J}, \mathsf{K}$. The first one is easy: the matrix $\mathbf{h}$ has an rs-element $h_{rs} = \langle\chi_r|\mathsf{h}|\chi_s\rangle = \int \chi_r^*(\mathbf{r}_1)\mathsf{h}\phi_s(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1$, but the others are more difficult and are found as in the following examples.

Example 4.4 The electron density function

Suppose we want the rs-element of the matrix representing J, defined in (4.11), using the χ-basis. When J acts on any function of $\mathbf{r}_1$ it simply multiplies it by $\int g(1,2)P(\mathbf{r}_2,\mathbf{r}_2)\mathrm{d}\mathbf{r}_2$, and our first job is to find the matrix $\mathbf{P}$ representing the density function in the χ-basis. This density is twice the sum over all the doubly-occupied orbitals, which we'll now denote by ϕ_K (using capital letters as their labels, so as not to mix them up with the basis functions $\chi_r, \chi_s etc.$. So the total density becomes

$$P(\mathbf{r}_2;\mathbf{r}_2) = 2\sum_K \phi_K(\mathbf{r}_2)\phi_K^*(\mathbf{r}_2) = 2\sum_K(\sum_t c_t^K\chi_t(\mathbf{r}_2)(\sum_u c_u^K\chi_u(\mathbf{r}_2))^* = \sum_{t,u} P_{tu}\chi_t\chi_u^*,$$

where $P_{tu} = 2\sum_K c_t^K c_u^K$. (Note that the summation indices have been re-named t, u as r, s are already in use. Also, when there's no room for 'K' as a subscript you can always put it at the top – it's only a label!))

The electron density function $P(\mathbf{r}_1;\mathbf{r}_2)$, first used in (4.11), generally contains *two* independent variables, the ordinary density of electric charge in electrons/unit volume arising on putting $\mathbf{r}_2 = \mathbf{r}_1$. When the function is written in finite basis form as

$$P(\mathbf{r}_1;\mathbf{r}_2) = 2\sum_K \phi_K(\mathbf{r}_1)\phi_K^*(\mathbf{r}_2) = 2\sum_K(\sum_t c_t^K\chi_t(\mathbf{r}_1)(\sum_u c_u^K\chi_u(\mathbf{r}_2))^* = \sum_{t,u} P_{tu}\chi_t(\mathbf{r}_1)\chi_u^*(\mathbf{r}_2), \tag{4.16}$$

the square array $\mathbf{P}$, here with elements P_{tu}, is an example of a **density matrix**. You will find how important density matrices can be when you begin to study the physical properties of molecules. Here we're going to use them simply in defining the Coulomb and exchange operators.

Example 4.5 The Coulomb operator

To get $\langle\chi_r|\mathsf{J}|\chi_s\rangle$ we first express the operator J, which is just a multiplying factor, in terms of the χ-basis:

$$\Big[\int \mathrm{d}\mathbf{r}_2(1/r_{12})P(\mathbf{r}_2;\mathbf{r}_2) = \int g(1,2)\sum_{t,u} P_{tu}\chi_t(\mathbf{r}_2)\chi_u^*(\mathbf{r}_2)\mathrm{d}\mathbf{r}_2.$$

This multiplier, when substituted in the matrix element expression $\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\chi_r^*(\mathbf{r}_1)\mathsf{J}\chi_s(\mathbf{r}_1)$ then gives (check it out!)

$$\langle\chi_r|\mathsf{J}|\chi_s\rangle = \sum_{t,u} P_{tu}\langle\chi_r\chi_u|g|\chi_s\chi_t\rangle,$$

where the first indices on the two sides of the operator come from the $\mathbf{r}_1$ integration, while the second indices (u, t) come from the $\mathbf{r}_2$.

From Example 4.5, the Coulomb operator in (4.11) is represented in the finite χ-basis by a matrix $\mathbf{J}(\mathbf{P})$ i.e. as a 'function' of the electron **density matrix**, with elements

$$J_{rs} = \sum_{t,u} P_{tu}\langle\chi_r\chi_u|g|\chi_s\chi_t\rangle. \tag{4.17}$$

The matrix defined in this way allows one to calculate the expectation value of the energy of an electron in orbital $\phi_K = \chi\mathbf{c}^K$, arising from its Coulomb interaction with the whole electron distribution.

Example 4.6 The exchange operator

To get $\langle\chi_r|\mathsf{K}|\chi_s\rangle$ we first express the operator K, which is an **integral operator**, in terms of the χ-basis: from (4.11), taking the operand $\phi(\mathbf{r}_1)$ to be $\chi_s(\mathbf{r}_1)$, we get $\mathsf{K}\chi_s(\mathbf{r}_1) = \left[\int \mathrm{d}\mathbf{r}_2(1/r_{12})P(\mathbf{r}_1;\mathbf{r}_2)\chi_s(\mathbf{r}_2)\right]$, where the integration over $\mathbf{r}_2$ is included in this first step. The next step in getting the matrix element

$\langle\chi_r|\mathsf{K}|\chi_s\rangle$ is to multiply from the left by $\chi_r^*(\mathbf{r}_1)$ (complex conjugate in the 'bra' factor) and then do the remaining integration over $\mathbf{r}_1$. The result is

$$\langle\chi_r|\mathsf{K}|\chi_s\rangle = \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 (1/r_{12})\chi_r^*(\mathbf{r}_1)\sum_{t,u} P_{tu}\chi_t(\mathbf{r}_1)\chi_u^*(\mathbf{r}_1)\chi_s(\mathbf{r}_2) = \sum_{t,u} P_{tu}\langle\chi_r\chi_u|g|\chi_t\chi_s\rangle.$$

Here the first indices (r, t) on the two sides of the operator come from the $\mathbf{r}_1$ integration, while the second indices (u, s) come from the $\mathbf{r}_2$; but note the **exchange** of indices in the 'ket'.

From Example 4.6, the exchange operator in (4.11) is represented in the finite χ-basis by a matrix $\mathbf{K}(\mathbf{P})$, again as a 'function' of the electron **density matrix**, but now with elements

$$K_{rs} = \sum_{t,u} P_{tu}\langle\chi_r\chi_u|g|\chi_t\chi_s\rangle. \tag{4.18}$$

This result allows one to calculate the expectation value of the energy of an electron in orbital $\phi_K = \boldsymbol{\chi}\mathbf{c}^K$, arising from its **exchange** interaction with the whole electron distribution.

We've finished!! We can now go back to the operator forms of the Hartree-Fock equations and re-write them in the modern matrix forms, which are ideal for offering to an electronic computer. Equation (4.1), which gave the expectation value of the total electronic energy in the form

$$\begin{aligned}\bar{E} &= 2\sum_i\langle\phi_i|\mathsf{h}|\phi_i\rangle + \sum_i\langle\phi_i|\mathsf{J}|\phi_i\rangle - \tfrac{1}{2}\textstyle\sum_i\langle\phi_i|\mathsf{K}|\phi_i\rangle \\ &= 2\sum_i\langle\phi_i|(\mathsf{h} + \tfrac{1}{2}\mathsf{G})|\phi_i\rangle \quad (\mathsf{G} = \mathsf{J} - \tfrac{1}{2}\mathsf{K})\end{aligned}$$

now becomes (dropping the orbital label 'k' to the subscript position now there are no others, and remembering that the 'dagger' conveniently makes the column $\mathbf{c}_k$ into a row and adds the star to every element)

$$\begin{aligned}\bar{E} &= 2\sum_k \mathbf{c}_k^\dagger\mathbf{h}\mathbf{c}_k + \sum_k \mathbf{c}_k^\dagger\mathbf{J}\mathbf{c}_k - \tfrac{1}{2}\textstyle\sum_k \mathbf{c}_k^\dagger\mathbf{K}\mathbf{c}_k \\ &= 2\sum_k \mathbf{c}_k^\dagger(\mathbf{h} + \tfrac{1}{2}\mathbf{G})\mathbf{c}_k \quad (\mathbf{G} = \mathbf{J} - \tfrac{1}{2}\mathbf{K})\end{aligned} \tag{4.19}$$

The operator eigenvalue equation (4.10) for getting the best possible orbitals, which was

$$\mathsf{F}\phi_k = \epsilon_k\phi_k \qquad (\mathsf{F} = \mathsf{h} + \mathsf{G}),$$

now becomes, in finite basis approximation,

$$\mathbf{F}\mathbf{c}_k = \epsilon_k\mathbf{c}_k \qquad (\mathbf{F} = \mathbf{h} + \mathbf{G}), \tag{4.20}$$

The last two equations represent the prototype approach in applying quantum mechanics to the 'real' many-electron systems we meet in Physics and Chemistry. Besides providing a solid platform on which to build all the applications that follow in Book 12, they provide the underlying pattern for most current developments which aim to go beyond the Independent-Particle Model.

Chapter 5

Atoms: the building blocks of matter

5.1 Electron configurations and electronic states

Chapter 6 of Book 11 dealt with the simplest of all atoms – Hydrogen, in which one electron moves in the field of a positive nucleus of atomic number $Z = 1$. The eigenstates of the Hamiltonian H were also eigenstates of the angular momentum operators, L^2 and one component of **angular momentum**, chosen as L_z. The definite values of the energy and momentum operators were then $E_n = -\frac{1}{2}(Z^2/n^2)$, $L(L+1)$ and M (all in atomic units of $\mathrm{e_H}$, $\hbar^2$ and $\hbar$, respectively), where n, L, M are **quantum numbers**. But here we're dealing with a very different situation, where there are in general *many* electrons. Fortunately, the angular momentum operators L_x, L_y, L_z, and similar operators for **spin**, all follow the same **commutation rules** for any number of electrons. This means we don't have to do all the work again when we go from Hydrogen to, say, Calcium with 20 electrons – the same rules still serve and very little needs changing. (You may want to read again the parts of Chapter 5 (Book 11) that deal with angular momentum.)

Here we'll start from the commutation rules for (orbital) angular momentum in a 1-electron system. The operators $\mathsf{L}_x, \mathsf{L}_y, \mathsf{L}_z$ satisfy the equations

$$\begin{aligned}(\mathsf{L}_x\mathsf{L}_y - \mathsf{L}_y\mathsf{L}_x) &= i\mathsf{L}_z,\\ (\mathsf{L}_y\mathsf{L}_z - \mathsf{L}_z\mathsf{L}_y) &= i\mathsf{L}_x,\\ (\mathsf{L}_z\mathsf{L}_x - \mathsf{L}_x\mathsf{L}_z) &= i\mathsf{L}_y,\end{aligned} \tag{5.1}$$

which followed directly from the rules for position and linear momentum operators (see Example 5.4 in Book 11). For a many-electron system the components of *total* angular momentum will be

$$\mathsf{L}_x = \sum_i \mathsf{L}_x(i), \quad \mathsf{L}_y = \sum_i \mathsf{L}_y(i), \quad \mathsf{L}_z = \sum_i \mathsf{L}_z(i),$$

where $\mathsf{L}_x(i)$ for example is an angular momentum operator for Particle i, while the unnumbered operators L_x etc refer to components of total angular momentum. We want to show that these operators satisfy exactly the same equations (4.1).

Example 5.1 Commutation rules for total angular momentum

From the definitions it follows that

$$\begin{aligned}
\mathsf{L}_x\mathsf{L}_y - \mathsf{L}_y\mathsf{L}_x &= \left(\sum_i \mathsf{L}_x(i)\right)\left(\sum_j \mathsf{L}_y(j)\right) - \left(\sum_j \mathsf{L}_y(j)\right)\left(\sum_i \mathsf{L}_x(i)\right) \\
&= \sum_{i\neq j} [\mathsf{L}_x(i)\mathsf{L}_y(j) - \mathsf{L}_y(j)\mathsf{L}_x(i)] + \sum_j i\mathsf{L}_z(j) \\
&= i\mathsf{L}_z.
\end{aligned}$$

Note that the double sum with $i \neq j$ is zero because the operators commute when they refer to different particles, but satisfy the equations (5.1) when $i = j$ – giving the single sum which is $i\mathsf{L}_z$. (And don't confuse i, the imaginary unit, with i as a summation index!)

The other equations in (5.1) arise simply on changing the names of the indices.

Everything we know about the commutation properties of 1-electron operators is now seen to be true for the N-electron operators obtained by summing over all particles: in particular H, L^2, L_z all commute with each other, for any value of N, when H is a central-field Hamiltonian. This means that we can find **stationary states** in which the electronic energy, the square of the angular momentum and one of its components (taken by convention as defining the z-axis) can all have simultaneously definite values, which don't change in time. This was the conclusion reached in Chapter 5 of Book 11, for a *one*-electron system. It was summarized in a 'semi-classical' picture (Figure 12), indicating how the description of orbital motion had to be changed in going from classical to quantum mechanics.

Other important operators are the 'step-up' and 'step-down' operators, whose properties were derived in Examples 1, 2 and 3 of Chapter 6, Book 11. They are defined as $\mathsf{L}^+ = \mathsf{L}_x + i\mathsf{L}_y$ and $\mathsf{L}^- = \mathsf{L}_x - i\mathsf{L}_y$ and work on any angular momentum eigenstate $\Psi_{L,M}$, with quantum numbers L, M, to change it into one with M 'stepped up', or 'stepped down', by one unit. Their properties are thus

$$\begin{aligned}
\mathsf{L}^+\Psi_{L,M} &= \sqrt{(L-M)(L+M+1)}\Psi_{L,M+1}, \\
\mathsf{L}^-\Psi_{L,M} &= \sqrt{(L+M)(L-M+1)}\Psi_{L,M-1},
\end{aligned} \tag{5.2}$$

where the numerical multipliers ensure that the 'shifted' states, $\Psi_{L,M\pm1}$ will also be normalized to unity, $\langle\Psi_{L,M\pm1}|\Psi_{L,M\pm1}\rangle = 1$. These operators change only the eigenstates of L_z, leaving a state vector which is still an eigenstate of H and L^2 with the same energy and total angular momentum. And, from what has been said already, they may be used without change for systems containing any number of electrons. So we can now start thinking about 'real' atoms of any kind!

The electronic structures of the first four **chemical elements** are pictured, in IPM approximation, as the result of filling the two lowest-energy **atomic orbitals**, called '1s' and '2s'. (You should read again the parts of Chapter 6, Book 11, cuments/Books/Book12:The **electron configurations** of the first ten elements, in increasing order of atomic number, are

Hydrogen[1s^1] Helium[1s^2] Lithium[1s^{2}2s^1] Beryllium[1s^{2}2s^2]

in which the first two s-type AOs are filling (each with up to two electrons of opposite spin component, $\pm\frac{1}{2}$), followed by six more, in which the p-type AOs (p_x, p_y, p_z) are filling with up to two electrons in each.

Boron[1s^{2}2s^{2}2p^1] Carbon[1s^{2}2s^{2}2p^2] Nitrogen[1s^{2}2s^{2}2p^3]

Oxygen[1s^{2}2s^{2}2p^4] Fluorine[1s^{2}2s^{2}2p^5] Neon[1s^{2}2s^{2}2p^6]

Here the names of the AOs are the ones shown in Figure 15 of Book 11, the leading integer being the **principal quantum number** and the letter being the orbital *type* $(\mathrm{s, p, d, f}, ...)$. Remember the letters just stand for the types of series ('sharp', 'principal', 'diffuse', 'fine') found in the atomic spectra of the elements, arising from particular electronic transitions: in fact they correspond to values $0, 1, 2, 3$,.. of the quantum number L. (The energy-level diagram below (Figure 5.1) will remind you of all that.)

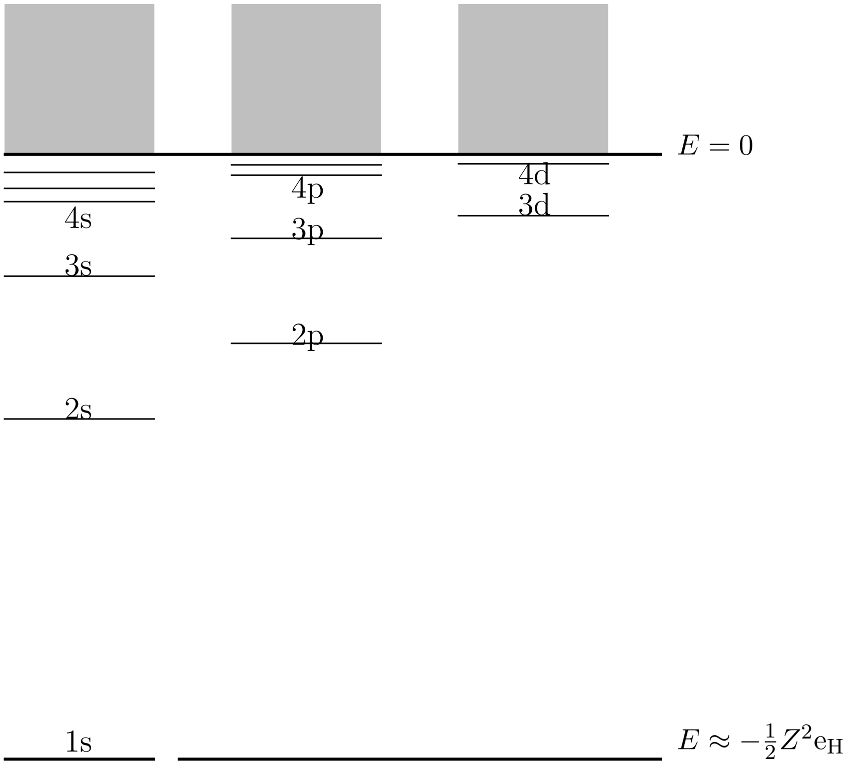


Figure 5.1 Orbital energies in an H-like atom (schematic)

Note especially that the energy levels differ slightly from those for a strictly Coulombic central field: the levels of given principal quantum number n normally lie in the energy order E_n(s)< E_n(p)< E_n(d)<... because in a real atom the orbitals with angle-dependent wave functions are on the average further from the nucleus and the electrons they hold are therefore not as tightly bound to it. As the number of electrons (Z) increases this effect becomes bigger, owing to the 'screening' produced by the electrons in the more tightly bound 'inner' orbitals. Thus, the upward trend in the series of levels such as 3s, 3p, 3d becomes more marked in the series 4s, 4p, 4d, 4f.

The first few atoms, in order of increasing atomic number Z, have been listed above along with the ways in which their electrons can be assigned to the available atomic orbitals – in ascending order of energy. The elements whose atoms have principal quantum numbers going from $n = 3$ up to $n = 10$ are said to form a **Period**, in which the corresponding quantum shells 'fill' with up to two electrons in every orbital. This is the first *'short period'*. Chemists generally extend this list, to include all the 92 naturally occuring atoms and a few more (produced artificially), by arranging them in a **Periodic Table** which shows how similar chemical properties may be related to similar electronic structures. More about that later.

Now that we have a picture of the probable **electron configurations** of the first few atoms, we have to start thinking about the wave functions of the corresponding electronic **states of a configuration**. For the atoms up to Beryllium, with its filled 1s and 2s orbitals, the ground states were non-degenerate with only one IPM wavefunction. But in Boron, with one electron in the next (2p) energy level, there may be several states as there are three degenerate 2p-type wavefunctions – usually taken as $2p_x$, $2p_y$, $2p_z$, or as $2p_{+1}, 2p_0, 2p_{-1}$, where the second choice is made when the unit angular momentum is quantized so that $\langle \mathsf{L}_z \rangle = +1,\ 0,\ -1$, respectively. The next element, Carbon, is even more interesting as there are now two electrons to put in the three degenerate p-orbitals. We'll study it in some detail, partly because of its importance in chemistry and partly because it gives you the key to setting up the many-electron state functions for atoms in general. (Before starting, you should read again Section 2.2 of Book 11, where we met a similar problem in dealing with *spin* angular momentum and how the spins of two or more particles could be coupled to give a whole range of total spins.)

First we note that the IPM states of the Carbon $(2p)^2$ configuration can all be built up from spin-orbital products with six factors of the type $\psi(l_i, m_i, s_i|\mathbf{x}_i) \quad (i = 1, 2, ...6)$. Here the 1-electron orbital angular momentum quantum numbers are denoted by lower-case letters l, m, leaving capitals (L, M) for *total* angular momentum; and s_i is used for the 1-electron 'up'- or 'down'-spin eigenvalue, always $\pm\frac{1}{2}$. For example $\psi(1, -1, +\frac{1}{2}|\mathbf{x}_5)$ means that Electron 5, with space-spin coordinates $\mathbf{x}_5$, occupies a $2p_{-1}$ orbital with spin factor α.

Next, it is clear that we don't have to worry about antisymmetrizing in looking for the angular momentum eigenfunctions: if a single product is an eigenfunction so will be the antisymmetrized product (every term simply containing re-named electron labels). So we can drop the electronic variables $\mathbf{x}_i$, taking the factors to be in the standard order $i = 1, 2, ..., 6$, and with this understanding, the typical spin-orbital product for the Carbon $(2p)^2$ configuration can be indicated as

$$(l_1, m_1, s_1)(l_2, m_2, s_2)....(l_5, m_5, s_5)(l_6, m_6, s_6).$$

The first four factors refer to a *closed shell* in which the first two orbitals, 1s and 2s, both correspond to zero angular momentum ($l_1 = l_2 = 0$) and are each 'filled' with two electrons of opposite spin. With the notation you're used to, they could be written as $(1s\alpha)(1s\beta)(2s\alpha)(2s\beta)$ and define the **closed-shell 'core'**. Wave functions for the quantized electronic states of this configuration are constructed in the following examples.

Example 5.2 The Carbon $(2p)^2$ configuration

The leading spin-orbital product, to which the six electrons are assigned in standard order, can be denoted by Product $= (1s\alpha)(1s\beta)(2s\alpha)(2s\beta)\ (l_5, m_5, s_5)(l_6, m_6, s_6)$. (We start from the 'top' state, in which the angular momentum quantum numbers have their maximum values $l_5 = l_6 = 1,\ m_5 = m_6 = 1$ for the 2p-orbital with highest z-component, and $s_5 = s_6 = \frac{1}{2}$ for the 'up-spin' α states. You can check that this product has a *total* angular momentum quantum number $M = 2$ for the orbital operator $\mathsf{L}_z = \mathsf{L}_z(1) + \mathsf{L}_z(2) + ... + \mathsf{L}_z(6)$ by noting that the first four 1-electron operators all multiply their corresponding orbital factors by zero, the eigenvalue for an 's-type' function; while the last two operators each give the same product, multiplied by 1. Thus, the operator sum has the effect $\mathsf{L}_z(\text{Product}) = 2 \times (\text{Product})$. In the same way, the total *spin* angular momentum operator $\mathsf{S}_z = \mathsf{S}_z(1) + \mathsf{S}_z(2) + ... + \mathsf{S}_z(6)$, will act on "Product" to multiply it by $\frac{1}{2} + \frac{1}{2} = 1$, the only non-zero contribution to the z-component eigenvalue coming from the last two spin-orbitals, which are each multiplied by $\frac{1}{2}$.

In short, in dealing with angular momentum, *we can completely ignore the spin-orbitals of a closed-shell core* and work only on the spin-orbital product of the 'open shell' that follows it. We can also re-name the two electrons they hold, calling them 1 and 2 instead of 5 and 6, and similarly for the operators that work on them – it can't make any difference! And now we can get down to the business of constructing all the eigenstates.

Let's denote the general state, with quantum numbers L, M and S, M_S, by $\Psi_{L,M;S,M_S}$ or the 'ket' $|L, M; S, M_S\rangle$. So the 'top' state will be $|L, L; S, S\rangle$; and we know from above that in terms of spin-orbitals this is $(l_1, l_1; \frac{1}{2}, \frac{1}{2})(l_2, l_2; \frac{1}{2}, \frac{1}{2}) = (2p_{+1}\alpha)(2p_{+1}\alpha)$, showing only the open-shell AOs. Here we've put $M = L$ for the 'top' orbital angular momentum and $m_s = s = \frac{1}{2}$ for the up-spin state.

First concentrate on the *orbital* quantum numbers, letting those for the spin 'sleep' (we needn't even show them). All the theory we need has been done in Chapter 6 of Book 11, where we found that

$$\mathsf{L}^-\Psi_{L,M} = \sqrt{(L+M)(L-M+1)}\Psi_{L,M-1}, \tag{5.3}$$

So if we apply the step-down operator $\mathsf{L}^- = \mathsf{L}^-(1) + \mathsf{L}^-(2)$ to the 'top' state we shall find (with $M = L = 2$) $\mathsf{L}^-\Psi_{2,2} = \sqrt{(2+2)(2-2+1)}\Psi_{2,2-1} = 2\Psi_{2,1}$. And to express this result in terms of orbital products we simply have to apply the 1-electron operators $\mathsf{L}^-(1)$

and $\mathsf{L}^-(2)$ to the individual factors in the orbital product $(2p)_{+1})(2p_{+1})$. We'll do that next.

Example 5.3 The orbital eigenstates

The many-electron eigenstates of the total spin operators, L^2 and L_z, can all be derived from the 'top' state $\Psi_{L,M}$ with quantum numbers $L = 2$ and $M = 2$. From now on, we'll use p_{+1}, p_0, p_{-1} to denote the three 2p-functions, with $l = 1$, and $m = +1, 0, -1$, so as not to confuse numbers and names!

The 1-electron step-down operator $\mathsf{L}^-(i)$ (any i) acts as follows:

$$\mathsf{L}^-(i)p_{+1}(i) = \sqrt{2}p_0(i),\ \mathsf{L}^-(i)p_0(i) = \sqrt{2}p_{-1}(i),\ \mathsf{L}^-(i)p_{-1}(i) = 0 \times p_{-1}(i),$$

– according to (5.2) with l, m in place of L, M.

Thus, to get $\Psi_{2,1}$ from $\Psi_{2,2}$ we use (5.2) and find $\mathsf{L}^-\Psi_{2,2} = \sqrt{4\times 1}\Psi_{2,1}$; so $\Psi_{2,1} = \frac{1}{2}\mathsf{L}^-\Psi_{2,2}$. To put this result in terms of orbital products, we note that $\mathsf{L}^- = \mathsf{L}^-(1) + \mathsf{L}^-(2)$ for the two electrons of the open shell and obtain

$$\Psi_{2,1} = \tfrac{1}{2}\mathsf{L}^-\Psi_{2,2} = \tfrac{1}{2}[\sqrt{2}p_0(1)p_{+1}(2) + p_{+1}(1)\sqrt{2}p_0(2)].$$

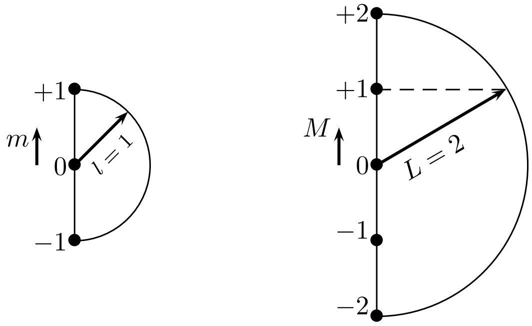
Here the first term in the square brackets results when the operator $\mathsf{L}^-(1)$ works on the 'top' state $\Psi_{2,2} = p_{+1}(1)p_{+1}(2)$ and the second term results from the operator $\mathsf{L}^-(2)$ for Electron 2. (The electron labels will not always be shown when they refer to the wave function arguments as they are always taken to be in the order $1, 2$.)

Continuing in this way, we find all five states with $L = 2$. They are shown below, listed according to their quantum numbers (L, M).

- $(2,\ \ 2)$ $\Psi_{2,2} = p_{+1}p_{+1}$
- $(2,\ \ 1)$ $\Psi_{2,1} = \mathsf{L}^-\Psi_{2,2} = (p_0p_{+1} + p_{+1}p_0)/\sqrt{2}$
- $(2,\ \ 0)$ $\Psi_{2,0} = \mathsf{L}^-\Psi_{2,1} = [p_{-1}p_{+1} + 2p_0p_0 + p_{+1}p_{-1}]/\sqrt{3}$
- $(2,-1)$ $\Psi_{2,-1} = \mathsf{L}^-\Psi_{2,0} = (p_{-1}p_{+1} + p_{+1}p_{-1}/\sqrt{2}$
- $(2,-2)$ $\Psi_{2,-2} = p_{-1}p_{-1}$

The five angular momentum eigenstates obtained in Example 5.3, all with the same total angular momentum quantum number $L = 2$, have M values going down from $+2$ to -2 in unit steps. Remember, however, that they arise from two electrons, each in a p-state with $l = 1$ and possible m-values $+1,\ 0\ -1$. This is an example of **angular momentum coupling**, which we first met in Chapter 6 of Book 11 in dealing with electron **spins**. There is a convenient 'vector model' for picturing such coupling in a 'classical' way. The unit angular momentum of an electron in a p-type orbital is represented by an arrow of unit length $l = 1$ and its components $m = 1,\ 0\ -1$ correspond to different orientations of the arrow: 'parallel coupling' of two such angular momenta is shown by putting their arrows in line to give a resultant angular momentum of 2 units. This angular momentum vector, with quantum number $L = 2$, may also be pictured as an arrow but its allowed (i.e. observable) values may now go from $M = L$, the 'top' state, down to $M = -L$. Again, this picture suggests that the angular momentum vector can only be found with $2L + 1$ allowed orientations in space; but remember that such ideas are not to be taken seriously – they only remind us of how we started the journey from classical physics into quantum mechanics, dealt with in detail in Book 11.

What we have found is summarized in the **Vector diagrams** of Figure 5.2.



(a) $l = 1$ (b) $L = 2$

Figure 5.2
Vector diagrams for angular momentum

Figure 5.2(a) indicates with an arrow of unit length the angular momentum vector for one electron in a p-orbital (quantum number $l = 1$). The allowed values of the z-component of the vector are $m = 0, \pm 1$ and the eigenstates, are indicated as bold dots at $m = +1$ (arrow up), $m = -1$ (arrow down), and $m = 0$ (arrow perpendicular to vertical axis, zero z-component).

Figure 5.2(b) indicates with an arrow of length 2 units the resultant angular momentum of the two 'p-electrons' with their unit vectors in line ('parallel coupled'). The broken line shows the projection of the $L = 2$ vector on the vertical axis, the bold dot corresponding to the eigenstate with $L = 2, M = +1$.

But are there other states, obtained by coupling the two unit vectors in different ways? Example 2.2 in Book 11, where we were dealing with *spin* angular momentum, suggests that there may be – and suggests also how we might find them. The eigenstate indicated by the bold dot at $M = +1$ in Figure 4.2(b) was found to be $\Psi_{2,1} = (p_0 p_{+1} + p_{+1} p_0)/\sqrt{2}$ and both terms are eigenstates of the operator $\mathsf{L}_z = \mathsf{L}_z(1) + \mathsf{L}_z(2)$. So any other linear combination will also be an eigenstate with $M = +1$. But we are looking for the simultaneous eigenstates of the commuting operators L^2 and L_z; and we know that two such states must be *orthogonal* when they have different eigenvalues. It follows that the state $\Psi = (p_0 p_{+1} - p_{+1} p_0)/\sqrt{2}$, which is clearly orthgonal to $\Psi_{2,1}$, will be the eigenstate we are looking for with eigenvalues $(L = 1, M = 1)$ i.e. the 'top state' of another series. It is also normalized (check it, remembering that the 'shift' operators were chosen to conserve normalization of the eigenstates they work on) and so we can give Ψ the subscripts $1, 1$. From $\Psi_{1,1} = (p_0 p_{+1} - p_{+1} p_0)/\sqrt{2}$, we can start all over again, using the step-down operator to get first $\Psi_{1,0}$ and then $\Psi_{1,-1}$.

Finally, we can look for an eigenstate with $M = 0$ orthogonal to $\Psi_{1,0}$. This must be a simultaneous eigenstate with a different value of the L quantum number: it can only be the missing $\Psi_{0,0}$.

Now we have found all the simultaneous eigenstates of the orbital angular momentum operators we can display them all in the diagram below:

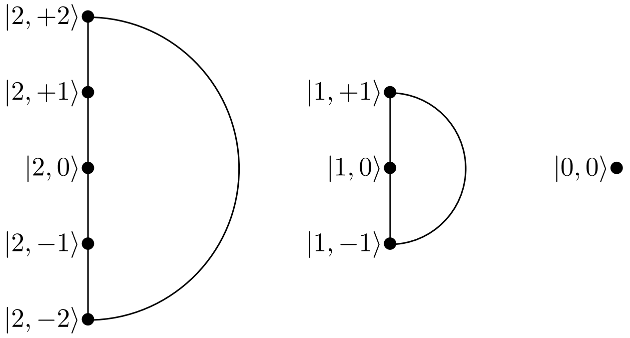


Figure 5.3 Angular momentum eigenstates $|L, M\rangle$ for a p^2 configuration

The eigenstates with angular momentum quantum numbers L, M correspond to the bold dots, arranged as 'ladders' for the three cases $L = 2, \quad L = 1, \quad L = 0$. A state of given M can be changed to one with $M \to M \pm 1$ by applying a 'step-up' or 'step-down' operator. A state of given L can be sent into one with $L \to L - 1$ (a horizontal shift) by making it orthogonal to the one of given L, the M-value being unchanged. Note how convenient it is to give the eigenstates in Dirac notation, with their quantum numbers inside a 'ket' vector $|\quad\rangle$, instead of using subscripts on a Ψ – even more so when we include other labels, for energy and spin, so far left 'sleeping'. Remember also that the vector diagrams are not in any sense 'realistic': for example the square of a total angular momentum, with operator L^2, has an eigenvalue $L(L+1)$, L being simply the maximum value $M = L$ of a measured component along an arbitrary z-axis. Nevertheless, we shall soon find how useful they are in classifying and picturing the origin of atomic spectra.

First of all, however, we must learn how to calculate the energies of the stationary states of *many*-electron atoms, using the rules developed in Chapter 3.

5.2 Calculation of the total electronic energy

In Chapter 3 we used Slater's rules (3.7) to derive an IPM approximation to the energy expectation value for a wave function expressed as an antisymmetrized spin-orbital product

$$\Psi = (1/N!)^{1/2} \sum_{\mathsf{P}} \epsilon_{\mathsf{P}} \mathsf{P}[\psi_1 \psi_2 \ldots \psi_N] \tag{5.4}$$

of N singly-occupied spin-orbitals (supposed orthonormal). This provided a basis for Hartree-Fock theory, in which the spin-orbitals are optimized to give a good approximation to the energy of a closed shell ground state.

For the Carbon atom, the basic spin-orbital product for this state would seem to have the explicit form

$$\psi_1\psi_2 \dots \psi_6 = (1s\alpha)(1s\beta)(2s\alpha)(2s\beta)(2p_{+1}\alpha)(2p_{+1}\beta),$$

but now we have to recognise the *degeneracy* and the need to couple the angular momenta of the electrons in the p-orbitals. The last section has shown how to do this: we start from the 'top state', with maximum z-component ($L_z = 2, S_z = 1$ in atomic units) and set up a whole range of states by applying the shift operators $\mathsf{L}^-, \mathsf{S}^-$ to obtain other simultaneous eigenfunctions with lower quantum numbers (see Fig. 5.3).

The 'top state', before antisymmetrizing as in (5.4) will now have the associated product

$$\psi_1\psi_2 \dots \psi_6 = (1s\alpha)(1s\beta)(2s\alpha)(2s\beta)(2p_{+1}\alpha)(2p_{+1}\alpha) \tag{5.5}$$

and the states with lower values of M have been found in Example 5.3. The next one 'down' will be derived by antisymmetrizing the product

$$(1s\alpha)(1s\beta)(2s\alpha)(2s\beta)[(p_0\alpha)(p_{+1}\alpha) + (p_{+1}\alpha)(p_0\alpha)]/\sqrt{2}$$

and this will give a wavefunction $\Psi = (1/\sqrt{2})(\Psi_1 + \Psi_2)$, where

$$\begin{aligned} \Psi_1 &= \sqrt{N!}\,\mathsf{A}[(1s\alpha)(1s\beta)(2s\alpha)(2s\beta)(p_0\alpha)(p_{+1}\alpha)] \\ \Psi_2 &= \sqrt{N!}\,\mathsf{A}[(1s\alpha)(1s\beta)(2s\alpha)(2s\beta)(p_{+1}\alpha)(p_0\alpha)]. \end{aligned} \tag{5.6}$$

Here, according to (3.4), each of the two terms is a *normalized* antisymmetrized product of six spin-orbitals – but they *differ* in the choice of the last two. In getting Slater's rules for finding the 1- and 2-electron contributions to the expectation value of the Hamiltonian we considered only the case $\langle \mathsf{H} \rangle = \langle \Psi | \mathsf{H} | \Psi \rangle$, where the functions in the 'bra' and the 'ket' were derived from exactly the same spin-orbital product. So we could use them to get the diagonal matrix elements H_{11} and H_{22} but *not* an 'off-diagonal' element such as $H_{12} = \langle \Psi_1 | \mathsf{H} | \Psi_2 \rangle$.

Let's now look at the general spin-orbital product $\psi_1\psi_2 \dots \psi_R \dots \psi_N$, using $R, S, T, U, \dots$ to label particular factors, and try to get the matrix element $\langle \Psi' | \mathsf{H} | \Psi \rangle$, in which the antisymmetrized product Ψ' differs from Ψ by having a spin-orbital ψ'_R in place of ψ_R

This will be given by an expression similar to (3.7) but the 1-electron part $\sum_R \langle \psi_R | \mathsf{h} | \psi_R \rangle$ will be replaced by the *single term* $\langle \psi'_R | \mathsf{h} | \psi_R \rangle$, while the 2-electron part will be replaced by the *single sum* $\sum_{S(\neq R)} [\langle \psi'_R \psi_S | \mathsf{g} | \psi_R \psi_S \rangle - \langle \psi'_R \psi_S | \mathsf{g} | \psi_S \psi_R \rangle]$.

When the spin-orbital products contain *two* non-matching pairs, $\psi'_R \neq \psi_R$ and $\psi'_S \neq \psi_S$, the 1-electron part will always contain a zero overlap integral $\langle \psi'_T | \psi_T \rangle$ when $T = R$ *or* $T = S$ – so no 1-electron term can arise. On the other hand, the 2-electron part will be replaced by the single term $[\langle \psi'_R \psi'_S | \mathsf{g} | \psi_R \psi_S \rangle - \langle \psi'_R \psi'_S | \mathsf{g} | \psi_S \psi_R \rangle]$. (To prove all these results you should go back to Examples 3.2 and 3.3, noting that *except in the cases indicated* the products of overlap factors will contain zeros.)

We can now collect all the matrix element rules obtained so far, using the antisymmetrizer $\sqrt{N!}\,\mathsf{A}$ as defined in (3.4):

Given $\Psi = \sqrt{N!}\,\mathsf{A}[\psi_1\psi_2 \dots \psi_N]$,
the diagonal matrix element $\langle\Psi|\mathsf{H}|\Psi\rangle$ is given by

$$\langle\Psi|\mathsf{H}|\Psi\rangle = \textstyle\sum_R \langle\psi_R|\mathsf{h}|\psi_R\rangle + \frac{1}{2}\sum'_{R,S}[\langle\psi_R\psi_S|\mathsf{g}|\psi_R\psi_S\rangle - \langle\psi_R\psi_S|\mathsf{g}|\psi_S\psi_R\rangle],$$

but with a single replacement, giving $\Psi' = \sqrt{N!}\,\mathsf{A}[\psi_1\psi_2 \dots \psi'_R \,..\, \psi_N]$,
the off-diagonal matrix element $\langle\Psi'|\mathsf{H}|\Psi\rangle$ is given by

$$\langle\Psi'|\mathsf{H}|\Psi\rangle = \langle\psi'_R|\mathsf{h}|\psi_R\rangle + \textstyle\sum_{S(\neq R)}[\langle\psi'_R\psi_S|\mathsf{g}|\psi_R\psi_S\rangle - \langle\psi'_R\psi_S|\mathsf{g}|\psi_S\psi_R\rangle]$$

and with *two* replacements, giving $\Psi' = \sqrt{N!}\,\mathsf{A}[\psi_1\psi_2 \dots \psi'_R \,..\, \psi'_S \,..\, \psi_N]$,
the off-diagonal matrix element $\langle\Psi'|\mathsf{H}|\Psi\rangle$ is given by

$$\langle\Psi'|\mathsf{H}|\Psi\rangle = [\langle\psi'_R\psi'_S|\mathsf{g}|\psi_R\psi_S\rangle - \langle\psi'_R\psi'_S|\mathsf{g}|\psi_S\psi_R\rangle].$$

(5.7)

Now we know how to get both diagonal and off-diagonal matrix elements of the Hamiltonian H, between antisymmetrized spin-orbital products, we can calculate the total electronic energies of all the many-electron states belonging to a given configuration. As an example, let's find the total electronic energy of the Carbon atom ground state. Experimentally, this is known to be triply degenerate, the three states corresponding to the angular momentum eigenstates $|L, M\rangle$ with $L = 1$, $M = 0, \pm 1$ (see Fig. 5.3).

The 'top state' of the three is an eigenstate of orbital angular momentum, $\Psi_{L,M}$, with quantum numbers $L = M = 1$. It was derived, just after Fig.4.2, by antisymmetrizing the spin-orbital product

$$(\text{closed shell}) \times (1/\sqrt{2})(p_0p_{+1} - p_{+1}p_0) \times (\text{spin factor}).$$

Here the closed-shell spin-orbitals are not shown, while p_0, p_{+1} are the orbital eigenstates with $l = 1, m = 0$ and $l = 1, m = 1$, respectively. (Just as the letters s, p, d, f are used to denote 1-electron eigenstates with l=0, 1, 2, 3, the corresponding capital letters are used to label the many-electron eigenstates with $L = 0, 1, 2, 3$.) So the degenerate ground state of Carbon is a 'P state' and we 'll use $\Psi^{(P)}$ to denote its wave function.

Example 5.2 Total electronic energy of the Carbon ground state

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There are two spin-orbital products, to which the six electrons are to be assigned. Here we'll simplify things by dealing only with the electrons outside the closed-shell $1s^22s^2$ core, re-labelling them as '1' and '2' and taking both to be in α spin states. The corresponding wave function Ψ^P then arises on antisymmetrizing the function

$$(1/\sqrt{2})[p_0(\mathbf{r}_1)p_{+1}(\mathbf{r}_2) - p_{+1}(\mathbf{r}_1)p_0(\mathbf{r}_2)] \times \alpha(s_1)\alpha(s_2)$$

– which is a linear combination $F = (F_1 - F_2)/\sqrt{2}$ of the two spin-orbital products

$$\begin{aligned} F_1 &= p_0(\mathbf{r}_1)\alpha(s_1)p_{+1}(\mathbf{r}_2)\alpha(s_2) \\ F_2 &= p_{+1}(\mathbf{r}_1)\alpha(s_1)p_0(\mathbf{r}_2)\alpha(s_2). \end{aligned}$$

The resultant 2-electron wave function is thus $\Psi^{(P)} = (\Psi_1 - \Psi_2)/\sqrt{2}$, where the two antisymmetrized and normalized components are $\Psi_1 = \sqrt{2}\,\mathsf{A}\,F_1$ and $\Psi_2 = \sqrt{2}\,\mathsf{A}\,F_2$. The energy of the open-shell electrons in the field of the core will then be

$$\bar{E}_P = \langle\Psi^{(P)}|\mathsf{H}|\Psi^{(P)}\rangle = (1/\sqrt{2})^2(H_{11} + H_{22} - H_{12} - H_{21}),$$

where H_{11} etc. are matrix elements of the Hamiltonian between the two components of $\Psi^{(P)}$ and may be evaluated in terms of the orbital integrals, using the rules (5.7).

Here we'll simply indicate the evaluation of H_{11} etc. with the spin-orbitals $\psi_1 = p_0\,\alpha$ and $\psi_2 = p_{+1}\,\alpha$ used in Ψ_1 and Ψ_2 :

$$\begin{aligned} \langle\Psi_1|\mathsf{H}|\Psi_1\rangle &= \langle\psi_1|\mathsf{h}|\psi_1\rangle + \langle\psi_2|\mathsf{h}|\psi_2\rangle + \langle\psi_1\psi_2|\mathsf{g}|\psi_1\psi_2\rangle - \langle\psi_1\psi_2|\mathsf{g}|\psi_2\psi_1\rangle \\ \langle\Psi_2|\mathsf{H}|\Psi_2\rangle &= \langle\psi_2|\mathsf{h}|\psi_2\rangle + \langle\psi_1|\mathsf{h}|\psi_1\rangle + \langle\psi_2\psi_1|\mathsf{g}|\psi_2\psi_1\rangle - \langle\psi_2\psi_1|\mathsf{g}|\psi_1\psi_2\rangle \\ \langle\Psi_1|\mathsf{H}|\Psi_2\rangle &= \langle\psi_1\psi_2|\mathsf{g}|\psi_2\psi_1\rangle - \langle\psi_1\psi_2|\mathsf{g}|\psi_1\psi_2\rangle \end{aligned}$$

When the Hamiltonian contains no spin operators (the usual first approximation) the diagonal 1-electron integrals each give the energy ϵ_{2p} of a 2p-electron in the field of the $1s^2 2s^2$ core, but off-diagonal elements are zero because they are between different eigenstates. The 2-electron terms reduce to 'Coulomb' and 'exchange' integrals, similar to those used in Chapter 3, involving different 2p-orbitals. So it's a long and complicated story, but the rules in (5.7) provide all that's needed (apart from a bit of patience!).

The Carbon ground state in Example 5.2 is described as ^{3}P (triplet-P) because it has *spin* quantum number $S = 1$ and therefore 3 components, with $M_S = 0, \pm 1$. But it is also degenerate owing to the three possible z-components of the *orbital* angular momentum, with $M_{(L)} = 0, \pm 1$, for $L = 1$. As we shall see shortly, this degeneracy is removed – or 'broken' – when small terms are included in the Hamiltonian. First, there is a term describing the interaction between the magnetic field arising from orbital motion of the electron (see Book 10) and the magnetic dipole associated with electron spin. This gives rise to a **fine structure** of the energy levels, which are separated but remain threefold degenerate for different values of M_S; only when an external magnetic field is applied, to fix a definite axis in space, is this remaining degeneracy broken – an effect called **"Zeeman splitting"** of the energy levels.

The energy-level structure of the lowest electronic states of the Carbon atom is indicated later in Figure 5.4, which shows the positions of the first few levels as determined experimentally by Spectroscopy.

There are other states belonging to the electron configuration $2p^2$, whose energies have not so far been considered. They are *singlet* states, labelled in Fig. 5.4 as ^{1}D and ^{1}S; why have we not yet found them? The reason is simply that we started the energy calculation using a wave function with only 'spin-up' electrons outside the closed shell $1s^2 2s^2$ and got the other functions by applying only the *orbital* step-down operator L^-: this leaves unchanged the spin factor $\alpha(s_1)\alpha(s_2)$ which represents a triplet state with $S = 1$. In fact, the Pauli Principle tells us at once that only the ^{3}P state is then physically acceptable: it has an orbital factor which is *antisymmetric* under exchange of electronic variables and can therefore be combined with the symmetric spin factor to give a wave function which is antisymmetric under electron exchange. The next example explains the results, which are indicated in Figure 5.4.

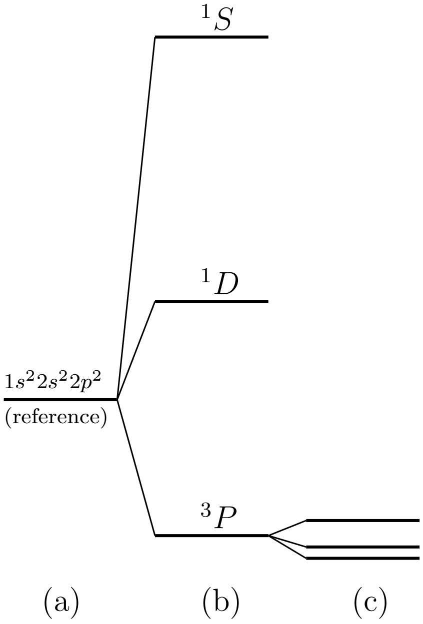

Figure 5.4 Lowest levels of Carbon

The Figure is very roughly to scale. In (a) the electron repulsion between the 2p electrons is left out, while (b) shows the effect of including it through the 2-electron integrals (described as "electrostatic splitting"). The levels in column (c) indicate the 'fine structure' arising from the coupling of orbital and spin angular momentum (not yet studied). The Zeeman splitting, caused by applying a magnetic field is even smaller and is not shown. The remarkable fact is that experiment and theory are usually in fair agreement in giving us a picture of the electronic structure of free atoms. And, indeed this agreement extends to our understanding of interacting atoms and therefore to the whole of Chemistry – which, as we noted in Section 2.5, wouldn't even exist without Pauli's Exclusion Principle!

So let's round off the section by looking briefly at the upper states belonging to the electron configuration $1s^22s^22p^2$ of the Carbon atom.

Example 5.3 Importance of the Pauli Principle

For the reasons given above, it's no use looking for the energies of the ^{1}D and ^{1}S states by starting from the spin-orbital product (5.5) and using the step-down operator L^-: as long as the spin factor $\alpha(s_1)\alpha(s_2)$ is left unchanged we can only get triplet states. However, we can reduce the value of M_S by applying the operator S^-, which changes the $\alpha\alpha$-product into $(\beta\alpha+\alpha\beta)/\sqrt{2}$ (check it!). And when we attach this factor to the orbital eigenstate $|2,+2\rangle$ in Fig. 5.3 the result is $p_{+2}(\mathbf{r}_1)p_{+2}(\mathbf{r}_2) \times [\beta(s_1)\alpha(s_2) + \alpha(s_1)\beta(s_2)]/\sqrt{2}$.

This is a linear combination of the two spin-orbital products

$$\begin{aligned} F_1 &= p_{+1}(\mathbf{r}_1)\beta(s_1)p_{+1}(\mathbf{r}_2)\alpha(s_2) \\ F_2 &= p_{+1}(\mathbf{r}_1)\alpha(s_1)p_{+1}(\mathbf{r}_2)\beta(s_2), \end{aligned}$$

namely $F = (F_1 + F_2)/\sqrt{2}$; but it still cannot give a wave function that satisfies the Pauli Principle, being totally *symmetric* under electron exchange. If we antisymmetrize F it just disappears!

Remember, however, that the step-down operator L^- changed the quantum number M in a state $|L, M\rangle$ but not (see Fig. 5.3) the value of L. To change L we had to find a second combination of the component states in $|L, M\rangle$, *orthogonal* to the first. It's just the same for the spin eigenfunctions; and the orthogonal 'partner' of $(F_1 + F_2)/\sqrt{2}$ is clearly $(F_1 - F_2)/\sqrt{2}$, which has a singlet spin factor with $S = M_S = 0$.

All we have to do, then, to get the singlet D-states is to use the original orbital eigenfunctions but attaching the spin factor $[\beta(s_1)\alpha(s_2) - \alpha(s_1)\beta(s_2)]/\sqrt{2}$ in place of the triplet factor $\alpha(s_1)\alpha(s_2)$. As the five states are degenerate it's enough to calculate the electronic energy for any one of them e.g. the 'top' state, with (after antisymmetrizing) the wave function $\Psi_{(L=2;S=0)}$. This is the linear combination $\Psi^{(D)} = (\Psi_1 - \Psi_2)/\sqrt{2}$ of the antisymmetrized products

$$\begin{aligned} \Psi_1 &= \sqrt{2}\mathsf{A}[p_{+1}(\mathbf{r}_1)\beta(s_1)p_{+1}(\mathbf{r}_2)\alpha(s_2)] \\ \Psi_2 &= \sqrt{2}\mathsf{A}[p_{+1}(\mathbf{r}_1)\alpha(s_1)p_{+1}(\mathbf{r}_2)\beta(s_2)]. \end{aligned}$$

The calculation continues along the lines of Example 5.2: the energy of the open-shell electrons in the field of the core will now be

$$\bar{E}_D = \langle\Psi^{(D)}|\mathsf{H}|\Psi^{(D)}\rangle = (1/\sqrt{2})^2(H_{11} + H_{22} - H_{12} - H_{21}),$$

where H_{11} etc. are matrix elements of the Hamiltonian between the two components of $\Psi^{(D)}$ and may be evaluated in terms of the orbital integrals, using the rules (4.7), just as in the case of $\Psi^{(P)}$.

A similar calculation can be made for the singlet S state. (Try to do it by yourself!)

You must have been wondering what makes a system 'jump' from one quantum state to another. We met this question even in Book 10 when we were first thinking about electromagnetic radiation and its absorption or emission by a material system; and again in the present Book 11 when we first studied the energy levels of a 1-electron atom and the 'spectral series' arising from *transitions* between the corresponding states. The interaction between radiation and matter is a very difficult field to study in depth; but it's time to make at least a start, using a very simple model.

5.3 Spectroscopy: a bridge between experiment and theory

Notes to the reader

Before starting this section, you should remind yourself of the **electromagnetic spectrum** (Section 6.5 of Book 10) and of "Hydrogen – the simplest atom of all" (Chapter 6 of Book 11), where you studied the energy levels of the H-atom and the series of **spectral lines** arising from **transitions** between different levels. We're now coming back to the question asked at the end of Chapter 6, namely "What *makes* an electron jump?" So you already know what the answer will be: eigenstates of the Hamiltonian are *stationary* and remain so until you disturb the sytem in some way. Such a disturbance is a **perturbation** and depends on the time at which it is applied.

Suppose the system we're considering has a complete set of stationary-state eigenfunctions of its Hamiltonian H. As we know from Book 11, these satisfy the Schrödinger equation including the time,

$$\mathsf{H}\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t}, \tag{5.8}$$

even when H itself does not depend on t. The eigenfunctions may thus develop in time through a time-dependent **phase factor**, taking the general form $\Psi_n \exp -(i/\hbar)E_n t$, where E_n is the nth energy eigenvalue. (You can verify that this is a solution of (5.8), provided E_n satisfies the time-independent equation $\mathsf{H}\Psi = E\Psi$.)

Now suppose $\mathsf{H} = \mathsf{H}^0 + \mathsf{V}(t)$, where $\mathsf{V}(t)$ describes a small **time-dependent perturbation** applied to the 'unperturbed' system – whose Hamiltonian we now call H^0. And let's expand the eigenfunctions of H in terms of those of H^0, putting

$$\Psi(t) = \sum_n c_n(t)\Psi_n \exp -(i/\hbar)E_n t,$$

where the expansion coefficient $c_n(t)$ changes slowly with time (the exponential factor usually oscillates very rapidly). On substituting this 'trial function' in (5.8) it follows that

$$-\frac{\hbar}{i}\sum_n \left(\frac{\mathrm{d}c_n}{\mathrm{d}t} - \frac{i}{\hbar}E_n c_n\right)\Psi_n \exp -(i/\hbar)E_n t = \sum_n \mathsf{H}\Psi_n \exp -(i/\hbar)E_n t,$$

and on taking the scalar product from the left with the eigenvector Ψ_m we get (only the term with $n = m$ remains on the left, owing to the factor $\langle\Psi_m|\Psi_n\rangle$)

$$\left(i\hbar\frac{\mathrm{d}c_m}{\mathrm{d}t} + E_m c_m\right)\exp -(i/\hbar)E_m t = \sum_n c_n[\langle\Psi_m|\mathsf{H}^0|\Psi_n\rangle + \langle\Psi_m|\mathsf{V}(t)|\Psi_n\rangle]\exp -(i/\hbar)E_n t.$$

Since the orthonormal set of solutions of the unperturbed equation $\mathsf{H}^0\Psi_n = E_n\Psi_n$ must satisfy $\langle\Psi_m|\mathsf{H}^0|\Psi_n\rangle = E_n\langle\Psi_m|\Psi_n\rangle = E_n\delta_{mn}$, substitution in the last equation gives (check it!)

$$i\hbar\frac{\mathrm{d}c_m}{\mathrm{d}t} = \sum_n c_n V_{mn}(t)\exp[(i/\hbar)(E_m - E_n)]t, \tag{5.9}$$

where $V_{mn}(t)$ is a time-dependent matrix element of the perturbation operator:

$$V_{mn}(t) = \langle\Psi_m|\mathsf{V}(t)|\Psi_n\rangle.$$

Now (5.9) is an *infinite* system of simultaneous equations; and we don't even know the exact eigenfunctions of H^0 – which, to be complete, will include functions forming a *continuum*. So it all looks pretty hopeless! The only way forward is to think about very special cases which lead to equations you can solve. That's what we do next.

We start by supposing that the perturbation V depends on time only through being 'switched on' at time $t = t_0$ and finally 'switched off' at a later time t, staying constant, and very small, between the two end points. Note that V may still be an *operator* (not just a *numerical* constant.) If the system is *initially* known to be in an eigenstate Ψ_n with $n = i$, then the initial values of all c_m will be $c_m(0) = 0$ for $m \neq i$, while $c_i(0) = 1$.

From (5.9), putting all c_n's on the right-hand side equal to zero except the one with $n = i$, we find a single differential equation to determine the initial rate of change of all $c_m(t)$: it will be

$$i\hbar \frac{\mathrm{d}c_m}{\mathrm{d}t} = V_{mi}(t)\exp{(i/\hbar)(E_m - E_i)t},$$

which is a key equation for the first-order change in the coefficients (and means approximating all coefficients on the right in (5.9) by their initial values).

When the operator V is time-independent, the initial value $c_i(0) = 1$ will have changed after time t to

$$c_i(t) = 1 - \frac{i}{\hbar}V_{ii} \times t,$$

while the other coefficients, initially zero, will follow from (5.9) with $m \neq i$:

$$\begin{aligned} c_m(t) &= -\frac{i}{\hbar}\int_0^t V_{mi}(t)\exp[(i/\hbar)(E_m - E_i)t]\mathrm{d}t \\ &= -\frac{i}{\hbar}V_{mi}\left[\frac{\exp(i/\hbar)(E_m - E_i)t}{(i/\hbar)(E_m - E_i)}\right]_0^t \\ &= \frac{V_{mi}}{E_m - E_i}[1 - \exp(i/\hbar)(E_m - E_i)t] \end{aligned} \tag{5.10}$$

Now you know (see Book 11, Chapter 3) that $|c_m(t)|^2$ will give the *probability* of observing the system in state Ψ_m, with energy E_m, at time t after starting in the initial state Ψ_i at $t = 0$. Thus,

$$\begin{aligned} |c_m(t)|^2 &= \frac{|V_{mi}|^2}{(E_m - E_i)^2}[1 - \exp(i/\hbar)(E_m - E_i)t] \times [1 + \exp(i/\hbar)(E_m - E_i)t] \\ &= \frac{|V_{mi}|^2}{(E_m - E_i)^2}\left(2\sin\frac{(E_m - E_i)}{2\hbar}t\right)^2, \end{aligned}$$

where in the second step you had to do a bit of trigonometry (Book 2, Chapter 3).

On setting the energy difference $(E_m - E_i) = x$, this result becomes

$$P(i \to m) = |c_m(t)|^2 = 4\frac{|V_{mi}|^2}{x^2}\left(\sin\frac{t}{2\hbar}x\right)^2 \tag{5.11}$$

and, if you think of this as a function of x, it shows a very sharp peak at $x = 0$ (which means $E_m \approx E_i$). The form of the peak is like that shown below in Figure 5.5.

By treating x as a continuous variable we can easily get the *total* probability, $\sum_m P(i \to m)$, that the system will go into *any* state close to a **final state** of 'given' energy E_f. For this purpose, we suppose the states are distributed with density $\rho(E_m)$ per unit range around one with energy E_f. In that case (5.11) will yield a *total* probability of transition from initial state Ψ_i to a final state with energy close to E_f, namely

$$W(i \to f) = \sum_m P(i \to m) \to \int P(i \to m)\rho(E_m)\mathrm{d}E_m.$$

This quantity can be evaluated by using a definite integral well known to Mathematicians;

$$\int_{-\infty}^{+\infty} \frac{\sin^2 \alpha x}{x^2} F(x)\mathrm{d}x = \pi\alpha F(0) \tag{5.12}$$

where $F(x)$ is any 'well-behaved' function of x. This means that the "delta function"

$$\delta(0\,; x) = (\pi\alpha)^{-1} \frac{\sin^2 \alpha x}{x^2}, \tag{5.13}$$

when included in the integrand of $\int F(x)\mathrm{d}x$, simply picks out the value of the function that corresponds to $x = 0$ and cancels the integration. It serves as the kernel of an integral operator, already defined in Book 11 Section 9, and is a particular representation of the **Dirac delta function**.

On using (5.12) and (5.13), with $\alpha = (t/2\hbar)$, in the expression for $W(i \to f)$, we find (do the substitution, remembering that $x = E_m - E_i$)

$$W(i \to f) = \int P(i \to m)\rho(E_m)\delta(0, x)\mathrm{d}E_m = 4V_{mi}^2 \rho(E_m) \times \frac{\pi t}{2\hbar} = \frac{2\pi t}{\hbar} V_{mi}^2 \rho(E_f) \tag{5.14}$$

where the delta function ensures that $x = E_i - E_m = 0$ and consequently that transitions may occur only when the initial and final states have the same energy, $E_m \approx E_f = E_i$. In other words, since $E_m \approx E_i$ the Energy Conservation Principle remains valid in quantum physics, within the limits implied by the Uncertainty Principle.

For 'short' times (still long on an 'atomic' scale) this quantity is proportional to t and allows us to define a **transition rate**, a probability per unit time, as

$$\boxed{w(i \to f) = \tfrac{2\pi}{\hbar} |V_{fi}|^2 \rho(E_f).} \tag{5.15}$$

This formula has very many applications in quantum physics and is generally known as **Fermi's Golden Rule**. In this first application, to a perturbation not depending on time, the energy of the system is conserved.

The form of the transition probability $P(i \to f)$, from which (5.15) was derived, is shown below in Figure 5.5 and is indeed 'sharp'. The half-width of the peak is in fact h/t and thus diminishes with time, being always consistent with what is allowed by Heisenberg's uncertainty principle for the energy of the states.

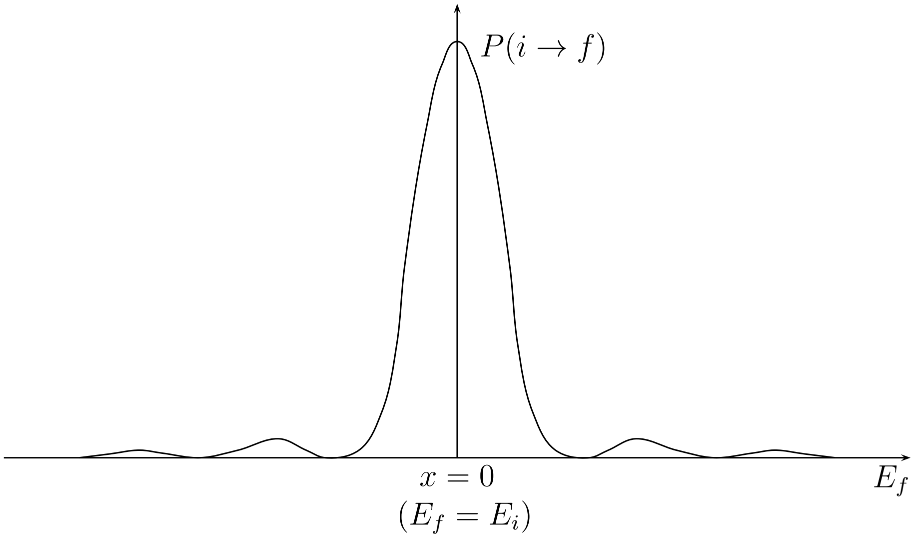

Figure 5.5 Probability of a transition (see text)

As a second example, let's think about the absortion and emission of radiation, which lie at the heart of all forms of Spectroscopy. The quanta of energy are carried by **photons**, but in Book 10 radiation was described in terms of the electromagnetic field in which the electric and magnetic field vectors, **E** and **B** oscillate at a certain frequency, depending on the type of radiation involved (very low frequency for radio waves, much higher for visible light – ranging from red up to blue – and much higher still for X-rays and cosmic rays). That was the 'classical' picture of light as a 'wave motion'. But in quantum physics, a ray of light is pictured as a stream of photons; and much of Book 11 was devoted to getting an understanding of this "wave-particle duality". The picture that finally came out was that a quantum of radiant energy could best be visualized as a highly concentated 'packet' of waves, sharing the properties of classical fields and quantum particles. (Read Chapter 5 of Book 11 again if you're still mystified!)

So now we'll try to describe the interaction between an electronic system (consisting of 'real' particles like electrons and nuclei) and a photon field in which each photon carries energy $\epsilon = h\nu$, where ν is the frequency of the radiation and h is **Planck's constant**. This is the 'semi-classical' picture, which is completely satisfactory in most applications and allows us to go ahead without needing more difficult books on **quantum field theory**.

The first step is to think about the effect of an oscillating perturbation of the form

$$\mathsf{V}(t) = \mathsf{V}e^{i\omega t} + \mathsf{V}^{\dagger}e^{-i\omega t} \quad (\omega > 0), \tag{5.16}$$

the operator V being small and time-independent, applied to a system with Hamiltonian H^0 and eigenstates $\Psi_n \exp -(i/\hbar)E_n t$, with energy E_n.

Transitions may occur, just as they did in the case where there was no oscillating field and the frequency-dependent factors were absent. But now there are two terms in the perturbation and each will have its own effect. The argument follows closely the one used when the ω-terms were missing, but the equation for the time-dependent coefficient $c_m(t)$ will now be a sum of two parts:

$$\begin{aligned} c_m(t) \quad &= \quad V_{mi} \left[\frac{[1 - \exp[(i/\hbar)(\hbar\omega + E_m - E_i)t]}{(\hbar\omega + E_m - E_i)} \right] \\ &+ \quad V^{\dagger}_{mi} \left[\frac{[1 - \exp[-(i/\hbar)(\hbar\omega - E_m + E_i)t]}{(\hbar\omega - E_m + E_i)} \right] . \end{aligned} \tag{5.17}$$

On putting $\omega = 0$, the first term reduces to the result given in (5.10), for a single constant perturbation: this was large only when $E_m \approx E_i$, but now it is large only when $E_m - E_i + \hbar\omega \approx 0$. The first term can therefore produce a transition from state Ψ_i to Ψ_m only when the radiation frequency $\nu\,(= \omega/2\pi)$ is such that $\hbar\omega = (h/2\pi)(2\pi\nu) \approx (E_i - E_m)$. The transition will thus occur only when $h\nu \approx E_i - E_m$. This corresponds to *emission* of a photon, leaving the system in a state with *lower* energy E_m.

In fact, the transition energy will not be *exactly* $E_i - E_m$ but rather $E_i - E_f$, where E_f will be an 'average' energy of the group of states into which the emitted electron 'lands'. The calculation is completed, as in the case of a constant perturbation, by assuming a density-of-states function $\rho(E_f)$ for the final state. In the case of emission, the probability of a transition into state Ψ_m at time t will be

$$P(i \to m) = |c_m(t)|^2 = \frac{|V_{mi}|^2}{(h\nu + E_m - E_i)^2} \left(2 \sin \frac{(\hbar\omega + E_m - E_i)}{2\hbar} t \right)^2 , \tag{5.18}$$

which you can get using the same argument that follows equation (5.10). Finally, following the same steps (do it!) that led to (5.14) you'll get the **transition rate**. The probability/unit time for emission of a photon of energy $h\nu\,(= \hbar\omega)$

$$w_(i \to f) = (2\pi/\hbar)|V_{fi}|^2 \rho(E_f)\delta(h\nu + E_f - E_i). \tag{5.19}$$

The *absorption* of a photon of energy $h\nu$ is brought about by the second term in (5.16) and the calculation of the transition rate runs along exactly parallel lines. Thus we find

Emission of a quantum of energy $h\nu$:
$w(i \to f) = (2\pi/\hbar)|V_{fi}|^2 \rho(E_f)\delta(h\nu + E_f - E_i)$
Absorption of a quantum of energy $h\nu$:
$w(i \to f) = (2\pi/\hbar)|V_{fi}|^2 \rho(E_f)\delta(h\nu - E_f + E_i)$

(5.20)

As the photon energy is a positive quantity, the final state in absorption will have *higher* energy than that in the initial state; and, as you can see, this is nicely taken care of by the delta-function. In (5.20) the Initial and Final states are labelled 'i' and 'f' and the delta-function has the form shown in Figure 5.5. Note that the delta-function peak for emission of a photon is exactly like that shown in the Figure, but the photon-frequency is given by putting $h\nu + E_f - E_i = 0$: this means that $h\nu = E_i - E_f$, so the final state has *lower* energy than the one the electron comes from; and that corresponds to the peak being displaced upwards, from energy $E_f \approx E_i$ in Figure 5.5 to $E_f \approx E_i - h\nu$ in the emission process. In the same way, the absorption of a photon of energy $h\nu$ would be shown by displacing the peak at energy E_f to one at $E_f \approx E_i + h\nu$.

It may seem that this chapter, with all its difficult theory, has not taken us far beyond the IPM picture we started from – where electrons were supposed independent and assigned to the AOs obtained by solving a 1-electron Schrödinger equation. But in fact we've come a very long way: we're now talking about a real *many*-electron system (and not *only* an atom!) and are already finding how far it's possible to go from the basic principles of quantum mechanics (Book 11) towards an *understanding* of the physical world. We haven't even needed a pocket calculator and we're already able to explain what goes on in Spectroscopy! Of course, we haven't been able to fill in all the details – which will depend on being able to calculate matrix elements like V_{if} (that require approximate *wave functions* for initial and final states). But we've made a good start.

5.4 First-order response to a perturbation

In Section 5.3 we were dealing with the effect of a small change in the Hamiltonian of a system, from H^0 to $\mathsf{H} = \mathsf{H}^0 + \mathsf{V}$, where the operator V was simply 'switched on' at time $t = 0$ and 'switched off' at time t. Now we'll ask what difference the presence of a time-independent V will make to the eigenstates Ψ_n of H^0, which we'll call the 'unperturbed' system. All the states will be *stationary* states and the time-dependent phase factors $\exp -(i/\hbar)E_n t$ may be dropped, having no effect on the expectation values of any time-independent quantities (look back at Section 5.3 of Book 11 if you need to). So we'll be dealing with the "Schrödinger equation without the time", $\mathsf{H}\Psi = E\Psi$.

We'll also want to get some *picture* of what the perturbation is doing to the system; and that will be provided by various **density functions**, which can show how the electron distribution is responding. The *probability* density $P(\mathbf{r})$ – the probability per unit volume of finding an electron at point $\mathbf{r}$ – is well known to you for a 1-electron system, as the squared modulus $|\phi(\mathbf{r})|^2$ of the wave function. But now we need to generalize the idea to a *many*-electron system – and to include the spin variables $s_1, s_2, \dots$ so we still have work to do.

As in Chapter 1, let's suppose we have a complete set of functions $\Phi_1, \Phi_2, \dots \Phi_k, \dots,$ in terms of which any wave function of the particle coordinates of the system can be expressed in the form

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N)=c_1\Phi_1(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N)+c_2\Phi_2(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N)+\ldots+c_k\Phi_k(\mathbf{x}_1,\mathbf{x}_2,\ldots\mathbf{x}_N)+\ldots, \tag{5.21}$$

where the expansion is, in principle, infinite and the functions of the **basis** are most conveniently taken to be normalized and orthogonal: $\langle\Phi_j|\Phi_k\rangle=\delta_{jk}$. Note that the basis functions have now been renamed as Φs ("Phi"s) so as not to mix them up with the eigenfunctions Ψs and remember that $\mathbf{x}_k$ stands for both position and spin variables $(\mathbf{r}_k,\, s_k)$.

In Section 1.3 an expansion of this kind was used for 1-electron functions and called a "linear variation function". Here, as in dealing with time development of the wave function in the last section, the basis used may consist of the energy eigenfunctions of the unperturbed operator H^0 (including positive-energy solutions for highly excited states!) We're not worrying about how difficult it may be to actually set up and calculate with such expansions –here it's enough to use them in building theories!

We know from Section 1.3 that the eigenvalue equation $\mathsf{H}\Psi=E\Psi$ is then equivalent to an (*infinite*) set of linear equations, $\mathbf{Hc}=E\mathbf{c}$, of which the first three will be

$$\begin{aligned}(H_{11}-\bar{E})c_1+H_{12}c_2+H_{13}c_3&=0,\\ H_{21}c_1+(H_{22}-\bar{E})c_2+H_{23}c_3&=0,\\ H_{31}c_1+H_{32}c_2+(H_{33}-\bar{E})c_3&=0.\end{aligned}$$

Here, on solving, $\bar{E}$ will give an upper bound to the lowest energy E_1 and $c_1\Psi_1+c_2\Psi_2+c_3\Psi_3$ will give a best approximation to the corresponding wave function Ψ_1. The matrix elements $H_{ij}=\langle\Phi_i|\mathsf{H}|\Phi_j\rangle$ must of course be calculated first and that will define how good the approximation can be.

The Perturbation Approach

In **perturbation theory** the basis functions are usually taken to be eigenfunctions of the operator H^0 of the unperturbed system, $\Phi_k=\Psi_k^0$, where $\mathsf{H}^0\Psi_k^0=E_k^0\Psi^0$. But here we'll keep the Φ-notation for the basis functions, bearing in mind that they may be either the unperturbed eigenfunctions themselves or arbitrary mixtures. In either case, the perturbation of the Hamiltonian will be denoted by H', so the perturbed system will have $\mathsf{H}=\mathsf{H}^0+\mathsf{H}'$. With the first choice, the matrix elements of H will then be simply

$$H_{kj}=\langle\Phi_k|\mathsf{H}|\Phi_j\rangle=E_k^0\delta_{kj}+H'_{kj} \tag{5.22}$$

and if we start from the matrix form $\mathbf{Hc}=E\mathbf{c}$ it is clear that all the off-diagonal elements of $\mathbf{H}$ will be small, containing only the perturbation operator. As a first approximation, the diagonal part that remains on neglecting them altogether has elements $H_{kk}=E_k^0+H'_{kk}$. In other words, $E_k\approx E_k^0+H'_{kk}$ and the corresponding matrix eigenvalue equation is satisfied by $c_k=1$, all other coefficients being zero. This result may be written

$$\delta^{(1)}E_k=H'_{kk}=\langle\Phi_k|\mathsf{H}'|\Phi_k\rangle,$$

where $\delta^{(1)}\mathrm{E}_k$ means "first-order change in E_k". On writing out in full the matrix element this becomes

$$\delta^{(1)}E_k = \int \Phi_k^*(\mathbf{x}_1, \mathbf{x}_2, \, ... \, \mathbf{x}_N)\mathsf{H}'\Phi_k(\mathbf{x}_1, \mathbf{x}_2, \, ... \, \mathbf{x}_N)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2 \, ... \, \mathrm{d}\mathbf{x}_i \, ... \mathrm{d}\mathbf{x}_N. \tag{5.23}$$

This is a very general result. The first-order change in the energy E_k of a state Ψ_k, produced by a perturbation H', can be approximated as the expectation value of the perturbation in the *unperturbed* state Φ_k. (Here, for simplicity, the state is taken to be non-degenerate.)

How to interpret this result: the electron density function

First we have to think about evaluating the matrix element of H', the change in the Hamiltonian, and that brings us back to the old problem of how to go from one particle to many. We start from the N-electron Hamiltonian $\mathsf{H} = \sum_i \mathsf{h}(i) + \frac{1}{2}\sum_{i,j} \mathsf{g}(i,j)$ and add a perturbation H'. The simplest kind of change is just a change of the field in which the electrons move, which changes the potential energy function $V(i)$ for every electron $i = 1, 2, ...N$. Thus H^0 becomes $\mathsf{H} = \mathsf{H}^0 + \mathsf{H}'$ with $\mathsf{H}' = \sum_i \delta\mathsf{h}(i) = \sum_i \delta V(i)$, since the KE operator is not changed in any way. And the matrix element in (5.23) therefore becomes

$$\begin{aligned}
\langle\Phi_k|\mathsf{H}'|\Phi_k\rangle &= \int \Phi_k^*(\mathbf{x}_1, \mathbf{x}_2, \, ... \, \mathbf{x}_N)\mathsf{H}'\Phi_k(\mathbf{x}_1, \mathbf{x}_2, \, ... \, \mathbf{x}_N)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2 \, ... \, \mathrm{d}\mathbf{x}_i \, ... \mathrm{d}\mathbf{x}_N \\
&= \int \Phi_k^*(\mathbf{x}_1, \mathbf{x}_2, \, ... \, \mathbf{x}_N) \sum_i \delta V(i)\Phi_k(\mathbf{x}_1, \mathbf{x}_2, \, ... \, \mathbf{x}_N)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2 \, ... \, \mathrm{d}\mathbf{x}_i \, ... \mathrm{d}\mathbf{x}_N.
\end{aligned}$$

Remember that a typical integration variable $\mathbf{x}_i$ really stands for the three components of the position vector $\mathbf{r}_i$ of Electron i, together with its 'spin variable' s_i, so the volume element $\mathrm{d}\mathbf{x}_i$ means $\mathrm{d}\mathbf{r}_i\mathrm{d}s_i$. Remember also that

$$\Phi_k^*(\mathbf{x}_1, \mathbf{x}_2, \, ... \, \mathbf{x}_N) \times \Phi_k(\mathbf{x}_1, \mathbf{x}_2, \, ... \, \mathbf{x}_N)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2 \, ... \, \mathrm{d}\mathbf{x}_i \, ... \mathrm{d}\mathbf{x}_N$$

gives the **probability** of finding electrons labelled $1, 2, ...i, ...N$ simultaneously in the corresponding volume elements. This is the basic interpretation of the Schrödinger wave function (see Book 11 Chapter 3) extended to a system of *many* particles.

If we had only two particles, described by a wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2)$, the probability of finding Electron '1' in volume element $\mathrm{d}\mathbf{x}_1$, and '2' at the same time in $\mathrm{d}\mathbf{x}_2$, would be $\Psi^*(\mathbf{x}_1, \mathbf{x}_2)\Psi(\mathbf{x}_1, \mathbf{x}_2)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2$, – the probabilities being "per unit volume". But the probability of finding Electron '1' in $\mathrm{d}\mathbf{x}_1$ and Electron '2' just *anywhere* would be obtained by summing (in this case integrating) over all possible positions of the second 'box' $\mathrm{d}\mathbf{x}_2$ i.e.

$$\mathrm{d}\mathbf{x}_1 \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2)\Psi(\mathbf{x}_1, \mathbf{x}_2)\mathrm{d}\mathbf{x}_2.$$

Owing to the antisymmetry principle, (2.15) in Chapter 2, the same result would follow if we wanted the probability of finding Electron '2' in 'box' $\mathrm{d}\mathbf{x}_1$, and Electron '1' just anywhere. (You can prove this by interchanging 1 and 2 in the wave function and noting that

$\Psi^*\Psi$ will be unchanged.) So, with two electrons, the integration only has to be done once – and the result then multiplied by 2. The probability of finding an electron, *no matter which* in $d\mathbf{x}_1$ can thus be denoted by $\rho(\mathbf{x}_1)d\mathbf{x}_1$, where $\rho(\mathbf{x}_1) = 2\int \Psi^*(\mathbf{x}_1, \mathbf{x}_2)\Psi(\mathbf{x}_1, \mathbf{x}_2)d\mathbf{x}_2$ and is called the "one-electron probability density".

For N electrons a similar result will follow when you think of Electron '1' in 'box' $d\mathbf{x}_1$ and don't care where all the $(N-1)$ other electrons are: you get the probability of finding it there by integrating over all positions of the remaining volume elements. And as you'll get the same result for whichever electron you assign to 'box' $d\mathbf{x}_1$ you can define

$$\rho(\mathbf{x}_1) = N\int \Psi^*(\mathbf{x}_1\,\mathbf{x}_2,\, ...\,\mathbf{x}_N)\Psi(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N)d\mathbf{x}_2\, ...\, d\mathbf{x}_i\, ...d\mathbf{x}_N. \qquad (5.24)$$

as the probability per unit volume of finding an electron (no matter which) 'at' point $\mathbf{x}_1$.

Now we can come back to the Physics. The expectation value of H' in state $\Psi = \Phi_k$ will be the sum of N identical terms, coming from the 1-electron quantities $\delta V(i)$. It will thus be

$$\begin{aligned}\langle\Phi_k|\mathsf{H}'|\Phi_k\rangle &= \int \Phi_k^*(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N)\mathsf{H}'\Phi_k(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N)d\mathbf{x}_1 d\mathbf{x}_2\, ...\, d\mathbf{x}_i\, ...d\mathbf{x}_N \\ &= N\int \Phi_k^*(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N)\delta V(1)\Phi_k(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N)d\mathbf{x}_1 d\mathbf{x}_2\, ...\, d\mathbf{x}_i\, ...d\mathbf{x}_N.\end{aligned}$$

This can be nicely expressed in terms of the 1-electron density defined in (5.24) and gives for the first-order energy change (5.23)

$$\delta^{(1)}E_k = \langle\Phi_k|\mathsf{H}'|\Phi_k\rangle = \int \delta V(1)\rho(\mathbf{x}_1)d\mathbf{x}_1, \qquad (5.25)$$

– all expressed in terms of the space-spin coordinates of a single electron, just as if we were dealing with a *one*-electron system!

A generalization: the density *matrix*

Although (5.25) is a very useful result, as you'll see presently, you may want to know what happens if $\mathsf{H}' = \sum_i \delta\mathsf{h}(i)$ where $\delta\mathsf{h}(i)$ is a true operator, not just multiplication by a function $\delta V(i)$. In that case it seems that the reduction to (5.25) is not possible because the operator stands between Ψ^* and Ψ and will work only on the function that stands to its right. In the step before (5.25) we were able to bring the wave function and its complex conjugate together, to get the probability density, because

$$\Phi_k^*(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N)\delta V(1)\Phi_k(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N) = \delta V(1)\Phi_k(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N)\Phi_k^*(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N)$$

– the order of the factors doesn't matter when they are just multipliers. But you can't do that if $\delta\mathsf{h}(1)$ contains differential operators: $\partial/\partial z_1$, for example, will differentiate everything that stands to its right and contains coordinates of Electron '1'. Here we want the operator to work only on the Ψ factor, which contains $\mathbf{x}_1$, and *not* on Ψ^*. So we have to 'trick' the operator by writing $\Phi_k^*(\mathbf{x}_1', \mathbf{x}_2,\, ...\,\mathbf{x}_N)$, where $\mathbf{x}_1'$ is a new variable, instead of $\Phi_k^*(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N)$, changing it back to $\mathbf{x}_1$ *after* the operation.

That makes very little difference: the definition of the 1-electron density in (5.24) is replaced by that of a 1-electron density *'matrix'*, containing the two variables $(\mathbf{x}_1, \mathbf{x}_1')$:

$$\rho(\mathbf{x}_1; \mathbf{x}_1') = N\int \Psi(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N)\Psi^*(\mathbf{x}_1'\,\mathbf{x}_2,\, ...\,\mathbf{x}_N)d\mathbf{x}_2\, ...\, d\mathbf{x}_i\, ...d\mathbf{x}_N \qquad (5.26)$$

and the expectation value of $\mathsf{H}' = \sum_i \delta\mathsf{h}(i)$ is then given by

$$\langle\Psi|\mathsf{H}'|\Psi\rangle = \int [\delta\mathsf{h}(1)\rho(\mathbf{x}_1;\mathbf{x}'_1)]_{\mathbf{x}'_1=\mathbf{x}_1}\mathrm{d}\mathbf{x}_1, \tag{5.27}$$

where the integration is done *after* applying the operator and identifying the variables. So the generalization needed is very easy to make (you've done it before in Section 3.5).

As a first application, however, let's think of applying a uniform electric field to an atom and asking how it will change the energy E of any stationary state Ψ. (We'll drop the state label k as it's no longer needed.)

Example 5.5 Application of external field $\mathbf{F}$ to an atom

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(Note that we'll be in trouble if we use $\mathbf{E}$ for the electric field, as E is used everywhere for *energy*; so now we'll change to F when talking about the electric field. You may also need to refer back to Book 10.)

The components F_x, F_y, F_z of the field vector arise as the gradients of an **electric potential** $\phi(x,y,z)$ along the three axes in space,

$$F_x = -\frac{\partial\phi}{\partial x}, F_y = -\frac{\partial\phi}{\partial y}, F_z = -\frac{\partial\phi}{\partial z}$$

and an obvious solution is $\phi(x,y,z) = -xF_x - yF_y - zF_z$. (Check it by doing the partial differentiations.)

The change in potential energy of an electron (charge $-e$) at field point (x_i, y_i, z_i), due to the applied electric field, is thus $\delta V(i) = e(x_iF_x + y_iF_y + z_iF_z)$. We can use this in (5.25) to obtain the first-order change in energy of the quantum state $\Psi = \Phi_k$ produced by the field:

$$\delta^{(1)}E = e\int (x_iF_x + y_iF_y + z_iF_z)\rho(\mathbf{x}_1)\mathrm{d}\mathbf{x}_1.$$

Now the integration $\int(.....)\mathrm{d}\mathbf{x}_1$ is over both space and spin variables $\mathrm{d}\mathbf{x}_1 \equiv \mathrm{d}\mathbf{r}_1\mathrm{d}s_1$, but in this example $\delta\mathsf{h}$ contains no spin operators; and even when the wave function contains spin-orbitals, with spin factors $\alpha(s_i)$ and $\beta(s_i)$, the spin dependence will 'disappear' when the spin integrations are done. A 'spinless' density function can therefore be defined as $P(\mathbf{r}_1) = \int \rho(\mathbf{x}_1)\mathrm{d}s_1$ and the last equation re-written as

$$\delta^{(1)}E = \int \delta V(\mathbf{r}_1)P(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1 = e\int (x_iF_x + y_iF_y + z_iF_z)P(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1,$$

where the spinless density $P(\mathbf{r}_1)$ depends only on the spatial coordinates of a single point in 'ordinary' 3-space.

Example 5.5 has given a very transparent expression for the first-order energy change that goes with a modification of the potential field in which the N electrons of a system move. If the potential energy of a single electron at point $\mathbf{r}_1$ is changed by $\delta V(\mathbf{r}_1)$, the first-order energy change of the whole electron distribution will be (dropping the label '1' on the integration variable)

$$\delta^{(1)}E = \int \delta V(\mathbf{r})P(\mathbf{r})\mathrm{d}\mathbf{r} \tag{5.28}$$

– just as if the distribution were a 'smeared out' charge, with $P(\mathbf{r})\mathrm{d}\mathbf{r}$ electrons per unit volume at point $\mathbf{r}$.

This is an example of the **Hellman-Feynman theorem** which, as we'll see in the next chapter, is enormously important in leading to a simple picture of the origin of the forces that hold atoms together in molecules. The result is accurate if the wave function is exact or has been obtained by certain types of variational method, but its main value lies in providing clear pictorial interpretations of difficult theory. It can also lead to simple expressions for many quantities that are easily measured experimentally. Thus, in Example 5.5,

$$\delta^{(1)}E = e\int (xF_x + yF_y + zF_z)P(\mathbf{r})\mathrm{d}\mathbf{r}$$

allows us to evaluate the components of the electric moment of a system. In classical physics, a charge q_i has an **electric moment vector** defined as "position vector $\mathbf{r}_i$ from origin to charge, × charge" with components $\mu_x = x_i q_i$, $\mu_y = y_i q_i$, $\mu_z = z_i q_i$ and when there are several charges the total electric moment vector will have components $\mu_x = \sum_i x_i q_i$, etc. The potential energy of that system of charges, in an applied field $\mathbf{F}$, is $-\mu\cdot\mathbf{F}$. In quantum physics, the expression given above has exactly this form (check it out!) provided the electric moment components are calculated as $\mu_x = \int x(-e)P(\mathbf{r})\mathrm{d}\mathbf{r}$ etc. and again this confirms the 'charge cloud' interpretation, following (5.28), with $P(\mathbf{r})$ electrons/unit volume, each carrying a charge $-e$.

Before going on to calculate the density functions for a few many-electron atoms we confirm that (5.24) (and with it (5.26)) are correct for any N-electron system and lead to simple expectation values of 1-electron quantities.

Example 5.6 The 1-electron density matrix

Probability of Electron 1 in volume element $\mathrm{d}\mathbf{x}_1$ is

$$\mathrm{d}\mathbf{x}_1 \int \Psi(\mathbf{x}_1\,\mathbf{x}_2,\,...\,\mathbf{x}_N)\Psi^*(\mathbf{x}_1,\mathbf{x}_2,\,...\,\mathbf{x}_N)\mathrm{d}\mathbf{x}_2\,...\,\mathrm{d}\mathbf{x}_i\,...\mathrm{d}\mathbf{x}_N$$

where the Ψ^* function has been written on the right, ready for defining the density *matrix*.

Since the product $\Psi\Psi^*$ is invariant against interchange of electrons, the same result would be obtained for finding 'Electron i' in $\mathrm{d}\mathbf{x}_1$. With N electrons, the final result for the electron density is thus correctly given in (5.24) as the sum of N contributions. The corresponding density matrix follows on changing the variable $\mathbf{x}_1$ in the Ψ^* factor to $\mathbf{x}_1'$, giving

$$\rho(\mathbf{x}_1;\mathbf{x}_1') = N\int \Psi(\mathbf{x}_1\,\mathbf{x}_2,\,...\,\mathbf{x}_N)\Psi^*(\mathbf{x}_1',\mathbf{x}_2,\,...\,\mathbf{x}_N)\mathrm{d}\mathbf{x}_2\,...\,\mathrm{d}\mathbf{x}_i\,...\mathrm{d}\mathbf{x}_N.$$

The expectation value of any 1-electron operator sum, $\sum_i \mathsf{h}(i)$, is thus

$$\langle \sum_i \mathsf{h}(i)\,\rangle = \int_{\mathbf{x}_1'\to\mathbf{x}_1} [\mathsf{h}(1)\rho(\mathbf{x}_1;\mathbf{x}_1')]\mathrm{d}\mathbf{x}_1,$$

where the prime is removed before doing the integration. We note in passing that this general result reduces to the one given in (3.7) for an IPM wave function with occupied spin-orbitals $\psi_1,\psi_2,...\psi_i,...\psi_N$. Thus, on putting

$$\rho(\mathbf{x}_1;\mathbf{x}_1') = \psi_1(\mathbf{x}_1)\psi_1^*(\mathbf{x}_1') + \,...\, + \psi_N(\mathbf{x}_1)\psi_N^*(\mathbf{x}_1'),$$

the expectation value becomes

$$\langle \sum_i \mathsf{h}(i) \rangle = \langle \psi_1 | \mathsf{h} | \psi_1 \rangle + \ldots + \langle \psi_N | \mathsf{h} | \psi_N \rangle$$

– exactly as in (3.7).

Example 5.6 has verified the expression for the density function (5.24) and has given its form in terms of the occupied spin-orbitals in an IPM wave function. Thus

$$\rho(\mathbf{x}_1) = \psi_1(\mathbf{x}_1)\psi_1^*(\mathbf{x}_1) + \psi_2(\mathbf{x}_1)\psi_2^*(\mathbf{x}_1) + ... + \psi_N(\mathbf{x}_1)\psi_N^*(\mathbf{x}_1) \tag{5.29}$$

is the 1-electron density function, while

$$\rho(\mathbf{x}_1; \mathbf{x}_1') = \psi_1(\mathbf{x}_1)\psi_1^*(\mathbf{x}_1') + \psi_2(\mathbf{x}_1)\psi_2^*(\mathbf{x}_1') + ... + \psi_N(\mathbf{x}_1)\psi_N^*(\mathbf{x}_1') \tag{5.30}$$

is the 1-electron density *matrix*, the two variables corresponding to row and column indices in a matrix representation of a density *operator* ρ. The primed and unprimed variables are shown here in a corresponding 'standard' order.

We haven't forgotten about the spin! If you write $\mathbf{x}_1 = \mathbf{r}_1 s_1$ and aren't interested in whether the spin is 'up' ($s = +\frac{1}{2}$) or 'down' ($s = -\frac{1}{2}$), then you can 'sum' over both possibilities to obtain a spinless density function $P(\mathbf{r}_1) = \int \rho(\mathbf{r}_1, s_1 \mathrm{d}s_1$. This is the probability/unit volume of finding an electron, of either spin, at point $\mathbf{r}_1$ in ordinary 3-space. The terms in (5.29) depend on spin-orbitals $\psi_i(\mathbf{x}) = \phi_i(\mathbf{r})\theta(s)$ where the spin factor θ may be α or β; and $\rho(\mathbf{x}_1)$ may therefore be written as a sum of the form

$$\rho(\mathbf{x}_1) = P_\alpha(\mathbf{r}_1)\alpha(s_1)\alpha^*(s_1) + P_\beta(\mathbf{r}_1)\beta(s_1)\beta^*(s_1), \tag{5.31}$$

in which the α- and β-terms are

$$P_\alpha(\mathbf{r}_1) = \sum_{i\,(\alpha)} \phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}_1), \qquad P_\beta(\mathbf{r}_1) = \sum_{i\,(\beta)} \phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}_1). \tag{5.32}$$

Here the first sum comes from occupied spin-orbitals with α spin factors and the second from those with β factors. The density matrix may clearly be written in a similar form, but with an extra variable coming from the 'starred' spin-orbital and carrying the prime.

The results (5.29) – (5.32) all followed from Example 5.6 and the definition

$$\rho(\mathbf{x}; \mathbf{x}') = \sum_i \psi_i(\mathbf{x})\psi_i^*(\mathbf{x}'),$$

which gave

$$\langle \Psi | \sum_i \mathsf{h}(i) | \Psi \rangle = \int [\mathsf{h}\rho(x; x')]_{(\mathbf{x}' \to \mathbf{x})} \mathrm{d}\mathbf{x}.$$

These are the IPM forms of the 1-electron density functions and their main properties.

When electron interaction is admitted we shall need corresponding results for 2-electron densities: these are derived in the next example.

Example 5.7 The 2-electron density matrix

The derivation follows closely that in Example 5.6: Probability of Electron 1 in $\mathrm{d}\mathbf{x}_1$ and Electron 2 simultaneously in $\mathrm{d}\mathbf{x}_2$

$$= \mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2 \int \Psi^(\mathbf{x}_1\,\mathbf{x}_2,\, ...\,\mathbf{x}_N)\Psi^*(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N)\mathrm{d}\mathbf{x}_3 \,...\, \mathrm{d}\mathbf{x}_i \,...\mathrm{d}\mathbf{x}_N$$

Here the Ψ^* function has been written on the right, ready for defining the density *matrix*, and the first two volume elements are kept 'fixed'. Again, Electrons i and j would be found in $\mathrm{d}\mathbf{x}_1$ and $\mathrm{d}\mathbf{x}_2$, respectively, with exactly the same probability. But the pair could be chosen from the N electrons in $N(N-1)$ different ways (with one already chosen there are only $N-1$ others to choose from). Adding all these identical probabilities means that the total probability of finding *any* two electrons in $\mathrm{d}\mathbf{x}_1$ and $\mathrm{d}\mathbf{x}_2$ will be

$$\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2 \int \Psi^(\mathbf{x}_1\,\mathbf{x}_2,\, ...\,\mathbf{x}_N)\Psi^*(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N)\mathrm{d}\mathbf{x}_3 \,...\, \mathrm{d}\mathbf{x}_i \,...\mathrm{d}\mathbf{x}_N.$$

Let's denote this 'pair' probability by $\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2\pi(\mathbf{x}_1, \mathbf{x}_2)$ (π being the Greek letter 'p'), so that – on dropping the volume elements – the **pair *density*** is $\pi(\mathbf{x}_1, \mathbf{x}_2) = \int \Psi^(\mathbf{x}_1\,\mathbf{x}_2,\, ...\,\mathbf{x}_N)\Psi^*(\mathbf{x}_1, \mathbf{x}_2,\, ...\,\mathbf{x}_N)\mathrm{d}\mathbf{x}_3 \,...\, \mathrm{d}\mathbf{x}_i \,...\mathrm{d}\mathbf{x}_N$. The corresponding 2-electron *density matrix* follows when we put primes on the arguments $\mathbf{x}_1$ and $\mathbf{x}_2$ in the function Ψ^* on the right; the result is denoted by $\pi(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2)$ and the pair probability results on identifying the primed and unprimed variables. Thus $\pi(\mathbf{x}_1, \mathbf{x}_2) = \pi(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2)$.

As in Example 5.6, the 2-electron density matrix for a system with an IPM wave function can be written down by inspection of the results obtained in Chapter 3. Thus, from (3.7) the expectation value of the electron interaction term $\sum'(i,j)\mathsf{g}(i,j)$ is given as

$$\langle\Psi|\sum{}'(i,j)\mathsf{g}(i,j)|\Psi\rangle = \sum_{(i,j)}(\langle\psi_i\psi_j|\mathsf{g}(1,2)|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\mathsf{g}(1,2)|\psi_j\psi_i\rangle)$$

where $\mathsf{g}(1,2)$ is the 2-electron operator acting on functions of $\mathbf{x}_1$ and $\mathbf{x}_2$. (Labels are needed to indicate two space-spin *variables.*) Note that the second matrix element has the spin-orbital labels exchanged in the ket factor, giving the 'exchange' term.

The first matrix element can be written

$$\langle\psi_i\psi_j|\mathsf{g}(1,2)|\psi_i\psi_j\rangle = \int \psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)\mathsf{g}(1,2)\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2,$$

while the second, with a minus sign, is similar but with labels exchanged in the ket factor.

As in the case of the 1-electron densities, we can express this as

$$\int \psi_i^*(\mathbf{x}_1)\psi_j^*(\mathbf{x}_2)\mathsf{g}(1,2)\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2 = \int [\mathsf{g}(1,2)\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\psi_i^*(\mathbf{x}'_1)\psi_j^*(\mathbf{x}'_2)]_{(\mathbf{x}'_1\to\mathbf{x}_1, \mathbf{x}'_2\to\mathbf{x}_2)}\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2$$

and similarly for the second term.

Now define

$$\pi(\mathbf{x}_1, \mathbf{x}_2) = \sum_{(i,j)}(\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\psi_i^*(\mathbf{x}'_1)\psi_j^*(\mathbf{x}'_2) - \psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\psi_i^*(\mathbf{x}'_1)\psi_j^*(\mathbf{x}'_2))$$

as the 2-electron density matrix. With this definition the many-electron expectation value becomes

$$\langle\Psi|\sum{}'_{(i,j)}\mathsf{g}(i,j)|\Psi\rangle = \int [\mathsf{g}(1,2)\pi(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2)]_{(\mathbf{x}'_1\to\mathbf{x}_1, \mathbf{x}'_2\to\mathbf{x}_2)}\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2.$$

and when the operator $\mathsf{g}(i,j)$ does not touch the spin variables the integrations over spin can be done first:

$$\langle\Psi|\sum\nolimits'_{(i,j)}\mathsf{g}(i,j)|\Psi\rangle = \int[\mathsf{g}(1,2)\Pi(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2)]_{(\mathbf{r}'_1\to\mathbf{r}_1,\mathbf{r}'_2\to\mathbf{r}_2)}\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2,$$

where the upper-case Greek letter Π is used to denote the spinless 2-electron density matrix. (Remember that upper-case "rho", which is "P" in the Greek alphabet, was used for the spinless 1-electron density – that way you won't get mixed up.)

The conclusions from Examples 5.6 and 5.7 for a state Ψ, represented by a single antisymmetrized spin-orbital product and normalized to unity as in (3.4), are collected below:

Typical terms in the expectation value of the Hamiltonian (3.1) are

$\langle\Psi|\sum_i \mathsf{h}(i)|\Psi\rangle = \sum_i\langle\psi_i|\mathsf{h}|\psi_i\rangle = \int[\mathsf{h}\rho(\mathbf{x};\mathbf{x}')]_{(\mathbf{x}'\to\mathbf{x})}\mathrm{d}\mathbf{x}$,

where the **1-electron density matrix** is
$\rho(\mathbf{x};\mathbf{x}') = \sum_i \psi_i(\mathbf{x})\psi_i^*(\mathbf{x}')$

and $\langle\Psi|\sum'_{(i,j)}\mathsf{g}(i,j)|\Psi\rangle = \int[\mathsf{g}(1,2)\pi(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2)]_{(\mathbf{x}'_1\to\mathbf{x}_1,\mathbf{x}'_2\to\mathbf{x}_2)}\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2$,

where the **2-electron density matrix** is

$\pi(\mathbf{x}_1,\mathbf{x}_2) = \sum_{(i,j)}(\psi_i(\mathbf{x}_1)\psi_j(\mathbf{x}_2)\psi_i^*(\mathbf{x}'_1)\psi_j^*(\mathbf{x}'_2) - \psi_j(\mathbf{x}_1)\psi_i(\mathbf{x}_2)\psi_i^*(\mathbf{x}'_1)\psi_j^*(\mathbf{x}'_2))$

(5.33)

Note that the arguments in the density functions no longer serve to label the electrons – they simply indicate space-spin 'points' at which electrons may be found. Now, in the next Example, we'll see how things work out in practice.

Example 5.8 Density functions for some atoms

At the beginning of Chapter 5, in Section 5.1, we listed the electron configurations of the first ten atoms of the Periodic Table. The first four involved only the two lowest-energy AOs, ϕ_{1s} and ϕ_{2s}, which were singly or doubly occupied by electrons. A doubly occupied orbital appeared once with spin factor α and once with spin factor β, describing electrons with 'up-spin' and 'down-spin', respectively. The corresponding **spin-orbitals** were denoted by $\psi_1 = \phi_{1s}\alpha$, $\psi_2 = \phi_{1s}\beta$, $\psi_3 = \phi_{2s}\alpha$, $\psi_4 = \phi_{2s}\beta$ and, on putting in the space and spin variables, the spin-orbital $\phi_{1s}(\mathbf{r})\alpha(s)$ will describe an electron at point $\mathbf{r}$ in 3-space, with spin s. Remember that $\mathbf{r} = x,y,z$ (using Cartesian coordinates), while s is a discrete variable with only two values, $s = \frac{1}{2}$ for an 'up-spin' electron or $-\frac{1}{2}$ for 'down-spin'. Now we can begin.

The **Hydrogen atom** (H) has one electron in a doubly degenerate ground state, described by spin-orbital $\phi_{1s}\alpha$ or $\phi_{1s}\beta$. The 1-electron density function for the up-spin state will therefore be

$$\rho(\mathbf{x}) = \psi_1(\mathbf{x})\psi_1^*(\mathbf{x}) = \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r})\alpha(s)\alpha^*(s)$$

and the 1-electron density *matrix* will be

$$\rho(\mathbf{x};\mathbf{x}') = \psi_1(\mathbf{x})\psi_1^*(\mathbf{x}') = \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r}')\alpha(s)\alpha^*(s').$$

The 'spinless' counterparts of these functions follow, as we guessed in Example 5.5, by integrating over the unwanted variable (in this case spin) after removing the prime. (Remember we always use orthonormal spin functions, so $\langle\alpha|\alpha\rangle = 1$, $\langle\alpha|\beta\rangle = 0$, etc. Thus we find the spinless density

$$P(\mathbf{r}) = \int \rho(\mathbf{x})\mathrm{d}s = \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r}) \int \alpha(s)\alpha^*(s)\mathrm{d}s = \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r})$$

and the spinless density *matrix* $P(\mathbf{r};\mathbf{r}') = \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r}')$ – just as if the wave function contained orbitals with no spin factors.

The **Helium atom** (He) has a non-degenerate ground state, with two electrons in the 1s AO, but to satisfy the Pauli principle its wave function must be an *antisymmetrized* spin-orbital product (3.4) and we must therefore use (5.29) and (5.30). For the ground state, the results are

$$\rho(\mathbf{x}) = \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r})\alpha(s)\alpha^*(s) + \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r})\beta(s)\beta^*(s)$$

and

$$\rho(\mathbf{x};\mathbf{x}') = \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r}')\alpha(s)\alpha^*(s') + \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r}')\beta(s)\beta^*(s').$$

The densities of up-spin and down-spin electrons are clearly, from (5.32),

$$P_\alpha(\mathbf{r}) = \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r}), \qquad P_\beta(\mathbf{r}) = \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r})$$

and the corresponding density matrices are

$$P_{\alpha\alpha}(\mathbf{r},\mathbf{r}') = \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r}'), \qquad P_{\beta\beta}(\mathbf{r},\mathbf{r}') = \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r}').$$

The up-spin and down-spin components of the total electron density are equal whenever the spin-orbitals are doubly occupied: Total density $= P_\alpha(\mathbf{r})+P_\beta(\mathbf{r})$. But the *difference* of the densities is also an important quantity: it is called the **spin density** and is usually defined as $Q(\mathbf{r}) = \frac{1}{2}(P_\alpha(\mathbf{r}) - P_\beta(\mathbf{r}))$. (The $\frac{1}{2}$ is the spin angular momentum in units of $\hbar$, so it is sensible to include it – remembering that the electron charge density $-eP(\mathbf{r})$ is measured in units of charge, with $e = 1$.)

The **Lithium atom** (Li) has a degenerate ground state, the third electron being in the 2s orbital with up-spin or down-spin. The electron density function for the up-spin state follows from (5.29) as

$$\rho(\mathbf{x}) = \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r})\alpha(s)\alpha^*(s) + \phi_{1s}(\mathbf{r})\phi_{1s}^*(\mathbf{r})\beta(s)\beta^*(s) + \phi_{2s}(\mathbf{r})\phi_{2s}^*(\mathbf{r})\alpha(s)\alpha^*(s).$$

You can do the rest yourself. The new features of this atom are (i) an **inner shell** of two electrons, with equal but opposite spins, in a tightly bound 1s orbital, and (ii) a **valence shell** holding one electron, in a diffuse and more weakly bound 2s orbital, with no other electron of opposite spin. This atom has a resultant spin density, when in the up-spin state, $Q(\mathbf{r}) = \frac{1}{2}\phi_{2s}(\mathbf{r})\phi_{2s}^*(\mathbf{r})$ and this 'free' spin density, almost entirely confined to the valence shell, is what gives the system its **chemical properties**.

Beryllium (Be) is another 'closed-shell' system, with only doubly-occupied orbitals, and like Helium shows little chemical activity.

Boron (B), with one more electron, must start filling the higher- energy p-type AOs such as $2p_x, 2p_y, 2p_z$ and the next few atoms bring in important new ideas.

5.5 An interlude: the Periodic Table

In Section 5.2 we listed the first ten chemical elements, in order of increasing atomic number, together with their electron configurations; and in the following sections we have developed in detail the methods for constructing IPM approximations to the wave functions that describe their electronic structures. These methods are rather general and in principle serve as a basis for dealing in a similar way with atoms of atomic number $Z > 10$. Many years ago Mendeleev and other Chemists of the day showed (on purely empirical grounds) how the elements of all the known atoms could be arranged in a Table, in such a way as to expose various regularities in their chemical behaviour as the atomic number Z increased. In particular, the elements show a *periodicity* in which certain groups of atoms possess very similar properties even when their Z-values are very different. As more and more elements were discovered it became important to classify their properties and show how they could be related to our increasing understanding of electronic structure. Parts of the resultant **Periodic Table**, in its modern form, are given below.

First we indicate the 'Short Periods', along with the electron configurations of the atoms they include (atomic numbers being attached as superscripts to their chemical symbols):

Periodic Table: the two short periods

^{3}Li	^{4}Be	^{5}B	^{6}C	^{7}N	^{8}O	^{9}F	^{10}Ne
$2s^1$	$2s^2$	$2s^22p^1$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2s^22p^5$	$2s^22p^6$

^{11}Na	^{12}Mg	^{13}Al	^{14}Si	^{15}P	^{16}S	^{17}Cl	^{18}A
$3s^1$	$3s^2$	$3s^23p^1$	$3s^23p^2$	$3s^23p^3$	$3s^23p^4$	$3s^23p^5$	$3s^23p^6$

In these periods the order in which the available orbitals are filled is exactly as suggested by the first and second columns of Figure 5.1. The lowest energy AO is occupied by one electron in Hydrogen and two electrons in Helium – two atoms not usually counted as forming a Period. The next two AOs, in ascending energy order, come from the quantum shell with principal quantum number $n = 2$ and account for the electron configurations of all the atoms in the first short period. Lithium and Beryllium hold only electrons in an orbital of 2s type; but the next AO is of 2p type and is three-fold degenerate, so Carbon, for example, will have the configuration with 2 electrons in the 2s AO and 2 electrons to be distributed among the 2p AOs (no matter *which*). When spin is taken into account, the ground states and low-lying excited states of the atoms in the short periods may be set up by angular momentum coupling methods, following the pattern of Example 5.2, to give all the resultant 'states of the configuration'.

Things become more complicated in the longer periods because, as Figure 5.1 suggests, the AO energies of orbitals in quantum shells with $n \geq 3$ may be so close together that it is not easy to guess the order in which they will be filled. The quantum shell with principal quantum number $n = 4$ starts with the atoms Potassium (K) and Calcium (Ca), with the expected configurations $4\mathrm{s}^1$ and $4\mathrm{s}^2$ (outside the filled shells with $n = 1, 2, 3$), and continues with the first long period (shown below).

Periodic Table: the first long period

^{21}Sc	^{22}Ti	^{23}V	^{24}Cr	^{25}Mn	^{26}Fe	^{27}Co	^{28}Ni	^{29}Cu	^{30}Zn
$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$

– and continuing :

^{31}Ga	^{32}Ge	^{33}As	^{34}Se	^{35}Br	^{36}Kr
$-4p^1$	$-4p^2$	$-4p^3$	$-4p^4$	$-4p^5$	$-4p^6$

If you look at that, along with Figure 5.1, you'll see that the 3d AOs have started to fill *before* the 4s because their orbital energies are in this case slightly lower. The atom of Zinc (Zn), with electron configuration $3\mathrm{d}^{10}4s^2$, has a complete shell with all 3d orbitals full; the next atom is Gallium (Ga), which starts taking on electrons in the 4p orbitals – on top of the filled 4s-3d shell (shown as a $-$). The atoms from Gallium up to Krypton (Kr) have configurations similar to those in the short periods, in which the three p orbitals are filling. The chemical properties of the six resultant atoms resemble those of the atoms in the two short periods shown above, ending with another inert gas (Kr) – like Neon (Ne) and Argon (A). In fact, such properties depend little on the inner-shell electrons which simply provide an 'effective field' for the electrons occupying the 'outer-shell' orbitals. The role of the atoms in Chemistry, which we begin to study in the next chapter, depends mainly on their outermost orbitals and that's why inner shells are often not shown in the Periodic Table – as listed above, where the Argon-like filled orbitals are shown only as a dash ($-$).

The whole Periodic Table, including over a hundred known chemical elements, is of such fundamental importance in Chemistry that it is nowadays displayed in schools and universities all over the world. Here you've seen how it relates to the electronic stuctures of the 'building blocks' from which all matter is constructed. More of that in later chapters, but first a bit more quantum mechanics.

5.6 Effect of small terms in the Hamiltonian

Most atoms do not have closed-shell ground states and, as we saw in the last section, that makes them much more interesting. In particular, electron configurations with degenerate AOs that are incompletely filled can show a rich variety of electronic states. Even when the separation of atomic energy levels is very small it is easy to observe experimentally with present-day techniques: these usually require the application of strong magnetic fields which allow one to 'see' the effects of coupling between the applied field and any free spins – which carry **magnetic dipoles** (see Book 10). The spin-field (Zeeman) interaction gives rise to a perturbation of the form

$$\mathsf{H}'_Z = g\beta \sum_i \mathbf{B} \cdot \mathsf{S}(i), \tag{5.34}$$

where $\beta = e\hbar/2m$ is called the "Bohr magneton" (don't confuse it with a spin eigenstate), $\mathbf{B}$ is the flux density of the magnetic field, and g is a number very close to 2 (which indicates that spin is twice as effective as orbital motion of a charge in producing a magnetic dipole).

The 'normal' interaction between the field and an electron with orbital angular momentum $\mathsf{L}(i)$ gives a perturbation

$$\mathsf{H}'_{\text{mag}} = \beta \sum_i \mathbf{B} \cdot \mathsf{L}(i), \tag{5.35}$$

which represents a classical field-dipole interaction). In both cases the summation is over all electrons.

There are many other interaction terms, which you don't even need to know about, but for a free atom there are some simplifications and it's fairly easy to see how the fine structure of the energy levels can arise and how the states can be classified. So we'll end this chapter by using what we already know about spin and orbital angular momenta. The unperturbed states of a Carbon $2p^2$ configuration, with energy levels represented in Figure 5.4, were constructed as linear combinations of antisymmetrized products of spin-orbitals so as to be simultaneous eigenstates of the commuting operators H, L^2, L_z, S^2, S_z (all in IPM approximation). But the fine structure of the triplet P level, indicated in Column (c), was not accounted for – though it was put down to "spin-orbit coupling", which could be admitted as a perturbation. Classically, the interaction energy between two magnetic dipoles $\mathbf{m}_1, \mathbf{m}_2$ is usually taken to be proportional to their scalar product $\mathbf{m}_1 \cdot \mathbf{m}_2$, so it will be no surprise to find that in quantum mechanics the spin-orbit perturbation operator, arising from the spin dipole and the orbital dipole, takes the approximate form (main term only)

$$\mathsf{H}'_{SL}(i) = \sum_i f(r_i)\mathsf{S}(i) \cdot \mathsf{L}(i), \tag{5.36}$$

where the factor $f(r_i)$ depends on distance r_i of Electron i from the nucleus, but is also proportional to nuclear charge Z and therefore important for heavy atoms.

To understand the effect of such terms on the levels shown in Fig. 5.4, we remember that eigenstates of the operators $\mathsf{L}^2, \mathsf{L}_z$ and $\mathsf{S}^2, \mathsf{S}_z$ can be coupled to give eigenstates of *total* angular momentum, represented by the operators $\mathsf{J}_x, \mathsf{J}_y, \mathsf{J}_z$, defined as

$$\mathsf{J}_x = \mathsf{L}_x + \mathsf{S}_x, \quad \mathsf{J}_y = \mathsf{L}_y + \mathsf{S}_y, \quad \mathsf{J}_z = \mathsf{L}_z + \mathsf{S}_z,$$

and that these operators have exactly the same commutation properties as *all* angular momentum operators (reviewed in Section 5.1). Thus, it should be possible to find simultaneous eigenstates of the operators $\mathsf{J}^2 = \mathsf{J}_x^2 + \mathsf{J}_y^2 + \mathsf{J}_z^2$, and J_z, with quantum numbers (J, M_J), and also the shift operators $\mathsf{J}^+ = \mathsf{J}_x + i\mathsf{J}_y$ and $\mathsf{J}^- = \mathsf{J}_x - i\mathsf{J}_y$. To check that this really *is* possible, let's start from the orbital and spin eigenstates (already found) with quantum numbers (L, M_L) and (S, M_S), calling them Φ_{L,M_L} and Θ_{S,M_S}, respectively. The product of the 'top' states, with $M_L = L$ and $M_S = S$, is clearly an eigenstate of $\mathsf{J}_z = \mathsf{L}_z + \mathsf{S}_z$ because each operator works only on 'its own' eigenfunction (orbital or spin), giving $\mathsf{J}_z(\Phi_{L,M_L=L}\Theta_{S,M_S=S}) = L+S(\Phi_{L,M_L=L}\Theta_{S,M_S=S})$, and this means the product function is an eigenfunction of J_z with the maximum available quantum number $M_J = L+S$, which implies that $J = L+S$ is the quantum number for the corresponding eigenstate of J^2. This really *is* the top state because it can't be stepped up ($\mathsf{J}^+ = \mathsf{L}^+ + \mathsf{S}^+$ and the product will be annihilated by one or other of the two operators). On the other hand, $(\Phi_{L,L}\Theta_{S,S})$ can be stepped *down* by using ($\mathsf{J}^- = \mathsf{L}^- + \mathsf{S}^-$). This will give a function with L and S unchanged, which is a combination of $\Phi_{L,L-1}\Theta_{S,S}$ and $\Phi_{L,L}\Theta_{S,S-1}$ with J unchanged but M_J reduced by 1.

You've done all this before! There will be another combination, orthogonal to the first and still with the J_z quantum number reduced to $M_J - 1$, and this must be the top state of a new series with $J = L+S-1$. If you do the same operations all over again you can reduce the M_J-value to $L+S-2$ and then, by finding an orthogonal combination, arrive at the top state of a new series with $J = M_J = L+S-2$. As you can see, this gets terribly tedious. But it can be done and the conclusion is easy enough to visualize: you add vectors by adding their corresponding components. In adding orbital and spin angular momentum vectors you start with the vectors 'in line', so $J = M_J = M_L + M_S$, only the quantized z-components being significant; and then you step down by using the J^- operator to get all the $2J+1$ states of the series with the same $J = M+S$. Then you move to the series with $J = M+S-1$ and M_J going down from J to $-J$ in integer steps, corresponding to the allowed projections of an arrow of length J on the z-axis. By carrying on in that way you find all the **vector-coupled states** with

$$J = L+S, \quad L+S-1, \quad L+S-2, \quad ...., |L-S|.$$

Since J is a positive number the process must stop when the next step would violate this condition; that's why the last state has a J value which is the *magnitude* of the difference in lengths of the L- and S-vectors.

We can now come back to Figure 5.4 and the splitting of the energy levels in Column (c). In principle we could estimate the effect of the perturbation terms (5.34), (5.35) and (5.36) by getting their matrix elements relative to the unperturbed functions and then solving a system of secular equations, along the lines of Section 5.4; but it's much nicer, if you don't want any numerical detail, to use the fact that the $2L+1$ orbital eigenstates of L^2 and the $2S+1$ spin eigenstates of S^2 may in general be *mixed* by the perturbation to produce eigenstates of the operators J^2 and J_z, which also commute with the Hamiltonian. We've just found how the vector-coupled states that result can be labelled in terms of the eigenvalues J and M_J; and we know that states with different sets of eigenvalues will in general have different energies.

The levels in Figure 5.4 result from the unperturbed 2-electron states with quantum numbers $L = 1, M_L = 1, 0, -1$ and $S = 1, M_S = 1, 0, -1$ and for each choice of L and S we can obtain all the allowed spin-coupled states of given J and M_J. Moreover, the unperturbed states have been constructed from antisymmetrized spin-orbital products and the Pauli Principle is thus taken care of from the start. Let's take the possible states one at a time:

$\underline{L = 2,\ S = 1}$

In Example 5.3 this case was ruled out, being completely symmetric under electron exchange, so $J = L + S = 3$ is excluded. But with $S = 0$ we pass to the next

$\underline{L = 2\ S = 0\ J = 2}$

$L = 2$ means this is a D state (2 units of orbital angular momentum) and $S = 0$ means this is a spin singlet, so the full state label is ^{1}D as shown in Fig.5.4

$\underline{L = 1\ S = 1\ J = 2}$

$L = 1$ means this is a P state (1 unit of orbital angular momentum) and $S = 1$ means this is a spin tripet, so the full state label is ^{3}P as shown in Fig. 5.4 with some fine structure resulting from spin-orbit coupling. When $J = 2$ there are $2J + 1 = 5$ states of different M_J: these are the Zeeman states, which are degenerate in the absence of an external magnetic field. But the top state ($J = M_J = 2$) can be stepped down to give a series with $J = 1$, still ^{3}P states, J being $J = L + S - 1$ with $L = 1$ and $S = 1$. Another step down gives $J = L + S - 2 = 0$, a single state with the L- and S-vectors anti-parallel coupled. To label these component states, of which there are 9 (=5+3+1), it is usual to add a subscript to the *'term symbols'* shown in Fig. 5.4, giving the value of J. The states of the ^{3}P multiplet are then labelled $^3\mathrm{P}_2, {}^3\mathrm{P}_1, {}^3\mathrm{P}_0$, in descending order of energy. The highest-energy state of the multiplet is the one in which the magnetic dipoles point in the same direction; the lowest is that in which their arrows are opposed – just as in Classical Physics.

Of course, we're still using an IPM picture, which is only a poor approximation, but it's amazing how much understanding we can get from it – even without any numerical calculations. The tiny shifts of the energy levels, brought about by the small terms in the Hamiltonian, are described as "**fine structure**". When observed spectroscopically they give important information about the electronic structure of the atoms: first of all they tell us *what* atom we are looking at (no two atoms give exactly the same 'finger prints') and secondly they tell us whether or not there are singly occupied orbitals, containing un-paired spins that are free to couple with the spins of other atoms. So they are useful for both **chemical analysis** and for understanding **chemical reactivity** – so much so that most of our big hospitals have expensive equipment for detecting the presence of unpaired spins in the atoms of the cells in our bodies!

Chapter 6

Molecules: first steps –

6.1 When did molecules first start to form?

You first started learning about how atoms could combine, to form molecules, in Chapter 1 of Book 5. Since then, in Book 6, you've learnt more about matter in general and the history of our planet Earth as a member of the Solar System. You must have been struck by the time-scale on which things happen and the traces they leave behind in the rocks, like the fossil remains of creatures that lived here many millions of years ago. And in Books 7-9 you learnt about the **evolution** of all those creatures (including ourselves!), starting from the earliest and simplest forms of life. Before studying molecules in more detail you may be wondering where the atoms themselves came from; and that takes us back to the beginning of the Universe. We'll have to tell the story in the light of what we know now (or at least *think* we know, on the basis of all the evidence we have).

About 14 billion years ago, all the particles in the present Universe were very close together in a 'ball' of unbelievably dense matter. This ball exploded as a result of the interactions that drove the particles apart: we now call that event the **Big Bang**. The particles spread out in empty space, at great speed, to form an **Expanding Universe** which is still getting bigger and bigger. As they interacted, the particles eventually began to form atoms – first of all those of Hydrogen, the lightest known atom, consisting of one **proton** and one **electron**. So at one stage the Universe could be pictured as a dense cloud of Hydrogen. But it didn't stay that way.

What happened in the early Universe?

The atomic *nuclei* (protons) could also come together in pairs to form new nuclei, those of the Helium ion He^{2+} (the 2+ indicating that the neutral Helium *atom* has lost two electrons to give a bare nucleus with two units of positive charge). This process is called **nuclear fusion** and was first mentioned in Book 4 Section 8.3 (which you should read again before going on). When two protons fuse in this way the total mass of the system is reduced by a factor of about 0.7×10^{-2} and since a proton has a mass $\approx 1.66\times10^{-27}$ kg the mass *lost* will be $\approx (0.7\times10^{-2})(1.66\times10^{-27}\,\mathrm{kg}) = 2.324\times10^{-29}\,\mathrm{kg}$

Now in Section 8.3 of Book 4, you learnt that mass is a form of *energy* and that the two things are related by Einstein's famous formula $E = mc^2$, where c is the speed with which light travels ($\approx 3 \times 10^8 \mathrm{ms}^{-1}$). The mass lost when two protons fuse is thus equivalent to an energy

$$E = mc^2 = (2.324 \times 10^{-29}\,\mathrm{kg}) \times (9 \times 10^{16}\,\mathrm{m}^2\mathrm{s}^{-2}) = (20.916 \times 10^{-13})\,\mathrm{kg\,m}^2\,\mathrm{s}^{-2}.$$

But the energy unit here is the **Joule**: $1\,\mathrm{J} = 1\,\mathrm{kg\,m}^2\,\mathrm{s}^{-2}$. That may not seem much, but if you remember that the 'chemical' unit of quantity is the 'mole' this must be multiplied by the Avogadro number L, the number of systems it contains. The fusion energy of 1 mole of proton pairs thus comes out as

$$(0.602 \times 10^{24}) \times (20.916 \times 10^{-13})\,\mathrm{J} = 12.59 \times 10^{11}\,\mathrm{J} = 12.59 \times 10^{8}\,\mathrm{kJ}.$$

Let's compare that with the energy released in burning 1 mole of hydrogen gas (often used as a rocket fuel). In that case (read section 3.2 of Book 5) the **reactants** are 1 mole of hydrogen molecules (H_2) plus 1 mole of Oxygen molecules (O_2); and the **products** are 1 mole of water molecules (H_2O). The energy change when the reactants go to the products is $\Delta H = H_{\mathrm{P}} - H_{\mathrm{R}}$, where H stands for "Heat content per mole". On putting in the experimental values of these quantities for Hydrogen, Oxygen and Water, the result is $-571.6\,\mathrm{kJ}$, the minus sign meaning that the total heat content goes *down* and the energy *released* by burning 1 mole of Hydrogen is 571.6 kJ.

That should be compared with the energy released in the fusion of 1 mole of proton pairs, which we found to be $1.259 \times 10^9\,\mathrm{kJ}$ – over a *thousand million* kJ. So in the early Universe there was no shortage of energy; its gaseous contents must have existed at an unbelievably high temperature!

What happened in the very early stages?

At the beginning of the first 10 billion years after the Big Bang, as it began to cool, the Universe contained a 'mish-mash' of particles with strange names like 'quarks' and 'gluons' (given to them by the people who discovered them), forming a continuous 'sea' called a **plasma**. That phase lasted only up to about *one second* after the BB and was followed by the appearance of heavier particles, mainly protons, electrons and neutrons – collectively known as 'baryons' – composed of quarks 'glued together' by the gluons.

(It's almost impossible to *observe* the quarks and gluons because if ever they get out of a baryon they have a vanishingly short lifetime and seem to just disappear – until recently nobody knew that a proton was composed of three quarks, held together by gluons! To find what was inside a proton or a neutron you had to smash it open by firing other particles at it and observing what came out; and to give these 'projectiles' enough energy to do that they had to be accelerated to speeds close to that of light. **Particle accelerators** are nowadays being built, at great expense, to do that job.)

Then, between about 3 and 20 mins after the BB, when the temperature and density of the plasma had fallen to a low enough level, the baryons started coming together to form other nuclei, such as He^{2+}, by the fusion reaction described above.

Much later, between about 200 and 400 *thousand years* after BB, the positively charged nuclei began to capture electrons from the plasma to form stable neutral particles, mainly neutrons, H-atoms and He-atoms together with a few of the other light atoms, like Carbon, that you've already met. These are the atoms needed in building simple molecules, which we'll study in detail in the rest of this chapter. (You might like to read a preview of them in Book 5.)

From that point on there followed a long period, still going on, of 'structure formation'. First the atoms came together in small groups, which attracted other groups and became much bigger (think of a snowball rolling down a hill and picking up more snow on the way until it becomes a giant snowball): after billions of years these gigantic structures became the first **stars**; and started coming together in 'star-clusters' or **'galaxies'**. The galaxy we see in the night sky and call the "Milky Way" was formed in this way between 7 and 10 billion years ago and one of the stars in this galaxy is our **Sun**. The whole Solar System, the Sun and the Planets that move in orbits around it, came into existence about 8 or 9 billion years after the Big Bang; so planet Earth, the part of the Universe we feel we know best, is about $4\frac{1}{2}$ billion years old!

But how do we know all that?

We see the stars in the night sky because they *shine*: they emit radiation in the form of **photons**, which travel through space at the enormous speed of $\approx 3 \times 10^8 \mathrm{ms}^{-1}$ (three hundred million metres per second!) and the light we observe using ordinary ('optical') telescopes consists only of photons in a very narrow range of frequencies (as you'll remember from Book 10, Section 6.5). Most of the light that reaches us is 'invisible' but it can all be 'seen' by the instruments available to us nowadays – and it all carries information about where it came from. We also have **radio telescopes**, for example, that pick up the radiation from distant stars. All this radiation can be analised by **spectrometers**, which give detailed information about the electronic origins of the light they take in (as you learnt in Section 5.3 of the present Book 12).

If you really think about all this you'll come to some amazing conclusions. First of all the *distances* between stars are so large that it's most convenient to measure them in **'light years'**; 1 light year is the distance travelled by a photon in 1 year and is about 9.5×10^{12}km. The nearest stars to our own Sun are about 4 light years away; so the light that we see coming from them started in processes that happened 4 years ago. But more distant stars in the Milky Way galaxy were formed as long as 13 billion years ago and any radiation that comes from them must therefore have been on the way for no less than about 13 billion years.

The light that reaches us here on the Earth, from the Milky Way, is very dim and its spectrum is 'foggy' showing little sign of the sharp lines found in atomic spectra observed in the laboratory. But against this background there is always one extremely faint line at a wavelength of 21.106 cm in the microwave region of the spectrum. Where could it come from?

When the first atoms began to form, so long ago, they were almost exclusively Hydrogen (one proton plus one electron). And, as you know from Section 5.3, when one of them makes a transition from one electronic state to another, of lower energy, a photon of frequency ν is emitted with $h\nu = E_{initial} - E_{final}$. The lowest electronic state is a ^{2}S doublet, the two 1s levels differing in spin ($\pm\frac{1}{2}$), but now we must remember that the *proton* is also a spin-$\frac{1}{2}$ particle and that the two spins ($S = \frac{1}{2}$ for the electron and $I = \frac{1}{2}$ for the proton) can couple to give a total spin angular momentum with quantum number F, say, with possible values $F = \frac{1}{2} + \frac{1}{2} = 1$ and $F = \frac{1}{2} - \frac{1}{2} = 0$. As a result of this **nuclear hyperfine coupling** the lowest energy level of the H-atom becomes a doublet with a minute energy separation, confirmed here and now in the laboratory, of 5.874 $\times 10^{-6}$ eV. This is the energy of a quantum of radiation of wavelength 21.106 cm.

What does all this mean? When we say "here and now" we mean "here on Earth" and "now at the time of making the experimental measurement". But the event we were talking about – the emission of a photon from an atom in a distant part of the Universe – took place about 13 billion light years away, which means 13 billion years *before* our laboratory experiments! The predicted energy separation comes from calculations that depend on all the laws of 'everyday' Physics (from Classical Mechanics (Book 4) to Electromagnetism (Book 10) and Quantum Mechanics (Book 11) – as long as extremely high energies or relativistic velocities are not involved. We can hardly escape the remarkable conclusion that

> **The Laws of Physics are invariant against changes of position or time of the system to which they are applied; and that must have been true for at least 13 billion years.**

Many details remain to be filled in: for example, theory shows that the 21 cm transition is in fact 'forbidden' and would probably take place not more than once in 10 million years! But the number of H atoms in the Milky Way is so enormous that the *total* probability of a transition is enough to account for the observed spectral line.

In summary: the fundamental laws of physics are OK and any variations in the behaviour of matter are normally due to changes in external conditions such as temperature and density (which may both reach unimaginable values). Now we're all set to start thinking about the next step in the evolution of the Universe: what makes the atoms stick together to form molecules?

6.2 The first diatomic systems

As you've learnt from Section 6.1, the early Universe once consisted of a hot plasma of electrons, neutrons, and protons (H^+) that had not yet picked up electrons to become neutral Hydrogen atoms (H) – together with a trace of Helium nuclei (He^{2+}) already formed by proton fusion.

Let's imagine what can happen when a proton meets a Hydrogen atom. There will then be a composite system, with two protons sharing one electron, namely a **hydrogen molecule ion**.

As usual we apply quantum mechanics to this system by first of all setting up the Hamiltonian operator. We should really suppose all three particles are moving, but we'll use an approximation that allows for the fact that a proton has a mass almost 2000 times that of an electron. The rapidly moving electron then 'sees' the nuclei at any instant as if they were at rest in fixed positions. The three-body problem then becomes in effect a one-electron problem with Hamiltonian

$$\mathsf{h} = -\tfrac{1}{2}\nabla^2 - \left(\tfrac{1}{r_a} + \tfrac{1}{r_b}\right), \tag{6.1}$$

where r_a and r_b denote distances of the electron from nuclei 'a' and 'b' and atomic units are used throughout. The ∇^2-operator works on the electronic coordinates, to be denoted by $\mathbf{r}$, and will have a form depending on the coordinate system chosen. The energy levels of the electron are then found by solving the eigenvalue equation

$$\mathsf{h}\phi = \epsilon\phi. \tag{6.2}$$

The energy of the whole system in this 'fixed nucleus' approximation will then be

$$E = 1/R_{ab} + \epsilon, \tag{6.3}$$

where ϵ denotes the electronic energy eigenvalue and R_{ab} is the internuclear distance. (Note that in atomic units the proton charges are $Z_a = Z_b = 1$ and that the first term in E is their classical Coulomb repulsion energy.) This procedure is called the **Born-Oppenheimer separation** of electronic and nuclear motion. Heavy particles (like nuclei) move in good approximation according to classical physics with E, calculated in this way, serving as a potential energy function.

But then we meet the next big problem. For an atom we had 'ready-made' atomic orbitals, with the well-known forms (1s, 2s, 2p, 3s, 3p, 3d, etc.) first discussed in Book 11, but here we know nothing about the forms of the **molecular orbitals** that will be needed in building corresponding approximations to the *molecular* wave functions. First of all, then, we need to find how to describe the one-electron system that remains when the electron is taken away. This system is experimentally well-known: it is the Hydrogen molecule ion, H_2^+.

How can we get a reasonable first approximation to the lowest-energy molecular orbital (MO)? When the electron is close to Nucleus a, the term $1/r_\mathrm{a}$ will be so big that $1/r_\mathrm{b}$ may be neglected in (6.1). The MO will then 'shrink' into an *atomic* orbital (AO) for a single hydrogen atom. We'll denote this AO by $\chi_a(\mathbf{r})$, as we're going to use AOs as **basis functions** out of which more general wave functions, such as MOs, can be constructed. In this process a general MO, call it ϕ, must change according to $\phi(\mathbf{r}) \rightarrow c_a\chi_a(\mathbf{r})$, since this will satisfy the same single-atom eigenvalue equation for any value of a numerical factor c. Similarly, when $\mathbf{r}$ is close to the second nucleus $\phi(\mathbf{r})$ will approach a numerical multiple of the AO $\chi_b(\mathbf{r})$. It follows that an electron in the field of both nuclei may be fairly well represented by an MO of the form

$$\phi(\mathbf{r}) = c_a\chi_a(\mathbf{r}) + c_b\chi_b(\mathbf{r}) \tag{6.4}$$

where the constants c_a, c_b are still to be chosen (e.g. by taking them as variable parameters and using the variation method of Section 1.3) to find the MO of minimum energy. This should give at least a rough description of the ground state.

In fact, however, no calculation is needed because the molecule ion is *symmetrical* across a plane perpendicular to the molecular axis, cutting the system into two equal halves. There is no reason to expect the electron to be found with different probability on the two sides of the symmetry plane and this implies that the values of the coefficients c_a, c_b can differ, at most, in sign: $c_b = \pm c_a$. Two acceptable approximate MOs are thus, putting $c_b = c_a = N_B$ in one MO and $c_b = -c_a = N_A$ in the other

$$\phi_B(\mathbf{r}) = N_B[\chi_a(\mathbf{r}) + \chi_b(\mathbf{r})], \qquad \phi_A(\mathbf{r}) = N_A[\chi_a(\mathbf{r}) - \chi_b(\mathbf{r})]. \tag{6.5}$$

This case arises only for **homonuclear** diatomic molecules – in which the two nuclei are identical. It is important because very many common diatomic molecules, such as H_2, N_2, O_2, are of this type.

The solutions just found are typical **Bonding and Antibonding MOs**; so called for reasons that will soon become clear. The constants N_A, N_B are normalizing factors, chosen to give unit probability of finding the electron *somewhere* in space. For normalization we require

$$N_B^2\langle\phi_B|\phi_B\rangle = N_B^2(2 + 2S_{ab}) = 1,$$

where $S_{ab} = \langle\chi_a|\chi_b\rangle$ is the **overlap integral** between the two AOs. In this way we find MOs

$$\phi_B(\mathbf{r}) = \frac{\chi_a(\mathbf{r}) + \chi_b(\mathbf{r})}{\sqrt{2 + 2S_{ab}}} \tag{6.6}$$

for the Bonding MO, and

$$\phi_A(\mathbf{r}) = \frac{\chi_a(\mathbf{r}) - \chi_b(\mathbf{r})}{\sqrt{2 - 2S_{ab}}} \tag{6.7}$$

for the Antibonding MO. The following Figure 6.1 gives a very schematic picture of the two MOs.

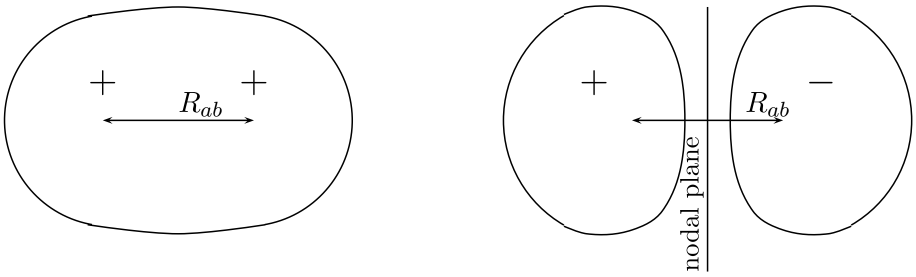


Figure 6.1 Schematic representation of the two lowest-energy MOs for H_2^+.

Here, for the ion, $\mathsf{H} = \mathsf{h}$, the 1-electron Hamiltonian, and the distinct quantities to be calculated are (using a common notation and supposing the AOs are normalized)

$$\alpha_a = \langle\chi_a|\mathsf{h}|\chi_a\rangle, \quad \beta_{ab} = \langle\chi_a|\mathsf{h}|\chi_b\rangle, \quad \alpha_b = \langle\chi_b|\mathsf{h}|\chi_b\rangle, \quad S_{ab} = \langle\chi_a|\chi_b\rangle. \tag{6.8}$$

As in Section 1.3 of Chapter 1, the conditions for a stationary value then reduce to

$$\begin{aligned}(\alpha_a - \bar{E})c_a &= -(\beta_{ab} - \bar{E}S_{ab})c_b \\ (\beta_{ab} - \bar{E}S_{ab})c_a &= -(\alpha_b - \bar{E})c_b.\end{aligned}$$

But when the system is symmetrical, as already noted, we know that $c_b = \pm c_a$ and in that case just one equation is enough to give us both eigenvalues. Thus, putting $\alpha_a = \alpha_b = \alpha$ and choosing $c_b = c_a$, the first equation reduces to $(\alpha + \beta) - \bar{E}(1 + S) = 0$; while on choosing $c_b = -c_a$ it reduces to $(\alpha - \beta) - \bar{E}(1 - S) = 0$. The approximate energies of the two states $\phi_B(\mathbf{r}), \phi_A(\mathbf{r})$, may then be written

$$\bar{E}_B = \frac{\alpha + \beta}{1 + S} = \frac{\alpha(1 + S) + \beta - \alpha S}{1 + S}, \qquad \bar{E}_A = \frac{\alpha - \beta}{1 - S} = \frac{\alpha(1 - S) - \beta + \alpha S}{1 - S},$$

where the numerators have been re-arranged so as to 'separate out' the leading terms. In this way we find

$$\bar{E}_B = \alpha + \frac{\beta - \alpha S}{1 + S}, \qquad \bar{E}_A = \alpha - \frac{\beta - \alpha S}{1 - S}. \tag{6.9}$$

Since α is the energy expectation value of an electron very close to one nucleus alone and (like β) has a negative value, it follows that the Bonding MO ϕ_B has a *lower* energy ($\bar{E}_B$) than the free- atom AO, while the Antibonding MO ϕ_A has a *higher* energy ($\bar{E}_A$). Note, however, that the upward displacement of the free-atom energy level in going to the antibonding level is greater than the downward dispacement in going to the bonding level, owing to the overlap term. All this is shown very nicely in a **correlation diagram** which shows how the energies of the AOs on two identical atoms are related to those of the MOs which result when the atoms are combined to form a **homonuclear diatomic molecule** – a 'homonuclear diatomic', for short.

Such a diagram, describing the formation of H_2, is shown in Figure 6.2, energy levels for the separate atoms being indicated on the left and right with the MO energies in the centre.

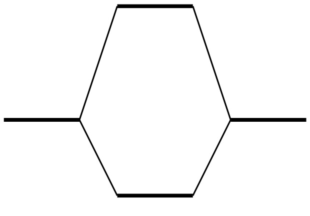


Figure 6.2 Energies of orbitals in a homonuclear diatomic.

AO levels shown left and right
MO levels shown in the centre.

Remember that we're still talking about a *one*-electron system, the hydrogen molecule positive ion, and that this is *homonuclear*. But before going to the neutral molecule, with two electrons, we may want to think also about other 2-electron systems such as HeH^+, with one of the Hydrogens (H) replaced by a Helium atom (He) and one of the three electrons taken away – giving you the **Helium Hydride positive ion**. In that case we'll have a **heteronuclear system** in which the two nuclei are different and the forms of the acceptable MOs must also be changed. Helium hydride is a very rare species, though it was important in the very early stages of the developing Universe, when there weren't many atoms around – only the very lightest ones like hydrogen and helium had already formed. But it gives us a general 'pattern' or **prototype** for the study of heteronuclear diatomic systems, which are present in great abundance in today's world. So it's worth looking at the system briefly, in the example that follows:

Example 6.1 A heteronuclear system: HeH^+.

HeH^+ is a system with two electrons moving in the field of two nuclei, but it differs from the hydrogen molecule in having a Helium nucleus (with charge $Z = 2$) in place of one of the protons. Let's take it as 'Nucleus a' in our study of H_2 and ask what MOs can be formed from the AOs χ_a and χ_b when the different atoms come together. We first take one electron away, leaving the doubly-positive ion HeH^{2+} for which the MOs may be determined. The 1-electron Hamiltonian then looks much the same as in the case of H_2^+, given in (6.1), except that the $(1/r_a)$-term will have $Z = 2$ in the numerator instead of $Z = 1$. But this is enough to destroy the symmetry and the acceptable MOs will no longer have the simple forms (6.4). Instead we must go back to the stationary value conditions to determine the mixing coefficients c_a, c_b.

Again, using β and S for short (in place of β_{ab}, S_{ab}), the coefficients may be eliminated by division to give the single equation

$$(\alpha_a - \bar{E})(\alpha_b - \bar{E}) - (\beta - S\bar{E})^2 = 0.$$

This can be solved by the method you first used in Book 1 (Section 5.3), to give two approximate eigenvalues $\bar{E}_B$ (lower energy) and $\bar{E}_A$ (upper energy). These correspond to the 'Bonding' and 'Antibonding' levels for a homonuclear system (see Figure 6.2), but solving the quadratic equation by the standard method doesn't give a simple result comparable with (6.4).

Instead, we use a simple approximation which shows directly how much the AO energies for the free atoms (roughly α_a and α_b) are respectively 'pushed down', to give $\bar{E}_B$, and 'pushed up', to give $\bar{E}_A$. The *interaction*, which does this, is caused by the term $(\beta - S\bar{E})^2$. If we neglect this term, $\bar{E} \approx \alpha_a$ – the lower of the two AO energies (corresponding to $Z = 2$) – so let's use this approximation to estimate the effect of the *other terms*: the last equation is then replaced by

$$(\alpha_a - \bar{E})(\alpha_b - \alpha_a) - (\beta - \alpha_a S)^2 = 0,$$

which gives (check it!)

$$\bar{E} - \alpha_a = -\frac{(\beta - \alpha_a S)^2}{\alpha_b - \alpha_a}.$$

This is the approximation to the lowest root of the quadratic equation, which we called $\bar{E}_B$, the energy of the Bonding MO.

A similar argument (you should try it) shows that the higher AO energy α_b is pushed *up* as a result of the mixing, giving an approximation to the energy of the Antibonding MO.

The results from Example 6.1 may be summarized as follows. The Bonding and Antibonding MOs used in describing the interaction of two different atoms to yield a heteronuclear diatomic molecule have corresponding MO energies

$$\bar{E}_B = \alpha_a - \frac{(\beta - \alpha_a S)^2}{\alpha_b - \alpha_a}, \qquad \bar{E}_A = \alpha_b + \frac{(\beta - \alpha_b S)^2}{\alpha_b - \alpha_a}. \tag{6.10}$$

These results should be compared with those in (6.5) and (6.6), which apply to a homonuclear molecule. In particular

- the lower of the two energy levels, in this case α_a, is pushed down to give the Bonding level $\bar{E}_B$. But whereas the shift for a homonuclear molecule was roughly β it is now roughly proportional to the *square* of β (neglecting the small overlap term $\alpha_a S$), divided by the difference of the free-atom energies $\alpha_b - \alpha_a$;
- the upper free-atom level is *raised* by a similar amount, to give the energy $\bar{E}_A$ of the Antibonding MO;
- these effects are both much smaller than in the case of a homonuclear system, unless the free-atom energies are close together. They are of 'second order' in the interaction term β.

The correlation diagram in Figure 6.2 is now replaced by the one shown below:

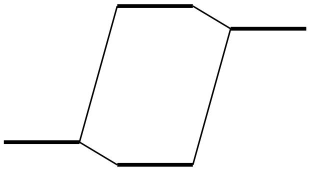


Figure 6.3 Energies of orbitals in a heteronuclear diatomic.

AO levels shown left and right
MO levels shown in the centre.

It's time to say why we're talking about "bonding" and "antibonding" orbitals. You'll remember from Book 5 that sometimes atoms 'stick together' to form molecules and other structures – gases, liquids, solids and so on. Until the early part of the last century this had to be accepted as a general 'property of matter' and further details had to be investigated experimentally. Only now, following the development of Quantum Mechanics, are we in a position to say *why* atoms behave like that. This property is called **valency**: when an atom usually sticks to only *one* other atom it is said to be *mono*-valent. But some atoms, such as Carbon, often combine with one, two, three or more others; they have a variable valency, making them *poly*-valent and giving them the possibility of forming a very rich variety of molecular structures.

The chemical bond

In Book 5, where you first met molecules, they were often represented in terms of 'ball and stick models': the 'balls' represented the atoms, while the 'sticks' that conected them, stood for the **chemical bonds** that held them together. This is still a widely used way of picturing molecules of all kinds, ranging from simple diatomics to the gigantic structures studied in the Life Sciences (see Book 9), where the molecules may contain many thousands of atoms arranged in long chains and carrying the **genetic code**.

Here, however, we are concerned with the 'sticks' that join the different atoms: what are they and how do they work? At bottom, they must be associated with the electrons and nuclei that carry negative and positive electric charge and with their *interaction energy*. And we have just seen how it is possible for even the single electron of a Hydrogen atom to enter a state of *lower energy* by bringing up a second proton, so that the electron is attracted to two positive nuclei instead of one. In that case we are imagining the formation of a molecular ion H_2^+, in which the electron occupies a Bonding MO.

Let's examine this case in more detail. In equation (6.9) we have an expression for the energy of an electron in the Bonding MO ϕ_B, as a function of the parameters α, β, and S (the 'Coulomb', 'resonance', and 'overlap' integrals). These parameters depend on the geometry of the system (i.e. the positions of the two nuclei) and are not too difficult to calculate in terms of the internuclear separation R. When this is done, the electronic energy of the system can be plotted against R and is found to increase steadily, going towards the energy of a free hydrogen atom, namely $-\frac{1}{2}e_H$, in the long-range limit $R \to \infty$. This is shown in the curve labelled "Electronic energy" in Figure 6.4 (below); but this has no *minimum* – which would indicate a stable diatomic system. So what's wrong?

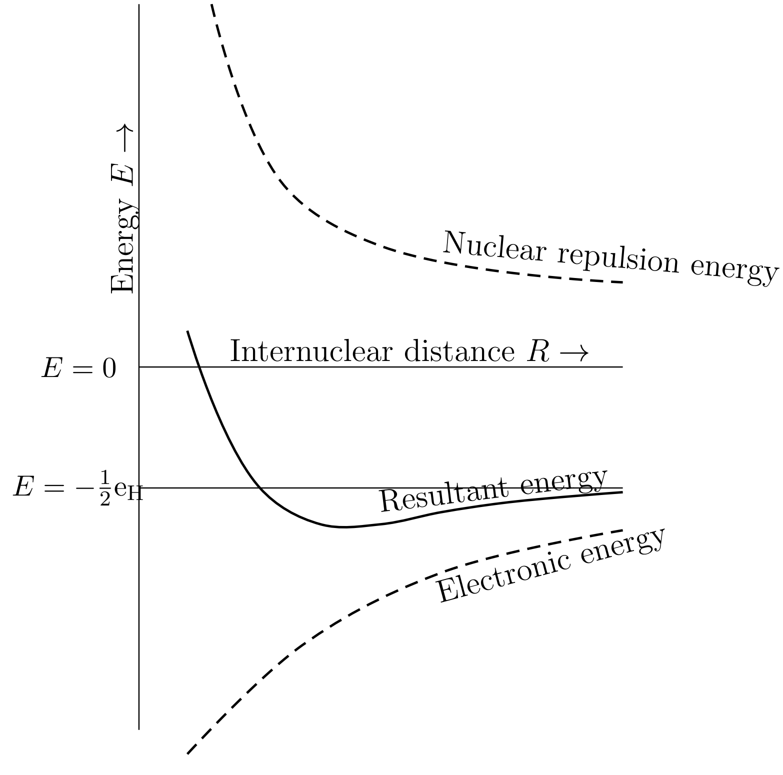


Figure 6.4 Energy curves for the Hydrogen molecule ion
Resultant energy E has its minimum at $R \approx 2\,a_0$

The fact is simply that we haven't yet included the energy of *repulsion* between the two nuclei: this is $E_{\rm nuc} \propto (1/R)$ and goes from a large positive value, when the nuclei are close together, to zero when $R \to \infty$. We didn't even include this term in the Hamiltonian (6.1) as it didn't depend on the *electronic* variables. Strictly it should be included (the protons are part of the system!); but then the expectation value $\bar{E} = \langle\phi|\mathsf{H}|\phi\rangle$, for any normalized state with wave function $\phi(\mathbf{r})$ would contain an additive constant $E_{\rm nuc}$, which can be put in at the end of the calculation. When this is done, the total energy of the system becomes the sum of two terms; the repulsion energy $E_{\rm nuc}$ and $\bar{E}_B$, the energy of the electron in the Bonding MO. The two terms are 'in competition', one falling as R increases, the other rising; and together they give a total energy $E(R)$ which shows a shallow minimum at a certain value $R = R_0$. This means there is a **chemical bond** between the two atoms, with 'bond length' R_0, *say*. The variation of all three energy terms, as functions of internuclear distance, is shown in Figure 6.4; and the total energy that results behaves as in the curve labelled "Resultant energy".

Of course, this is not for the normal hydrogen *molecule* but rather the *molecule ion* that remains when one electron is taken away. However, the energy of H_2 behaves in a very similar way: the electronic energy expression has just the same form as for any 2-electron system, as given in (2.8). The big difference is that the 1-electron terms, $\langle\Psi|\mathsf{h}(1)|\Psi\rangle$ and $\langle\Psi|\mathsf{h}(2)|\Psi\rangle$, and the 2-electon term $\langle\Psi|g(1,2)|\Psi\rangle$, are much more difficult to evaluate. Remember that the wave function we're going to use is a product $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_B(\mathbf{r}_1)\phi_B(\mathbf{r}_2)$, where both electrons are shown in the Bonding M0 ϕ_B, which decribes the state of lowest energy $2E_B$ when the interelectronic repulsion energy, $J = \langle\Psi|g(1,2)|\Psi\rangle$, is neglected. Since J is positive the total electronic energy will now have a lowest possible expectation value

$$\bar{E} = 2E_B + J,$$

corresponding to the molecular ground state. This has the same form as that for the 2-electron *atom*; but the 1-electron part, $2E_B$, will now depend on the attraction of the electron to *both* nuclei – and therefore on their separation R, which determines their positions in space. Apart from this weak dependence on R, the total electronic energy of the system will behave in much the same way as for the ion H_2^+, while the inter*nuclear* repulsion energy remains unchanged as $E_{\rm nuc}$.

The relevant energy curves for both the normal molecule and its positive ion are therefore rather similar in form. Those for the ion are shown above. The value of R at which the energy has its minimum is usually called the **equilibrium bond length** and is denoted by $R_{\rm e}$ while the energy difference between that at the minimum and that for $R \to \infty$ is called the **dissociation energy**, denoted by $D_{\rm e}$. The term "equilibrium" is of course not quite correct – the nuclei are in fact moving and it is an approximation to do the calculation as if they were at rest, for a series of fixed values of R. But it is usually a decent first approximation which can later be refined to take account of vibration and rotation of the system around its equilibrium configuration; and anyway we've made more serious approximations already in using such a simple form of the electronic wave function.

6.3 Interpretation of the chemical bond

Figure 6.4 showed the existence of a *minimum energy* when the two nuclei of a diatomic molecule were at a certain distance R_e, which we called the equilibrium bond length, but offers no explanation of how the bond originates – where does it come from? But another way of saying that the system is in equilibrium is to say that the distribution of electrons must produce forces, acting on the nuclei, that balance the force of repulsion between their positive charges. And we know already that the electron density function $P(\mathbf{r})$, defined in Chapter 5 for a general many-electron system, will give us a way of calculating the energy of interaction between the nuclei and the electron distribution.

The charges on the two nuclei produce an electric field and the potential energy function for unit charge at point $\mathbf{r}$ in that field will be $V(\mathbf{r})$; so the electron/nuclear interaction energy for one electron will be $-eV(\mathbf{r})$. When the electronic charge is, in effect, 'smeared out' with a density $P(\mathbf{r})$ electrons/unit volume, the total interaction energy will be

$$V_{\text{en}} = \int -eV(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{6.11}$$

We now want to know how the contributions to V_{en} can arise from different parts of the electron distribution. We start with a very simple example: one electron in an MO, which may be of 'bonding' or 'anti-bonding' type.

Example 6.2 Analysis of the electron density.

Let's think of an electron in a molecular orbital built up from two atomic orbitals, χ_1, χ_2, as the linear combination $\phi = c_1\chi_1 + c_2\chi_2$. The electron density function will then be (using for simplicity normalized and real MO functions)

$$P(\mathbf{r}) = c_1^2\chi_1(\mathbf{r})^2 + 2c_1c_2\chi_1(\mathbf{r})\chi_2(\mathbf{r}) + c_2^2\chi_2(\mathbf{r})^2.$$

There are three parts to the density, two 'orbital densities' and one 'overlap density';

$$d_1(\mathbf{r}) = \chi_1(\mathbf{r})^2,\ d_2(\mathbf{r}) = \chi_2(\mathbf{r})^2,\ d_{12}(\mathbf{r}) = \chi_1(bfr)\chi_2(\mathbf{r})/S_{12},$$

where $S_{12} = \langle\chi_1|\chi_2\rangle$ and all three terms are therefore normalized to unity. On writing $c_1^2 = P_{11},\ c_2^2 = P_{22},\ c_1c_2 = P_{12}$, the electron density takes the form

$$P(\mathbf{r}) = q_1d_1(\mathbf{r}) + q_2d_2(\mathbf{r}) + q_{12}d_{12}(\mathbf{r}).$$

Here $q_1 = P_{11}, q_2 = P_{22}, q_{12} = 2S_{12}P_{12}$ are the *quantities of charge*, in electron units, associated with the 'orbital' and 'overlap' densities. Provided the MO is correctly normalized, the sum of the qs must be 1 electron: $q_1 + q_2 + q_{12} = 1$. The individual qs indicate in a formal way the electron 'populations' of the various regions in space.

The following Figure 6.5 gives a very schematic picture of the electron distribution in the H_2^+ ion, according to the LCAO approximation, for the two states in which the electron occupies the Bonding MO (left) or the Anti-bonding MO (right).

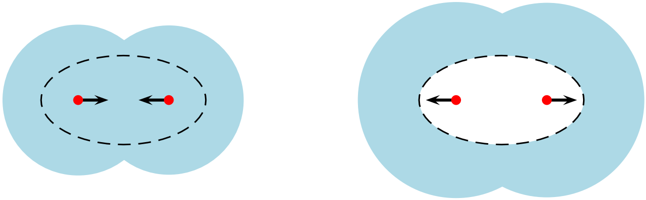


Figure 6.5 Electron density pictures (schematic) see text

The positive nuclei are shown as red dots while the distribution of electronic charge (negative) is shown in lightblue. In the bonding state the nuclei are attracted towards the accumulation of negative charge in the bond region (marked by the broken line), the forces acting on them being indicated by the short black arrows. The 'overlap density' in Example 6.5 contains a quantity of negative charge q_{12} and this provides most of the attractive force (the separate AO densities being centrosymmetric and giving no net force on their nuclei). But in the anti-bonding state the overlap density appears with a negative sign and is therefore 'scooped out' of the total electron density, the density removed being indicated in white i.e. as a 'hole' in the total density. Note that normalization of the Anti-bonding MO requires that the charge removed from the bond region must go into the two centrosymmetric AO regions. Each nucleus is therefore pulled towards the enlarged outer parts of the total density, as well as feeling the full Coulomb repulsion of the other nucleus. In this way the origin of the various energy curves in Figure 6.4 receives a nice physical explanation.

It is a simple matter to generalize the conclusions from Example 6.5 to a basis containing any number of AOs $\chi_i(\mathbf{r})$ and to any kind of *many*-electron wave function. We define normalized AO and overlap densities

$$d_i(\mathbf{r}) = \chi_i(\mathbf{r})^2, \quad d_{ij}(\mathbf{r}) = \chi_i(\mathbf{r})\chi_j(\mathbf{r})/S_{ij} \tag{6.12}$$

and write the electron density function in the usual form (cf.(5.29)), taking for simplicity real functions, $P(\mathbf{r}) = \sum_{ij} P_{ij}\chi_i(\mathbf{r})\chi_j(\mathbf{r})$. In terms of the densities defined in (6.12) it follows that

$$P(\mathbf{r}) = \sum_i q_i d_i(\mathbf{r}) + \sum_{i<j} q_{ij} d_{ij}(\mathbf{r}), \tag{6.13}$$

where the orbital and overlap charges are

$$q_i = P_{ii}, \quad q_{ij} = 2S_{ij}P_{ij} \tag{6.14}$$

and the restriction of the double summation to terms with $i < j$ makes sure that each overlap is counted only once.

This conclusion is valid for any N-electron wave function expressed in finite basis form with any number of basis functions χ_i, which need not even be AOs (though we often continue to use the term in, for example, the "LCAO approximation"). Nowadays the 'charges' 'q_i' and 'q_{ij}' are usually called orbital and overlap "populations" of the regions defined by the functions χ_i and their products $\chi_i\chi_j$; and this way of describing the results of electronic structure calculations is called "electron population analysis". It will be used often when we study particular molecules.

6.4 The total electronic energy in terms of density functions. The force concept in Chemistry

In Chapter 5 we obtained a general expression for the electron density function $\rho(\mathbf{x}_1)$ for an N-electron system of particles with spin, using $\mathbf{x}_i$ to denote the space-spin variables of Particle i. The probability of finding Particle '1' in volume element $\mathrm{d}\mathbf{x}_1 = \mathrm{d}\mathbf{r}_1\mathrm{d}s_1$ was

$$\mathrm{d}\mathbf{x}_1 \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N)\Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N)\mathrm{d}\mathbf{x}_2 \dots \mathrm{d}\mathbf{x}_N,$$

obtained by integrating over all 'positions' of the *other* particles. And, since the same result will be obtained for whichever electron is found in volume element $\mathrm{d}\mathbf{x}_1$ at point $\mathbf{x}_1$, multiplication by N will give equation (5.24). Thus, the probability/unit volume of finding a particle, *no matter which*, at point $\mathbf{x}_1$ will be

$$\rho(\mathbf{x}_1) = N \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N)\Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N)\mathrm{d}\mathbf{x}_2 \dots \mathrm{d}\mathbf{x}_N. \tag{6.15}$$

Remember that this is the probability density with spin variable included. If we're not interested in spin it's enough to sum over both spin possibilities by integrating over the spin variable s_1 to obtain a *spinless* density function $P(\mathbf{r}_1) = \int \rho(\mathbf{x}_1)\mathrm{d}s_1$. The result is the probability density for finding a particle, of *either* spin in a volume element $\mathbf{r}_1$ (e.g. $\mathrm{d}x_1\mathrm{d}y_1\mathrm{d}z_1$) at point $\mathbf{r}_1$ in ordinary 3-space. If you look back at Examples 5.6 and 5.7 in the last chapter you'll find that you've done all this before for atoms, thinking mainly of IPM-type wave functions. But the results apply to any kind of wave function (approximate or exact and for any kind of system). So now we're ready to deal with molecules.

The 1- and 2-electron density matrices, including dependence on spin variables, are

$$\rho(\mathbf{x}_1; \mathbf{x}_1') \quad \text{and} \quad \pi(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2').$$

They determine the expectation values of operator sums, such as $\sum_i \mathsf{h}(i)$ and $\sum_{i,j} \mathsf{g}(i,j)$, in any state Ψ. For example

$$\langle\Psi| \textstyle\sum_i \mathsf{h}(i)|\Psi\rangle = \int_{\mathbf{x}_1' \to \mathbf{x}_1} \mathsf{h}(1)\rho(\mathbf{x}_1; \mathbf{x}_1')\mathrm{d}\mathbf{x}.$$

From now on, to simplify the text, let's remember that the primes are only needed when an *operator* works on a density matrix, being removed immediately after the operation – so we'll stop showing them, writing the expectation values as

$$\boxed{\begin{aligned}&\langle\Psi|\textstyle\sum_i \mathsf{h}(i)|\Psi\rangle = \displaystyle\int \mathsf{h}(1)\rho(\mathbf{x}_1)\mathrm{d}\mathbf{x}_1,\\ &\langle\Psi|\textstyle\sum_{i,j} \mathsf{g}(i,j)|\Psi\rangle = \displaystyle\int \mathsf{g}(1,2)\pi(\mathbf{x}_1,\mathbf{x}_2)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2.\end{aligned}} \tag{6.16}$$

and remembering what the short forms mean.

When tiny spin-dependent terms are neglected these results may be reduced in terms of the 'spinless' density matrices $P(\mathbf{r}_1;\mathbf{r}'_1)$ and $\Pi(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2)$. The counterparts of (6.16) apply when the operators do not touch the spin variables; they become instead

$$\boxed{\begin{aligned}&\langle\Psi|\textstyle\sum_i \mathsf{h}(i)|\Psi\rangle = \displaystyle\int \mathsf{h}(1)P(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1,\\ &\langle\Psi|\textstyle\sum_{i,j} \mathsf{g}(i,j)|\Psi\rangle = \displaystyle\int \mathsf{g}(1,2)\Pi(\mathbf{r}_1\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\end{aligned}} \tag{6.17}$$

and involve only the *position* variables of typical particles

In what follows we'll use the reduced forms in (6.17), which apply when relativistic corrections are ignored. The total electronic energy of any system of N electrons, moving around a set of fixed nuclei, can then be expressed in a very simple and transparent form. The 1-electron operator for an electron at point $\mathbf{r}_1$ in ordinary 3-space is $\mathsf{h}(1) = -\frac{1}{2}\nabla^2(1)+V(\mathbf{r}_1)$ (kinetic energy plus potential energy in field of the nuclei), while the 2-electron operator for electrons at points $\mathbf{r}_1$ and $\mathbf{r}_2$ is simply the Coulomb repulsion energy, $\mathsf{g}(1,2) = 1/r_{12}$ (in atomic units), r_{12} being the interelectronic distance (the length of the vector separation $\mathbf{r}_2 - \mathbf{r}_1$). On putting these terms in the energy expectation value formula $E = \langle\Psi|\mathsf{H}|\Psi\rangle$, we find (do it!)

$$\boxed{\mathrm{E}\text{= -}\tfrac{1}{2}\int \nabla^2(1)P(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1 + \int V(1)P(\mathbf{r}_1) + \tfrac{1}{2}\int g(1,2)\Pi(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2} \tag{6.18}$$

Here the three terms are, respectively, T the total kinetic energy; V_{en}, the potential energy of a smeared out electronic charge in the field of the nuclei; and the average potential energy V_{ee} due to pairwise repulsions described by the 2-electron density $\Pi(\mathbf{r}_1,\mathbf{r}_2)$.

The Hellmann-Feynman theorem

In Section 6.3 we gave a pictorial interpretation of the chemical bond in terms of the electron density function $P(\mathbf{r})$. According to classical physics, the positively charged nuclei in a molecule would 'feel' the forces due to the distribution of negative charge in which they were embedded. But in quantum mechanics the function $P(\mathbf{r})$ gives only the *probability* of finding an electron at point $\mathbf{r}$ in 3-space; we must show that the system behaves *as if* this function were a density of negative charge. We must *define* the force acting on any nucleus in terms of things like the energy – which we know how to calculate.

To do that we first imagine the molecule to be in equilibrium, the total energy being stationary against small changes of any kind – in the wave function and in the potential energy function $V(\mathbf{r})$ (e.g. due to a field applied from outside the molecule, or change of nuclear positions). Since

$$E = \int \mathsf{h}(1)P(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1 + \tfrac{1}{2}\int \mathsf{g}(1,2)\Pi(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2,$$

the first-order changes to be considered result from $\delta\mathsf{h}$ and the density functions $\delta P(1)$ and $\delta\Pi(1,2)$. The total first-order energy change will therefore be (noting that the operators $\nabla^2(1)$ and $\mathsf{g}(1,2)$ remain unchanged)

$$\delta E = \int \delta\mathsf{h}(1)P(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1 + \int \mathsf{h}(1)\delta P(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1 + \tfrac{1}{2}\int g(1,2)\delta\Pi(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \tag{6.19}$$

and the stationary value condition will follow on equating this quantity to zero.

Now suppose that the density functions have been fully optimized by varying the energy in the absence of any perturbation term $\delta\mathsf{h}(1)$. In that case only the last two terms remain in (6.19) and their sum must be equated to zero. Thus

The first-order energy change arising from the perturbation $\mathsf{h}(1) \rightarrow \mathsf{h}(1) + \delta\mathsf{h}(1)$ is given by $\delta E = \int \delta\mathsf{h}(1)P(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1$, provided the wave function Ψ is fully optimized in the absence of the perturbation.

(6.20)

This is usually called the "Hellmann-Feynman theorem in its general form". It was discovered by Hellmann (1937) for the special case where the perturbation was due to a change of nuclear position and independently, two years later, by Feynman. In thinking about the *forces* that hold the nuclei together in a molecule we first have to define them: if we move one nucleus, nucleus n say, through a distance δX_n in the direction of the x-axis, we'll change the total energy of the molecule by an amount δE given in (6.20). And in this case $\delta\mathsf{h}(1) = \delta V_n(\mathbf{r}_1)$, the corresponding change in potential energy of an electron at point $\mathbf{r}_1$ in the field of the nucleus.

Now the *rate* of decrease of this potential energy is the limiting value of $-\delta V_n(\mathbf{r}_1)/\delta X_n$ as $X_n \to 0$ and measures the x-component of the *force* acting between Nucleus n and an electron at point $\mathbf{r}_1$. Thus we may write

$$-\frac{\partial V_n(\mathbf{r}_1)}{\partial X_n} = F_{nx}(\mathbf{r}_1)$$

and this defines the force component on Nucleus n due to an electron at $\mathbf{r}_1$.

A similar argument applies to the *total* electronic energy E due to interaction with all the electrons: its rate of decrease on moving Nucleus n through a distance X_n will be $-\partial E/\partial X_n$ and will give the x-component F_{nx} of the total force exerted on Nucleus n by all the electrons. Thus

$$-\frac{\partial E}{\partial X_n} = F_{nx}$$

defines the x-component of total force on Nucleus n due to interaction with the whole electron distribution.

Having defined the forces, in terms of energy derivatives, we return to (6.20). Here, putting $\delta\mathsf{h}(1) = \delta V_n(\mathbf{r}_1)$, dividing by δX_n and going to the limit $\delta X_n \to 0$, we find

$$F_{nx} = \int F_{nx}(\mathbf{r}_1)P(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1. \tag{6.21}$$

In words, the x-component of the total force on any nucleus (n) may be computed by adding (integrating) the contributions arising from all elements of the charge cloud. This is true for any component and therefore the force *vector* acting on any nucleus in the molecule can be calculated in exactly the same way: once the electron density has been computed by quantum mechanics the forces holding the nuclei together may be given an entirely classical interpretation. When the molecule is in equilibrium it is because the forces exerted on the nuclei by the electron distribution are exactly balanced by the repulsions between the nuclei – as they were in Figure 6.4.

This beautiful result seems too good to be true! Apparently only the electron density function $P(\mathbf{r}_1)$ is needed and the 2-electron function $\Pi(\mathbf{r}_1, \mathbf{r}_2)$, which is vastly more difficult to calculate, doesn't come into the picture. So what have we overlooked?

In deriving (6.21) we simply took for granted that the variational wave function Ψ was *fully optimized*, against all the parameters it may contain. But in practice that is hardly ever possible. Think, for example, of an LCAO approximation, in which the atomic orbitals contain size parameters (orbital exponents) and the coordinates of the points around which they are centred: in principle such parameters should be varied in the optimization, allowing the orbitals to expand or contract or to 'float away' from the nuclei on which they are located. In practice, however, that is seldom feasible and the Hellmann-Feynman theorem remains an idealization – though one which is immensely useful as a qualitative tool for understanding molecular structure even at a simple level.

Chapter 7

Molecules: Basic Molecular Orbital Theory

7.1 Some simple diatomic molecules

We start this chapter by going back to the simple theory used in Chapter 6, to see how well it works in accounting for the main features of molecules formed from the elements in the first row of the Periodic Table.

In Section 6.2 we studied the simplest possible diatomic system, the Hydrogen molecule positive ion H_2^+, formed when a proton approaches a neutral Hydrogen atom. And even in Chapter 5 we had a glimpse of the Periodic Table of all the elements: the first ten atoms, with their electron configurations, are

Hydrogen[$1s^1$] Helium[$1s^2$] Lithium[$1s^2 2s^1$] Beryllium[$1s^2 2s^2$]

in which the first two s-type AOs are filling (each with up to two electrons of opposite spin component, $\pm\frac{1}{2}$), followed by six more, in which the p-type AOs (p_x, p_y, p_z) are filling with up to two electrons in each.

Boron[$1s^2 2s^2 2p^1$] Carbon[$1s^2 2s^2 2p^2$] Nitrogen[$1s^2 2s^2 2p^3$]

Oxygen[$1s^2 2s^2 2p^4$] Fluorine[$1s^2 2s^2 2p^5$] Neon[$1s^2 2s^2 2p^6$]

Helium, with two electrons in the 1s shell, doesn't easily react with anything; it is the first Inert Gas atom. So let's turn to Lithium, with one 2s electron outside its $(1s)^2$ inner shell, and ask if this would react with an approaching atom of Hydrogen. We could, for example, try to calculate the total electronic energy E using the Self-Consistent Field method (see Chapter 4) and then adding the nuclear repulsion energy, as we did for the molecule H_2 in Section 6.2. Again, as we don't have any 'ready-made' *molecular* orbitals we have to build them out of a set of **basis functions**, $\chi_1,\ \chi_2,\ ...\ \chi_i\ ...$ and it seems most reasonable to choose these as the *atomic* obitals of the atoms we are dealing with, writing the MO ϕ as

$$\phi = c_1\chi_1 + c_2\chi_2 + \ ......\ c_m\chi_m \tag{7.1}$$

for a basis of m functions. This is the famous LCAO (linear combination of atomic orbitals) approximation, which is the one most widely used in molecular structure calculations. In principle, if the basis set is large enough, this could be a fairly accurate approximation.

As you learnt in Chapter 4 (you should go back there for the details) the MOs should really be determined by solving the operator equation

$$\mathsf{F}\phi = \epsilon\phi \quad [\text{the Hartree} - \text{Fock equation}] \tag{7.2}$$

but the best we can do, in LCAO approximation, is to choose the expansion coefficients so as to minimize the calculated value of the total electronic energy E. The best approximate MOs of the form (7.1), along with their corresponding orbital energies (ϵ) are then determined by solving the **secular equations**

$$\mathbf{Fc} = \epsilon\mathbf{c}, \tag{7.3}$$

where $\mathbf{c}$ is the column of expansion coefficients in (7.1) and $\mathbf{F}$ is the square matrix representing the effective Hamiltonian F – which has elements $F_{ij} = \langle\chi_i|\mathsf{F}|\chi_j\rangle$.

(Note that this simple form of the secular equations, depends on using **orthogonal** basis functions; but if overlap is not small enough to be neglected it may be removed by choosing new combinations – work which is easily done by modern computers.)

In a first example, we summarize an early SCF calculation on the LiH system.

Example 7.1 The Lithium Hydride molecule: LiH.

In the SCF calculation by Ransil (1960) the AO basis used consisted of the 1s, 2s and 2p orbitals of the Lithium atom, together with a single 1s orbital for the Hydrogen. The basis functions were thus χ_{1s}, χ_{2s}, χ_{2p}, χ_H, where the first three are centred around the Li nucleus (only one p function is needed, that with symmetry around the bond axis) and the last is a 1s-type function, centred on the proton. The Lithium 1s AO is tightly localized around the nucleus ($Z = 3$) and in good approximation does not mix with the other functions. The MOs that come from the 4-electron SCF calculation are then found to be

$$\phi_{1\sigma} \approx \chi_{1s}; \quad \phi_{2\sigma} \approx 0.323\chi_{2s} + 0.231\chi_{2p} + 0.685\chi_H.$$

The electron configuration of the molecule will then be, with four electrons, LiH[$1\sigma^2 2\sigma^2$].

This indicates a Lithium inner shell, similar to that in the free atom, and a bonding MO 2σ containing 2 electrons. But the bonding MO is not formed from one 2s AO on the Lithium atom, overlapping with the Hydrogen 1s AO; instead, it contains *two* AOs on the Lithium atom. If we want to keep the simple picture of the bond, as resulting from the overlap of two AOs, one on each atom, we must accept that the 'AO's need not be 'pure' but may be *mixtures* of AOs on a single centre. Ransil's calculation shows that a much clearer description of LiH is obtained by rewriting his MO in the form

$$\phi_{2\sigma} \approx 0.397\chi_{hyb} + 0.685\chi_H,$$

where $\chi_{hyb} = 0.813\chi_{2s} + 0.582\chi_{2p}$ is called a *hybrid* orbital and this kind of mixing is called *hybridization*. The general form of this Lithium hybrid AO is indicated below in Figure 7.1, in which the contour lines correspond to given values of the function χ_{hyb}. The broken line marks the 'nodal surface' separating negative and positive values of χ_{hyb}. The energy is lowered by hybridization, which increases the strength of the bonding by putting more electron density (i.e. negative charge) between the positive nuclei; but this is offset by the energy $\epsilon_{2p} - \epsilon_{2s}$ needed to 'promote' an electron from a 2s state to a 2p state. So hybridization is favoured for AOs of similar energy and resisted when their energy difference is large.

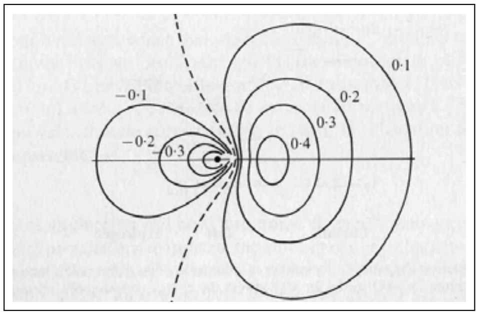


Figure 7.1 Contour map for the s-p hybrid orbital χ_{hyb}

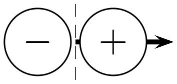
The capacity of an atom to form chemical bonds with other atoms is known as **valency** and is often measured by the number of bonds it can form. Lithium in LiH is *mono*-valent, but Oxygen in H_2O is *di*-valent and Carbon in CH_4 is *quadri*-valent. But many atoms show variable valency, depending on the nature of the atoms they combine with and on the degree of hybridization involved. In Example 7.1 the Lithium atom is said to be in a "valence state", depending on the degree of 2s-2p mixing, and this may usefully be decribed in terms of the electron populations introduced in Section 6.3. If the hybrid orbital is written as the mixture $\chi_{hyb} = a\chi_{2s} + b\chi_{2p}$, an electron in χ_{hyb} gives a probability density $P_{hyb} = a^2\chi_{2s}^2 + b^2\chi_{2p}^2 + 2ab\chi_{2s}\chi_{2p}$. Integration over all space gives unity (1 electron), with a^2 coming from the 2s density, b^2 from the 2p and nothing from the last term (the AOs being orthogonal). We can then say that the 2s and 2p AOs have electron populations a^2 and b^2, respectively, in the molecule. The electron configuration of the Lithium atom, in the molecule, could thus be written Li[$1s^2 2s^{0.661} 2p^{0.339}$] (according to Example 7.1) the numbers being the values of a^2 and b^2 for an electron in the 'valence orbital' χ_{hyb}. The atom never actually passes through a 'valence state'; but the concept is none the less valuable. For example, the idea that a fraction of an electron has been 'promoted' from a 2s orbital to an empty 2p shows why hybridization, to produce strong bonds, is most common for elements on the left side of the Periodic Table, where the 2s-2p energy separation is small.

Now let's try something a bit more complicated. If we replace Lithium by Carbon we shall have *four* electrons outside the tightly-bound 1s shell, two of them in the next-higher energy 2s orbital and two more in the slightly-higher energy 2p orbitals ($2p_x$,$2p_y$,$2p_z$). These four are not too strongly bound to prevent them taking part in bonding with other atoms, so they are are all available as **valence electrons**. And if we go two places further along the First Row we come to Oxygen, which has six electrons outside its $1s^2$ inner shell – all available, to some degree, for bonding to other atoms. The energy difference between the 2s and 2p orbitals increases, however, with increasing nuclear charge; and as a result the elements C and O have rather different valence properties. In the next example we'll try to understand what can happen when these two atoms come together and begin to share their valence electrons.

Example 7.2 The Carbon monoxide molecule: CO.

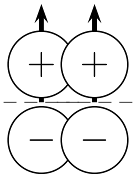
The $1s^2$ inner shells, or 'cores', of both atoms are so strongly bound to their nuclei that the main effect they have is to 'screen' the positive charges (Ze, with Z=6 for the carbon atom and Z=8 for oxygen); the 'effective' nuclear charges are then closer to $Z_{eff} = 4$, for C, and 6 for O. We'll therefore think about only the valence electrons, asking first what MOs can be formed to hold them.

We already know that the AOs on two different atoms tend to combine in pairs, giving one bonding MO along with an anti-bonding partner; and that this effect is more marked the more strongly the AOs *overlap*. Think of the 2s AOs as spheres and the 2p AOs as 'dumbells',



Here the + and − parts indicate regions in which the wave function χ is positive or negative. Unlike an s-type AO, one of p-type is associated with a definite *direction* in space, indicated by the arrow. For the CO molecule, the 2s AOs on the two centres will not overlap strongly as they come together, owing to their size difference (the oxygen 2s being smaller – can you say why?). They might give a weakly bonding MO, consisting mainly of the oxygen 2s AO, which we'll call $1\sigma_s^*$) as it would be the first MO with rotational symmetry around the 2-centre axis. On the other hand, the oxygen $2p_z$ AO pointing along the axis towards the carbon would have a fairly good overlap with the carbon 2s AO. In that case we might expect, as usual, two MOs; one bonding (call it $2\sigma_s$) and the other anti-bonding ($2\sigma_s^*$.)

However, there are *three* 2p AOs on each centre, the $2p_x$ and $2p_y$, both transverse to the bond axis (along which we've directed the $2p_z$ AO). They are of π-type symmetry and, when pairs of the same type come close together, they will have a good side-to-side or 'lateral' overlap:



In summary, the orbitals available for holding the 10 valence electrons would seem to be

•1σ – the first MO of σ type, mainly Oxygen 2s

•2σ – a bonding MO, formed from Carbon 2s and Oxygen $2p_z$

•3σ – an anti-bonding MO, the partner of 2σ

•$1\pi_x$ – a π-bonding MO, formed from $2p_x$ AOs on C and O

•$1\pi_y$ – a π-bonding MO, formed from $2p_y$ AOs on C and O

To assign the electrons to these MOs we look at the probable correlation diagram.

The correlation diagram for the CO molecule, with neglect of hybridization on one or both atoms, would seem to be that shown below in Figure 7.2:

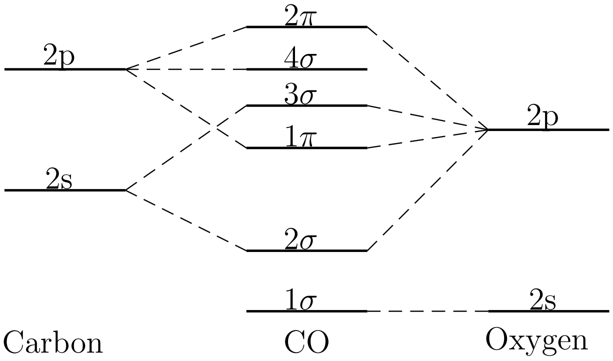


Figure 7.2 Correlation diagram for CO, no hybrids

Notice that the 2p AOs take part in both $\sigma-$ and π-type MOs: the 2σ and 3σ MOs will each have a $2p_z$ component (also symmetrical around the CO axis) while the 1π MO is degenerate, with $1\pi_x$ and $1\pi_y$ MOs containing only $2p_x$ and $2p_y$ AOs, respectively. The $1\pi_x$ and $1\pi_y$ MOs are formed from the 'side-by-side' overlap of 2p AOs perpendicular to the CO axis (shown pictorially in Example 7.2). The highest occupied MO (often called the "HOMO") is 3σ and is apparently *anti*-bonding.

This all looks a bit strange, because we know from Example 1 that the mixing of AOs is likely to be much more widespread, mixtures of AOs on each centre giving 1-centre *hybrids* which can better describe the results of a good SCF calculation. Moreover, experiment shows the picture to be quite wrong! In particular the main CO σ bond is very strong, while here it would be largely 'cancelled' by the anti-bonding effect of the electrons in the 3σ MO. There is also evidence for a lone pair of electrons smeared out behind the Carbon, but here there seems to be no MO to hold them. We must ask how this picture is changed on admitting hybridization: the conclusion is shown in Figure 7.3 below.

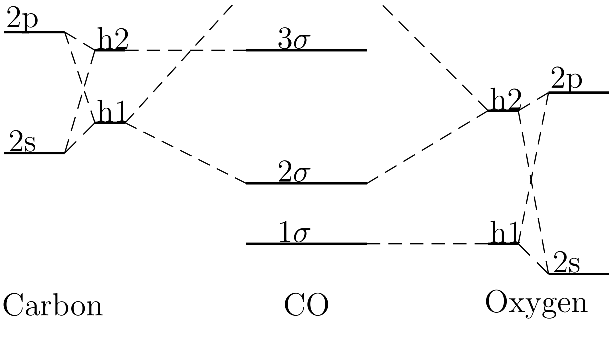


Figure 7.3 Correlation diagram for CO, with hybrid AOs

Even without doing a full SCF calculation, a qualitative argument leads easily to the same conclusion. By allowing for the mixing of 2s and 2p AOs on Carbon and on Oxygen (s and p orbital energies being fairly close together), the correlation diagram in Figure 7.2 must be re-drawn. The result is that shown in Figure 7.3, where the 2s and 2p orbital energies are again indicated on the extreme left (for Carbon) and extreme right (for Oxygen). But now, when these AOs are allowed to mix – forming hybrids, the (2s) AO of lower energy must be raised in energy – owing to the inclusion of a bit of 2p character; while the energy of an electron in the upper AO must be lowered, by inclusion of 2s character. The effects of s-p hybridization are indicated by the broken lines connecting the hybrid energies with the energies of their 'parent' AOs.

The probable orbital energies of the MOs in the CO molecule are shown in the centre of the diagram. The broken lines now show how the MO energy levels arise from the hybrid levels to which they are connected. The energies of the π-type MOs are not affected by the hybridization (containing only 2p$_x$ and 2p$_y$ AOs) and remain as in Figure 7.2 – with the 1π level (not shown)lying between the 2σ and 3σ MO energies.

When we assign the 10 valence electrons to these MOs we find

- a pair of electrons in the 1σ MO, which is mainly Oxygen 2s;
- a pair in the 2σ MO, the bonding combination of strongly overlapping hybrids, pointing towards each other along the bond axis;
- two pairs in the bonding 1π-type MOs, transverse to the bond axis; and
- a pair in the 3σ MO, which is mainly a Carbon hybrid and is too high in energy to mix with σ-type AOs on the other atom.

Now let's look at the electron density (density of negative charge), which is given, as a function of position in space, by $|\phi|^2$ for an electron in the MO ϕ. (If you're not yet ready to follow all the details you can skip the following part, in small type, and come back to it later.)

The first MO (above) gives a density $|\phi|^2$ roughly spherical and strongly bound to the Oxygen 1s^2 'core', but leaning slightly away from the Carbon (can you say why?)

The second MO gives a density concentrated on and around the CO axis, between the two atoms, providing a strong σ bond

The third MO is degenerate, with density contributions $|\phi_x|^2$ and $|\phi_y|^2$ where, for example, $\phi_x = c_a\phi^a_{2p_x} + c_b\phi^b_{2p_x}$ – a linear combination of 2p$_x$ AOs on the two atomic centres. At a general point P(x, y, z), a 2p$_x$ AO has the form $xf(r)$, where distances are measured from the nucleus and the function $f(r)$ is spherically symmetrical. If you rotate a 2p$_x$ AO around the z axis it will change only through the factor x; and the same will be true of the combination ϕ_x.

The whole electron density function will thus change only through a factor $x^2 + y^2 = r_z^2$, where r_z is the distance of Point P from the CO bond axis. A 'slice' of density, of thickness dz, will be a circular disk of charge – with a hole in the middle because r_z falls to zero on the bond axis. The two π bonds together therefore form a hollow 'sleeve' of electron density, with the σ distribution inside – along the axis.

The 3σ HOMO now comes *below* the 4σ *anti-bonding* MO and does not diminish the strong σ bond in any way. It provides essentially a lone-pair electron density, localized mainly on the Carbon. Moreover, this density will point away from the CO σ-bond because h2 and h1 stand for *orthogonal* orbitals – and h1 points into the bond.

In summary, it seems that when hybridization is admitted everything can be understood!

The CO molecule should have a **triple bond**, a strong σ bond supported by two weaker π bonds; and the Carbon should have a region of lone-pair electron density on the side away from the C≡O triple bond – all in complete agreement with its observed chemical properties.

7.2 Other First Row homonuclear diatomics

The CO molecule has 10 (=4+6) valence electrons outside the $1s^2$ cores and is therefore **'isoelectronic'** with the Nitrogen molecule, N_2, which is homonuclear and therefore has a symmetrical correlation diagram. The molecules, Nitrogen (N_2,) Oxygen (O_2) and Fluorine (F_2), with 10, 12 and 14 valence electrons, respectively, all have similar energy-level diagrams; but differ in the way the levels are filled as electrons are added. This is all part of the so-called "aufbau approach" ("aufbau" being the German word for "building up") in which electrons are added one at a time to the available orbitals, in ascending order of orbital energy. The First Row atoms use only 1s,2s and 2p AOs, in which only the 2s and 2p AOs take part in molecule building (see for example Figure 7.2). But in homonuclear diatomics the two atoms are identical and the correlation diagram is simpler because orbitals of identical energy interact very strongly and hybridization may often be neglected. For First Row atoms a typical diagram is shown in Figure 7.4, below.

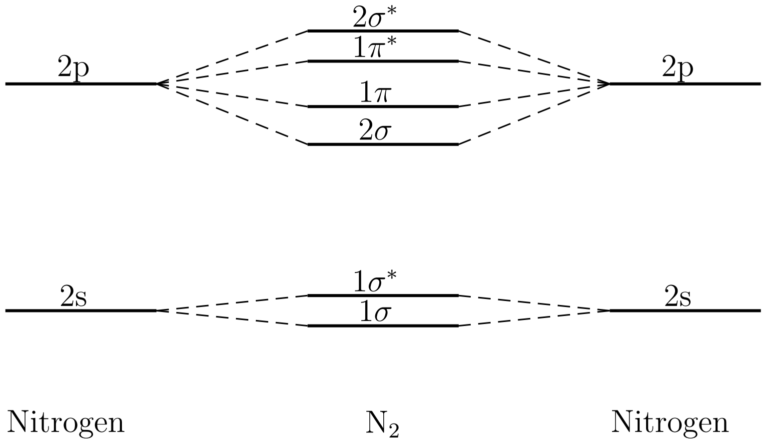


Figure 7.4 Correlation diagram for N_2, no hybrids

Note that the 2s AOs give rise to the bonding and anti-bonding MOs denoted by 1σ and 2σ (first and second valence MOs of σ symmetry, but the 2p AOs, three on each centre, give MOs of both σ and π type. For clarity it is sometimes useful to use an alternative notation in which, for example, the first valence MO and its anti-bonding partner are called 1σ and $1\sigma^*$. The MOs can then be put in order of increasing energy and displayed as

$$1\sigma \quad \Rightarrow \quad 1\sigma^* \quad \Rightarrow \quad 2\sigma_z \quad \Rightarrow \quad (1\pi_x, 1\pi_y) \quad \Rightarrow \quad (1\pi_x^*, 1\pi_y^*) \quad \Rightarrow \quad 2\sigma_z^*$$

where the arrows indicate increasing order of orbital energies and the subscript z refers to the bond axis, while x and y label the transverse axes. The π-type MOs are degenerate, x and y components having identical energies.

The electron configurations of most of the homonuclear diatomics in the First Row conform to the above order of their MO energy levels. Let's take them one at a time, starting again with Nitrogen.

Nitrogen

Following the aufbau procedure, the first two of the ten valence electrons should go into the 1σ MO with opposite spins; the next two will go into its antibonding partner $1\sigma^*$ – more or less undoing the bonding effect of the first pair; two more go into the $2\sigma_z$ MO which is strongly bonding, being formed from $2p_z$ AOs pointing towards each other. But then there are four MOs, all of π type, formed from the $2p_x$ and $2p_y$ AOs on the two atoms, which are perpendicular to the σ bond: they are $1\pi_x$, $1\pi_y$ and their anti-bonding partners ($1\pi_x^*$, $1\pi_y^*$) – all before we come to $2\sigma_z^*$, which is well separated from $2\sigma_z$ owing to the strong overlap of the component $2p_z$ AOs. The remaining four of the 10 valence electrons nicely fill the two bonding MOs and give two bonds of π type.

The end result will be that N_2 has a *triple* bond and the electron configuration

$$1\sigma^2\, 1\sigma^{*\,2} 2\sigma_z^2\, 1\pi_x^2\, 1\pi_y^2.$$

The next First Row diatomic will be

Oxygen

Here there are 12 valence electrons, two more than in N_2, and they must start filling the *anti*-bonding π-type MOs. But we know that when two orbitals are degenerate electrons tend to occupy them singly: so $1\pi_x^{*1}\, 1\pi_y^{*1}$ is more likely than, say, $1\pi_x^{*2}$. And each antibonding π electron will 'cancel' half the effect of a bond *pair*.

The probable result is that O_2 will have a *double* bond and an electron configuration such as

$$1\sigma^2\, 1\sigma^{*2}\, 2\sigma_z^2\, 1\pi_x^2\, 1\pi_y^2\, 1\pi_x^{*1}\, 1\pi_y^{*1}.$$

Moreover, the electrons in the singly-occupied MOs may have their spins parallel-coupled – giving a triplet ground state ($S = 1$). This means that Oxygen may be a **paramagnetic** molecule, attracted towards a magnetic field. All this is in accord with experiments in the laboratory. Of course, the 'theory' we are using here is much too simple to predict things like spin coupling effects (we haven't even included electron interaction!) but experiment confirms that the last two electrons do indeed have their spins parallel-coupled to give a triplet state.

Fluorine

The electron configuration for the molecule F_2 is obtained by adding two more valence electrons. This will complete the filling of the π-type anti-bonding MOs, to give the configuration

$$1\sigma^2\, 1\sigma^{*2}\, 2\sigma_z^2\, 1\pi_x^2\, 1\pi_y^2 1\pi_x^{*2} 1\pi_y^{*2}.$$

The pairs of electrons in the $1\pi_x^*$ and $1\pi_y^*$ MOs then take away the effect of those in the corresponding bonding MOs, removing altogether the π bonding to leave a single σ bond.

Neon

The molecule Ne_2 does not exist! Neon is an **inert gas**, like Helium, its atoms not forming covalent bonds with anything. The reason is simply that, on adding two more electrons, every bonding MO has an anti-bonding partner that is also doubly occupied. Every Row of the Periodic Table that ends with the filling of a 'shell' of s- and p-type AOs has a last atom of inert-gas type: the inert-gas atoms are Helium (He), Neon (Ne), Argon (A), Krypton (Kr), Xenon (Xe), Radon (Rn), with values of the principal quantum number n going from $n = 1$ up to $n = 6$.

Here we are dealing only with the First Row, that ends with Neon and contains only the first 10 elements, but we started from Nitrogen (atomic number $Z = 7$) and continued in order of increasing Z. The atom before that is Carbon, the most important of the ones we left out. So let's do it now.

Carbon

Carbon has only 4 valence electrons outside its $1s^2$ core, so if a C_2 molecule exists we should have to assign 8 electrons to energy levels like the ones shown in Figure 7.4 – corresponding to the MOs

$$1\sigma, \quad 1\sigma^*, \quad 2\sigma_z, \quad (1\pi_x,\, 1\pi_y), \quad (1\pi_x^*,\, 1\pi_y^*), \quad 2\sigma_z^*.$$

Before we start, however, remember that the s- and p-type energy levels get closer together as the effective nuclear charge ($Z_{\mathrm{eff}} \approx Z - 2$) gets smaller; and this means that the 2s and $2p_z$ AOs must be allowed to mix, or 'hybridize', as in Figure 7.3, where the mixing gives rise to hybrids h_1 and h_2. h_1 is largely 2s, but with some $2p_z$ which makes it 'lean' into the σ bond; h_2, being orthogonal to h_1, will be largely $2p_z$, but pointing away from the bond. This will be so for both Carbons. The correlation diagram should then have the form

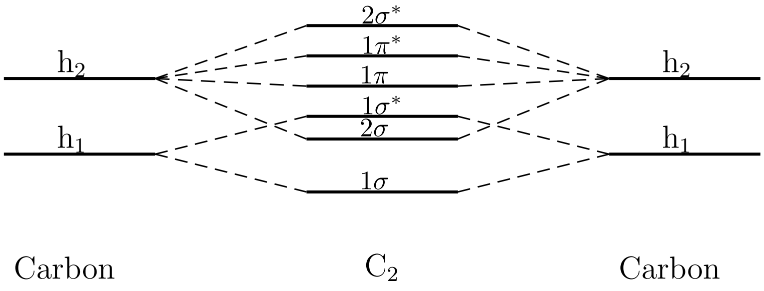


Figure 7.5 Correlation diagram for C_2, with hybrids

– where the h_1 and h_2 levels are now relatively close together and the order of the MO levels they lead to is no longer 'standard'. The order in which they are filled up, in the 'aufbau', will now be

$$1\sigma, \quad 2\sigma_z, \quad 1\sigma^*, \quad (1\pi_x, 1\pi_y), \quad (1\pi_x^*, 1\pi_y^*), \quad 2\sigma_z^*,$$

as you can see from Figure 7.5.

For C_2, however, we have only 8 valence electrons. The expected electron configuration in the ground state will therefore be

$$1\sigma^2\, 2\sigma_z^2\, 1\sigma^{*\,2}\, 1\pi_x^1\, 1\pi_y^1,$$

where the last two electrons have been put in the two degenerate 1π MOs. Electrons in the 1σ MO and its anti-bonding partner should therefore give no effective bonding, the first σ bond coming from the 2σ MO – which arises from strongly overlapping hybrids, pointing towards each other along the z axis. The strong σ bond would be supplemented by two 'half' π bonds; so the C_2 molecule could be pictured as a double-bonded system C=C, with electron density similar to that in N_2 but with the 'sleeve' of π density containing only 2 electrons instead of 4. Moreover, the ground state could be either a *triplet*, with $S = 1$, or a singlet ($S = 0$), since the Pauli principle does not come in when the two electrons are in different orbitals. As in the case of Oxygen, the theory is much too simplified for predicting singlet-triplet energy differences: experiment shows the ground state is this time a singlet.

But what about the electrons in the 1σ and $1\sigma^*$ MOs? These orbitals are built as combinations of hybrids pointing *away from* the C−C bond (remember h_1 is orthogonal to h_2, which points *into* the bond). You can think of these 'sleeping' electrons as lone pairs, sticking out at the back of each Carbon atom. Consequently, the C_2 molecule will be easily attacked by any positively charged species – attracted by a region of negative charge density. In fact, C_2 is a highly reactive system and does not exist for long as an independent molecule – as the next example will suggest.

Example 7.3 What will happen if C_2 is approached by a proton?

To keep things symmetrical let's suppose a proton comes close to each of the two Carbons. In that case all the 8 valence electrons will 'feel' an attraction towards two centres, each with effective positive charge $Z_{\text{eff}} = 3$. This will be similar to that for Nitrogen ($Z = 7$, $Z_{\text{eff}} = 7 - 2 = 5$ and the energy level diagram would therefore look more like that for the N_2 molecule, shown in Figure 7.4.

But in fact we are talking about a system with only 8 valence electrons, which would correspond to the doubly positive *ion* N_2^{++}, and our model is a bit unrealistic – because bare protons do not float about in space waiting to be put wherever we please! They are usually found in the company of an electron – in the atom of Hydrogen. And if the protons bring their electrons with them where will they go?

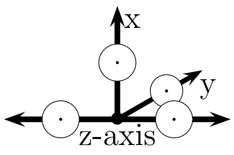
The actual C_2 system (forgetting for the moment about the protons we've added) would have the electron configuration $1\sigma^2\, 2\sigma_z^2\, 1\sigma^{*\,2}\, 1\pi_x^1\, 1\pi_y^1$, – with places waiting for the two extra electrons. When they are filled, the system will have a closed-shell ground state with all MOs doubly occupied. But the system is no longer C_2: we've added two Hydrogen atoms and made a new molecule H−C≡C−H. We're doing Chemistry!

Of course, the orbitals in the new molecule H−C≡C−H, which is called **Acetylene**, are not quite the same as in C_2: the lone-pair orbitals (h_2), which we imagined as "sticking out at the back of each Carbon atom" now have protons embedded in them and describe two C−H bonds. Here, in dealing with our first **polyatomic molecule**, we meet a new problem: acetylene apparently has two CH single bonds and one CC triple bond. We are thinking about them as if they were independently localized in different regions of space; but in MO theory the bonding is described by *non*-localized orbitals, built up as linear combinations of much more localized AOs. All the experimental evidence points towards the existence of localized bonds with characteristic properties. For example, the **bond energies** associated with CC and CH links are roughly additive and lead to molecular **heats of formation** within a few per cent of those measured experimentally. Thus, for acetylene, taking the bond energies of C−H and C≡C as 411 and 835 kJ mol^{-1}, respectively, gives an estimated heat of formation of 1657 kJ mol^{-1} – roughly the observed value. (If you've forgotten your Chemistry you'd better go back to Book 5; Science is all one!)

Next we'll ask if similar ideas can be applied in dealing with other polyatomic molecules.

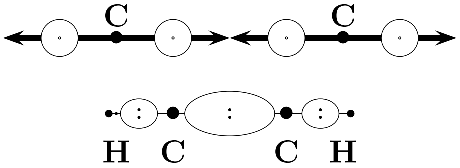
7.3 Some simple polyatomic molecules; localized bonds

The discussion of H−C≡C−H can easily be put in pictorial form as follows. Each Carbon atom can be imagined as if it were in a **valence state**, with two of its four valence electrons in hybrid orbitals sticking out in opposite directions along the z axis and the other two in its $2p_x$ and $2p_y$ AOs. This state can be depicted as



where the Carbon is shown as the bold dot in the centre, while the bold arrows stand for the hybrids h_1 and h_2, pointing left and right. The empty circles with a dot in the middle indicate they are singly occupied. The arrows labelled 'x' and 'y' stand for the $2p_x$ and $2p_y$ AOs, pointing in the positive directions (− to +), and the circles each contain a dot to stand for single occupation.

The electronic stucture of the whole molecule H−C≡C−H can now be visualized as



where the upper diagram represents the two Carbon atoms in their valence states (π-type MOs not indicated); while the lower diagram shows, in very schematic form, the electronic structure of the molecule H$-$C$\equiv$C$-$H that results when they are brought together and two Hydrogens are added at the ends. The C$\equiv$C triple bond arises from the σ-type single bond, together with the π_x- and π_y-type bonds (not shown) formed from side-by-side overlap of the $2p_x$ and $2p_y$ AOs. The two dots indicate the pair of electrons occupying each localized MO.

Acetylene is a *linear* molecule, with all four atoms lying on the same straight line. But exactly the same principles apply to two- and three-dimensional systems. The **Methyl radical** contains four atoms, lying in a plane, Carbon with three Hydrogens attached. **Methane** contains five atoms, Carbon with four attached Hydrogens. The geometrical forms of these systems are experimentally well known. The radical (so-called because it is not a stable molecule and usually has a very short lifetime) has its Hydrogens at the corners of an equilateral triangle, with Carbon at the centre; it has been found recently in distant parts of the Universe, by astronomical observation, and suggests that Life may exist elswhere. Methane, on the other hand, is a stable gas that can be stored in cylinders and is much used in stoves for cooking; its molecules have four Hydrogens at the corners of a regular tetrahedron, attached to a Carbon at the middle. These shapes are indicated in Figure 7.6 below.

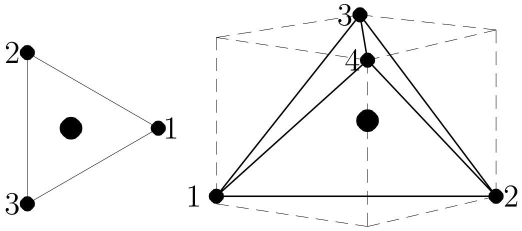


Figure 7.6 Shapes of the Methyl radical and the Methane molecule

In the Figure the large black dots indicate Carbon atoms, while the smaller ones show the attached Hydrogens. In the Methyl radical (left) the Hydrogens are at the corners of a flat equilateral triangle. In Methane (right) they are at the corners of a **regular tetrahedron**, whose edges are shown by the solid lines. The tetrahedron fits nicely inside a cube, which conveniently tells you the coordinates of the four Hydrogens: using $\mathsf{e}_x\,\mathsf{e}_y$, e_z to denote unit vectors parallel to the cube edges, with Carbon as the origin, unit steps along each in turn will take you to H4 (top corner facing you) so its coordinates will be (1,1,1). Similarly, if you reverse the directions of two of the steps (along e_x and e_y, say) you'll arrive at H3, the 'back' corner on the top face, with coordinates $(-1,-1,1)$. And if you reverse the steps along e_y and e_z you'll get to H1 (left corner of bottom face), while reversing those along e_1 and e_3 will get you to H2 (right corner of bottom face).

That's all a bit hard to imagine, but it helps if you make a better drawing, with e_z as the positive z axis coming out at the centre of the top face, e_x as the x axis coming out at the centre of the left-hand face, and e_y as the y axis coming out at the centre of the right-hand face. Keep in mind the definition of a right-handed system; rotating the x axis towards the y axis would move a corkscrew along the z axis.

In fact, however, it's easiest to remember the coordinates of the atoms themselves: they will be H4(+1,+1,+1) – top corner facing you; H3(-1,-1,+1) – top corner behind it;
H2(+1,-1,-1) – bottom corner right; H1(-1,+1,-1) – bottom corner left and that means their position vectors are, respectively,

$$\mathsf{h}_4 = \mathsf{e}_x + \mathsf{e}_y + \mathsf{e}_z, \quad \mathsf{h}_3 = -\mathsf{e}_x - \mathsf{e}_y + \mathsf{e}_z, \quad \mathsf{h}_2 = \mathsf{e}_x - \mathsf{e}_y - \mathsf{e}_z, \quad \mathsf{h}_1 = -\mathsf{e}_x + \mathsf{e}_y - \mathsf{e}_z,$$

relative to Carbon at the origin.

The Methyl radical is easier to deal with, being only 2-dimensional. A bit of simple geometry shows that (taking the Carbon atom as origin (0,0), with Hydrogens on a unit circle, x axis horizontal and y axis vertical) the Hydrogens have coordinates H1$(1,0)$, H2$(-\frac{1}{2}, \frac{1}{2}\sqrt{3})$, H3$(-\frac{1}{2}, -\frac{1}{2}\sqrt{3})$. Their position vectors are thus (given that $\sqrt{3} = 1.73205$)

$$\mathsf{h}_1 = \mathsf{e}_x, \quad \mathsf{h}_2 = -0.5\mathsf{e}_x + 0.8660\mathsf{e}_y, \quad \mathsf{h}_3 = -0.5\mathsf{e}_x - 0.8660\mathsf{e}_y.$$

Example 7.4 An sp hybrid pointing in any direction

How can we get sp hybrids that point from the Carbon atoms in Figure 7.6 to all the attached Hydrogens? Let's suppose the hybrid pointing towards H1 in the Methyl radical is

$$\mathrm{h}_1 = N(\mathrm{s} + \lambda \mathrm{p}_1),$$

where s and p_1 $(= \mathrm{p}_x)$ are normalized s and p AOs. The constant λ determines how much p-character is mixed in and N is a normalizing factor. An exactly similar hybrid pointing towards H2 will be $\mathrm{h}_2 = \mathrm{s} + \lambda\mathrm{p}_2$, where p_2 is obtained by rotating p_1 $(=\mathrm{p}_x)$ through +120° around a z axis normal to the plane, while s remains unchanged.

Instead of dealing with things one at a time let's think of the general case: we want to set up a similar hybrid pointing in *any direction*. You'll remember that a unit vector v of that kind can always be written $\mathsf{v} = l\mathsf{e}_x + m\mathsf{e}_y + n\mathsf{e}_z$, where l, m, n are called the **direction cosines** of the vector, relative to the unit vectors e_x, e_y, e_z along the x-,y-,z-axes. We've already found such vectors $(\mathsf{h}_1, \mathsf{h}_2, ...)$ for the Hydrogens, relative to Carbon as the origin, so we don't need to do the work again.

Whichever vector we choose as v, the hybrid pointing along v will be $\mathrm{h}_v = \mathrm{s} + \lambda\mathrm{p}_v$, where p_v is constructed just like $\mathrm{p}_1 = \mathsf{r}\cdot\mathsf{e}_x$, but with e_x replaced by v. Thus $\mathrm{p}_v = (x\mathsf{e}_x + y\mathsf{e}_y + z\mathsf{e}_z)\cdot\mathsf{v}$ – and this will work just as well in 3 dimensions (e.g. for Methane).

Now $\mathrm{p}_x = xF(\mathsf{r})$, where $F(\mathsf{r})$ is a spherically symmetric function of position with $\mathsf{r} = x\mathsf{e}_x + y\mathsf{e}_y + z\mathsf{e}_z$; so for the Methyl radical, taking $\mathsf{v} = \mathsf{h}_1 = \mathsf{e}_x$ gives $\mathrm{p}_1 = xF(\mathsf{r})$ (as it must!), since e_x, e_y, e_z are orthogonal unit vectors. But putting $\mathsf{v} = \mathsf{h}_2$ gives

$$\begin{aligned} \mathrm{p}_2 &= (x\mathsf{e}_x + y\mathsf{e}_y + z\mathsf{e}_z) \cdot (-0.5\mathsf{e}_x + 0.8660\mathsf{e}_y)F(\mathsf{r}) \\ &= -0.5xF(\mathsf{r}) + 0.8660yF(\mathsf{r}) \\ &= -0.5\mathrm{p}_x + 0.8660\mathrm{p}_y \end{aligned}$$

and putting $\mathsf{v} = \mathsf{h}_3$ gives $\mathrm{p}_3 = -0.5\mathrm{p}_x - 0.8660\mathrm{p}_y$.

For a 3-dimensional array (e.g. Methane) the same procedure will give

$$\begin{aligned} \mathrm{p}_v &= (x\mathsf{e}_x + y\mathsf{e}_y + z\mathsf{e}_z) \cdot (l\mathsf{e}_x + m\mathsf{e}_y + n\mathsf{e}_z)F(\mathsf{r}) \\ &= lxF(\mathsf{r}) + myF(\mathsf{r}) + nzF(\mathsf{r}) \\ &= l\mathrm{p}_x + m\mathrm{p}_y + n\mathrm{p}_z, \end{aligned}$$

where l, m, n are the direction cosines of the vector pointing to *any* attached atom.

Now that we know how to make hybrid orbitals that point in any direction we only need to normalize them. That's easy because the 'squared length' of h_1 (in function space!) is $\langle \mathrm{h}_1|\mathrm{h}_1\rangle = N^2(1+\lambda^2)$, and the s- and p-type orbitals are supposed to be normalized and orthogonal ($\langle \mathrm{s}|\mathrm{s}\rangle = \langle \mathrm{p}_x|\mathrm{p}_x\rangle = 1$, $\langle \mathrm{s}|\mathrm{p}_x\rangle = 0$). And it follows that $N^2 = 1/(1+\lambda^2)$.

The amount of s character in a hybrid will be the square of its coefficient, namely $1/(1+\lambda^2)$, while the amount of p character will be $\lambda^2/(1+\lambda^2)$; and these fractions will be the same for every hybrid of an equivalent set. The *total* s content will be related to the number of hybrids in the set: if there are only two, as in Acetylene, the single s orbital must be equally shared by the two hybrids, giving $2/(1+\lambda^2) = 1$ and so $\lambda^2 = 1$. With p_1 directed along the positive z axis and p_2 along the negative, the two normalized hybrids are thus

$$\mathrm{h}_1 = \frac{1}{\sqrt{2}}(\mathrm{s} + \mathrm{p}_1), \quad \mathrm{h}_2 = \frac{1}{\sqrt{2}}(\mathrm{s} + \mathrm{p}_2), \tag{7.4}$$

just as we found earlier.

With three equivalent hybrids, the case of **trigonal hybridization**, each must have an s content of $\frac{1}{3}$ and a similar calculation shows $3/(1+\lambda^2) = 1$ and so $\lambda^2 = 2$ On choosing the axes as in Example 4, we get

$$\mathrm{h}_1 = \frac{1}{\sqrt{3}}(\mathrm{s} + \sqrt{2}\mathrm{p}_1), \quad \mathrm{h}_2 = \frac{1}{\sqrt{3}}(\mathrm{s} + \sqrt{2}\mathrm{p}_2), \quad \mathrm{h}_3 = \frac{1}{\sqrt{3}}(\mathrm{s} + \sqrt{2}\mathrm{p}_3). \tag{7.5}$$

Finally, with four equivalent hybrids (the case of **tetrahedral hybridization**), we get in the same way (check it!)

$$\mathrm{h}_1 = \tfrac{1}{2}(\mathrm{s} + \sqrt{3}\mathrm{p}_1), \quad \mathrm{h}_2 = \tfrac{1}{2}(\mathrm{s} + \sqrt{3}\mathrm{p}_2), \quad \mathrm{h}_3 = \tfrac{1}{2}(\mathrm{s} + \sqrt{3}\mathrm{p}_3), \quad \mathrm{h}_4 = \tfrac{1}{2}(\mathrm{s} + \sqrt{3}\mathrm{p}_4), \tag{7.6}$$

which point towards the corners of a regular tetrahedron, numbered as in Figure 7.6, and inclined at $109°28'$ to each other.

These definitions apply, in fair approximation, to a wide range of systems in which the hybrids are not exactly equivalent (e.g. where the attached atoms are not all the same, or where some may even be missing). The following are typical examples, all making use of roughly tetrahedral hybrids: CH_4, NH_3, H_2O, NH_4^+. Figure 7.7 gives a rough schematic picture of the electronic structure and shape of each of these systems.

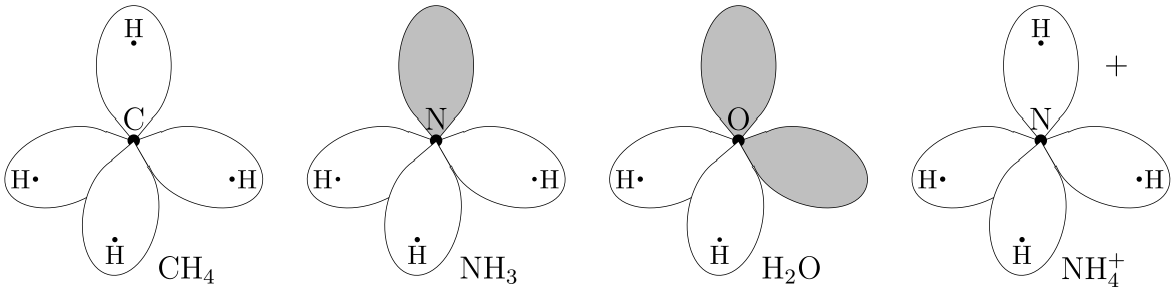


Figure 7.7 Electronic structures of four similar systems

In CH_4 the CH bonds are represented as four lobes of electron density, each of them starting on the Carbon nucleus and containing a Hydrogen nucleus. The angle between any two bonds is $109°28'$ (the 'tetrahedral angle') and all bonds are exactly equivalent.

In NH_3, Ammonia, the three NH bonds are equivalent, just changing places under rotation around the vertical axis; but the fourth lobe of electron density (shown shaded) is different from the others and contains no nucleus – it represents a 'lone pair' of electrons. The NH bonds are inclined at about 107° to each other and so form the edges of an equilateral pyramid, with the lone pair sticking up from the apex.

The water molecule H_2O has *two* lone pairs (shaded grey) and the H-O-H bond angle is about 105°; so the molecule is V-shaped and the bonds are about 4° closer than the tetrahedral angle would suggest.

The fourth system NH_4^+ is a *positive ion*, which could be formed from the Ammonia molecule by inserting a proton (unit positive charge) into its lone pair. All four NH bonds then become exactly equivalent, the extra positive charge being equally shared among them, and H-N-H angle goes back to its tetrahedral value. The capacity of a molecule to accept a proton in this way means it is able to act as an **alkali** (or **base**).

Hybridization is a very important concept: besides allowing us to get a clear picture of electronic structure and its relationship to molecular shape (**stereochemistry**) it gives insight into the probable *chemical properties* of molecules. More on that in later chapters: here we only note that the observed variations in bond angles when some of the atoms in a molecule are replaced by others (called **substitution**), or are taken away, can also be interpreted electronically. Thus the trends in bond angle, following the changes C $\rightarrow$ N $\rightarrow$ O, can be understood when electron interactions (not included at the IPM level) are recognized: in NH_3, for example, the lone pair electrons repel those of the bond pairs and this reduces the H-N-H bond angles from $\approx 109°$ to the observed 107°.

At this point it seems we are getting a good understanding of molecular electronic structure in terms of **localized MOs**, built up from overlapping AOs on adjacent centres in the molecule. But we started from a much more complete picture in the general theory of Chapter 4, where every orbital was constructed, in principle, from a set of AOs centred on all the nuclei in the molecule. In that case the MOs of an IPM approximation of LCAO form would extend over the whole system: they would come out of the SCF calculation as completely **nonlocalized MOs**. We must try to resolve this conflict.

7.4 Why can we do so well with *localized* MOs?

That's a good question, because Chapter 4 (on the Hartree-Fock method) made it seem that a full quantum mechanical calculation of molecular electronic structure would be almost impossible to do – even with the help of big modern computers. And yet, starting from a 2-electron system and using very primitive ideas and approximations, we've been able to get a general picture of the charge distribution in a many-electron molecule and of how it holds the component atoms together.

So let's end this section by showing how "simple MO theory", based on localized orbitals, can come out from the quantum mechanics of many-electron systems. We'll start from the Hartree-Fock equation (4.12) which determines the 'best possible' MOs of LCAO form, remembering that this arises in IPM approximation from a single antisymmetrized product of spin-orbitals:

$$\Psi_{SCF} = \sqrt{N!}\mathsf{A}[\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\ ...\psi_N(\mathbf{x}_N). \tag{7.7}$$

With the usual notation the spin-orbitals for a 10-electron system, such as the water molecule, are

$$\psi_1(\mathbf{x}_1) = \phi_1(\mathbf{r}_1)\alpha(s_1), \psi_2(\mathbf{x}_2) = \phi_1(\mathbf{r}_2)\beta(s_2),\ ....\ \psi_5(\mathbf{x}_{10}) = \phi_5(\mathbf{r}_{10})\beta(s_{10}),$$

and the spatial functions are normally taken to be mutually orthogonal.

We know that this many-electron wave function leads to the 1-electron density function (spin included)

$$\rho(\mathbf{x}_1) = \psi_1(\mathbf{x}_1)\psi_1^*(\mathbf{x}_1) + \psi_2(\mathbf{x}_1)\psi_2^*(\mathbf{x}_1) + ... + \psi_N(\mathbf{x}_1)\psi_N^*(\mathbf{x}_1) \tag{7.8}$$

and that for a closed-shell ground state the spin dependence can be removed by integration to give the ordinary electron density

$$P(\mathbf{r}_1) = 2[\phi_1(\mathbf{r}_1)\phi_1^*(\mathbf{r}_1) + \phi_2(\mathbf{r}_1)\phi_2^*(\mathbf{r}_1) +\ ....\ + \phi_5(\mathbf{r}_1)\phi_5^*(\mathbf{r}_1)]$$

– a sum of orbital densities, times 2 as up-spin and down-spin functions give the same contributions.

The spinless density *matrix* (see Chapter 5; and (5.33) for a summary) is very similar:

$$P(\mathbf{r}_1;\mathbf{r}_1') = 2[\phi_1(\mathbf{r}_1)\phi_1^*(\mathbf{r}_1') + \phi_2(\mathbf{r}_1)\phi_2^*(\mathbf{r}_1') +\ ....\ + \phi_N(\mathbf{r}_1)\phi_N^*(\mathbf{r}_1')] \tag{7.9}$$

and gives the ordinary electron density on identifying the two variables, $P(\mathbf{r}_1) = P(\mathbf{r}_1;\mathbf{r}_1)$. These density functions allow us to define the effective Hamiltonian F used in Hartree-Fock theory and also give us, in principle, all we need to know about chemical bonding and a wide range of molecular properties.

The question is now whether, by setting up new mixtures of the spatial orbitals, we can obtain alternative forms of the same densities, without disturbing their basic property of determining the 'best possible' one-determinant wave function. To answer the question, we collect the equations in (4.12), for all the orbitals of a closed-shell system, into a single matrix equation

$$\mathsf{F}\boldsymbol{\phi} = \boldsymbol{\phi}\boldsymbol{\epsilon}, \tag{7.10}$$

where the orbitals are contained in the *row matrix*

$$\boldsymbol{\phi} = (\phi_1\, \phi_2 \,....\, \phi_{N/2})$$

and $\boldsymbol{\epsilon}$ is a *square matrix* with the orbital energies ϵ_1, ϵ_2, ..., $\epsilon_{N/2}$ as its diagonal elements, all others being zeros. (Check this out for a simple example with 3 orbitals!)

Now let's set up new linear combinations of the orbitals $\bar{\phi}_1$, $\bar{\phi}_2$, ... $\bar{\phi}_{N/2}$, and collect them in the row matrix

$$\bar{\boldsymbol{\phi}} = (\bar{\phi}_1,\, \bar{\phi}_2,\, ...\, \bar{\phi}_{\mathrm{N}/2}).$$

The set of complex conjugate functions, $\bar{\phi}_i^*$, is then written as a column, obtained by transposing the row and putting the star on each of its elements – an operation indicated by a 'dagger' (†). With these conventions, which you may remember from Chapter 4, the new mixtures can be related to the old by the matrix equation

$$\bar{\boldsymbol{\phi}} = \boldsymbol{\phi}\mathbf{U} \tag{7.11}$$

where the square matrix $\mathbf{U}$ has elements U_{rs} which are the 'mixing coefficients' giving $\bar{\phi}_s = \sum_r \phi_r U_{rs}$. The new density matrix can be expressed as the row-column matrix product

$$\bar{P}(\mathbf{r}_1;\mathbf{r}_1') = \bar{\boldsymbol{\phi}}\,\bar{\boldsymbol{\phi}}^\dagger$$

and is then related to that before the transformation, using (7.11), by

$$\begin{aligned} \bar{P}(\mathbf{r}_1;\mathbf{r}_1') &= \boldsymbol{\phi}\mathbf{U}(\boldsymbol{\phi}\mathbf{U})^\dagger \\ &= \boldsymbol{\phi}\mathbf{U}(\mathbf{U}^\dagger\boldsymbol{\phi}^\dagger) \\ &= P(\mathbf{r}_1;\mathbf{r}_1') \quad \text{(provided } \mathbf{U}\mathbf{U}^\dagger = \mathbf{1}. \end{aligned} \tag{7.12}$$

Here we've noted that $(\mathbf{AB})^\dagger = (\mathbf{B}^\dagger\mathbf{A}^\dagger)$ and the condition on the last line means that $\mathbf{U}$ is a **unitary matrix**.

That was quite a lot of heavy mathematics, but if you found it tough go to a real application in the next Example, where we relate the descriptions of the water molecule based on localized and non-localized MOs. You should find it much easier.

Example 7.5 Transformation from localized to non-localized orbitals: H_2O

To show what the matrix $\mathbf{U}$ looks like let's use (7.11) to pass from the basis of localized orbitals $\bar{\boldsymbol{\phi}}$, which we set up by intuition ('guess work'), to non-localized orbitals similar to those that come from an SCF calculation – putting them in the row matrix $\boldsymbol{\phi}$.

To do that we need to express (7.11) the other way round, but that's easy because when both orbital sets are orthonormal (as we suppose) $\mathbf{U}$ will be unitary, $\mathbf{U}\mathbf{U}^\dagger = \mathbf{1}$. So multiplying from the right by $\mathbf{U}^\dagger$ gives $\bar{\boldsymbol{\phi}}\mathbf{U}^\dagger = \boldsymbol{\phi}$.

We want to choose $\mathbf{U}^\dagger$, then, so that the orbitals in $\boldsymbol{\phi}$ are completely *de*-localized over the whole molecule; and we know that these orbitals will be of various types as a result of molecular symmetry. Some will be symmetric under a reflection that interchanges left and right, others will be anti-symmetric – changing only in sign – and so on.

In Figure 7.4 the H_2O molecule is inscribed in a cube, for comparison with the other systems, and here it's convenient to use the same figure. The atoms of H1–O–H2 then lie in the xz-plane, with O as origin and z-axis pointing upwards (above the H atoms). This plane is a **symmetry plane**, the molecule being symmetric under reflection across it; but the xy-plane is a second plane of symmetry, across which the H atoms simply change places under reflection. The two reflections are both **symmetry operations**, which leave the system apparently unchanged. Another kind of symmetry operation may be a *rotation*, like that of half a turn (through 180°) about the z-axis – which also interchanges the H atoms. These three operations are usually denoted by σ_1, σ_2 for the reflections and C_2 for the rotation; together with the "identity operation" E (do nothing!) they form the **symmetry group** of the system. (If you've forgotten about such things,turn back to Chapter 7 of Book 11 – or even to Chapter 6 of Book 1!)

The localized orbitals we have in mind for the water molecule were constructed from the valence hybrids h_1, h_2 overlapping with the Hydrogen 1s AOs (let's call them H_1 and H_2) to give two **bond orbitals**

$$\bar{\phi}_1 = a\mathrm{h}_1 + b\mathrm{H}_1, \quad \bar{\phi}_2 = a\mathrm{h}_2 + b\mathrm{H}_2.$$

Here the bonds are equivalent, so the mixing coefficients a, b must be the same for both of them. The remaining 4 of the 8 valence electrons represent two lone pairs and were assigned to the next two hybrids h_3 and h_4, which we may now denote by

$$\bar{\phi}_3 = \mathrm{h}_3 \text{ and } \bar{\phi}_4 = \mathrm{h}_4.$$

What about the non-localized MOs? These will be put in the row matrix $\boldsymbol{\phi} = (\phi_1\, \phi_2\, \phi_3\, \phi_4)$ and should serve as approximations to the MOs that come from a full valence-electron SCF calculation. There are only four occupied SCF orbitals, holding the 8 valence electrons, and for a symmetrical system like H_2O they have simple symmetry properties. The simplest would be symmetric under rotation C_2, through 180° around the z-axis, and also under reflections σ_1, σ_2 across the xz- and yz-planes. How can we express such orbitals in terms of the localized set $\bar{\boldsymbol{\phi}}$? Clearly $\bar{\phi}_1$ and $\bar{\phi}_2$ are both symmetric under reflection σ_1 across the plane of the molecule, but they change places under the rotation C_2 and also under σ_2 – which interchanges the H atoms. For such operations they are neither symmetric nor anti-symmetric; and the same is true of $\bar{\phi}_3$ and $\bar{\phi}_4$. However, the combination $\bar{\phi}_1 + \bar{\phi}_2$ clearly *will* be fully symmetric. Reflection sends the positive combination into itself, so $\bar{\phi}_1 + \bar{\phi}_2$ is symmetric, but $\bar{\phi}_1 - \bar{\phi}_2$ becomes $\bar{\phi}_2 - \bar{\phi}_1$ and is therefore anti-symmetric under C_2 and σ_2. Moreover, the symmetric and anti-symmetric combinations are both *delocalized* over both bonds and can be used as

$$\phi_1 = (1/\sqrt{2})(\bar{\phi}_1 + \bar{\phi}_2), \quad \phi_2 = (1/\sqrt{2})(\bar{\phi}_1 - \bar{\phi}_2),$$

where we remembered that all orbitals are supposed to be orthonormal. Similarly, the localized and non-localized lone-pair orbitals are related by

$$\phi_3 = (1/\sqrt{2})(\bar{\phi}_3 + \bar{\phi}_4), \quad \phi_4 = (1/\sqrt{2})(\bar{\phi}_3 - \bar{\phi}_4).$$

Finally, these results may be put in matrix form, $\boldsymbol{\phi} = \bar{\boldsymbol{\phi}}\mathbf{U}^\dagger$, where the matrix $\mathbf{U}^\dagger$ is

$$\mathbf{U}^\dagger = \begin{pmatrix} x & x & 0 & 0 \\ x & \bar{x} & 0 & 0 \\ 0 & 0 & x & x \\ 0 & 0 & x & \bar{x} \end{pmatrix}$$

(x and $\bar{x}$ standing for $\frac{1}{2}\sqrt{2}$ and $-\frac{1}{2}\sqrt{2}$.) It is easy to confirm that this matrix is unitary. Each column contains the coefficients of a nonlocalized MO in terms of the four localized MOs; so the first expresses ϕ_1 as the combination found above, namely $(1/\sqrt{2})(\bar{\phi}_1 + \bar{\phi}_2)$, while the fourth gives $\phi_4 = (1/\sqrt{2})(\bar{\phi}_3 - \bar{\phi}_4)$. In each case the sum of the coefficients squared is unity (normalization); and for two columns the sum of corresponding products is zero (orthogonality).

In summary, Example 7.5 has shown that

$$\phi_1 = (1/\sqrt{2})(\bar{\phi}_1 + \bar{\phi}_2) \text{ and } \phi_2 = (1/\sqrt{2})(\bar{\phi}_1 - \bar{\phi}_2) \tag{7.13}$$

are delocalized combinations of localized bond orbitals, behaving correctly under symmetry operations on the molecule and giving exactly the same description of the electron distribution. The same is true of the lone pair orbitals: they may be taken in localized form as, $\bar{\phi}_3$ and $\bar{\phi}_4$, which are clearly localized on different sides of a symmetry plane, or they may be combined into the delocalized mixtures

$$\phi_3 = (1/\sqrt{2})(\bar{\phi}_3 + \bar{\phi}_4) \text{ and } \phi_4 = (1/\sqrt{2})(\bar{\phi}_3 - \bar{\phi}_4) \tag{7.14}$$

The localized and non-localized orbital sets give entirely equivalent descriptions of the electron distribution, provided they are related by a unitary transformation $\boldsymbol{\phi} = \bar{\boldsymbol{\phi}}\mathbf{U}^\dagger$. In the case of the water molecule

$$\mathbf{U}^\dagger = \begin{pmatrix} x & x & 0 & 0 \\ x & \bar{x} & 0 & 0 \\ 0 & 0 & x & x \\ 0 & 0 & x & \bar{x} \end{pmatrix}, \tag{7.15}$$

where x and $\bar{x}$ stand for the numerical coefficients $\frac{1}{2}\sqrt{2}$ and $-\frac{1}{2}\sqrt{2}$. Thus, for example, the localized lone pairs are $\bar{\phi}_3 = \mathrm{h}_3$ and $\bar{\phi}_4 = \mathrm{h}_4$, and their contribution to the total electron density P is $2|\mathrm{h}_3|^2 + 2|\mathrm{h}_4|^2$ (two electrons in each orbital).

After transformation to the delocalized combinations, given in (7.14), the density contribution of the lone pairs is expressed as (Note that the 'square modulus' |...| is used as the electron density P is a *real* quantity, while the functions may be complex.)

$$\begin{aligned} 2|\phi_3|^2 + 2|\phi_4|^2 &= |(\mathrm{h}_3 + \mathrm{h}_4)|^2 + |(\mathrm{h}_3 - \mathrm{h}_4)|^2 \\ &= (|\mathrm{h}_3|^2 + |\mathrm{h}_4|^2 + 2|\mathrm{h}_3\mathrm{h}_4|) + (|\mathrm{h}_3|^2 + |\mathrm{h}_4|^2 - 2|\mathrm{h}_3\mathrm{h}_4|) \\ &= 2|\mathrm{h}_3|^2 + 2|\mathrm{h}_4|^2 \end{aligned}$$

– exactly as it was before the change to non-localized MOs.

You can write these results in terms of the usual s, p_x, p_y, p_z AOs (you should try it!), getting

$$\phi_3 = \sqrt{2}(\mathrm{s} + \mathrm{p}_z), \qquad \phi_4 = \sqrt{2}(\mathrm{p}_x + \mathrm{p}_y).$$

Evidently, $|\phi_3|^2$ describes a lone-pair density lying along the symmetry axis of the molecule (sticking out above the Oxygen) while $|\phi_4|^2$ lies in the plane of the molecule and describes a 'halo' of negative charge around the O atom.

The water molecule provided a very simple example, but (7.14) and all that follows from it are quite general. Usually the transformation is used to pass from SCF MOs, obtained by solving the Hartree-Fock equations, to *localized* MOs, which give a much clearer picture of molecular electronic structure. In that case (7.11) must be used, with some suitable prescription to define the matrix **U** that will give **maximum localization** of the transformed orbitals. Many such prescriptions exist and may be applied even when there is no symmetry to guide us, as was the case in Example 7.5: they provide a useful link between Quantum Mechanics and Chemistry.

7.5 More Quantum Chemistry – the semi-empirical treatment of bigger molecules

At IPM level, we've already explored the use of **Molecular Orbital** (MO) theory in trying to understand the electronic structures of some simple molecules formed from atoms of the First Row of the Periodic Table, which starts with Lithium (3 electrons) and ends with Neon (10 electrons).

Going along the Row, from left to right, and filling the available AOs (with up to two electrons in each) we obtain a complete 'shell'. We made a lot of progress for **diatomic molecules** (*homonuclear* when both atoms are the same, *heteronuclear* when they are different) and even for a few bigger molecules, containing 3,4, or more atoms. After finding the forms of rough approximations to the first few MOs we were able to make *pictures* of the molecular electronic structures formed by adding electrons, up to two at a time, to the 'empty' MOs. And, remember, these should really be solutions of the Schròdinger equation for one electron in the field provided by the *nuclei* and all *other* electrons: they are not 'buckets' for holding electrons! – they are *mathematical functions* with sizes and shapes, like the AOs used in Section ... to describe the regions of space in which the electron is most likely to be found.

In the approach used so far, the MOs that describe the possible *stationary states* of an electron were approximated as **Linear Combinations of Atomic Orbitals** on the separate atoms of the molecule (the LCAO approximation). On writing

$$\phi = c_1\chi_1 + c_2\chi_2 + \ \dots c_n\chi_n = \sum_i c_i\chi_i, \tag{7.16}$$

the best approximations we can get are determined by solving a set of **secular equations**.

In the simple case $n = 3$ these have the form (see equation (4.15) of Section 4)

$$\begin{pmatrix} h_{11} & h_{12} & h_{13} \\ h_{21} & h_{22} & h_{23} \\ h_{31} & h_{32} & h_{13} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \epsilon \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}. \tag{7.17}$$

In Section 4 we were thinking about a much more refined many-electron approach, with as many basis functions as we wished, and an *effective* Hamiltonian F in place of the 'bare nuclear' operator h. The Fock operator F includes terms which represent interaction with all the other electrons, but here we use a strictly 1-electron model which contains only interaction with the nuclei. The matrix elements h_{ij} are then usually treated as disposable parameters, whose values are chosen by fitting the results to get agreement with any available experimetal data. And the overlap integrals $S_{ij} = \langle\chi_i|\chi_j\rangle$ are often neglected for $i \neq j$. This is the basis of **semi-empirical MO theory**, which we explore further in this section.

Let's start by looking at some simple **hydrocarbons**, molecules that contain only Carbon and Hydrogen atoms, beginning with Acetylene (C_2H_2) – the linear molecule $\mathrm{H} - \mathrm{C} \equiv \mathrm{C} - \mathrm{H}$, studied in Example 7.3, where the simplest picture of the electronic structure was found to be

$$\phi^2_{\mathrm{CH}}\phi^2_{\mathrm{CC}\sigma z}\phi^2_{\mathrm{CC}\pi x}\phi^2_{\mathrm{CC}\pi y}\phi^2_{\mathrm{CH}}.$$

That means, you'll remember, that two electrons occupy the MO ϕ_{CH} localized around the left-hand CH bond; another two occupy $\phi_{\mathrm{CC}\sigma z}$, a σ-type MO localized around the C–C (z) axis; two more occupy a π-type MO $\phi_{\mathrm{CC}\pi x}$ formed from $2\mathrm{p}_x$ AOs; two more occupy a similar MO $\phi_{\mathrm{CC}\pi y}$ formed from $2\mathrm{p}_y$ AOs; and finally there are two electrons in the right-hand CH bond. That accounts for all 10 valence electrons! (2 from the Hydrogens and 2×4 from the Carbons) And in this case the localized MOs are constructed from the same number of AOs.

Now suppose the MOs came out from an approximate SCF calculation as general linear combinations of the 10 AOs, obtained by solving secular equations like () but with 10 rows and columns. What form would the equations have? The matrix elements h_{ij} for pairs of AOs χ_i, χ_j would take values $h_{ii} = \alpha_i$, say, along the diagonal ($j = i$); and this would represent the expectation value of the effective Hamiltonian h for an electron sitting in χ_i. (This used to be called a "Coulomb" integral, arising from the electrostatic interaction with all the nuclei.) The off-diagonal elements $h_{ij}, (j \neq i)$ would arise jointly from the way χ_i and χ_j 'overlap' (*not* the overlap *integral*, which we have supposed 'negligible'). It is usually denoted by β_{ij} and is often referred to as a 'resonance' integral because it determines how easily the electron can 'resonate' between one AO and the other. In semi-empirical work the αs and βs are looked at as the 'disposable parameters' referred to above.

In dealing with **hydrocarbons** the αs may be given a common value α_{C} for a Carbon valence AO α_{H} for a Hydrogen AO. The βs are given values which are large for AOs with a heavy overlap (e.g. hybrids pointing directly towards each other), but are otherwise neglected (i.e. given the value zero). This is the **nearest-neighbour approximation**. To see how it works out let's take again the case of Acetylene.

Example 7.6 Acetylene – with 10 AOs

Choose the AOs as the hybrids used in Example 7.3. Those with σ symmetry around the (z) axis of the molecule are:

- χ_1 = left-hand Hydrogen 1s AO
- χ_2 = Carbon σ hybrid pointing towards Hydrogen (χ_1)
- χ_3 = Carbon σ hybrid pointing towards second Carbon (χ_4)
- χ_4 = Carbon σ hybrid pointing towards first Carbon (χ_3)
- χ_5 = Carbon σ hybrid pointing towards right-hand Hydrogen
- χ_6 = right-hand Hydrogen 1s AO

The other Carbon hybrids are of x-type, formed by including a $2p_x$ component, and y-type, formed by including a $2p_y$ component. They are

- χ_7 = x-type hybrid on first Carbon, pointing towards second
- χ_8 = x-type hybrid on second Carbon, pointing towards first
- χ_9 = y-type hybrid on first Carbon, pointing towards second
- χ_{10} =y-type hybrid on second Carbon, pointing towards first

You should draw pictures of all these hybrid combinations and decide which pairs will overlap to give non-zero βs.

To determine the form of the secular equations we have to decide which AOs are 'nearest neighbours', so let's make a very simple diagram in which the AOs $\chi_1,\ ...\ \chi_{10}$ are indicated by short arrows showing the way they 'point' (usually being hybrids). As the molecule is linear, the arrows will be arranged on a straight line as in Figure 7.8 below:

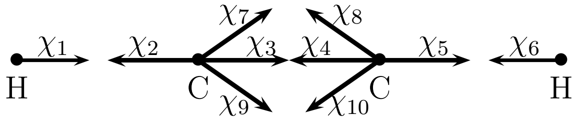


Figure 7.8 Overlapping orbital pairs in C_2H_2

From the Figure, the diagonal elements in the matrix of the 1-electron Hamiltonian, $\mathbf{h}$, will be $h_{ii} = \langle \chi_i | \mathsf{h} | \chi_i \rangle$; so

$$h_{11} = \alpha_{\mathrm{H}},\ h_{22} = h_{33} = h_{44} = h_{55} = \alpha_{\mathrm{C}},\ h_{66} = \alpha_{\mathrm{H}},$$

(all with σ symmetry around the z-axis) and, if we take all the Carbon hybrids as approximately equivalent,

$$h_{77} = h_{88} = h_{99} = h_{10,10} = \alpha_{\mathrm{C}}.$$

$$h_{77} = h_{88} = h_{99} = h_{10,10} = \alpha_{\mathrm{C}}.$$

The off-diagonal elements $h_{ij} = \langle\chi_i|\mathsf{h}|\chi_j\rangle$ will be neglected, in nearest-neighbour approximation, except for $\chi_i\chi_j$ pairs that point towards each other. The pairs (1,2) and (5,6) may be given a common value denoted by $\beta_{\rm CH}$, while (3,4),(7,8),(9,10) may be given a common value $\beta_{\rm CC}$. For short, we'll use just β for the C-C resonance integral and β' for the one that links C to H.

Since i and j are row- and column- labels of elements in the matrix $\mathbf{h}$, it follows that the approximate form of $\mathbf{h}$ for the Acetylene molecule is

$$\begin{pmatrix} \alpha' & \beta' & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \beta' & \alpha & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \beta & \alpha & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha & \beta' & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta' & \alpha' & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \alpha & \beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \alpha & \beta \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \beta & \alpha \end{pmatrix} \qquad (7.18)$$

The secular equations contained in the matrix $\mathbf{hc} = \epsilon\mathbf{c}$ then break up into pairs, corresponding to the 2×2 'blocks' along the diagonal of (7.18). The first pair, for example, could be written

$$(\alpha' - \epsilon)c_1 + \beta' c_2 = 0, \quad \beta' c_1 + (\alpha - \epsilon)c_2 = 0$$

and the solution is easy (you've done it many times before!): by 'cross-multiplying' you eliminate the coefficients and get

$$(\alpha' - \epsilon)(\alpha - \epsilon) - (\beta')^2 = 0,$$

which is a simple quadratic equation to determine the two values of ϵ for which the two equations can be solved (are 'compatible'). These values, the 'roots', are (look back at Section 5.3 of Book 1 if you need to!)

$$\epsilon = \tfrac{1}{2}(\alpha + \alpha') \pm \tfrac{1}{2}\sqrt{(\alpha - \alpha')^2 + 4(\beta')^2)}. \qquad (7.19)$$

Since the αs and βs are all negative quantities (do you remember why?) the lowest root will be $\epsilon_1 = \frac{1}{2} - \frac{1}{2}\sqrt{(\alpha + \alpha')^2 + 4(\beta')^2}$ and this will be the orbital energy of an electron in the localized MO describing the CH bond. To get the form of this bonding MO all you have to do is substitute $\epsilon = \epsilon_1$ in either of the two equations leading to (8.4): this will determine the *ratio* of the coefficients and their absolute values then follow from the normalization condition $c_1^2 + c_2^2 = 1$. This has been done in detail for some simple diatomic molecules in Section 6.2, which you may want to read again.

All the localized MOs follow in exactly the same way from the other diagonal blocks in (7.18). For the bonds involving similar AOs the equations contain no 'primed' quantities and (7.19) gives $\epsilon_1 = \alpha + \beta,\ \epsilon_2 = \alpha - \beta$ for the bonding and antibonding combinations. In that case the corresponding normalized MOs are

$$\text{Bonding}: \quad \phi_1 = (\chi_1 + \chi_2)/\sqrt{2}, \quad \text{Antibonding}: \quad \phi_2 = (\chi_1 - \chi_2)/\sqrt{2}, \tag{7.20}$$

just as for a homonuclear *diatomic* molecule (Section 7.2). In other words the IPM picture, with *nearest-neighbour approximations*, views the molecule as a superposition of independent 2-electron bonds, each one consisting of two electrons in a localized MO extending over only two centres. In this extreme form of the IPM approximation, the total electronic energy is represented as a sum

$$E_{\text{total}} \approx \sum_{rs(pairs)} E_{(rs)}, \tag{7.21}$$

where $E_{(rs)} = 2\epsilon_{(rs)}$ and is the energy of two electrons in the bonding MO formed from an overlapping pair of AOs χ_r, χ_s.

The total electronic energy of the Acetylene molecule would thus be

$$E_{\text{total}} \approx 2E_{\text{CH}} + 3E_{\text{CC}}$$

– corresponding to 2 CH bonds and 3 CC bonds (taken as being equivalent).

From Acetylene to Ethane and Ethylene

In Acetylene the Carbons, which are each able to form bonds with up to *four* other atoms (as in Methane, CH_4, shown in Figure 7.7), are each bonded with only *one* other atom. The CC triple bond seems a bit strange, with each Carbon using 3 of its 4 valencies to connect it only with another Carbon! – and the triple bond is apparently quite different from that in the diatomic Nitrogen molecule $N \equiv N$, described in Section 7.2 as one bond of σ type with two somewhat weaker π-type bonds. Instead we've described it in terms of hybrid AOs, one pair (χ_3, χ_4), pointing directly towards each other, and two pairs pointing away from the molecular axis and able to form only 'bent' bonds. In fact, however, both descriptions are acceptable when we remember that the hybrid AOs are simply *linear combinations* of 2s and 2p AOs and the three pairs of localized MOs formed by overlapping the hybrids are just alternative combinations. In Section 7.4 we found how two alternative sets of *orbitals* could lead to exactly the same total *electron density*, provided the mixing coefficients were chosen correctly so as to preserve normalization and orthogonality conditions. So don't worry! – you can use either type of MOs and get more or less the same overall description of the electronic structure. Any small differences will arise from using one set of 'standard' s-p hybrids in a whole series of slightly different molecular situations (as in Figure 7.7).

Ethane and Ethylene illustrate two main categories of carbon compounds: in Ethane the Carbon forms four σ-type bonds with other atoms (we say all carbon valencies are *saturated*), leading to "saturated molecules"; but in Ethylene only three carbon valencies are used in that way, the fourth being involved in somewhat weaker π-type bonding, and

Ethylene is described as an "unsaturated molecule". Let's deal first with Ethane and similar molecules.

The Ethane molecule

Ethane has the formula C_2H_6, and looks like two CH_3 groups with a σ bond between the two Carbons. Its geometry is indicated in Figure 7.9 below:

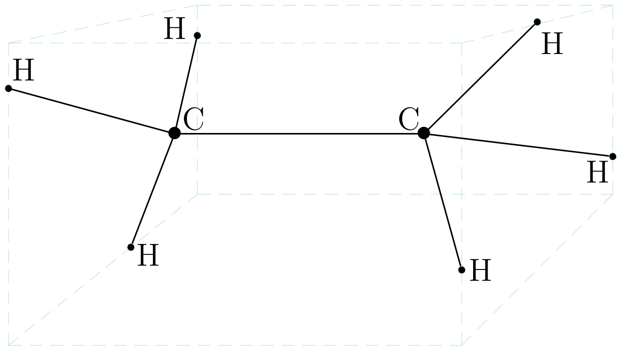


Figure 7.9 Geometry of the Ethane molecule

Here the molecule is shown sitting inside a rectangular box (indicated by the light blue broken lines) so you can see its 3-dimensional form. Each Carbon uses one of its four hybrids to make a sigma bond with the other Carbon, while its three remaining hybrids connect it with Hydrogens. The right-hand CH_3 group is rotated around the C−C axis, relative to the CH_3 on the left; this is called the "staggered conformation" of the molecule. The energy variation in such a rotation is a tiny fraction of the total electronic energy; in the "eclipsed conformation", where each group is the mirror image of the other across a plane perpendicular to the C−C axis, cutting the molecule in two, the total energy is about 12 kJ/mol higher – but this is less than (1/20,000)th of the total energy itself! The energy difference between the two conformations is a rotational 'barrier height' but is clearly much too small to be predicted with the crude approximations we are using. In IPM approximation with inclusion of only nearest neighbour interactions the total electronic energy for either conformation would be simply

$$E_{\text{total}} \approx 6E_{\text{CH}} + E_{\text{CC}}$$

and this does not depend on rotation of one group relative to the other. (To be reminded of energy units go back to Book 5, Section 3.1)

Ethane is the second member of the series starting with methane, often called the **Paraffin series**. The next one is Propane C_3H_8, formed by adding another CH_2 group between the two Carbons in Ethane. Because there is so little resistence to twisting around a C−C single bond, such chains are very flexible. They are also chemically stable, not reacting easily with other molecules as all valencies are saturated. Members of the series with the shortest chains form gases, becoming liquids as the chain length increases (e.g. gasolene with 7-9 Carbons and kerosene with 10-16 Carbons) and finally solid paraffin. Obviously they are very important commercially.

The Ethylene molecule

In this molecule, with the formula C_2H_4, each Carbon is connected to only two Hydrogens and the geometry of the molecule is indicated in Figure 7.10 here two CH_2 groups lie in the same plane (that of the paper) and are connected by a C−C sigma bond. Each Carbon has three valencies engaged in sigma-bonding; the fourth involving the remaining 2p AO, sticking up normal to the plane of the molecule and able to take part in π bonding.

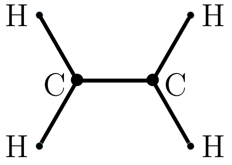


Figure 7.10 Geometry of Ethylene

Molecules with Carbons of this kind are said to be "*conjugated*" and **conjugated molecules** form an important part of carbon chemistry. The Ethylene molecule is flat, with Carbon 2p orbitals normal to the plane and overlapping to give a π bond; there is thus a CC double bond, which keeps the molecule flat, because twisting it around the CC bond reduces the lateral overlap of the 2p orbitals and hence the degree of π bonding. Unsaturated hydrocarbons like Ethylene are generally planar for the same reason. They can all be built up by replacing one of the Hydrogens by a trivalent Carbon  and saturating two of the extra valencies by adding two more Hydrogens. From Ethylene we obtain in this way C_3H_6 (The Allyl radical), which has 3 π electrons and is a highly reactive "free radical".

The Butadiene molecule

On replacing the right-most Hydrogen of Allyl by another CH_2 group, we obtain the molecule pictured in Figure 7.11 which is called "Butadiene":

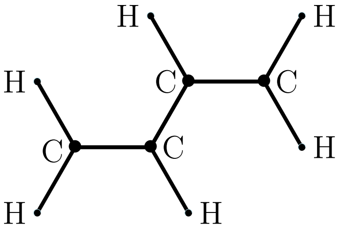


Figure 7.11 The Butadiene molecule

As you can see, the chain of Carbons is not straight but 'zig-zag' – as a result of the trigonal symmetry of the electron distribution around each Carbon. But, if we think about the π electrons alone – as if they moved in the field of a 'rigid framework' provided by the σ-bonded atoms – that's not important: in a nearest-neighbour approximation all that matters is the pattern of connections due to lateral overlap of 2p AOs on adjacent Carbons. In the early applications of quantum mechanics to molecules this approximation turned up an amazing number of chemically important results. So let's use Butadiene to test our theoretical approach:

Example 7.7 Butadiene: electronic structure of the π-electron system

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In the present approximation we think only of the C – C – C – C chain and set up the secular equations for a π electron in the field of the σ-bonded framework. The effective Hamiltonian has diagonal matrix elements α for every Carbon and off-diagonal elements β for every pair of nearest neighbours, the rest being neglected. The equations we need are therefore (check it out!)

$$\begin{pmatrix} \alpha-\epsilon & \beta & 0 & 0 \\ \beta & \alpha-\epsilon & \beta & 0 \\ 0 & \beta & \alpha-\epsilon & \beta \\ 0 & 0 & \beta & \alpha-\epsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

There are solutions only for values of ϵ which make the determinant of the square matrix zero. How can we find them?

The first line of the matrix equation above reads as

$$(\alpha-\epsilon)c_1 + \beta c_2 = 0$$

and it would look better if you could get rid of the α and β, which are just parameters that can take any values you choose. So why not divide all terms by β, which doesn't change anything, and denote $(\alpha-\epsilon)/\beta$ by $-x$? The first equation then becomes $-xc_1 + c_2 = 0$ and the whole matrix equation becomes

$$\begin{pmatrix} -x & 1 & 0 & 0 \\ 1 & -x & 1 & 0 \\ 0 & 1 & -x & 1 \\ 0 & 0 & 1 & -x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

There are solutions only for values of x which make the determinant of the square matrix zero; and if you know how to solve for x you can get all the energy levels for any values of the adjustable parameters α, β.

The equation to determine the acceptable values of x is thus

$$\begin{vmatrix} -x & 1 & 0 & 0 \\ 1 & -x & 1 & 0 \\ 0 & 1 & -x & 1 \\ 0 & 0 & 1 & -x \end{vmatrix} = 0 \tag{7.22}$$

You may remember the rule for evaluating a determinant (it was given first just after equation (6.10) in Book 2). Here we'll use it to evaluate the 4×4 determinant of the square matrix on the left in (7.22). Working along the first row and denoting the value of the 4×4 determinant by $\Delta_4(x)$ (it's a function of x) we get *in the first step*

$$\Delta_4(x) = \begin{vmatrix} -x & 1 & 0 & 0 \\ 1 & -x & 1 & 0 \\ 0 & 1 & -x & 1 \\ 0 & 0 & 1 & -x \end{vmatrix} = (-x)\begin{vmatrix} -x & 1 & 0 \\ 1 & -x & 1 \\ 0 & 1 & -x \end{vmatrix} - (1)\begin{vmatrix} 1 & 1 & 0 \\ 0 & -x & 1 \\ 0 & 1 & -x \end{vmatrix} + \text{etc.}$$

The next step is to use the same rule to evaluate each of the 3×3 determinants. You'll need only the first two as the others are multiplied by zero. The first one is

$$\begin{vmatrix} -x & 1 & 0 \\ 1 & -x & 1 \\ 0 & 1 & -x \end{vmatrix} = (-x)\begin{vmatrix} -x & 1 \\ 1 & -x \end{vmatrix} - (1)\begin{vmatrix} 1 & 1 \\ 0 & -x \end{vmatrix} + (0)\begin{vmatrix} 1 & -x \\ 0 & 1 \end{vmatrix}$$

The second one is

$$\begin{vmatrix} 1 & 1 & 0 \\ 0 & -x & 1 \\ 0 & 1 & -x \end{vmatrix} = (1)\begin{vmatrix} -x & 1 \\ 1 & -x \end{vmatrix}$$

– the other 2×2 determinants being multiplied by zeros.

Any 2×2 determinant

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - cb$$

– as follows from the rule you're using (check it) and it's therefore easy to work back from this point and so evaluate the original 4×4 determinant $\Delta_4(x)$. The final result is (check it!) $\Delta_4(x) = x^4 - 3x^2 + 1$ and depends only on the *square* of x. That shows at once that the set of energy levels will be symmetrical around $x = 0$; and if we put $x^2 = y$ the consistency condition $\Delta_4(x) = 0$ becomes $y^2 - 3y + 1 = 0$. This simple quadratic equation has roots $y = (3 \pm \sqrt{5})/2$, which lead to $x = \pm\sqrt{(1.618)}$, or $x = \pm\sqrt{(0.618)}$; and therefore to energy levels

$$\epsilon = \alpha \pm x\beta = \alpha \pm 1.272\beta, \text{ or } \alpha \pm 0.786\beta.$$

Since α and β are both negative quantities the level for the plus sign is below the 'datum' α and corresponds to a 'bonding' state, while that with the negative sign lies symmetrically above the datum and corresponds to an 'antibonding' state.

The calculation above, for a chain of four Carbons, could be repeated for a chain of six Carbons (called "Hexatriene") but would involve dealing with a 6×6 determinant; and with N Carbons we would have to deal with an $N \times N$ determinant – quite a lot of work! Sometimes, however, it is simpler to solve the simultaneous equations directly: the method is shown in Example 7.8 that follows.

Example 7.8 Butadiene: a simpler and more general method

Again we calculate the electronic structure of the π-electron system of Butadiene, but this time we work directly from the secular equations, which follow from (7.22) as

$$\begin{aligned} (\alpha - \epsilon)c_1 + \beta c_2 + 0c_3 + 0c_4 &= 0c_1 \\ \beta c_1 + (\alpha - \epsilon)c_2 + \beta c_3 + 0c_4 &= 0c_2 \\ 0c_1 + \beta c_2 + (\alpha - \epsilon)c_3 + \beta c_4 &= 0c_3 \\ 0c_1 + 0c_2 + \beta c_3 + (\alpha - \epsilon)c_4 &= 0c_4, \end{aligned}$$

where the sum of terms on the left of the equality must vanish for every line. In short,

$$(\alpha-\epsilon)c_1+\beta c_2=0, \quad \beta c_1+(\alpha-\epsilon)c_2+\beta c_3=0, \quad \beta c_2+(\alpha-\epsilon)c_3+\beta c_4=0, \quad \beta c_3+(\alpha-\epsilon)c_4=0.$$

Let's now write c_m for the mth coefficient (in the order 1,2,3,4), divide each equation by β, and again put $(\alpha-\epsilon)/\beta=-x$. The whole set of equations can then be written as a single one:

$$c_{m-1}-xc_m+c_{m+1}=0,$$

where m takes the values 1,2,3 and 4 in turn and we exclude any values such as 0 or 5 that lie outside that range. These are 'boundary conditions' which tell us there are no coefficients below m=1 or above m=4. The number of atoms in the chain (call it N) is not important as long as we insist that c_0 and c_{N+1} should be zero. So now we can deal with **polyene chains** of any length!

To complete the calculation we can guess that the coefficients will follow the up-and-down pattern of waves on a string, like the wave functions of an electron in a 1-dimensional box – behaving like $\sin m\theta$ or $\cos m\theta$ or a combination of the two. It's convenient to use the complex forms $\exp(\pm)im\theta$ and on putting $c_m=\exp(im\theta)$ in the key equation above we get the condition

$$\exp\, i(m-1)\theta - x\exp\, m\theta + \exp\, i(m+1)\theta = 0.$$

Taking out a common factor of $\exp\, im\theta$, this gives $e^{i\theta}+e^{-i\theta}-x=0$, so the 'wavelength' θ must be related to the energy x by $x=2\cos\theta$.

Since changing the sign of m gives a solution of the same energy, a more general solution will be

$$c_m = A\exp(im\theta)+B\exp(-im\theta)$$

where A and B are arbitrary constants, which must be chosen to satisfy the boundary conditions: the first of these, $c_0=A+B=0$, gives

$$c_m = A[\exp(im\theta)-\exp(-im\theta)] = C\sin(m\theta), \quad (C=2A)$$

while the second, taking $m=N+1$, becomes

$$c_{N+1}=C\sin{(N+1)\theta}=0.$$

This is satisfied only when $(N+1)\theta=k\pi$ where k is *any positive integer* and is essentially a *quantum number* for the kth state of the system. The wavelength in the kth state is thus $\theta=k\pi/(N+1)$; so the MO ϕ_k will be $\phi_k=\sum c_m\chi_m$ with AO coefficient $c_m=C\ \sin\, mk\pi/(N+1)$ and will have corresponding orbital energy $x_k=C\ \cos(k\pi/(N+1)$.

From Example 7.8, the MOs ϕ_k for a polyene chain of N Carbons are $\phi_k=\sum c_m^{(k)}\chi_m$, where the mth AO coefficient is (after normalizing – check it!)

$$c_m^{(k)} = C_k\sin\left(\frac{mk\pi}{N+1}\right) \qquad (C_k=\sqrt{2/(N+1)}). \tag{7.23}$$

The corresponding orbital energies are $\epsilon_k=\alpha+\beta x_k$, with

$$x_k = 2\cos\left(\frac{k\pi}{N+1}\right). \tag{7.24}$$

The energy levels are thus symmetrically disposed around $\epsilon=\alpha$, which may be taken as a reference level. As $N\to\infty$ the levels become closer and closer, eventually forming a continuous **energy band** extending from $\epsilon = \alpha + 2\beta$ up to $\alpha - 2\beta$. (Remember α and β are both negative.) All this is shown below in Figure 7.12.

It should be noted that when the number of Carbons is odd there is always a Non-bonding MO: it is very important, giving the molecule its 'free-radical' character – the highest occupied orbital leading to a highly reactive system with a very short lifetime.

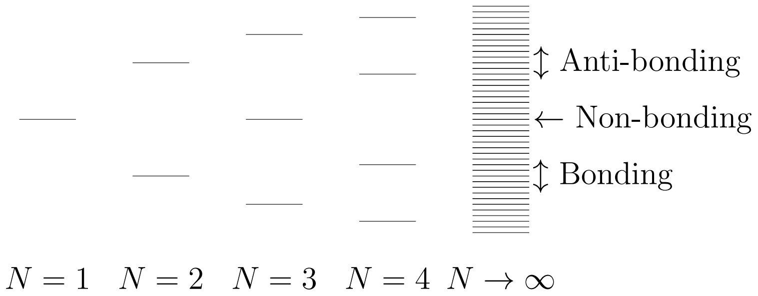


Figure 7.12 MO energy levels in a chain of N Carbon atoms

The reference level ($N = 1$) in Figure 7.12 has $\epsilon = \alpha$. As $N \to \infty$ the levels become very close, forming an **energy band** extending from $\epsilon = \alpha + 2\beta$ up to $\alpha - 2\beta$. (Remember α and β are both negative.) It should be noted that when the number of Carbons is odd there is always a Non-bonding MO: it is very important, giving the molecule its 'free-radical' character – the highest occupied orbital leading to a highly reactive system with a very short lifetime.

It is also interesting to ask what happens if you join the ends of a chain molecule to form a ring – a 'cyclic' molecule. In Example 7.9 we find the question is easily answered by making a simple change of the boundary conditions used in Example 7.8.

Example 7.9 Making rings – cyclic polyenes

If we join the ends of a chain of N Carbons, keeping the system flat with adjacent atoms connected by strong σ bonds, we obtain a ring molecule in which every Carbon provides one π electron in a 2p AO normal to the plane. In nearest neighbour approximation, the equations to determine the MO coefficients are unchanged – except that the AOs χ_1 and χ_N will become neighbours, so there will be a new non-zero element in the first and last rows of the matrix $\mathbf{h}$. For a 6-Carbon ring, called **Benzene**, h_{16} and h_{61} will both have the value β instead of zero. The secular equations will then become

$$\begin{aligned}
(\alpha - \epsilon)c_1 + \beta c_2 + \beta c_6 &= 0, \\
\beta c_1 + (\alpha - \epsilon)c_2 + \beta c_3 &= 0, \\
\beta c_2 + (\alpha - \epsilon)c_3 + \beta c_4 &= 0, \\
\beta c_3 + (\alpha - \epsilon)c_4 + \beta c_5 &= 0, \\
\beta c_4 + (\alpha - \epsilon)c_5 + \beta c_6 &= 0, \\
\beta c_1 + \beta c_5 + (\alpha - \epsilon)c_6 &= 0,
\end{aligned}$$

where the terms at the end of the first line and the beginning of the last line are 'new': they arise because now the Carbon with AO coefficient c_1 is connected to that with AO coefficient c_6.

On putting $(\alpha - \epsilon)/\beta = -x$, as before, and dividing throughout by β, the first and last of the secular equations become, respectively,

$$-xc_1 + c_2 + c_6 = 0 \quad \text{and} \quad c_1 + c_5 - xc_6 = 0,$$

but all the other equations have the 'standard' form

$$c_{m-1} - xc_m + c_{m+1} = 0$$

with m taking values $2, 3, 4, 5$. The first equation does not fit this pattern because, putting $m = 1$, it would need a term c_0 – which is missing. The last equation also does not fit – because with $m = 6$ it would need a term c_7, which is also missing.

To get round this problem we use a simple trick. We allow them to exist but make a change of interpretation: on counting round the ring in the direction of increasing m we note that $m = 6 + 1$ brings us back to the *seventh* atom, which coincides with the *first* – so $c_7 = c_1$ and $c_8 = c_2$ etc. – and in general $c_{m+N} = c_m$ for a ring of N atoms. This is called a **periodic boundary condition** and on putting $c_m = \exp(im\theta)$, as before, we must now require that $\exp(im\theta) = \exp i(m+N)\theta$.

The acceptable values of θ are thus limited to the solutions of $\exp(iN\theta) = 1$, which are $\theta = 2\pi k/N$, where k is an integer (positive, negative, or zero). The MOs and their energies are thus determined in general by

$$c_m^{(k)} = A_k \exp(2\pi imk/N), \qquad x_k = 2\cos(2\pi k/N) \quad (k = 0, \pm1, \pm2, \pm3).$$

To summarize what came out from Example 7.9, joining the ends of a long polyene chain to form a ring leaves the formula for the energy levels, namely (7.24), more or less unchanged –

$$\epsilon_k = \alpha + 2\beta \cos\left(\frac{2\pi k}{N}\right) \tag{7.25}$$

– with N instead of $N + 1$, but gives a *complex* MO with AO coefficients

$$c_m^{(k)} = A_k \exp\left(\frac{2\pi imk}{N}\right) \quad (A_k = 1/\sqrt{N}). \tag{7.26}$$

However, changing the sign of k in (7.24) makes no difference to the energy, so the solutions in (7.26) can be combined in pairs to give *real* MOs with AO coefficients

$$a_m^{(k)} = C_k \sin\left(\frac{2\pi mk}{N}\right), \qquad b_m^{(k)} = C_k \cos\left(\frac{2\pi mk}{N}\right),$$

where C_k is again chosen to normalize the function. On putting $N = 6$, for example, the three bonding π-type MOs for the **Benzene molecule** can be written as

$$\begin{aligned}
\phi_1 &= (1/\sqrt{6})(\chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 + \chi_6) \\
\phi_2 &= -(1/2\sqrt{3})(\chi_1 + 2\chi_2 + \chi_3 - \chi_4 - 2\chi_5 - \chi_6) \\
\phi_3 &= (1/2)(\chi_1 - \chi_3 - \chi_4 - 2\chi_5 + \chi_6).
\end{aligned} \tag{7.27}$$

The molecule forms a sweet-smelling liquid of great importance in the chemical industry. It is used in the manufacture of drugs, dyes, plastics and even explosives and is the first in a whole 'family' of molecules called **polyacenes**, formed by joining benzene rings together with one side in common and the loss of corresponding H atoms. All such molecules have numerous **derivatives**, formed by replacing one or more of the attached Hydrogens by other chemical groups such as $-\mathrm{CH}_3$ (methyl) or $-\mathrm{OH}$ (the **hydroxyl group**).

The next two members of the polyacene family are Naphthalene and Anthracene, as shown below:

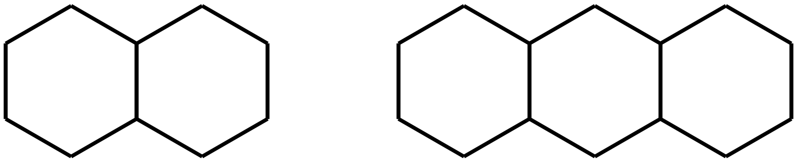


Figure 7.13 Naphthalene (left) and Anthracene (right)

Note that in pictures representing molecules of this kind, which are generally called **aromatic hydrocarbons**, the attached Hydrogens are usually not shown. Such molecules are also important in the chemical industry: Naphthalene forms a solid whose smell repels insects such as moths, which attack woollen garments, and both molecules form a starting point for preparing biologically important substances such as cholesterol and sex hormones.

7.6 The distribution of π electrons in alternant hydrocarbons

In the early applications of quantum mechanics to chemistry, alternant molecules were of special importance: they could be dealt with using simple approximations and 'pencil-and-paper' calculations (long before electronic computers were available). Nevertheless they uncovered many general ideas which are still valid and useful, especially in this field.

An **alternant hydrocarbon** is one in which the conjugated Carbons, which you first met in Example 7.5, lie in a plane and each contribute one π electron in a 2p orbital normal to the plane. The Carbons, all with three sp hybrids involved in σ bonds, fall into two sets; obtained by putting a star against alternate atoms to get a 'starred set and an 'unstarred set' so that no two stars come next to each other. A chain of N atoms is clearly of this kind, but a ring with an odd number of atoms is not – for the 'starring' would have to end with two atoms coming next to each other. Alternant molecules have certain general properties, typical of those found in Example 7.5: the bonding and antibonding MOs have orbital energies in pairs, with $\epsilon = \alpha \pm x\beta$ equally spaced below and above the reference level α.

When the MOs are filled in increasing order of energy, by one electron from each conjugated Carbon, they give a simple picture of the **electron density** in the molecule. The MO

$$\phi_k = c_1\chi_1 + c_2\chi_2 + \dots + c_N\chi_N$$

gives an electron (probability) density contribution $c_r^2|\chi_r|^2$ to atom r and integration shows that c_r^2 represents the amount of electronic 'charge' associated with this atom by an electron in MO ϕ_k. Nowadays this quantity, summed over all π-type occupied MOs, is often called the "π-electron population" of the AO χ_r and is denoted by q_r.

The remarkable fact is that when the N electrons fill the available MOs, in increasing energy order, $q_r = 1$ for every conjugated Carbon – just as if every atom kept its own share of π electrons. Moreover, this result remains true even when the highest occupied MO contains only one electron, the number of conjugated centres being odd.

Just after Example 7.5, it was noted that a chain with an odd number of Carbons must contain a **non-bonding** MO, with $x = 0$ and therefore $\epsilon = \alpha$). Such NBMOs are important because they give rise to free-radical behaviour. In general they follow from the secular equations (see, for example, Example 7.5) because the one that connects the coefficient c_r with those of its neighbours c_s must satisfy

$$-xc_r + \sum_{s(r-s)} c_s = 0, \tag{7.28}$$

where $s(r-s)$ under the summation sign means " for atoms s connected with atom r", and when $x = 0$ the sum of AO coefficients over all atoms s connected with r must vanish. In the Allyl radical, for example, we could mark the end Carbons (1 and 3, say) with a 'star' and say that, as they are neighbours of Carbon 2, the NBMO must have $c_1 + c_3 = 0$. The normalized NBMO would then be (with the usual neglect of overlap) $\phi_{NBMO} = (\chi_1 - \chi_3)/\sqrt{2}$.

A more interesting example is the **Benzyl radical** where a seventh conjugated Carbon is attached to a Benzene ring, the 'starred' positions and corresponding AO coefficients are as shown below –

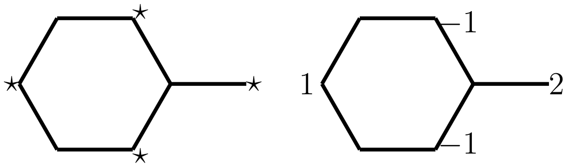
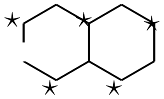


Figure 7.14 The Benzyl radical: starring of positions, and AO coefficients in the NBMO

To summarize: in the NBMO of an alternant hydrocarbon, the 'starring' of alternate centres divides the Carbons into two sets, 'starred' and 'unstarred'. On taking the AO coefficients in the unstarred set to be zero, the *sum* of those on the starred atoms to which any unstarred atom is connected must also be zero. Choosing the AO coefficients in this way satisfies the condition (8.13) whenever $x = 0$ and this lets you write down at least one NBMO just by inspection! The MO is normalized by making the sum of the squared coefficients equal to 1 and this means that an electron in the NBMO of the Benzyl radical will be found on the terminal Carbon with a probability of 4/7, compared with only 1/7 on the other starred centres. The presence of this odd 'unpaired' electron accounts for many of the chemical and physical properties of alternant hydrocarbons with one or more NBMOs. Such electrons easily take part in bonding with other atoms or chemical groups with singly occupied orbitals; and they are also easily 'seen' in electron spin resonance (ESR) experiments, where the magnetic moment of the spin couples with an applied magnetic field. The Benzyl radical, with its single loosely bound electron, is also easily converted into a Benzyl radical *anion* by accepting another electron, or into a *cation* by loss of the electron in the NBMO. The corresponding 'starred' centres then get a net negative or positive charge, which determines the course of further reactions.

To show how easy it is to play with such simple methods you could try to find the NBMO for the 'residual molecule' which results when you take away one CH 'fragment' from the Naphthalene molecule shown in Figure 7.14 The system that remains when you choose the 'top' Carbon on the right is



where the starred positions have been chosen as shown. You should try to attach the non-zero AO coefficients in the NBMO.

The NBMO is important in the discussion of **chemical reactions**. The 'taking away' of the CH group in this example actually happens (we think!) when an NO_2^+ group comes close to the Carbon: it is 'thirsty' for electrons and localizes two π electrons in the Carbon 2p AO, changing the hybridization so that they go into a tetrahedral hybrid and leave only 8 electrons in the 9-centre conjugated system of the residual molecule. The NO_2 group then bonds to the Carbon in this 'activated complex', which carries a positive charge (still lacking 1 electron of the original 10): an electron is then removed from the attached Hydrogen, which finally departs as a bare proton! Just before that final step, the energy (E') of the residual molecule is higher than the energy (E) of the original molecule and the difference $A = E' - E$ is called the **Activation Energy** of the nitration reaction.

Any change you can make in the original molecule (e.g. replacing another Carbon by a Nitrogen) that lowers the Activation Energy will make the reaction go more easily; and that's the kind of challenge you meet in Chemistry.

(Notice that we've been talking always about total π-electron energies, estimated as sums of orbital energies, and we're supposing that there are no big changes in the energies of the σ bonds. These are approximations that seem to work! – but without them there would be little hope of applying quantum mechanics in such a difficult field.)

It's time to move on – this is not a Chemistry book! But before doing so let's remember that nearly all the molecules we've been dealing with in this section have been built up from only two kinds of atom – Hydrogen, with just one electron, and Carbon, with six. And yet 'Carbon chemistry' is so important in our daily life that we can't do without it: hydrocarbons give us the fuels we need for driving all kinds of machines (in our factories) and vehicles (from scooters to heavy transport); also for heating and cooking; and for preparing countless other materials (from drugs to plastics and fabrics such as nylon).

Remember also that our own bodies are built up almost entirely from elements near the beginning of the Periodic Table, Carbon and Hydrogen in long chain molecules, along with small attached groups containing Nitrogen and Oxygen, and of course the Hydrogen and Oxygen in the water molecules (which make up over 50% of body mass). When Calcium and Phosphorus are added to the list (in much smaller quantities) these six elements account for about 99% of body mass!

7.7 Connecting Theory with Experiment

The main 'bridge' between so much abstract theory and the things we can measure in the laboratory, the **observables**, is provided by a number of **electron density functions**. In Chapter 4 we introduced a 'density matrix', in the usual finite-basis representation, where it was used to define the Coulomb and exchange operators of self-consistent field (SCF) theory. But because we were dealing with **closed-shell** systems, where the occupied orbitals occurred in pairs (one with spin factor α and a 'partner' with spin factor β) we were able to 'get rid of spin' by integrating over spin variables. Then, in studying the electronic structure and some of the properties of *atoms* (in Chapter 5), we took the idea of density functions a bit further and began to see how useful they could be in dealing with electronic properties. You should look again at the ideas developed in Examples 5.6 and 5.7 and summarized in the 'box' (5.33). Finally, in Chapter 6, we were able to extend the same ideas to molecules; so here you'll find nothing very new.

It will be enough to remind ourselves of the definitions and fill in some details. The spinless electron density function, for a system with an N-electron wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N)$ is

$$P(\mathbf{r}_1) = \int \rho(\mathbf{x}_1)\mathrm{d}s_1, \tag{7.29}$$

where $\rho(\mathbf{x}_1)$ is the density with spin included, as defined in (5.24), and arises from the product $|\Psi\Psi^*|$ on integrating over all variables except $\mathbf{x}_1$. Although the variable has been called $\mathbf{x}_1$ that's only because we chose the first of the N variables to keep 'fixed' in integrating over all the others: the electrons are indistinguishable and we get the same density function whatever choice we make – so from now on we'll often drop the subscript in *one*-electron functions, using just $P(\mathbf{r})$ or $\rho(\mathbf{x})$. The function $P(\mathbf{r})$ is often called, for short, the "charge density" since it gives us a clear picture of how the total electronic charge is 'spread out' in space.

We'll continue to use the N-electron Hamiltonian

$$\mathsf{H} = \sum_i \mathsf{h}(i) + \tfrac{1}{2}\textstyle\sum_{i\neq j} \mathsf{g}(i,j), \tag{7.30}$$

where $\mathsf{h}(i)$ and $\mathsf{g}(i,j)$ are defined in Chapter 2, through equations (2.2) and (2.3), and the 1-electron operator $\mathsf{h}(i)$ contains a term $V(i)$ for the potential energy of electron i in the field of the nuclei. The potential energy of the whole system follows in terms of the state function Ψ as

$$\begin{aligned}\langle\Psi|\sum_i V(i))|\Psi\rangle &= N\int \Psi^*(\mathbf{x}_1,\mathbf{x}_2,\,...\,\mathbf{x}_N)V(1)\Psi(\mathbf{x}_1,\mathbf{x}_2,\,...\,\mathbf{x}_N)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2\,...\,\mathrm{d}\mathbf{x}_N \\ &= \int V(1)\rho(\mathbf{x}_1)\mathrm{d}\mathbf{x}_1 \\ &= \int V(1)P(\mathbf{r}_1)\mathrm{d}\mathbf{r}_1,\end{aligned}$$

where the first step expresses the expectation value as N times the result for Electron 1; the next step puts it in terms of the density $\rho(\mathbf{x}_1)$ with spin included; and finally, since $V(1)$ is spin-independent, the spin integrations can be done immediately and introduce the 'spinless' density $P(\mathbf{r}_1)$ defined in (7.14)

The spinless density *'matrix'* is defined similarly:

$$P(\mathbf{r}_1;\mathbf{r}'_1) = \int_{s'_1=s_1} \rho(\mathbf{x}_1;\mathbf{x}'_1)\mathrm{d}s_1 \tag{7.31}$$

where $\rho(\mathbf{x}_1;\mathbf{x}'_1) = N\int \Psi(\mathbf{x}_1,\mathbf{x}_2,\,...\,\mathbf{x}_N)\Psi^*(\mathbf{x}'_1,\mathbf{x}_2,\,...\,\mathbf{x}_N)\mathrm{d}\mathbf{x}_2,\,...\,\mathbf{x}_N)$ is the density matrix with spin included, as defined in (5.26), the prime being used to protect the variable in Ψ^* from the action of any operator. To express the expectation value of an *operator* sum you can make similar steps (you should do it!) Thus, for the *kinetic* energy with operator $\mathsf{T}(i)$ for electron i,

$$\begin{aligned}\langle\Psi|\sum_i \mathsf{T}(i))|\Psi\rangle &= N\int \Psi^*(\mathbf{x}_1,\mathbf{x}_2,\,...\,\mathbf{x}_N)\mathsf{T}(1)\Psi(\mathbf{x}_1,\mathbf{x}_2,\,...\,\mathbf{x}_N)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2\,...\,\mathrm{d}\mathbf{x}_N \\ &= \int_{\mathbf{x}'_1=\mathbf{x}_1} \mathsf{T}(1)\rho(\mathbf{x}_1;\mathbf{x}'_1)\mathrm{d}\mathbf{x}_1 \\ &= \int_{\mathbf{r}'_1=\mathbf{r}_1} \mathsf{T}(1)P(\mathbf{r}_1;\mathbf{r}'_1)\mathrm{d}\mathbf{r}_1.\end{aligned}$$

Those are *one*-electron density functions, but in Example 5.7 we found it was possible to generalize to two- and many-electron densities in a closely similar way. Thus a 'pair' density (spin included) is defined as

$$\pi(\mathbf{x}_1,\mathbf{x}_2) = N(N-1)\int \Psi(\mathbf{x}_1,\mathbf{x}_2\,...\,\mathbf{x}_N)\Psi^*(\mathbf{x}_1,\mathbf{x}_2\,...\,\mathbf{x}_N)\mathrm{d}\mathbf{x}_3,\,...\,\mathbf{x}_N$$

and the density matrix follows on putting primes on the variables $\mathbf{x}_1,\mathbf{x}_2$ in the Ψ^* factor. With this definition, the expectation value of the electron interaction term in the Hamiltonian becomes (remember, the prime on the Σ means "no term with $j=i$")

$$\langle\Psi|\sum{}'_{(i,j)}\mathsf{g}(i,j)|\Psi\rangle = \int [\mathsf{g}(1,2)\pi(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2)]_{(\mathbf{x}'_1=\mathbf{x}_1,\mathbf{x}'_2=\mathbf{x}_2)}\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2.$$

As $\mathsf{g}(1,2)$ is just an inverse-distance electron repulsion, without spin dependence, the spin integrations can be performed immediately and the primes can be removed. The result is thus

$$\langle\Psi|\sum\nolimits'_{(i,j)}\mathsf{g}(i,j)|\Psi\rangle = \int[\mathsf{g}(1,2)\Pi(\mathbf{r}_1,\mathbf{r}_2)]\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2.$$

(The notation is consistent: Greek letters ρ and π are used for the density functions with spin included; corresponding capitals, P and Π for their spin-free counterparts.)

In summary, $\pi(\mathbf{x}_1,\mathbf{x}_2) = N(N-1)\int\Psi(\mathbf{x}_1,\mathbf{x}_2\ldots\mathbf{x}_N)\Psi^*(\mathbf{x}_1,\mathbf{x}_2\ldots\mathbf{x}_N)\mathrm{d}\mathbf{x}_3,\ \ldots\mathbf{x}_N$ and

$$\Pi(\mathbf{r}_1,\mathbf{r}_2) = \int\pi(\mathbf{x}_1,\mathbf{x}_2)\mathrm{d}s_1\mathrm{d}s_2 \tag{7.32}$$

is a 2-electron probability density: it gives the probability of two electrons (*any* two) being found simultaneously 'at' points $\mathbf{r}_1$ and $\mathbf{r}_2$ in ordinary 3-space, with all the others anywhere. (Remember this function is a *density*, so to get the actual probability of finding two electrons *in* tiny volume elements at points $\mathbf{r}_1$ and $\mathbf{r}_2$ you must multiply it by the volume factor $\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2$.)

The function $\Pi(\mathbf{r}_1,\mathbf{r}_2)$ describes the **correlation** between the motions of two electrons and in IPM approximation turns out to be non-zero only when they have the same spin. This is one of the main challenges to the calculation of accurate many-electron wave functions. Fortunately we can go a long way without meeting it!

Some applications

So far we've been thinking mainly of an isolated system, which can stay in a definite energy eigenstate 'forever' – such states being *stationary*. To make the system change you must do something to it; you must disturb it and a small disturbance of this kind is called a **perturbation**. The **properties** of the system are measured by the way it reacts to such changes.

Response to an applied electric field

The simplest properties of molecules are the ones that depend directly on the charge density, described by the function $P(\mathbf{r})$ defined in (7.29). And the simplest perturbation you can make is the one due to an electric field applied from outside the molecule. This will change the potential energy of Electron i in the Hamiltonian H, so that (using x, y, z for the components of an electron's position vector $\mathbf{r}$,

$$V(i) \to V(i) + \delta V(i).$$

When the 'external' field is uniform and is in the z-direction, it arises from the electric potential ϕ as $F_z = -\partial\phi/\partial z$; and we may thus choose

$\phi = -F_z z$, which takes the value zero at the origin of coordinates. The potential energy of electron i (of charge $-e$) due to the applied field is then $-e\phi = F_z ez$ and represents the change $\delta V(i)$ in the electron's potential energy. Thus a uniform field in the z-direction will produce a perturbation $\delta V(i) = F_z ez_i$, for every electron i. (Remember, F_z is used for the field strength so as not to mix it up with the *energy* E).

Supposing F_z to be constant, its effect will be to produce a small **polarization** of the system by urging the electron in the (negative) direction of the field (since the electron carries a negative charge $-e$) and this means the probability function will 'lean' slightly in the the field direction. This effect will be small: if the change in the wavefunction is neglected in a first approximation the change in expectation value of H will be, summing over all electrons,

$$\delta E = \langle \delta \mathsf{H} \rangle = \langle \delta V \rangle = F_z e \int zP(\mathbf{r})\mathrm{d}\mathbf{r}.$$

This may be written $\delta E = F_z \mu_z$ where $\mu_z$is the z-component of the **electric moment** of the electron charge density, which is an experimentally measurable quantity. Of course this is a 'first-order' result and doesn't depend on the perturbation of the density function $P(\mathbf{r})$, which is also proportional to the applied field but is more difficult to calculate. When that is done the result becomes $\delta E = F_z M_z + \frac{1}{2} {F_z}^2 \alpha_{zz}$, where α_{zz} is another experimentally measurable quantity; it is a component of the **electric polarizability tensor** but its calculation requires perturbation theory to *second order*.

Response to displacement of a nucleus

As a second example let's think of *internal* changes in the molecule, where the change δV in the electronic potential energy function is caused by the displacement of a single nucleus. Use X, Y, Z for the coordinates of a nucleus (n, say) and think of the displacement in which $X \rightarrow X + \delta X$. The change of interaction energy between electron i and nucleus n will be $\delta V(\mathbf{r}_i)$ from electron i. Summing over all electrons gives the total potential energy change $\delta V(\mathbf{r})$ at any point $\mathbf{r}$ due to the whole electron distribution; and we again use the result

$$\delta E = \langle \delta \mathsf{H} \rangle = \langle \delta V \rangle = \int \delta V(\mathbf{r})\mathrm{d}\mathbf{r}.$$

Now divide both sides by δX and go to the limit where $\delta X \to 0$, to obtain

$$F_{nx} = \int F_{nx}(\mathbf{r})P(\mathbf{r})\mathrm{d}\mathbf{r}, \qquad (7.33)$$

where you will remember that (by definition)

$$-(\partial E/\partial X) = F_{nx},$$

is the total force on nucleus n, and

$$-(\partial F_{nx}(\mathbf{r})/\partial X) = F_{nx}(\mathbf{r}),$$

is the force due to one electron at point $\mathbf{r}$.

This is the famous **Hellmann-Feynman theorem**, first derived in Chapter 6: in words it says that the forces acting on the nuclei (which oppose their mutual electrostatic repulsions –and keep the molecule together) can be calculated by 'summing' the attractions due to the amount of charge $P(\mathbf{r})\mathrm{d}\mathbf{r}$ in volume element $\mathrm{d}\mathbf{r}$ over the whole 'charge cloud'. The interpretation is purely 'classical': the electron probability density may be treated as a static distribution of negative charge in which the positive nuclei are embedded. In Chapter 6 we said "This beautiful result seems too good to be true!" and you should go through the derivation again to understand what conditions apply and why you must be cautious in using it. At least it gives a solid foundation for the ideas contained in Section 6.3, where we introduced **electron populations** of orbital and overlap regions in LCAO approximations to the density function $P(\mathbf{r})$.

There are very many other experimentally observable effects that depend directly on the electron density in a molecule (some already studied, like the energy shifts of inner shell electrons, perturbed from their free-atom values by the molecular environment; the response to the approach of charged chemical groups, such as radical ions and cations; and the whole field of electronic spectroscopy, which depends on the *time-dependent* perturbations due to oscillating fields; and so on. But to close this chapter it's worth trying to fill one gap in the theoretical methodology built up so far: we haven't said very much about *magnetic* properties – and yet some of the most powerful experimental techniques for getting information about atomic and molecular structure involve the application of strong :magnetic fields. One thinks in particular of **Nuclear Magnetic Resonance** (NMR) and **Electron Spin Resonance** (ESR), which bring in the *spins* of both electrons and nuclei. So we must start by thinking of how a system responds to the application of a magnetic field.

Response to an applied magnetic field

Again let's take the simplest case of a *uniform* field. Whereas an electric field – a vector quantity – $\mathbf{F}$ with scalar components F_x, F_y, F_z in a Cartesian system, can be defined as the **gradient** of a scalar potential function ϕ, that is not possible for a magnetic field. If you look at Chapter 4 of Book 10 you'll see why: briefly, $\mathrm{div}\,\mathbf{B} = 0$ at every point in free space; but if $\mathbf{B}$ were the gradient of some scalar potential ϕ_{mag} that wouldn't be possible in general. On the other hand, $\mathbf{B}$ *could* be the curl of some vector quantity, $\mathbf{A}$, say. (If you've forgotten about operators such as grad, div and curl, you'll need Book 10.)

Now we're ready to show how the *motion* of a particle of charge q is modified by the application of a magnetic field. First of all, remember how the kinetic energy T is defined: $T = (1/2m)\sum p_i^2$, where the index i runs over components x, y, z and p_x, for example, is the x-component of momentum $p_x = mv_x = m\dot{x}$ – $\dot{x}$ being short for the time-derivative $\mathrm{d}x/\mathrm{d}t$. Also, when there is a potential energy $V = V(x, y, z) = q\phi(x, y, z)$ the total energy of the particle is the **Hamiltonian function**

$$E = H(x, y, z, p_x, p_y, p_z) = T + V,$$

but the **Lagrangian function**

$$L(x, y, z, p_x, p_y, p_z) = T - V;$$

named after the French mathematician Lagrange, is equally important. Either can be used in setting up the same equations of motion, but here we'll use Lagrange's approach.

The Lagrangian for a single particle in a static electric field is thus

$$L = \tfrac{1}{2}mv^2 - q\phi,$$

in terms of the speed v of the particle. In terms of L, the momentum components can be expressed as $p_x = (\partial L/\partial \dot{x}) = (\partial T/\partial \dot{x})$, since ϕ is velocity-independent. In the presence of a magnetic field, however, we know there is a transverse force depending on the particle velocity vector v and the magnetic flux vector B. We want to add a term to L (which is a scalar), depending on charge, velocity and B (or A), which can lead to the correct form of this so-called **Lorentz force**.

The simplest possibility would seem to be the scalar product $q(\mathsf{v}\cdot\mathsf{A})$, which leads to

$$L = \tfrac{1}{2}mv^2 + q(\mathsf{v}\cdot\mathsf{A}) - q\phi, \tag{7.34}$$

and a 'generalized' momentum component

$$p_x = (\partial L/\partial\dot{x}) = m\dot{x} + qA_x - q\phi. \tag{7.35}$$

This leads to the correct Lorentz force

$$\mathsf{F}_{\text{mag}} = q\mathsf{v}\times\mathsf{B} = q\mathsf{v}\times\operatorname{curl}\mathsf{A}$$

when we calculate the rate of change of particle momentum arising from the term $q(\mathsf{v}\cdot\mathsf{A})$ in (7.34), as we show in Example 7.10

Example 7.10 Showing that the new equations lead to the correct Lorentz force.

We want to show that the field-modified equations, (**??**) and (**??**) lead to the Lorentz force $\mathsf{F}_{\text{mag}} = q\mathsf{v}\times\mathsf{B}$. First we write the Newtonian equations of motion $F_x = m\ddot{x}$ etc. (i.e. Force = mass x acceleration) in Lagrangian form, taking one component at a time. The left-hand side can be written

$$F_x = -(\partial U/\partial x) = (\partial L/\partial x)$$

(rate of decrease of potential energy U in the x-direction). The right-hand side depends only on velocity, through the kinetic energy $T = \frac{1}{2}m\dot{x}^2$: thus $\partial T/\partial\dot{x} = m\dot{x}$ and therefore

$$F_x = m\ddot{x} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial T}{\partial\dot{x}}\right) = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial\dot{x}}\right),$$

since the potential energy U does not depend on velocity.

The Newtonian equations can thus be replaced by

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{x}}\right) = \frac{\partial L}{\partial x}$$

– with similar equations for the y- and z-components.

Example 7.10 Showing that the new equations lead to the correct Lorentz force.

We want to show that the field-modified equations, (7.34) and (7.35) lead to the Lorentz force $\mathsf{F}_{\text{mag}} = q\mathsf{v} \times \mathsf{B}$. First we write the Newtonian equations of motion $F_x = m\ddot{x}$ etc. (i.e. Force = mass x acceleration) in Lagrangian form, taking one component at a time. The left-hand side can be written

$$F_x = -(\partial U/\partial x) = (\partial L/\partial x)$$

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since the potential energy U does not depend on velocity.
The Newtonian equations can thus be replaced by

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{x}}\right) = \frac{\partial L}{\partial x}$$

– with similar equations for the y- and z-components.

Turning now to the generalized momentum vector p, whose x-component is given in (**??**), when the applied fields are time-independent its rate of change will be

$$(\mathrm{d}/\mathrm{d}t)\mathsf{p} = (\mathrm{d}/\mathrm{d}t)m\mathsf{v} + q(\mathrm{d}/\mathrm{d}t)\mathsf{A}.$$

The first term on the right is the usual mass × acceleration of Newton's law (the second term being the change resulting from the magnetic field) and refers to the ordinary ‘mechanical’ momentum change. So we write the equation the other way round, as

$$m\dot{\mathsf{v}} = \dot{\mathsf{p}} - q\dot{\mathsf{A}}.$$

The time derivative of p follows from the Lagrangian equations of motion (at the beginning of this Example), namely (for the x-component),

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{x}}\right) = \frac{\partial L}{\partial x}.$$

Thus, $(\partial L/\partial \dot{x})$ – which is the generalized momentum x-component – has a time derivative $\dot{p_x}$ and this is equated to $(\partial L/\partial x)$. When the magnetic field is included it follows that

$$\dot{p_x} = (\partial L/\partial x) = -q(\partial \phi/\partial x) + qv_x\partial(A_x/\partial x).$$

The second term in the expression for $\mathsf{F} = m\dot{\mathsf{v}}$ is $-q\dot{\mathsf{A}}$ and as we have taken $\mathsf{A} = \frac{1}{2}\mathsf{B} \times \mathsf{r}$, we can easily calculate its time rate of change. On taking the components one at a time and remembering that the position vector r has components x, y, z. we obtain

$$\left(\frac{\mathrm{d}A_x}{\mathrm{d}t}\right) = \left(\frac{\partial A_x}{\partial t}\right) + \left(\frac{\partial A_x}{\partial x}\right)\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right) + \left(\frac{\partial A_x}{\partial y}\right)\left(\frac{\mathrm{d}y}{\mathrm{d}t}\right) + \left(\frac{\partial A_x}{\partial z}\right)\left(\frac{\mathrm{d}z}{\mathrm{d}t}\right),$$

with similar expressions for the y- and z-components. Note that the first term on the right will be zero because A has no explicit dependence on time.

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taking the components one at a time and remembering that the position vector r has components x, y, z. we obtain

$$\left(\frac{\mathrm{d}A_x}{\mathrm{d}t}\right) = \left(\frac{\partial A_x}{\partial t}\right) + \left(\frac{\partial A_x}{\partial x}\right)\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right) + \left(\frac{\partial A_x}{\partial y}\right)\left(\frac{\mathrm{d}y}{\mathrm{d}t}\right) + \left(\frac{\partial A_x}{\partial z}\right)\left(\frac{\mathrm{d}z}{\mathrm{d}t}\right),$$

with similar expressions for the y- and z-components. Note that the first term on the right will be zero because A has no explicit dependence on time.

On substituting both terms into the force equation $\mathsf{F} = m\dot{\mathsf{v}} = \dot{\mathsf{p}} - q\dot{\mathsf{A}}$ the x-component follows as

$$F_x = -q\frac{\partial \phi}{\partial x} + q\left[\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right)\dot{y} - \left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right)\dot{z}\right].$$

The two terms in round brackets can be recognised as, respectively, the z- and y-components of the vector $\mathrm{curl}\,\mathsf{A}$; and when the coefficients $\dot{y}$ and $\dot{z}$ are attached the result in square brackets is seen to be the x-component of the vector product $\mathsf{v} \times \mathrm{curl}\,\mathsf{A}$.

Finally, then, in vector notation $\mathsf{F} = q\mathsf{E} + q(\mathsf{v} \times \mathsf{B})$ where the electric field vector is here denoted by E, while the other term $\mathsf{F}_{\mathrm{mag}} = q(\mathsf{v} \times \mathrm{curl}\,\mathsf{A})$ is the **Lorentz force**.

Molecules in magnetic fields

In Section 6 of Chapter 5 we noted that whenever a system contained unpaired electrons there would be a tiny interaction between the **electron spin**, with its resultant magnetic dipole, and any external magnetic field. A free spin interacts with a magnetic field **B** through a 'coupling term' $g\beta\mathbf{B}\cdot\mathsf{S}$, where the 'g-value' is very close to 2 and $\beta = e\hbar/2m$ (the "Bohr magneton"). So there will be a small perturbation of the many-electron Hamiltonian of the form

$$\mathsf{H}'_{\mathrm{Z}} = g\beta\sum_i \mathbf{B}\cdot\mathsf{S}(i), \tag{7.36}$$

the summation being over all electrons. This is the spin-field "Zeeman interaction".

There will also be an interaction between the spin dipole and the magnetic field produced by **motion** of the electrons, which will depend on the *velocity* with which they are moving. In the case of an atom, the spatial motion around the nucleus was represented by an angular momentum operator, giving rise to **spin-orbit coupling** through a perturbation

$$\mathsf{H}'_{\text{mag}} = \beta \sum_i \mathbf{B} \cdot \boldsymbol{\mathsf{L}}(i). \tag{7.37}$$

By taking account of these two perturbations we were able to predict the **fine structure** of atomic energy levels, which could be 'seen' experimentally in electronic spectroscopy.

In the case of a molecule things are a bit more difficult: there will be *several* nuclei instead of one, so an electron is not in a spherically symmetrical field and will not be in a state of definite angular momentum – which is said to be 'quenched' by the presence of other nuclei. That means the velocity of the electron will be variable and spread out through space, corresponding to a 'current' of probability density; and in defining this we must take account of the magnetic field. We also need to generalize the **spin density**, defined as the excess of up-spin electron density, $P_\alpha(\mathbf{r})$, over down-spin, $P_\alpha(\mathbf{r})$ (see (5.32). We can, however, do both things at the same time by going back to first principles.

Property Densities

Suppose we are interested in some observable quantity, call it X, with associated operator $\mathsf{X}(i)$ for electron i. The expectation value of X, for the whole N-electron system will be

$$\begin{aligned} \langle\Psi|\mathsf{X}|\Psi\rangle &= \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N)\mathsf{X}\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2 \dots \mathrm{d}\mathbf{x}_N \\ &= N\int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N)\mathsf{X}(1)\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N)\mathrm{d}\mathbf{x}_1\mathrm{d}\mathbf{x}_2 \dots \mathrm{d}\mathbf{x}_N. \end{aligned}$$

– since every electron gives the same contribution as 'Electron 1'. By moving the Ψ^* factor to the right and changing variable $\mathbf{x}_1$ to $\mathbf{x}'_1$ (so the operator will not touch it), we can rewrite this result as

$$\langle\Psi|\mathsf{X}|\Psi\rangle = \int [\mathsf{X}(1)\rho(\mathbf{x}_1;\mathbf{x}'_1)]_{\mathbf{x}'_1=\mathbf{x}_1}\mathrm{d}\mathbf{x}_1,$$

where $\rho(\mathbf{x}_1;\mathbf{x}'_1)$ is the 1-electron **density matrix** and the two variables are identified *after* the operation with $\mathsf{X}(1)$.

The whole integrand in the last equation is an ordinary density function and, when integrated over all space, gives the expectation value of X for the whole system. We'll call it a **property density** for X and denote it by

$$\rho_X(\mathbf{x}) = [\mathsf{X}\rho(\mathbf{x};\mathbf{x}')]_{\mathbf{x}'=\mathbf{x}}, \tag{7.38}$$

where the subscripts on the variables in the *one-electron* density matrix, no longer necessary, are dropped from now on.

Spinless Properties

You've already dealt with similar density functions, usually for properties that are spin-independent. In that case you can integrate over spin variables immediately in getting the expectation value and obtain, instead of (7.38), a spinless density function

$$P_X(\mathbf{r}) = [\mathsf{X}\,P(\mathbf{r};\mathbf{r}')]_{\mathbf{r}'=\mathbf{r}}. \tag{7.39}$$

If you write V instead of X, for potential energy of the electrons in the field of the nuclei, and identify the variables straight away (V) being just a function of position in ordinary space), then all should be clear: the density of potential energy becomes

$$P_V(\mathbf{r}) = V(\mathbf{r})P(\mathbf{r}),$$

since V is just the multiplier $V(\mathbf{r})$. The density is thus the amount of potential energy per unit volume for an electron at point $\mathbf{r}$ and integration over all space gives the expectation value of the potential energy of the whole electron distribution.

Spin Density

Now let's think of the density of a component of **spin angular momentum** (if the electron is 'smeared out' in space, with probability density $P(\mathbf{r})$ per unit volume, then so is the spin it carries!). On taking $\mathsf{X} = \mathsf{S}_z$, and using (7.38) we get

$$\rho_{\mathsf{S}_z}(\mathbf{x}) = [\mathsf{S}_z\,\rho(\mathbf{x};\mathbf{x}')]_{\mathbf{x}'=\mathbf{x}}.$$

For any kind of wave function $\rho(\mathbf{x};\mathbf{x}')$ will have the form (Read Example 5.6 again, and what follows it, then think about it!)

$$\rho(\mathbf{x};\mathbf{x}') = P_\alpha(\mathbf{r};\mathbf{r}')\alpha(s)\alpha(s') + P_\beta(\mathbf{r};\mathbf{r}')\beta(s)\beta(s').$$

The spin operator in (7.40) will multiply $\alpha(s)$ by $\frac{1}{2}$, but $\beta(s)$ by $-\frac{1}{2}$ and then, removing any remaining primes, (7.40) will become (check it out!)

$$\rho_{\mathsf{S}_z}(\mathbf{r}) = \tfrac{1}{2}[P_\alpha(\mathbf{r}) - P_\beta(\mathbf{r})]. \tag{7.40}$$

This result, as you would expect, is simply (in words)

"Density of up-spin electrons minus density of down-spin, times magnitude of spin angular momentum".

Since ρ has usually been reserved for functions of the space-spin variable $\mathbf{x}$, the result is often written instead as

$$Q_z(\mathbf{r}) = \tfrac{1}{2}[P_\alpha(\mathbf{r}) - P_\beta(\mathbf{r})]. \tag{7.41}$$

Similar densities, Q_x, Q_y, may also be defined, but in practice the applied magnetic field (e.g. in NMR and ESR experiments) is usually chosen to fix the 'z-direction'.

Densities that depend on motion of the electrons

The other density functions needed refer to electronic *motion*, for generality in the presence of a magnetic field: they are a density of kinetic energy (which is a scalar quantity) and a current density (a vector density arising from the linear momentum).

Kinetic Energy Density

In (7.34) we proposed the kinetic energy operator $\mathsf{T} = \frac{1}{2}m\mathsf{v}^2 - e(\mathbf{\mathsf{v}}\cdot\mathbf{\mathsf{A}})$ for an electron moving in a magnetic field $\mathbf{B}$, arising from a **vector potential A**; and in this case we also derived a 'generalized' momentum operator(7.35), namely $\mathbf{\mathsf{p}} = m\dot{\mathbf{\mathsf{r}}} - e\mathbf{\mathsf{A}}$, whose first term is just the Newtonian quantity $m\mathbf{\mathsf{v}}$ – usually denoted by $\mathbf{\mathsf{p}}$ when there is no magnetic field. To avoid confusion it's convenient to give the generalized momentum vector a new symbol, writing it as

$$\boldsymbol{\pi} = m\dot{\mathbf{\mathsf{r}}} - e\mathbf{\mathsf{A}} \tag{7.42}$$

and calling it, by its usual name, the "gauge invariant momentum".

When there is no magnetic field, the 1-electron KE term in the Hamiltonian can be written $\mathsf{T} = (1/2m)\mathsf{p}^2$ and it would seem that a kinetic energy density could be defined (cf. (7.39)) as

$$P_{\mathsf{T}_0}(\mathbf{r}) = (1/2m)[\mathsf{p}^2\, P(\mathbf{r};\mathbf{r}')]_{\mathbf{r}'=\mathbf{r}},$$

where subscript zero indicates zero magnetic field.

Unfortunately this definition is not completely satisfactory because it leads to a quantity with both real and imaginary parts, whereas the kinetic energy contributions must be *both real and positive* at all points in space. One way out of this difficulty is simply to take the *real part* of the last expression as a more satisfactory definition; another is to replace the operator p^2 by $\mathbf{p}\cdot\mathbf{p}^\dagger$, where the adjoint operator $\mathsf{p}^\dagger$ (obtained by changing the sign of i) works on the variables in the wave function Ψ^*. In the second case the KE density becomes

$$P_{\mathsf{T}_0}(\mathbf{r}) = (1/2m)[\mathbf{p}\cdot\mathbf{p}^\dagger\, P(\mathbf{r};\mathbf{r}')]_{\mathbf{r}'=\mathbf{r}}. \tag{7.43}$$

(This is still not absolutely satisfactory if one wants to know how much KE comes from a finite part of space, when integrating to get the total expectation value, for it contains terms depending on the surface bounding the chosen region. But for all normal purposes, which involve integration over *all* space, it may be used.)

In the presence of a magnetic field the operator p is replaced by the 'generalized' momentum operator $\boldsymbol{\pi}$, defined in (7.42), and the natural generalization of the KE density is

$$P_{\mathsf{T}}(\mathbf{r}) = (1/2m)[\boldsymbol{\pi}\cdot\boldsymbol{\pi}^\dagger\, P(\mathbf{r};\mathbf{r}')]_{\mathbf{r}'=\mathbf{r}}. \tag{7.44}$$

Like the field-free result, this definition is normally satisfactory.

Probability current density

Whenever the probability distribution, described by the 1-electron density $P(\mathbf{r})$, is changing in time we need to know *how* it is changing. There will be a *flow* of density out of (or into) any volume element d$\mathbf{r}$ and it must be described in terms of a velocity component v_α ($\alpha = x,\ y,\ z$) in ordinary space. (Think of the wave packet discussed in Section ? of Book 11.)

Here we'll look for a current density function with components $J_\alpha(\mathbf{r})$ such that

$$P_{\mathsf{v}_\alpha}(\mathbf{r}) = (1/m)[\mathsf{p}_\alpha\, P(\mathbf{r};\mathbf{r}')]_{\mathbf{r}'=\mathbf{r}},$$

which we know will lead, on integrating over all space, to the expectation value $\langle \mathsf{v}_\alpha\rangle$ of electronic velocity along the α direction. Again this gives in general an unwanted imaginary component, which may be dropped; and when the magnetic field is admitted the most satisfactory definition is

$$P_{\mathsf{v}_\alpha}(\mathbf{r}) = m^{-1}\mathrm{Re}[\pi_\alpha\, P(\mathbf{r},\mathbf{r}')]_{\mathbf{r}'=\mathbf{r}}. \tag{7.45}$$

This gives a current density which is everywhere real and positive and gives the correct expectation value on integrating over all space.

Finite basis approximations

Of course, if we want to actually calculate a molecular electronic property we have to use an approximation in which the orbitals used (e.g. the MOs) are expressed as linear combinations of basis functions (e.g. AOs centred on the various nuclei). This finite basis approximation was first introduced in Chapter 4 (Section 4.4) and allows us to convert all equations into *matrix* equations. For example any MO

$$\phi_K = c_{K1}\chi_1 + c_{K2}\chi_2 + \;...\; + c_{Kr}\chi_r + \;...\; + c_{Km}\chi_m$$

can be expressed in matrix form, as the row-column product

$$\phi_K = (\chi_1\,\chi_2\,...\,\chi_m)\begin{pmatrix} c_{K1}\\ c_{K2}\\ ..\\ ..\\ c_{Km}\end{pmatrix} = \boldsymbol{\chi}\mathbf{c}_K, \tag{7.46}$$

where $\mathbf{c}_K$ stands for the whole *column* of expansion coefficients and $\boldsymbol{\chi}$ for the *row* of basis functions. So the X operator will be represented in the χ-basis by the matrix $\mathbf{X}$, with elements $X_{rs} = \langle\chi_r|\mathsf{X}|\chi_s\rangle$, and its expectation value for an electron in ϕ_K will be

$$\begin{aligned}\langle\phi_K|\mathsf{X}|\phi_K\rangle &= \sum_{r,s} c^*_{Kr}\langle\chi_r|\mathsf{X}|\chi_s\rangle c_{Ks}\\ &= \sum_{r,s} c^*_{Kr}X_{rs}c_{Ks}\\ &= \mathbf{c}_K{}^{\dagger}\mathbf{X}\mathbf{c}_K \end{aligned} \tag{7.47}$$

– so, you see, an operator (set in the special typeface as X) is *represented* by a corresponding matrix $\mathbf{X}$ (set in boldface), while a function, such as ϕ_K, is represented by a single-column matrix $\mathbf{c}_K$ containing its expansion coefficients; and the complex conjugate of a function is indicated by adding a 'dagger' to the symbol for its column of coefficients. Once you get used to the notation you can see at a glance what every equation means. As a simple illustration of how things work out in a finite basis we can use a very rough approximation to estimate the velocity expectation value for an electron moving along a 1-dimensional chain of Carbon atoms.

Example 7.11 Calculation of a ring current

In Example 7.9 we joined the ends of a chain of N Carbon atoms to make a ring, considering only the π electrons (one from each atom) and using Hückel approximations to calculate the MOs ϕ_k and corresponding energy levels ϵ_k. In the absence of an applied magnetic field, the electron velocity operator is $\mathsf{v} = (1/m)\mathsf{p}$ and we'll choose the momentum operator for a component p in the 'positive' direction (i.e. from Atom n to Atom $n+1$ as you go along the chain.)

Suppose we want the expectation value $\langle \mathsf{v} \rangle$ for motion in this direction and for any allowed value of k. Since any velocity operator $\mathsf{v} = (1/m)\mathsf{p}$ contains a factor $(\hbar/i)$, and is thus pure imaginary, its expectation value in any state with a real wave function must be zero. But Example 7.9 showed that, for a ring of N atoms, complex eigenfunctions of the form

$$\phi_k = A_k \sum_n \chi_n \exp(2\pi i n k/N) \quad (A_k = 1/\sqrt{N})$$

could be found. The MO of lowest energy is $\phi_0 = A_0(\chi_1 + \chi_2 + \ldots + \chi_6)$ and, being real, will have zero value of the velocity expectation value. But the MOs with $k = \pm 1$ form a degenerate pair, whose wave functions are complex conjugate. The expectation value in state ϕ_k will be $\langle \phi_k | \mathsf{v} | \phi_k \rangle = \sum_{n,n'} c_n^{(k)*} \langle \chi_n | \mathsf{v} | \chi_{n'} \rangle c_{n'}^{(k)}$ and tdo evaluate this quantity, which measures the expected electron probability current, we need only the matrix elements $\langle \chi_n | \mathsf{v} | \chi_{n'} \rangle$ and the AO coefficients $c_n^{(k)}$ (given above for any chosen k). If we were doing an energy calculation, with Hückel approximations, we'd have the 1-electron Hamiltonian h in place of v; and the n-n' matrix element would be given an empirically chosen value $\beta_{nn'}$ for nearest neighbour atoms, zero otherwise. But here the nearest neighbours of Atom n would have $n' = n + 1$ (for positive direction along the chain) and $n' = n - 1$ (for negative direction); and, as the operator v 'points' in the direction of increasing n, the $n \rightarrow n + 1$ matrix element would have a substantial (but imaginary) value ($i\gamma$, say). With this choice, the most suitable approximations would seem to be $\langle \chi_n | \mathsf{v} | \chi_{n+1} \rangle = i\gamma$ and $\langle \chi_n | \mathsf{v} | \chi_{n-1} \rangle = -i\gamma$, other matrix elements being considered negligible.

On using this very crude model, the expectation value of the velocity component for an electron in MO ϕ_k, for an N-atom chain, would be

$$\begin{aligned} \langle \phi_k | \mathsf{v} | \phi_k \rangle &= |A_k|^2 \sum_{n=1}^{n=N} [\exp(-2\pi i n k/N)(i\gamma) \exp(2\pi i (n+1) k/N) \\ &+ \exp(-2\pi i n k/N)(-i\gamma) \exp(2\pi i (n-1) k/N)]. \end{aligned}$$

This reduces to (Check it out!– noting that the summation contains N terms)

$$\langle \phi_k | \mathsf{v} | \phi_k \rangle = -2\gamma \sin(2\pi k/N).$$

The example confirms that, even without using a computer (or even a simple calculator!), it's often possible to obtain a good understanding of what goes on in a complicated many-electron system. Here we've found how an IPM approach with the simplest possible approximations can reveal factors that govern the flow of charge density along a carbon chain: a parameter γ (which depends on overlap of adjacent AOs) should be large and the flow will be faster in quantum states with higher values of a quantum number k. Pairs of states with equal but opposite values of k correspond to opposite directions of circulation round the ring; and the circulating current produces a magnetic dipole, normal to the plane of the ring. In cyclic hydrocarbons such effects are experimentally observable; and when the angular momentum operator p is replaced by the 'gauge invariant' operator $\boldsymbol{\pi}$ (which contains the vector potential of an *applied* magnetic field) it is possible to calculate a resultant **induced magnetic dipole** – again experimentally observable. In fact, the quantum number k in a ring current calculation is the analogue of an *angular momentum* quantum number in an atomic calculation. Chapter 7 has set out most of the mathematical tools necessary for an 'in depth' study of molecular electronic structure and properties – even if only at IPM level. But, for now, that's enough!

In Chapter 8, we'll start looking at more extended systems where there may be many thousands of atoms. Incredibly, we'll find it is still possible to make enormous progress.

Chapter 8

Some extended structures in 1-,2- and 3-dimensions

8.1 Symmetry properties of extended structures

In earlier chapters of this book we've often talked about "symmetry properties" of a system; these have been, for example, the exchange of two or more identical particles, or a geometrical operation such as a rotation which sends every particle into a new position. Such operations may form a **symmetry group** when they satisfy certain conditions. We have met **Permutation Groups** in introducing the Pauli Principle (Section 2.4 of Chapter 2); and **Point Groups**, which contain geometrical operations that leave one point in the system unmoved, in studying molecules (e.g. in Example 7.5 of this book). But when we move on to the study of extended structures such as crystals, in which certain structural 'units' may be repeated indefinitely (over and over again) as we go through the crystal, we must admit new symmetry operations – called **translations**. So this is a good point at which to review the old and start on the new.

The Point Groups

Here we'll use one or two simple examples to introduce general ideas and methods, without giving long derivations and proofs. As a first example let's look at the set of operations which, when applied to a square plate (or 'lamina'), leave it looking exactly as it did before the operation: these are the operations which "bring it into self-coincidence". They are named as shown in the following Figure 8.1, where those labelled with a C are all **rotations** around a vertical axis through the centre of the square, while those with a σ refer to **reflections** across a plane perpendicular to it (the arrow heads indicate a direction of rotation, while the double-headed arrows show what happens in a reflection). Thus, rotation C_4 sends the square corners labelled $1, 2, 3, 4$ into $2, 3, 4, 1$ and similarly σ_1 interchanges corners 2 and 4, leaving 1 and 3 where they were.

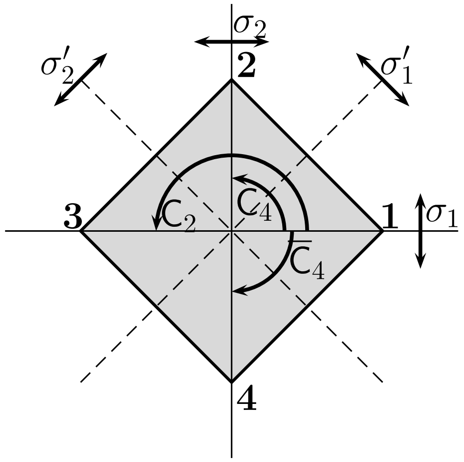


Figure 8.1 Symmetry operations: square lamina (see text)

Note that subscripts 1 and 2 on the reflection operations label different reflection planes and, when that is not enough, a prime has been added to the σ to show a different *type* of reflection (e.g. one which interchanges opposite sides of the square instead of opposite corners). The rotations C_n stand for those in the *positive* sense (anti- clockwise), through an angle $2\pi/n$, while $\overline{\mathsf{C}}_n$ stands for a similar operation, but in the *negative* sense (i.e. clockwise). In this example the operations do not include "turning the plate over", because the top and bottom faces may look different; if they looked exactly the same we'd have to include another symmetry operation for the interchange.

Note also that symmetry operations aren't always ones you can actually do! A reflection, for example, is easy to *imagine* – sending every point on the lamina into its 'mirror image' on the other side of the reflection plane – but could only be done by breaking the lamina into tiny pieces and re-assembling them!

The various operations, defined and named in Figure 8.1, can be collected and set out in a Table –as below:

Table 1

E	C_2	C_4	$\overline{\mathsf{C}}_4$
σ_1	σ_2	σ_1'	σ_2'

The operations in different boxes in Table 1 belong to different "classes" (e.g. rotations through the same angle but around different axes; or reflections across different planes) and E is used for the "identity" operation (do nothing!), which is in a class by itself.

Definition of a Group

Symmetry operations are combined by *sequential performance*: first perform one and then follow it by a second. Since each makes no observable change to the system, their combination is also a symmetry operation. The only way to see what is happening is to put a mark on the object (or to add numbers as in Figure 8.1). To describe the two operations "C_4 following σ_1" and their result we write

$$\mathsf{C}_4\sigma_1 = \sigma_1'.$$

The order in which the operations are made follows the usual convention, the one on the right acting first. Thus, if C_4 acts first, we find $\sigma_1\mathsf{C}_4 = \sigma_2'$ and the two 'products' do not, in general, commute: $\sigma_1\mathsf{C}_4 \neq \mathsf{C}_4\sigma_1$. Note that every operation has an *inverse*: for example $\mathsf{C}_4\overline{\mathsf{C}}_4 = \overline{\mathsf{C}}_4\mathsf{C}_4 = \mathsf{E}$ and some operations may be *self*-inverse, for example, $\sigma_1\sigma_1 = \mathsf{E}$. In general, the inverse of any operation R is denoted by R^{-1}, just as in 'ordinary' algebra.

In the language of Group Theory any collection of 'elements', with a **law of combination** like the one we've been using, containing an **identity** element E and an **inverse** R^{-1} for every element R, is called a **group**. The example we've been studying is called the $\mathbf{C}_{4v}$ **point group**: it contains symmetry operations that leave one point unmoved, have a 4-fold principle axis of rotation (normally taken as the 'vertical' axis) together with vertical reflection planes. There are molecules with symmetry groups more complicated than $\mathbf{C}_{nv}$, with an n-fold principle axis, but they can be dealt with in similar ways.

Subgoups, generators, classes

The elements in the first row of Table 1 form a group in themselves, $\mathbf{C}_4$;

we say C_4 is a **subgroup** of C_{4v}.

All the elements in C_4 can be expressed in terms of *one element* C_4: thus $\mathsf{C}_2 = \mathsf{C}_4\mathsf{C}_4 (= \mathsf{C}_4^2)$, $\overline{\mathsf{C}}_4 = \mathsf{C}_4^3$, $\mathsf{E} = \mathsf{C}_4^4$. We say C_4 is a **generator** of C_4.

If we take the elements in the first row of Table 1 and follow them (i.e. multiply from the left), in turn, with σ_1 we generate the elements in the second row. Thus, the whole group C_{4v} can be generated from only two elements, C_4 and σ_1. Often we need to work with only the generators of a group, since their properties determine the group completely.

The **classes** within a group each contain symmetry operations which are similar except that the axis, or reflection plane, to which they refer has itself been acted on by a symmetry operation. Thus, the reflection plane for σ_2 differs from that for σ_1 by a C_4 rotation; so σ_1 and σ_2 are in the same class – but this class does not include σ_1' or σ_2'.

Space Groups and Crystal Lattices

So far we've been looking only at Point Groups, where one point stays fixed in all symmetry operations. But in *extended* structures like crystals we must admit also the **translation** operations in which *all* points are shifted in the same direction and by the same amount. In symbols, a translation t sends the point with position vector r into an 'image' with $\mathsf{r}' = \mathsf{r} + \mathsf{t}$. Moreover, translations and point group operations (which we'll denote generally by R) can be combined. Thus, a rotation followed by a translation will send a point at r into an image at $\mathsf{r}' = \mathsf{R}\mathsf{r} + \mathsf{t}$. It is usual to denote this composite operation by $(\mathsf{R}|\mathsf{t})$ (not to be confused with a scalar product in quantum mechanics!), writing in symbols

$$\mathsf{r}' = (\mathsf{R}|\mathsf{t})\mathsf{r} = \mathsf{R}\mathsf{r} + \mathsf{t}. \tag{8.1}$$

It is then easily shown (do it!) that the law of combination for such operations is

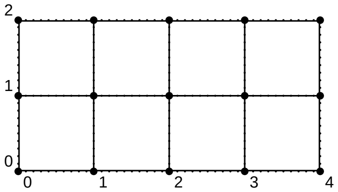
$$(\mathsf{R}|\mathsf{t})(\mathsf{S}|\mathsf{t}') = (\mathsf{R}\mathsf{S}|\mathsf{t} + \mathsf{R}\mathsf{t}') \tag{8.2}$$

and that the set of all such operations then forms a **Space Group**.

In the following example we show how just two **primitive translations**, call them a_1 and a_2, can be used to generate a **Crystal Lattice** in two dimensions. On adding a third primitive translation a_3 it is just as easy to generate a lattice for a real three-dimensional crystal.

Example 8.1 Generating a two-dimensional lattice

Let us take a_1 and a_2 as unit vectors defining x- and y-axes and combine them, without admitting any point group operations, to obtain a translation $\mathsf{t} = \mathsf{a}_1^{n_1}\mathsf{a}_2^{n_2}$: the translations commute, so the order in which the shifts are made is not important and the first factor simply means n_1 translations a_1 (e.g. $\mathsf{a}_1\mathsf{a}_1\mathsf{a}_1\mathsf{a}_1 = \mathsf{a}_1^4$ with the usual convention). And this translation moves a point at the origin to an image point with position vector $\mathsf{r}' = n_1\mathsf{a}_1 + n_2\mathsf{a}_2$ (it doesn't matter whether you think of $\mathsf{a}_1, \mathsf{a}_2$ as vectors or translations – it depends only on what you have in mind!). For $n_1 = 4, n_2 = 2$ you go to the top-right lattice point shown below:



If you allow n_1, n_2 to take all positive and negative values, from zero to infinity, you will generate an infinite square lattice in the xy-plane; the bold dots will then show all the **lattice points**.

Example 8.1 brings out one very important conclusion: when translations are combined with point group operations we have to ask *which* rotations or reflections are allowed. The combination $(\mathsf{R}|\mathsf{t})$ may not always be a symmetry operation – and in that case the operations will not be acceptable as members of a space group. Looking at the picture it is clear that if t is a translation leading from point (1,0) to (3,1) it *can* be combined with a rotation C_4, and then leads to another lattice point; but it *cannot* be combined with C_3 or C_6 because $(\mathsf{R}|\mathsf{t})$ would not lead to a lattice point for either choice of the rotation – and could not therefore belong to any space group. To derive all the possible space groups, when symmetrical objects are placed in an empty lattice of points, is a very long and difficult story (there are 320 of them!) – but it's time to move on.

Lattices and Unit Cells

In three dimensions we need to include *three* primitive translations $(\mathsf{a}_1, \mathsf{a}_2, \mathsf{a}_3)$ instead of two; and these vectors may be of different length and not at 90° to each other. If we stick to two, for ease of drawing, they will generate a lattice of the type shown below

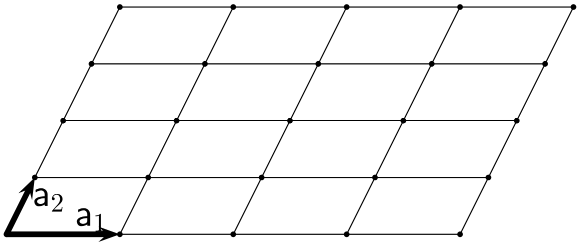


Figure 8.2 Lattice generated by translations a_1, a_2

A general lattice point will then have the position vector (in 3 dimensions)

$$\mathsf{r} = n_1\mathsf{a}_1 + n_2\mathsf{a}_2 + n_3\mathsf{a}_3, \tag{8.3}$$

where n_1, n_2, n_3 are *integers* (positive, negative, or zero). The scalar product that gives the square of the length of the vector (i.e. of the distance from the origin to the lattice point) is then

$$\begin{aligned} \mathsf{r}\cdot\mathsf{r} &= n_1^2(\mathsf{a}_1\cdot\mathsf{a}_1) + n_2^2(\mathsf{a}_2\cdot\mathsf{a}_2) + n_3^2(\mathsf{a}_3\cdot\mathsf{a}_3) \\ &\quad + n_1n_2(\mathsf{a}_1\cdot\mathsf{a}_2) + n_1n_3(\mathsf{a}_1\cdot\mathsf{a}_3) + n_2n_3(\mathsf{a}_2\cdot\mathsf{a}_3) \\ &= \sum_i n_i^2 S_{ii} + \sum_{i<j} n_in_jS_{ij}\ (S_{ij} = \mathsf{a}_i\cdot\mathsf{a}_j), \end{aligned} \tag{8.4}$$

where the S_{ij} are elements of the usual **metric matrix S** and i, j go from 1 to 3. When the vectors for the primitive translations are orthogonal and of equal length **S** is a multiple of the 3×3 unit matrix and the translations generate a *simple cubic* lattice, in which $(\text{distance})^2$ has the usual (Cartesian) form as a sum of squares of the vector components.

Using (8.3), with the oblique axes shown in Figure 8.2, the scalar product does not have that simple form; but we can get it back by setting up a new basis of '**reciprocal vectors**' (not a good name), denoted by $\mathsf{b}_1, \mathsf{b}_2$, in which a general vector v is expressed as $\mathsf{v} = v_1\mathsf{b}_1 + v_2\mathsf{b}_2$ – and choosing b_1 orthogonal to a_2, but with length reciprocal to that of a_1, and similarly for b_2. This makes $\mathsf{a}_1\cdot\mathsf{b}_1 = \mathsf{a}_2\cdot\mathsf{b}_2 = 1$, but $\mathsf{a}_1\cdot\mathsf{b}_2 = 0$ and a scalar product $(r_1\mathsf{a}_1 + r_2\mathsf{a}_2)\cdot(v_1\mathsf{b}_1 + v_2\mathsf{b}_2)$ will then take the usual form

$$\mathsf{r}\cdot\mathsf{v} = r_1v_1(\mathsf{a}_1\cdot\mathsf{b}_1) + r_2v_2(\mathsf{a}_2\cdot\mathsf{b}_2) + r_1v_2(\mathsf{a}_1\cdot\mathsf{b}_2) + r_2v_1(\mathsf{a}_2\cdot\mathsf{b}_1) = r_1v_1 + r_2v_2,$$

just as it would be for two general vectors in a (Cartesian) 2-dimensional space.

The same construction can be made in 3-space, with the primitive translations described by the vectors $\mathsf{a}_1, \mathsf{a}_2, \mathsf{a}_3$; and with basis vectors $\mathsf{b}_1, \mathsf{b}_2, \mathsf{b}_3$ defining the **reciprocal space**. But in this case the relationship between the two bases is not so direct: the b vectors must be defined as

$$\mathsf{b}_1 = \frac{\mathsf{a}_2\times\mathsf{a}_3}{[\mathsf{a}_1\,\mathsf{a}_2\,\mathsf{a}_3]},$$

with permutations $123 \rightarrow 231 \rightarrow 312$ giving $\mathsf{b}_2, \mathsf{b}_3$. Here $[\mathsf{a}_1\,\mathsf{a}_2\,\mathsf{a}_3] = \mathsf{a}_1 \cdot \mathsf{a}_2 \times \mathsf{a}_3$ is the *vector triple product* which gives the volume of a single **unit cell** of the lattice (If you turn back to Section 6.4 of Book 2, you'll see you did this long ago!)

Many metals have a crystal structure with a single atom at every lattice point and in a "free-electron model" we can think of the most loosely bound electrons as moving freely around the positively charged atomic 'cores' from which they came.

Example 8.2 Simple model of a crystal

Let us consider a **'fundamental volume'** containing a large number G^3 of unit cells, G in each of the three directions $\mathsf{a}_1, \mathsf{a}_2$ and a_3. You can think of this as defining a small crystal of the same shape as the unit cell.

First we'll forget about the atom cores and think of completely free electrons moving in a box provided by the **'empty lattice'**. We know that the energy eigenstates of a free electron are given by $\phi(\mathbf{r}) = M\exp(i\mathbf{r}\cdot\mathbf{p}/\hbar)$ where $\mathbf{r}$ and $\mathbf{p}$ represent its position and momentum vectors (as sets of components), while $\hbar = h/2\pi$ is Planck's constant and M is just a normalizing factor.

When we write position and momentum in the form $r_1\mathsf{a}_1 + r_2\mathsf{a}_2 + r_3\mathsf{a}_3$ and $p_1\mathsf{b}_1 + p_2\mathsf{b}_2 + p_3\mathsf{b}_3$, the scalar product $\mathbf{r}\cdot\mathbf{p}$ keeps its Cartesian form and the free-electron wave function becomes

$$\phi(\mathbf{r}) = N\exp(ir_1p_1/\hbar)\exp(ir_2p_2/\hbar)\exp(ir_3p_3/\hbar).$$

Now on changing $r_1\mathsf{a}_1$ to $(r_1 + G)\mathsf{a}_1$ we move from the origin to a point G lattice cells further on in the a_1 direction; and we want to impose the **periodic boundary condition** that the corresponding factor in the wave function is unchanged. This means that $\exp(iGp_1/\hbar)$ must be unity and this requires that the argument $Gp_1/\hbar$ must be a multiple of 2π. The same argument applies in the other directions, so we must insist that

$$Gp_1/\hbar = \kappa_1(2\pi), \qquad Gp_2/\hbar = \kappa_2(2\pi), \qquad Gp_3/\hbar = \kappa_3(2\pi),$$

where $\kappa_1, \kappa_2, \kappa_3$ are arbitrary (but very large) *integers*. In other words the only allowed momentum vectors are $\mathsf{p} = \hbar\mathsf{k}$, with components $p_1 = (2\pi/G)\kappa_1$ etc. – and the vectors are thus

$$\mathsf{p} = (\hbar\kappa_1/G)2\pi\mathsf{b}_1 + (\hbar\kappa_2/G)2\pi\mathsf{b}_1 + (\hbar\kappa_3/G)2\pi\mathsf{b}_3.$$

It is usual to write the results of Example 8.2 in the form $\mathsf{p} = \hbar\mathsf{k}$ where

$$\mathsf{k} = k_1(2\pi\mathsf{b}_1) + k_2(2\pi\mathsf{b}_2) + k_3(2\pi\mathsf{b}_3), \tag{8.5}$$

Here k is called a **vector of k-space** and the basis vectors are now taken as $2\pi\mathsf{b}_1,\ 2\pi\mathsf{b}_2,\ 2\pi\mathsf{b}_3$. The corresponding 1-electron wave function will then be (adding a normalising factor M)

$$\phi(\mathbf{r}) = M\exp(i\mathbf{r}\cdot\mathbf{p}/\hbar) = M\exp(i\mathbf{k}\cdot\mathbf{r}), \tag{8.6}$$

with quantized values of the k-vector components. (Remember that vector *components*, being sets of numbers, have usually been denoted by bold letters $\mathbf{r}$, while the abstract vectors they *represent* are shown in 'sans serif' type as r) The energy of the 1-electron state (8.6) can still be written in the free-electron form $\epsilon_k = (\hbar^2/2m)|\mathsf{k}|^2$, but when the axes are *oblique* this does not become a simple sum-of-squares (you have to do some trigonometry to find the squared length of the k-vector!) .

Of course an empty box, even with suitable boundary conditions, is not a good model for any real crystal; but it gives a good start by showing that the 'fundamental volume' containing G^3 lattice cells allows us to set up that number of quantized 1-electron states, represented by points in a certain **central zone** of k-space. Each state can hold two electrons, of opposite spin, and on adding the electrons we can set up an IPM description of the whole electronic structure of the crystal.

8.2 Crystal orbitals

In the 'empty-lattice' approximation, we have used free-electron wave functions of the form (8.6) to describe an electron moving with definite momentum vector $\mathsf{p} = \hbar\mathsf{k}$, quantized according to the size and shape of the fundamental volume.

Now we want to recognize the fact that in reality there is an internal structure due to the presence of atomic nuclei, repeated within every unit cell of the crystal. We're going to find that the 1-electron functions are now replaced by **crystal orbitals** of very similar form

$$\phi(\mathbf{r}) = M \exp(i\mathbf{k}\cdot\mathbf{r}) f_{\mathbf{k}}(\mathbf{r}), \tag{8.7}$$

where $f_{\mathbf{k}}(\mathbf{r})$ is a function with the periodicity of the lattice – having the same value at equivalent points in all the unit cells. This result was first established by the German physicist Bloch and the functions are also known as **Bloch functions**.

To obtain (8.7) most easily we start from the periodicity of the potential function $V(\mathbf{r})$: if we look at the point with position vector $\mathsf{r}+\mathsf{R}$, where R is the displacement

$$\mathsf{R} = m_1\mathsf{a}_1 + m_2\mathsf{a}_2 + m_3\mathsf{a}_3$$

and m_1, m_2, m_3 are integers, the potential must have the same value as at point r. And let's define an operator T_R such that $\mathsf{T}_\mathsf{R}\phi(\mathbf{r}) = \phi(\mathbf{r}+\mathbf{R})$. Applied to the potential function $V(\mathbf{r})$ it produces $\mathsf{T}_\mathsf{R}V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R})$, but this must have exactly the same value $V(\mathbf{r})$ as before the shift: the potential function is *invariant* against any displacement with integral m's. The same is true for the kinetic energy operator T and for the sum $\mathsf{h} = \mathsf{T} + V$, which is the 1-electron Hamiltonian in IPM approximation. Thus

$$\mathsf{T}_\mathsf{R}(\mathsf{h}\phi) = \mathsf{h}\mathsf{T}_\mathsf{R}\phi,$$

h being unchanged in the shift; and in other words the operators h and T_R must *commute*.

If we use $\mathsf{T}_1, \mathsf{T}_2, \mathsf{T}_3$ to denote the operators that give shifts $\mathsf{r} \rightarrow \mathsf{r}+\mathsf{a}_1$, $\mathsf{r} \rightarrow \mathsf{r}+\mathsf{a}_2$, $\mathsf{r} \rightarrow \mathsf{r}+\mathsf{a}_3$ (for the primitive translations) then we have *four commuting operators* $(\mathsf{h}, \mathsf{T}_1, \mathsf{T}_2, \mathsf{T}_3)$ and should be able to find simultaneous eigenfunctions ϕ, such that

$$\mathsf{h}\phi = \epsilon\phi, \quad \mathsf{T}_1\phi = \lambda_1\phi, \quad \mathsf{T}_2\phi = \lambda_2\phi, \quad \mathsf{T}_3\phi = \lambda_3\phi. \tag{8.8}$$

Now let's apply T_1 G times to $\phi(\mathbf{r})$, this being the number of unit cells in each direction in the fundamental volume, obtaining $(\mathsf{T}_1)^G\phi = \lambda_1{}^G\phi$. If we put $\lambda_1 = e^{i\theta_1}$ this means that $G\theta_1$ must be an integral multiple of 2π, so we can write $\theta_1 = (\kappa_1/G) \times (2\pi)$, where κ_1 is a positive or negative integer or zero. This is true also for λ_2 and λ_3; and it follows that in a general lattice displacement, $\mathsf{R} = m_1\mathsf{a}_1 + m_2\mathsf{a}_2 + m_3\mathsf{a}_3$,

$$\phi(\mathbf{r}+\mathbf{R}) = \mathsf{T}_{\mathsf{R}}\phi(\mathbf{r}) = \mathsf{T}_1^{m_1}\mathsf{T}_2^{m_2}\mathsf{T}_3^{m_3}\phi(\mathbf{r}).$$

On introducing the k-vector defined in (8.6), this result becomes

$$\phi(\mathbf{r}+\mathbf{R}) = \mathsf{T}_{\mathsf{R}}\phi(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{R})\phi(\mathbf{r}). \tag{8.9}$$

To show that a function $\phi(\mathbf{r})$ with this property can be written in the form (8.2) it is enough to apply the last result to the function $e^{i\mathbf{k}\cdot\mathbf{r}}f(\mathbf{r})$, where $f(\mathbf{r})$ is arbitrary: thus

$$e^{i\mathbf{k}\cdot\mathbf{R}}e^{i\mathbf{k}\cdot\mathbf{r}}f(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}e^{i\mathbf{k}\cdot\mathbf{r}}f(\mathbf{r}).$$

In other words we must have $f(\mathbf{r}+\mathbf{R}) = f(\mathbf{r})$ and in that case the most general crystal orbital will have the form

$$\phi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}f_{\mathbf{k}}(\mathbf{r}) \qquad (f_{\mathbf{k}}(\mathbf{r}) \text{ a periodic function}) \tag{8.10}$$

Here the subscript $\mathbf{k}$ has been added because the components of the k-vector are essentially quantum numbers labelling the states. There is thus a one-to-one correspondence between Bloch functions and free-electron wave functions, though the energy no longer depends in a simple way on the components $\mathbf{k}$ of the k-vector The simplest approximation to a crystal orbital is a linear combination of AOs on the atomic centres: thus, for a 1-dimensional array of lattice cells, with one AO in each, this has the general form

$$\phi = \sum_n c_n\chi_n, \tag{8.11}$$

where the χs are AOs on the numbered centres. We imagine the whole 1-dimensional crystal is built up by repeating the fundamental volume of G unit cells in both directions, periodicity requiring that $c_{n+G} = c_n$.

In the following example we assume zero overlap of AOs on different centres and use a nearest-neighbour approximation for matrix elements of the 1-electron Hamiltonian h. Thus, introducing the so-called coulomb and resonance integrals

$$\langle\chi_n|\mathsf{h}|\chi_n\rangle = \alpha, \quad \langle\chi_n|\mathsf{h}|\chi_{n+1}\rangle = \beta \tag{8.12}$$

Example 8.3 Crystal orbital for a 1-dimensional chain

With the approximations (8.12), the usual secular equations to determine the expansion coefficients in (8.11) then become (check it out!)

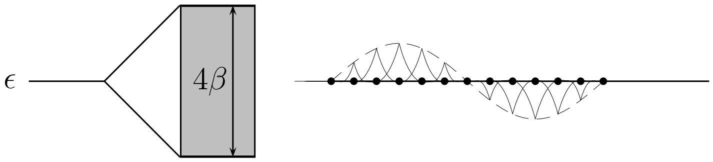
$$c_{n-1}\beta + (c_n - \epsilon)\alpha + c_{n+1}\beta = 0 \qquad \text{(all n)}$$

and are easily solved by supposing $c_n = e^{in\theta}$ and substituting. On taking out a common factor the condition becomes, remembering that $e^{i\theta} + e^{-i\theta} = 2\cos\theta, (\alpha - \epsilon) + 2\beta\cos\theta = 0$, which fixes ϵ in terms of θ.

To determine θ itself we use the periodicity condition $c_{n+G} = c_n$, which gives $e^{iG\theta} = 1$. Thus $G\theta$ must be an integral multiple of 2π and we can put $\theta = 2\pi\kappa/G$, where κ is a positive or negative integer or zero. Finally, the allowed energy levels and AO coefficients in (8.11) can be labelled by κ:

$$\epsilon_\kappa = \alpha + 2\beta\cos(2\pi\kappa/G), \quad c_n^\kappa = \exp(2\pi i\kappa n/G).$$

The energy levels for a 1-dimensional chain of atoms, in LCAO approximation, should therefore form an **energy band** of width 4β, where β is the interaction integral $\langle\chi_n|\mathsf{h}|\chi_{n+1}\rangle$ between neighbouring atoms. Figure 8.4, below, indicates these results for a chain of Hydrogen atoms, where every χ is taken to be a 1s orbital.



(a) (b)

Figure 8.4 Energy Band and part of Crystal Orbital
(schematic, see text)

The energy levels are equally spaced around ϵ for a free atom, G 'bonding' levels below and G 'anti-bonding' levels above. When the number of atoms in the fundamental volume is very large the levels become so close that they form an almost continuous band, indicated by the shaded area in (a). The crystal orbitals, being linear combinations of the AOs, have a wave-like form with a wavelength depending on the energy, as indicated in (b). If the nuclear charges were reduced to zero, the AOs would become broader and broader and the 'spiky' crystal orbital would go over into the plane wave for an empty lattice.

8.3 Polymers and plastics

It's time to look at some real systems and there's no shortage of them: even plastic bags are made up from long chains of atoms, mainly of Carbon and Hydrogen atoms, all tangled together; and so are the DNA molecules that carry the 'instructions' for building a human being from one generation to the next! All are examples of **polymers**.

In Example 8.3 we found crystal orbitals for the π-electrons of a carbon chain, using a nearest-neighbour approximation and taking the chain to be *straight*. In reality, however, carbon chains are never straight, and the C–C sigma bonds are best described in terms of *hybrid* AOs, inclined at 120° to each other. Polyene chains are therefore usually 'zig-zag' in form, even when the Carbon atoms lie in the same plane – as in the case shown below:

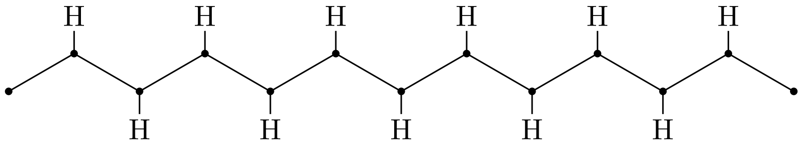


Figure 8.5 Picture showing part of a long polyene chain

In the figure, the black dots in the chain indicate the Carbon atoms of the 'backbone', to which the Hydrogens are attached. The molecule is (ideally) flat and each Carbon provides one electron in a π-type AO, which can be visualized as sticking up perpendicular to the plane of the paper. The system is a 'one-dimensional crystal' in which each unit cell contains four atoms, two Carbons and two Hydrogens. As C_2H_2 is the chemical formula for Acetylene (which you met in Example 7.3), a polyene of this kind is commonly called 'polyacetylene' ("many-acetylenes".)

In Example 8.3, we used a simplified model in which (i) the zig-zag chain was replaced by a straight chain; (ii) the unit cell contained only one Carbon atom, the Hydrogens still being left out; and (iii) each Carbon contributed only one electron to the π-type crystal orbitals, the more tightly-bound electrons simply providing an 'effective field' in the usual way. With *four* atoms in every unit cell, we should try to do better.

How to improve the model

If we continue to admit only the valence electrons, we shall need to consider at least 4+4+2 AOs in every unit cell (4 on each Carbon and 1 on each Hydrogen). So with R_n as the origin of the nth unit cell we shall have to deal with 10 AOs on each atom, indicating their type and position in the cell. However, to keep things simple, let's deal with only the two Carbons, calling them A and B, and taking only one AO on each. Thus χ^A will be centred on point r_A in the unit cell – i.e. at the position of the 'first' Carbon – and χ^B on point r_B, at the position of the 'second'. So their positions in the whole crystal lattice will be $\mathsf{R}_{n,A} = \mathsf{R}_n + \mathsf{r}_A$ and $\mathsf{R}_{n,B} = \mathsf{R}_n + \mathsf{r}_B$. We can then set up Bloch functions for each type of AO, such that

$$\phi_{A,\mathsf{k}}(\mathbf{r}) = \frac{1}{\sqrt{G}^3}\sum_m \exp(i\mathsf{k}\cdot\mathsf{R}_{m,A})\chi_{A,\mathsf{R}_{m,A}}(\mathbf{r}), \quad \phi_{B,\mathsf{k}}(\mathbf{r}) = \frac{1}{\sqrt{G}^3}\sum_n \exp(i\mathsf{k}\cdot\mathsf{R}_{n,B})\chi_{B,\mathsf{R}_{n,B}}(\mathbf{r}). \tag{8.13}$$

These functions will behave correctly when we go from the unit cell at the origin to any other lattice cell and, provided all χs are orthonormal, they are also normalized over the whole fundamental volume. The k-vector specifies the **symmetry species** of a function, under translations, and only functions with the same k can be mixed. Just as we can express a π-type MO between the two atoms of the unit cell as a linear combination $c_A\chi_A + c_B\chi_B$, we can write a π-type *crystal* orbital as

$$\phi = c_{A,\mathsf{k}}\phi_{A,\mathsf{k}} + c_{B,\mathsf{k}}\phi_{B,\mathsf{k}}, \tag{8.14}$$

where the mixing coefficients now depend on the k-vector and must be found by solving a secular problem, as usual.

To complete the calculation, we need approximations to the matrix elements of the 1-electron Hamiltonian between the two Bloch functions in (8.13): these depend on the corresponding elements between the AOs in all lattice cells and the simplest approximation is to take, as in (8.12), $\langle\chi_{A,\mathsf{R}_{m,A}}|\mathsf{h}|\chi_{A,\mathsf{R}_{m,A}}\rangle = \langle\chi_{B,\mathsf{R}_{n,B}}|\mathsf{h}|\chi_{B,\mathsf{R}_{n,B}}\rangle \approx \alpha_C^\pi$ (the same value for all Carbons) and $\langle\chi_{A,\mathsf{R}_{m,A}}|\mathsf{h}|\chi_{B,\mathsf{R}_{n,B}}\rangle \approx \beta_{CC}^\pi$, for nearest-neighbour Carbons (in the same or adjacent cells).

The results of Example 8.3 are unchanged, in this case, because the nearest-neighbour approximation does not depend on whether the two AOs are in the same or adjacent lattice cells. The forms of the energy band and the crystal orbitals remain as in Figure 8.4, with orbital energies distributed symmetrically around the reference level $\epsilon = \alpha_C^\pi$. On the other hand, when we include the hybrid AOs on each Carbon and the 1s AOs on the Hydrogens, we shall obtain several quite new energy bands – all lying at lower energy than the π band (which describes the most loosely bound electrons in the system). Some of these results are indicated in the figure below:

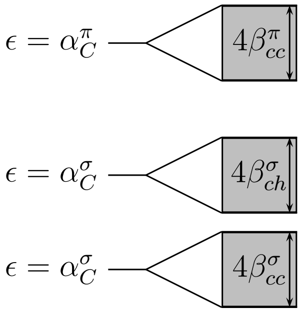


Figure 8.6 Polyacetylene energy bands

(a) - for Carbon π-type crystal orbitals

(b) - for σ-type orbitals: CH bonds

(c) - for σ-type orbitals: CC bonds

The top band (a) refers to the most loosely bound electrons, the reference level at $\epsilon = \alpha_C^\pi$ being the energy of an electron in a single Carbon $2\mathrm{p}_\pi$ AO. For a fundamental volume containing G unit cells the band arising from this AO will contain G levels, but as each Carbon provides only one π electron only $\frac{1}{2}G$ of the crystal orbitals will be filled (2 electrons in each, with opposite spins). That means that electrons will be easily excited, from the ground state into the nearby ‘empty’ orbitals; so a carbon chain of this kind should be able to conduct electricity. Polyacetylene is an example of an *unsaturated* chain molecule: such molecules are of industrial importance owing to the electrical properties of materials derived from them.

Electrons in the lower bands, such as (b) and (c), are more strongly bound – with crystal orbitals consisting mainly of σ-type AOs, which lie at much lower energy. Figure 8.6 is very schematic; the same reference level α_C^σ is shown for the hybrid AOs involved in the CH bonds and the CC bonds (which should lie much lower); and the band *widths* are shown equal in all three cases, whereas the resonance integrals (β) are much greater in magnitude for the AOs that overlap more heavily. So in fact such bands are much wider and may even overlap. On carefully counting the number of energy levels they contain and the number of atomic valence electron available it appears that the crystal orbitals in these lower energy bands are all likely to be *doubly-occupied.* In that case, as we know from Section 7.4, it is always possible to replace the completely delocalized crystal orbitals by unitary mixtures, without changing in any way the total electron density they give rise to, the mixtures being strongly localized in the regions corresponding to the traditional chemical bonds.

There will also be empty bands at much higher energy than those shown in Figure 8.6, but these will arise from anti-bonding combinations of the AOs and are usually of little interest.

Other types of polymer chains

The polyacetylene chain (Figure 8.5) is the simplest example of an *unsaturated* polymer: the Carbons in the 'backbone' all have only three saturated valences, the fourth valence electron occupying a $2p_\pi$ orbital and providing the partial π bonds which tend to keep the molecule flat. This valence electron may, however, take part in a 2-electron bond with another atom, in which case all four Carbon valences are saturated and the nature of the bonding with its neighbours is completely changed. The simplest *saturated* polymers are found in the **paraffin** series, which starts with methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and continues with the addition of any number of CH$_2$ groups. Nowadays, the paraffins are usually called **alkanes**.

Instead of the 'flat' polyacetylene chains, which are extended by adding CH groups, the alkanes are extended by adding CH_2 groups. The backbone is still a zig-zag chain of Carbons, but the CC links are now single bonds (with no partial 'double-bond' character) around which rotation easily takes place: as a result the long chains become 'tangled', leading to more rigid materials. If the chain is kept straight, as a 1-dimensional lattice, the unit cell contains the repeating group indicated below in Figure 8.7 (where the unit cell contents are shown within the broken-line circle).

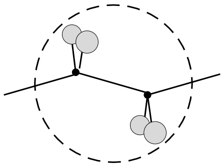


Figure 8.7 Repeating group (C_2H_4)
Individual CH_2 groups are perpendicular to the plane of the Carbon chain (above it and below it)

(Carbons shown in black, Hydrogens in grey)

The first few alkanes, with few C_2H_4 groups and thus low molecular weight, occur as gases; these are followed by liquid paraffins and then by solid waxes. But the chain lengths can become enormous, including millions of groups. The resultant high-density materials are used in making everything from buckets to machine parts, while the lower density products are ideal for packaging and conserving food. World production of this low-cost material runs to billions of tons every year!

8.4 Some common 3-dimensional crystals

In Section 8.1 we introduced the idea of a **crystal lattice**, in one, two and three dimensions, along with the simplest model – in which an 'empty lattice' was just thought of as a 'box' containing free electrons. Then, in Section 8.2, we improved the model by defining the **crystal orbitals**, as a generalization of the MOs used in Chapter 7 for discussing simple molecules. Finally, in Section 8.3, we began the study of some 'real' systems by looking at some types of '1-dimensional crystal', namely polymer chains built mainly from atoms of Hydrogen and Carbon. These simple chain molecules form the basis for most kinds of **plastics** – that within the last century have changed the lives of most of us.

Most common crystals, however, are 3-dimensional and bring in new ideas which we are now ready to deal with. The simplest of all (after solid Hydrogen) is **metallic Lithium**, a metal consisting of Lithium atoms, each with one valence electron outside a Helium-like closed shell. The atoms form a **body-centred cubic** lattice, with the unit cell indicated below:

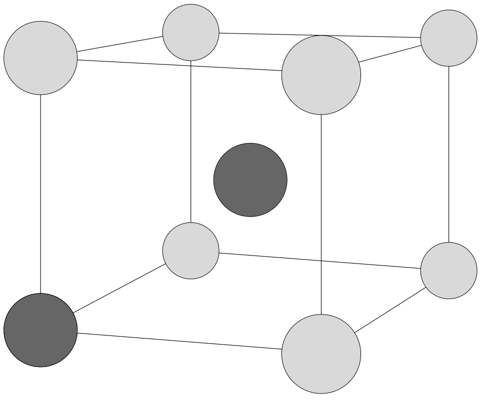


Figure 8.8 Indicating the unit cell of a body-centred cubic lattice

In the figure, atoms are shown as the shaded circles at the corners and centre of a cube. All lattice cells are identical, differing only by translations along the crystal axes; but the unit cell, containing *only* the two atoms shown with dark shading, 'generates' the whole crystal by repetition in that way. Note that the atom at the middle of the cube has *eight* nearest neighbours, four on the top face of the cube and four on the bottom face: the atoms shown with light-gray shading 'belong' to the surrounding lattice cells.

Again we'll use names A and B for the two atoms in the unit cell and suppose they are at positions r_A and r_B, relative to the origin of any cell. The 'global' position of A in a lattice cell with origin at R_m will then be $\mathsf{R}_m + \mathsf{r}_A$ and similarly for B. Bloch functions can be formed for each atom, just as in (8.13), which we repeat here;

$$\phi_{A,\mathsf{k}}(\mathbf{r}) = \frac{1}{\sqrt{G}^3}\sum_m \exp[i\mathsf{k}\cdot(\mathsf{R}_m+\mathsf{r}_A)]\chi_{A,\mathsf{R}_m}(\mathbf{r}), \quad \phi_{B,\mathsf{k}}(\mathbf{r}) = \frac{1}{\sqrt{G}^3}\sum_n \exp[i\mathsf{k}\cdot(\mathsf{R}_n+\mathsf{r}_B)]\chi_{B,\mathsf{R}_n}(\mathbf{r}). \tag{8.15}$$

These functions are normalized, over the fundamental volume containing G^3 cells, provided all AOs (namely the χs) are normalized and orthogonal.

(Remember that $\chi_{A,\mathsf{R}_m}(\mathbf{r})$ is an A-type AO centred on point r_A in the lattice cell with origin at R_m and similarly for $\chi_{B,\mathsf{R}_n}(\mathbf{r})$. Remember also that the wave vector k is defined in terms of the **reciprocal lattice** as

$$\mathsf{k} = k_1(2\pi\mathsf{b}_1) + k_2(2\pi\mathsf{b}_2) + k_3(2\pi\mathsf{b}_3)$$

and that with this definition the scalar products take the usual form with $\mathsf{k}\cdot\mathsf{r}_A = k_1(r_A)_1 + k_2(r_A)_2 + k_3(r_A)_3$, etc.)

The most general crystal orbital we can construct, using only the two Bloch functions (8.15), is

$$\phi = c_{A,\mathsf{k}}\phi_{A,\mathsf{k}} + c_{B,\mathsf{k}}\phi_{B,\mathsf{k}},$$

where the mixing coefficients follow from the usual secular equations. But matrix elements between the Bloch functions may now depend on the wave vector k. Thus,

$$h_{AA} = h_{BB} = \langle\phi_{A,\mathsf{k}}|\mathsf{h}|\phi_{A,\mathsf{k}}\rangle, \quad h_{AB} = \langle\phi_{A,\mathsf{k}}|\mathsf{h}|\phi_{B,\mathsf{k}}\rangle.$$

Example 8.4 Reducing the matrix elements

The matrix elements of h between the Bloch functions may be reduced as follows. The diagonal element becomes, using (8.15),

$$h_{AA} = \frac{1}{G^3}\sum_{m,n}\exp[-i\mathsf{k}\cdot(\mathsf{R}_m+\mathsf{r}_A)]\exp[+i\mathsf{k}\cdot(\mathsf{R}_n+\mathsf{r}_A)]\int\chi^*_{A,\mathsf{R}_m}\mathsf{h}\chi_{A,\mathsf{R}_n}\mathrm{d}\mathbf{r},$$

where the minus sign in the first exponential arises from the complex conjugate of the function on the left of the operator h, i.e. the function in the 'bra' part of the matrix element. The integral itself is α if the two functions are identical or β if they are nearest neighbours. Let's do the summation over n first, holding m fixed. When the two AOs are identical, the exponential factor is unity and the integral factor is α. On doing the remaining summation, this result will be repeated G^3 times – being the same for every lattice cell – and the normalizing factor will be cancelled. Thus $h_{AA} = \alpha_A, h_{BB} = \alpha_B$. This result does not depend at all on the wave vector k.

For the off-diagonal element we obtain, in a similar way,

$$h_{AB} = \frac{1}{G^3}\sum_{m,n}\exp[-i\mathsf{k}\cdot(\mathsf{R}_m+\mathsf{r}_A)]\exp[+i\mathsf{k}\cdot(\mathsf{R}_n+\mathsf{r}_B)]\int\chi^*_{A,\mathsf{R}_m}\mathsf{h}\chi_{B,\mathsf{R}_n}\mathrm{d}\mathbf{r},$$

but this contains the exponential factor

$$\exp[i\mathsf{k}\cdot(\mathsf{R}_n - \mathsf{R}_m + \mathsf{r}_B - \mathsf{r}_A)] = \exp i\mathsf{k}\cdot\boldsymbol{\rho}_{nm},$$

where $\boldsymbol{\rho}_{nm} = (\mathsf{R}_n - \mathsf{R}_m + \mathsf{r}_B - \mathsf{r}_A)$ is the vector distance from an atom of A-type, in lattice cell at R_m, to one of B-type in a cell at R_n. The double summation is over all B-neighbours of any A atom, so taking A in the unit cell at the origin and summing over nearest neighbours will give a contribution $(\sum_n \exp(i\mathsf{k}\cdot\boldsymbol{\rho}_{nm}) \times \langle\chi_A|\mathsf{h}|\chi_B\rangle$. This result will be the same for any choice of the cell at R_m, again cancelling the normalizing factor on summation. On denoting the **structure sum** by $\sigma_{AB}(\mathsf{k})$, the final result will thus be $h_{AB} = \beta_{AB}\sigma_{AB}(\mathsf{k})$, where β_{AB} is the usual 'resonance' integral for the nearest-neighbour pairs.

Example 8.4 has given for the matrix elements of the 1-electron Hamiltonian, between Bloch functions $\phi_{A,\mathsf{k}}$ and $\phi_{B,\mathsf{k}}$,

$$h_{AA} = \alpha_A, \quad h_{BB} = \alpha_B, \quad h_{AB} = \beta_{AB}\sigma_{AB}(\mathsf{k}). \tag{8.16}$$

Here, for generality, we allow the atoms or orbitals at r_A and r_B to be different; so later we can deal with 'mixed crystals' as well as the Lithium metal used in the present section. The secular determinant is thus

$$\begin{vmatrix} \alpha_A - \epsilon & \beta_{AB}\sigma_{AB}(\mathsf{k}) \\ \beta_{AB}\sigma^*_{AB}(\mathsf{k}) & \alpha_B - \epsilon \end{vmatrix} = 0, \tag{8.17}$$

where the 'star' on the second sigma arises because h_{BA} is the complex conjugate of h_{AB} while the AOs are taken as real functions. This quadratic equation for ϵ has roots, for atoms of the same kind ($\alpha_A = \alpha_B = \alpha$),

$$\epsilon_{\mathsf{k}} = \alpha \pm \beta_{AB}|\sigma_{AB}(\mathsf{k})|.$$

Since α and β_{AB} are negative quantities, the states of lowest energy are obtained by taking the upper sign. There will be G^3 states of this kind, resulting from the solution of (8.17) at all points in k-space i.e. for all values of k_1, k_2, k_3 in the wave vector $\mathsf{k} = k_1(2\pi\mathsf{b}_1) + k_2(2\pi\mathsf{b}_2) + k_3(2\pi\mathsf{b}_3)$. And there will be another G^3 states, of higher energy, which arise on taking the lower sign. The present approximation thus predicts two energy bands, of the kind displayed in Figure 8.6 for a 1-dimensional crystal (polyacetylene). We now look for a pictorial way of relating the energy levels ϵ_{k} within a band to the k-vector of the corresponding crystal orbitals.

Brillouin Zones and Energy Contours

The results in Example 8.3, for a 1-dimensional crystal, are echoed in 2 and 3 dimensions: a 3-dimensional crystal is considered in the next example.

Example 8.5 Bloch functions in three dimensions

A Bloch function constructed from AOs $\chi_{n_1n_2n_3}$ at each lattice point R_n will be $\phi = \sum_{n_1,n_2,n_3} c_{n_1n_2n_3}\chi_{n_1n_2n_3}$ and we try $c_{n_1n_2n_3} = \exp i(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)$.

Each factor $c_n = e^{in\theta}$ will be periodic within the fundamental volume of G lattice cells in each direction when $\theta = 2\pi\kappa/G$, κ being an integer. So the general AO coefficient will be

$$c^{\kappa_1\kappa_2\kappa_3}_{n_1n_2n_3} = \exp[2\pi i(n_1\kappa_1 + n_2\kappa_2 + n_3\kappa_3)/G],$$

where the three quantum numbers $\kappa_1, \kappa_2, \kappa_3$ determine the state; and the energy follows, as in Example 8.3, from the difference equation (in nearest neighbour approximation). Thus, the Bloch orbital energy becomes a sum of three terms, one for each dimension:

$$\epsilon_{\kappa_1\kappa_2\kappa_3} = \alpha + 2\beta_1 \cos(2\pi\kappa_1/G) + 2\beta_2 \cos(2\pi\kappa_2/G) + 2\beta_3 \cos(2\pi\kappa_3/G).$$

In terms of the wave vector k and its components in reciprocal space, the 3-dimensional Bloch function and its corresponding ϵ_{k} can now be written, assuming all atoms have the same α and all nearest-neighbour pairs have the same β,

$$\phi_{\mathsf{k}} = \sum_n \exp(i\mathsf{k}\cdot\mathsf{R}_n)\chi_n, \quad \epsilon_{\mathsf{k}} = \alpha + 2\beta\cos 2\pi k_1 + 2\beta\cos 2\pi k_2 + 2\beta\cos 2\pi k_3, \tag{8.18}$$

where χ_n is short for the AO $(\chi_{n_1n_2n_3})$ in the lattice cell at $\mathsf{R}_n = n_1\mathsf{a}_1 + n_2\mathsf{a}_2 + n_3\mathsf{a}_3$.

To get a simple picture of how ϵ_{k} depends on the k-vector components let's take a square lattice with only one AO per unit cell. In this 2-dimensional case the energy formula in (8.18) contains only the first two terms and can be written alternatively (simple trigonometry – do it!) as $\epsilon_{\mathsf{k}} = \alpha + 4\beta\cos\pi(k_1+k_2)\cos\pi(k_1-k_2)$. On taking the 'fundamental volume' to contain numbered lattice cells going from $-\frac{1}{2}G$ to $+\frac{1}{2}$G in each direction, the G^2 states will correspond to k_1 and k_2 each in the range $(-\frac{1}{2}, +\frac{1}{2})$. We can then define a **central zone** in k-space by taking $2\pi\mathsf{b}_1$ and $2\pi\mathsf{b}_2$ as coordinate axes, along which to plot values of k_1 and k_2. This is the **Brillouin zone** in the following Figure 8.9:

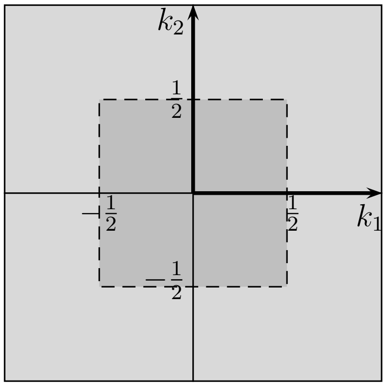


Figure 8.9 Zones in k-space

Brillouin zone bounded by the broken line contains G^2 states (k_1, k_2 each in range $(-\frac{1}{2}, +\frac{1}{2})$)

The formula $\epsilon_{\mathsf{k}} = \alpha + 4\beta\cos\pi(k_1+k_2)\cos\pi(k_1-k_2)$, obtained from (8.18) in the 2-dimensional case, then shows that the energy rises from a minimum $\alpha + 4\beta$ at the zone centre (where $k_1 = k_2 = 0$) to a maximum $\alpha - 4\beta$ at the zone corners. The 'top' and 'bottom' states thus define an **energy band** of width 8β.

Near the bottom of the band (β being negative), k_1 and k_2 are small and expanding the cosines in (8.18) gives the approximation (get it!)

$$\epsilon_{\mathsf{k}} = \alpha + 4\beta - 4\pi^2\beta(k_1^2 + k_2^2) + ... \tag{8.19}$$

– which is constant when $k_1^2 + k_2^2$ = constant. The **energy contours** in k-space are thus circular near the origin where $k_1 = k_2 = 0$. Remember that, in a free electron approximation, $\hbar\mathsf{k}$ represents the momentum vector and that $\epsilon_{\mathsf{k}} = (1/2m)\hbar^2|\mathsf{k}|^2$: if we compare this with the k-dependent part of (8.20) it is clear that $\hbar^2/2m$ must be replaced by $-4\pi^2\beta$ – suggesting that the electron in this crystal orbital behaves as if it had an **effective mass**

$$m_e = -2\pi^2\hbar^2/\beta. \tag{8.20}$$

This can be confirmed by asking how a wave packet, formed by combining functions ϕ_{k} with k-values close to k_1, k_2 travels through the lattice (e.g. when an electric field is appplied). (You may need to read again about wave packets in Book 11.) The result is also consistent with what we know already (e.g. that tightly-bound inner-shell electrons are described by wave functions that overlap very little, giving very small (and negative) β values: (8.20) shows they will have a very high effective mass – and thus almost zero mobility.

On the other hand, near the *corners* of a Brillouin zone, where $k_1, k_2 = \pm\frac{1}{2}$, things are very different. On putting $k_1 = \frac{1}{2} + \delta_1$, $k_2 = \frac{1}{2} + \delta_2$, (8.19) gives an energy dependence of the form (check it!)

$$\epsilon_{\mathsf{k}} = A + B(\delta_1^2 + \delta_2^2) + ... \tag{8.21}$$

– showing that the energy contours are again circular, but now around the corner points with $\epsilon_{\mathsf{k}} = \alpha - 4\beta$. Such states have energies at the *top* of the band; and the sign of B, as you can show, is negative. This indicates a *negative effective mass* and shows that a wave packet formed from states near the top of the band may go the 'wrong way'. In other words if we accelerate the packet it will be reflected back by the lattice! (Of course it couldn't go beyond the boundary of the Brillouin zone, because that is a 'forbidden' region.)

The forms of the energy contours are sketched below:

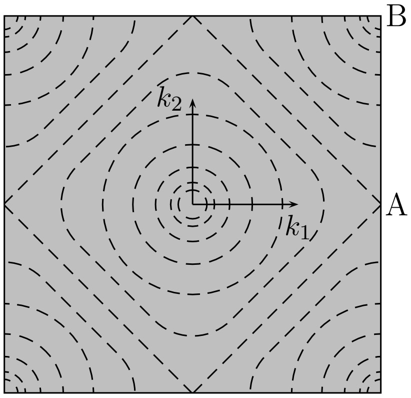


Figure 8.10 Central zone in k-space: energy contours

The contours of constant energy are indicated by the broken lines. The zone centre is at $k_1 = k_2 = 0$ and is the point of minimum energy Point A ($k_1 = \frac{1}{2}, k_2 = 0$) marks a corner of the square contour on which $\epsilon_{\mathsf{k}} = \alpha$ and Point B ($k_1 = k_2 = \frac{1}{2}$) corresponds to the maximum energy $\epsilon_{\mathsf{k}} = \alpha - 4\beta$.

Of course, you need practice to understand what the contour maps mean; but if you've used maps in the mountains you'll remember that walking along a contour means that you stay 'on the level' – the contour connects points at the same height. In Figure 8.10 the energy level depends on the two 'distances', k_1 and k_2, and corresponds exactly to a height above the energy minimum. So if you measure ϵ_{k} along a vertical axis above the plane of k_1 and k_2 you can make a 3-dimensional picture like the one below:

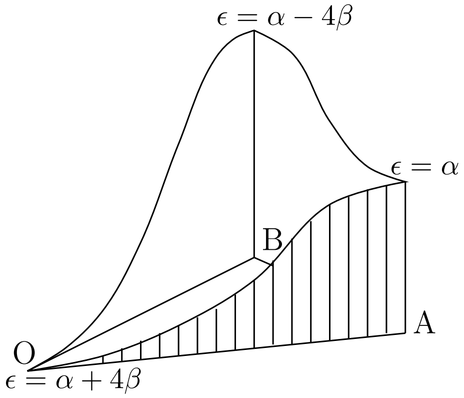


Figure 8.11 3D sketch of the energy surface

The sketch shows the part of the energy surface lying above the triangle OAB in Figure 8.10 (O being the centre of the Brillouin zone): the shaded 'wall' just indicates the front boundary of the region considered. If you put 8 pieces like that together you get the whole energy surface. Notice the symmetry of the contour map in Figure 8.10: on extending the map outside the zone boundary the contours are simply repeated – the Brillouin zone is simply the *central* zone in k-space.

With only one AO per lattice cell, the zone contains just G^2 distinct states (we chose a 2-dimensional crystal for simplicity) but if we took two AOs in each cell and solved the secular equation (8.18), for every point in k-space, we'd find another G^2 states corresponding to the second root. The new states define another energy band, of higher energy than the first, which are functions of the k-vector components at points within the same central zone. Mixing of the two Bloch functions has little effect on the states of lower energy, whose energies lie on the surface in Figure 8.11, but in general the upper surface will be separated from the lower by an **energy gap**.

Note that in talking about adding a second AO per cell we were simply thinking of extending the basis, from G^2 to $2G^2$ basis functions, so we would be doubling the number of *states* available – without changing the number of *electrons*. But if the second AO belongs to a real monovalent atom, then we also double the number of electrons available.

Many of the physical properties of real 3-dimensional crystals, such as the way they conduct heat and electricity, depend strongly on the highest occupied electronic states; so it is important to know how the available states are filled. Every crystal orbital can hold only two electrons, of different spin (Pauli Principle), so with only one monovalent atom per lattice cell there would be $2G^3$ states available for the G^3 valence electrons: the lowest energy band would be only *half full* and the next band would be completely empty. The crystal should be a good conductor of electricity, with electrons easily excited into upper orbitals of the lower band; and the same would be true with two monovalent atoms per cell ($4G^3$ states and $2G^3$ electrons). On the other hand, with two divalent atoms per cell there would be $4G^3$ valence electrons available and these would fill the lower energy band: in that case conduction would depend on electrons being given enough energy to jump the band gap.

Some mixed crystals

Even simpler than metallic Lithium, is **Lithium Hydride** LiH, but the molecule does not crystallize easily, forming a white powder which reacts violently with water – all very different from the soft silvery metal! On the other hand, **Lithium Fluoride** forms nice regular crystals with the same structure as common salt (Sodium Chloride, NaCl); they have the face-centred cubic structure, similar to that of the metal itself except that the Fluorine atoms lie at the centres of the cube faces instead of at the cube centre.

Salts of this kind are formed when the two atoms involved (e.g. Li and F; or Na and Cl) are found on opposite sides of the **Periodic Table**, which means their electrons are *weakly* bound (left side) or *strongly* bound (right side). You will remember from Section 6.2 that when the α-values of the corresponding AOs differ greatly the energy-level diagram for a diatomic molecule looks very different from that in the homonuclear case where the two atoms are the same: in LiF for example, using A and B to denote Fluorine and Lithium, the lowest-energy MO (Figure 6.3) has $\epsilon_1 \approx \alpha_A$ while its antibonding partner has the much higher energy $\epsilon_2 \approx \alpha_B$. The corresponding diatomic MOs, in the same approximation, are $\phi_1 \approx \chi_A$ and $\phi_2 \approx \chi_B$, as you can confirm (do it!) by estimating the mixing coefficients in $\phi \approx c_A\chi_A + c_B\chi_B$. In other words, the lowest-energy MO is roughly the same as the AO on the atom of greater **electron affinity** – meaning with the greater need to attract electrons. When the MOs are filled with electrons (2 in each MO) the Fluorine will grab two of the valence electrons, leaving the Lithium with none. The bonding between the two atoms is then said to be **ionic**, the Fluorine being pictured as the negative ion F^- and the Lithium as the positive ion Li^+. In that way both atoms achieve a *closed-shell* electronic structure in which their valence orbitals are all doubly occupied. The Fluorine, in particular, looks more like the **inert gas** Neon, at the end of this row in the Periodic Table.

When the salts form crystals similar considerations apply: the electronic structure of the crystal may be described by filling the available crystal orbitals, written as linear combinations of Bloch functions, and the mixing coefficients could be calculated by solving a set of secular equations at every point in k-space. But in the case of ionic crystals such difficult calculations can be avoided: looking ahead, we can guess that the Fluorine AO coefficients in the crystal orbitals will come out big enough to justify a picture in which the Fluorine has gained an electron, becoming F^{-}, while the Lithium has in effect lost its valence electron to become Li^{+}. In this way we come back to the 'classical' picture of ionic crystals, put forward long before the development of quantum mechanics!

The unit cell in the LiF crystal, well established experimentally by X-ray crystallography, has the form shown below.

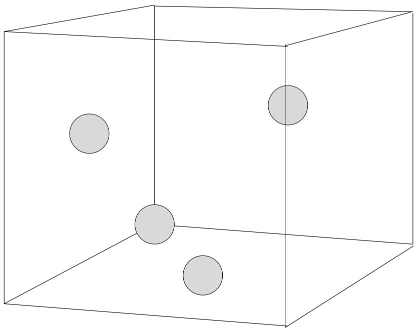


Figure 8.12 Fluorine ions (F^{-}) in the LiF unit cell

Only the positions of the Fluorine ions, which are much bigger than the Li^{+} ions, are indicated in Figure 8.12, one being at a cube corner and three others being at the centers of three faces. This forms part of the unit cell 'building block', from which the whole crystal can be constructed by adding similar blocks 'face-to-face' along the three axes. As you can see, the next block on the right will supply the missing F^{-} ion on the right-hand cube face, along with one at the bottom-right cube corner; and so it goes on if you add blocks in the other two directions (up/down and back/front). In that way every fluorine ion finds its own position in the lattice, no two 'wanting' to occupy the same place. The Lithium positive ions are added to this face-centred lattice to give the electrically neutral LiF crystal, with 4 ions of each kind per unit cell. (Three of the Li^{+} ions are found at the mid-points of the three cube edges that meet at the bottom-back corner, while the fourth is at the body-center of the cube; you might like to draw them in on Figure 8.12, along with all the other ions associated with that cubic cell in the crystal.)

So to do a quantum mechanical calculation, even at IPM level, it would be necessary to take account of 8 Bloch functions, solving an 8×8 secular problem at every point in k-space! and we're lucky to be able to understand the structure of the crystal without having to do such an enormous calculation. In the **classical theory of ionic crystals** we simply picture the crystal as an array of negatively and positively charged spheres attracting each other according to Coulomb's inverse-distance law. But what stops the ions all collapsing into each other to make all distances zero and the total energy minus infinity? That's the only point at which quantum mechanics must be used – and then it's enough to show how two closed-shell ions build up a strong repulsion as soon as their electron distributions begin to overlap. The classical picture works well if it is supposed that the energy of repulsion between two neighbouring ions has the form $E_{\text{rep}} = B\exp(r/\rho)$ where B and ρ are constants and r is the distance between the ion centres. Usually the constants are given empirical values so as to reproduce experimental data such as the unit cell distances and the total energy of the crystal. Even then the calculations are not simple, because the crystal contains millions of ions and care must be taken with *convergence* as more and more ions are included; but they are by now standard and give a good account of crystal properties. So let's now look ar something really new!

8.5 New materials

A few years ago the Nobel Prize in Physics 2010 was awarded jointly to two Russians, Andre Geim and Konstantin Novoselov, for their groundbreaking experimental work on the two-dimensional material **graphene**. Since then, thousands of scientific papers on this material and its remarkable properties have been published in all the world's leading journals. Graphene seems likely to cause a far bigger revolution in Science and Technology than that made by the discovery of plastics – and yet all the underlying theory was known more than 50 years ago and can be understood on the basis of what you've done so far.

A crystal of solid **graphite**, which contains only Carbon atoms lying on a 3-dimensional lattice, consists of 2-dimensional 'sheets' or 'layers', lying one on top of another. Each layer contains Carbons that are strongly bonded together, lying at the corners of a hexagon as in the benzene molecule, while the bonding between different layers is comparitively weak. Such a single layer forms the 2-dimensional crystal **graphene**, whose unit cell is shown in the figure 8.13 (left) along with that for the corresponding k-space lattice (right). Because graphene is so important it's worth showing how easy it is to construct all we need from very first principles.

Example 8.6 A bit of geometry – the hexagonal lattice

Of course you've been using simple vector algebra ever since Book 2, usually with a Cartesian basis in which a vector $\mathsf{v} = v_x\mathsf{i} + v_y\mathsf{j} + v_z\mathsf{k}$ is expressed in terms of its components relative to orthogonal unit vectors $\mathsf{i}, \mathsf{j}, \mathsf{k}$. So this is the first time you meet something new: the basis vectors we need in dealing with the graphene lattice are *oblique* though they can be expressed in terms of Cartesian unit vectors. Thus, in crystal space, Figure 8.13 (left), we can choose i, j as unit vectors pointing along AB and perpendicular to it (upwards). We then have

$$\mathsf{a}_1 = \tfrac{1}{2}\sqrt{3}\,\mathsf{i} - \tfrac{1}{2}\,\mathsf{j}, \quad \mathsf{a}_2 = \tfrac{1}{2}\sqrt{3}\,\mathsf{i} + \tfrac{1}{2}\,\mathsf{j}.$$

In reciprocal space (i.e. without the 2π factors), Figure 8.13 (right), we can define

$$\mathsf{b}_2 = \tfrac{1}{2}\,\mathsf{i} + \tfrac{1}{2}\sqrt{3}\,\mathsf{j}, \quad \mathsf{b}_1 = \tfrac{1}{2}\,\mathsf{i} - \tfrac{1}{2}\sqrt{3}\,\mathsf{j}$$

where b_2 and b_1 are respectively (note the order) perpendicular to a_1 and a_2). Thus, $\mathsf{a}_1 \cdot \mathsf{b}_2 = \mathsf{a}_2 \cdot \mathsf{b}_1 = 0$. On the other hand $\mathsf{a}_1 \cdot \mathsf{b}_1 = \frac{1}{4}\sqrt{3} + \frac{1}{4}\sqrt{3} = \frac{1}{2}\sqrt{3}$ and $\mathsf{a}_2 \cdot \mathsf{b}_2$ has the same value. As a result, any pair of vectors $\mathsf{u} = u_1\mathsf{a}_1 + u_2\mathsf{a}_2$ (in 'a-space') and $\mathsf{v} = v_1\mathsf{b}_1 + v_2\mathsf{b}_2$ (in 'b-space') will have a scalar product

$$\mathsf{u} \cdot \mathsf{v} = u_1v_1(\mathsf{a}_1 \cdot \mathsf{b}_1) + u_2v_2(\mathsf{a}_2 \cdot \mathsf{b}_2) = \tfrac{1}{2}\sqrt{3}(u_1v_1 + u_2v_2),$$

since the other terms are zero. We'd like to have a simpler result, like that for two vectors in an 'ordinary' (rectangular Cartesian) vector space. And we can get it if we replace the basis vectors $\mathsf{b}_1, \mathsf{b}_2$ by $\mathsf{b}_1^* = (\frac{1}{2}\sqrt{3})^{-1}\mathsf{b}_1$ and $\mathsf{b}_2^* = (\frac{1}{2}\sqrt{3})^{-1}\mathsf{b}_2$, for then the factors $(\frac{1}{2}\sqrt{3})$ cancel out. When the vectors u and v are written as $\mathsf{u} = u_1\mathsf{a}_1 + u_2\mathsf{a}_2$ and $\mathsf{v} = v_1\mathsf{b}_1^* + v_2\mathsf{a}_2$, we find (check it!)

$$\mathsf{u} \cdot \mathsf{v} = u_1 v_1 + u_2 v_2$$

– exactly as for any pair of vectors in a single rectangular Cartesian space.

Let's collect the two sets of basis vectors obtained in Example 8.6: the a-set define the 'real' ('crystal') space, while the b^*-vectors define the **reciprocal space**, which is set up only for mathematical convenience!

$$\begin{aligned} \mathsf{a}_1 &= \tfrac{1}{2}\sqrt{3}\,\mathsf{i} - \tfrac{1}{2}\,\mathsf{j}, \qquad & \mathsf{a}_2 &= \tfrac{1}{2}\sqrt{3}\,\mathsf{i} + \tfrac{1}{2}\,\mathsf{j} \\ \mathsf{b}_1^* &= (\sqrt{3})^{-1}\mathsf{i} - \mathsf{j}, \qquad & \mathsf{b}_2^* &= (\sqrt{3})^{-1}\mathsf{i} + \mathsf{j}. \end{aligned} \tag{8.22}$$

Thus,

$$\mathsf{a}_1 \cdot \mathsf{b}_1^* = (\mathsf{a}_2 \cdot \mathsf{b}_2^*) = 1$$

but we still have $\mathsf{a}_1 \cdot \mathsf{b}_2^* = \mathsf{a}_2 \cdot \mathsf{b}_1^* = 0$. So for any two vectors, u, v, the first expressed in crystal space and the second in reciprocal space, we have

$$(u_1\mathsf{a}_1 + u_2\mathsf{a}_2) \cdot (v_1\mathsf{b}_1^* + v_2\mathsf{b}_2^*) = (u_1 v_1 + u_2 v_2)$$

– just as if the two vectors belonged to an 'ordinary' Cartesian space.

Now we know that the vectors set up in (8.22) have the properties we need, we can look again at Figure 8.13, which shows how they appear in the graphene crystal space and corresponding k-space lattices:

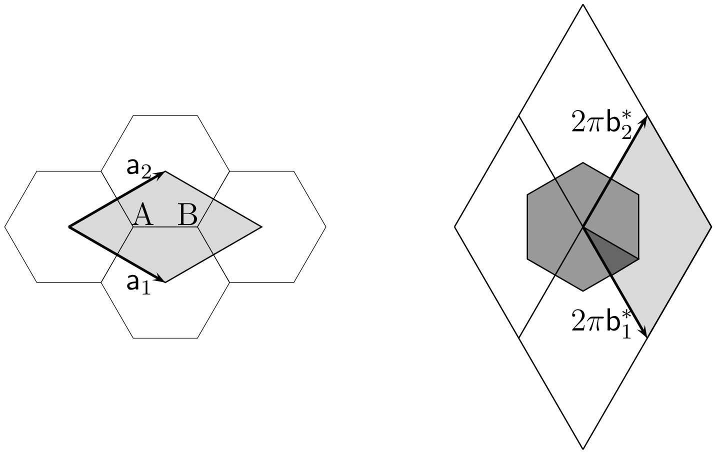


Figure 8.13 Crystal lattices and some unit cells (see text)

The left-hand side of Figure 8.13 shows part of the lattice in crystal space; one cell, the unit cell, contains Carbon atoms at A and B and is lightly shaded. The basis vectors a_1 and a_2 are shown as bold arrows. The right-hand side shows part of the corresponding lattice in k-space: the basis vectors $2\pi\mathsf{b}_1$ and $2\pi\mathsf{b}_2$ are each perpendicular (*respectively*) to $\mathsf{a}_2, \mathsf{a}_1$ and define a unit cell (lightly shaded) in k-space. The **central zone** in k-space is hexagonal (shown in darker shading) and is made up from 12 triangular pieces, one of which is shown, all equivalent under symmetry operations. You can imagine the 12 pieces come from the unit cell by 'cutting it into parts' and sliding them into new positions to fill the hexagon.

What we want to do next is to calculate the energy ϵ as a function of the coordinates (k_1, k_2) in k-space; then we'll be able to sketch the energy contours within the unit cell or the equivalent central zone.

Calculation of the energy surfaces

As in dealing with aromatic hydrocarbons, where the highest energy MOs are built up from π-type AOs and serve to describe electrons moving in an effective field, provided by a flat σ-bonded 'framework', the first approximation to calculations on a single graphite layer will start from this model. Again, with only two atoms in the unit cell, we shall need to solve a secular problem at every point in k-space to determine approximations to the crystal orbitals. And when we express these 1-electron crystal orbitals as linear combinations of Bloch functions in the form

$$\phi^{(\mathsf{k})} = c_{A,\mathsf{k}}\phi_{A,\mathsf{k}} + c_{B,\mathsf{k}}\phi_{B,\mathsf{k}}, \tag{8.23}$$

the optimum approximation will follow from the secular equation

$$\begin{vmatrix} h_{AA}(\mathsf{k}) - \epsilon & h_{AB}(\mathsf{k}) \\ h_{BA}(\mathsf{k}) & h_{BB}(\mathsf{k}) - \epsilon \end{vmatrix} = 0, \tag{8.24}$$

The matrix elements are between Bloch functions, namely $\phi_{A,\mathsf{k}}, \phi_{B,\mathsf{k}}$, where for example

$$\phi_{A,\mathsf{k}} = \frac{1}{G}\sum_m \exp[i\mathsf{k}\cdot(\mathsf{r}_A + \mathsf{R}_m)]\chi_{A,\mathsf{R}_m}$$

and χ_{A,R_m} is the AO at point $\mathsf{r}_A = (1/3)\mathsf{a}_1 + (1/3)\mathsf{a}_2$ in the lattice cell at R_m.

They can be reduced to those between the AOs as follows:

$$h_{AA} = \frac{1}{G^2}\sum_{\mathsf{R}_m}\int \chi^*_{A,\mathsf{R}_m}(\mathbf{r})\mathsf{h}\chi_{A,\mathsf{R}_m}(\mathbf{r})\mathrm{d}\mathbf{r} = \langle\chi_A|\mathsf{h}|\chi_A\rangle,$$

with an identical result for h_{BB}. (Note that $\langle\chi_A|\mathsf{h}|\chi_A\rangle$ is for the A-atom in the unit cell at the origin and that the summation is over G^2 equal lattice cells.) These diagonal matrix elements are independent of k :

$$h_{AA} = \langle\chi_A|\mathsf{h}|\chi_A\rangle, \quad h_{BB} = \langle\chi_B|\mathsf{h}|\chi_B\rangle. \tag{8.25}$$

The off-diagonal element, however, does depend on k :

$$h_{AB}(\mathsf{k}) = \frac{1}{G^2}\sum_{\mathsf{R}_m,\mathsf{R}_n} \exp[i\mathsf{k}\cdot(\mathsf{r}_B + \mathsf{R}_n - \mathsf{r}_A - \mathsf{R}_m)] \int \chi^*_{A,\mathsf{R}_m}(\mathbf{r})\mathsf{h}\chi_{B,\mathsf{R}_n}(\mathbf{r})\mathrm{d}\mathbf{r}.$$

We can make this look simpler by putting $\mathsf{R}_n + \mathsf{r}_B - \mathsf{r}_A = \rho_n$, which is the vector that goes from atom at A in the unit cell at $\mathsf{R}_m = 0$ to the atom at B in the lattice cell at R_n. Again there are G^2 identical terms in the double sum and the final result is thus

$$h_{AB}(\mathsf{k}) = \sum_n \exp(i\mathsf{k}\cdot\rho_n)\langle\chi_{A,0}|\mathsf{h}|\chi_{B,\mathsf{R}_n}\rangle. \tag{8.26}$$

The summation in the last equation can be broken into terms for A-atoms and B-atoms in the same or adjacent cells (nearest neighbours) and then in more distant cells (second and higher order neighbours). Equation (8.26) may thus be written

$$h_{AB}(\mathsf{k}) = h_1\sigma_1(\mathsf{k}) + h_2\sigma_2(\mathsf{k}) + \ ...,$$

where the terms rapidly get smaller as the A- and B-atoms become more distant. Here we'll deal only with the first approximation, evaluating $h_1\sigma_1(\mathsf{k})$ for nearest-neighbour contributions to $\sigma_1(\mathsf{k})$. We imagine atom A fixed and sum over the nearest B-type atoms; these will be B, in the same cell as A, and atoms at points B′ and B″ in adjacent cells to the left, one lower for B′ and one higher for B″. (Study carefully Figure 8.13, where you will see B′ is at the lower right corner of the next hexagon, while B″ is at its upper right corner.) The vector positions of the three B-atoms are given in terms of the Cartesian unit vectors i, j, by

$$\mathsf{r}_B = (2l)\mathsf{i} + 0\mathsf{j}, \quad \mathsf{r}_{B'} = \tfrac{1}{2}l\,\mathsf{i} - \tfrac{1}{2}\sqrt{3}l\,\mathsf{j} \quad \mathsf{r}_{B''} = \tfrac{1}{2}l\,\mathsf{i} + \tfrac{1}{2}\sqrt{3}l\,\mathsf{j},$$

where $l = 1/\sqrt{3}$ is the side-length of the hexagon. Their positions *relative to atom A* are thus

$$\mathsf{r}_B = l\,\mathsf{i} + 0\mathsf{j}, \quad \mathsf{r}_{B'} = -\tfrac{1}{2}l\,\mathsf{i} - \tfrac{1}{2}\,\mathsf{j}, \quad \mathsf{r}_{B''} = -\tfrac{1}{2}\,l\mathsf{i} + \tfrac{1}{2}\,\mathsf{j},$$

or, in terms of the a-vectors given in (8.22).

These are the corresponding ρ-vectors in (8.26); namely

$$\rho_B = (\mathsf{a}_1 + \mathsf{a}_2)/3, \quad \rho_{B'} = (1/3)\mathsf{a}_1 - (2/3)\mathsf{a}_2, \quad \rho_{B''} = -(2/3)\mathsf{a}_1 + (1/3)\mathsf{a}_2. \tag{8.27}$$

The contributions to the nearest-neighbour structure sum $\sigma(\mathsf{k})$ arise from atoms at the lattice points B, B′, B″ (from now on we drop the '1' subscript, standing for *first* neighbours) and thus give

$$\sigma(\mathsf{k}) = \exp(i\mathsf{k}\cdot\rho_B) + \exp(i\mathsf{k}\cdot\rho_{B'}) + \exp(i\mathsf{k}\cdot\rho_{B''}).$$

To evaluate these contributions, which all involve scalar products between vectors in 'real' space and those in k-space, we must remember that the latter contain a factor of 2π along with the reciprocal space basis vectors $\mathsf{b}_1^*, \mathsf{b}_2^*$. In fact, any $\mathsf{v}\cdot\mathsf{k}$ will take the usual form

$$\mathsf{v}\cdot\mathsf{k} = 2\pi(v_1k_1 + v_2k_2).$$

On substituting the ρ-vectors given in (8.27) and using this last result, we obtain finally

$$\sigma(\mathsf{k}) = [\exp(2\pi i/3)(k_1+k_2) + \exp(2\pi i/3)(k_1-2k_2) + \exp(2\pi i/3)(-2k_1+k_2). \tag{8.28}$$

The energy of the crystal orbitals ϵ, as a function of k, follows from the secular equation (8.24). The diagonal matrix elements of the Hamiltonian h, given in (8.25), become (with the usual notation) $h_{AA} = h_{BB} = \alpha$, while the off-diagonal element (8.26) becomes $h_{AB}(\mathsf{k}) = \beta\sigma(\mathsf{k})$, β being the usual 'resonance integral'. The energy eigenvalues $\epsilon(\mathsf{k})$ are finally

$$\epsilon(\mathsf{k}) = \alpha \pm \beta\sqrt{\sigma(\mathsf{k})\sigma^*(\mathsf{k})}, \tag{8.29}$$

where the upper sign gives the *lower*-energy solution (that of a bonding orbital), since β is a negative quantity.

The squared modulus of the structure sum $\sigma(\mathsf{k})$ in the energy expression (8.29) has the form

$$\sigma(\mathsf{k})\sigma^*(\mathsf{k}) = (\exp i\theta_1 + \exp i\theta_2 + \exp i\theta_3) \times (\exp -i\theta_1 + \exp -i\theta_2 + \exp -i\theta_3),$$

where

$$\theta_1 = (2\pi/3)(k_1 + k_2), \quad \theta_2 = (2\pi/3)(k_1 - 2k_2), \quad \theta_3 = (2\pi/3)(-2k_1 + k_2).$$

If you do the multiplication and note the properties of the exponentials you should find

$$\sigma(\mathsf{k})\sigma^*(\mathsf{k}) = 3 + 2\cos 2\pi(k_1) + 2\cos 2\pi(k_2) + 2\cos 2\pi(k_1 + k_2)$$

and hence

$$\epsilon(\mathsf{k}) = \alpha \pm \beta\sqrt{3 + 2\cos 2\pi(k_1) + 2\cos 2\pi(k_2) + 2\cos 2\pi(k_1 + k_2)}. \quad (8.30)$$

To get the coordinates (k_1, k_2) of points in k-space we first draw the hexagonal Brillouin zone, indicating the basis vectors $\mathsf{b}_1^*, \mathsf{b}_2^*$. Note that k_1, k_2 are the coefficients of $\mathsf{b}_1^*, \mathsf{b}_2^*$ in the k-vector. The result is shown in Figure 8.14 below (next page), where the end points of some particular k-vectors are marked with bold dots. The other diamond-shaped areas are the adjacent cells in k-space.

The higher of the two bold dots is a K-point (corner point of the hexagonal filled zone), while the lower is an M-point (mid-point of a side). To calculate the corresponding energies we must change to reciprocal-space coordinates, $\mathsf{k}_1, \mathsf{k}_2$, which go with the basis vectors $\mathsf{b}_1^*, \mathsf{b}_2^*$.

In fact, the coefficients of b_1^* and b_2^* are, apart from the missing 2π factor, the components of the properly scaled k-vector, denoted by k_1 and k_2.

The following picture shows the central zone in k-space and indicates, with bold dots, two of the most important points (a K-point and an M-point).

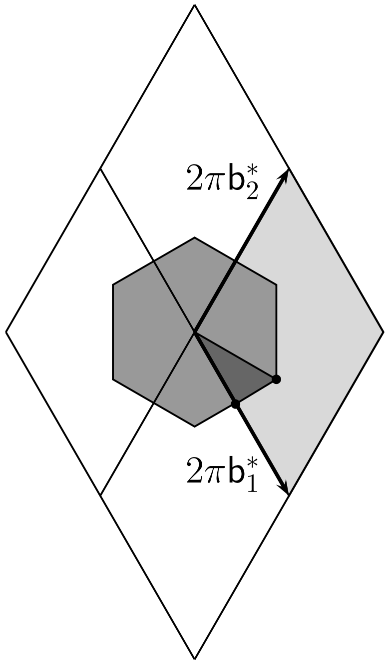


Figure 8.14 Filled zone in k-space (see text)

You can find the energy value at any point in k-space, using the energy expression (8.30) For example, at the centre of the hexagonal Brillouin zone $k_1 = k_2 = 0$ and (8.30) gives for $\epsilon(\mathsf{k})$ the value

$\alpha \pm \beta\sqrt{3 + 2\cos 2\pi(k_1) + 2\cos 2\pi(k_2) + 2\cos 2\pi(k_1 + k_2)}$,

In other words, $\epsilon = \alpha \pm \beta\sqrt{9} = \alpha \pm 3\beta$. The upper sign gives the absolute minimum $\epsilon = \alpha + 3\beta$ on the energy surface, while the lower sign gives the positive maximum energy for orbitals in a second energy band.

At the M-point on the right-hand side you should find $k_1 = k_2 = (3/4)$ and this leads to, on using (8.30),

$\epsilon(\mathsf{k}) = \alpha \pm \beta\sqrt{3 + 2\cos 2\pi(3/4) + 2\cos 2\pi(3/4) + 2\cos 2\pi(3/2)}$.

The result is thus $\epsilon = \alpha + \beta\sqrt{3 + 0 + 0 - 2} = \alpha + \beta$ at an M-point in the central Brillouin zone. Now let's turn to the general form of $\epsilon(k_1, k_2)$ throughout the zone:

Energy contours in the lowest-energy Brillouin zone

By evaluating (8.30) at a large number of points in k-space we can draw in the contour lines on which $\epsilon(\mathsf{k})$ is constant. This is of course a tedious job, but the results look nice and are sketched in the figure that follows.

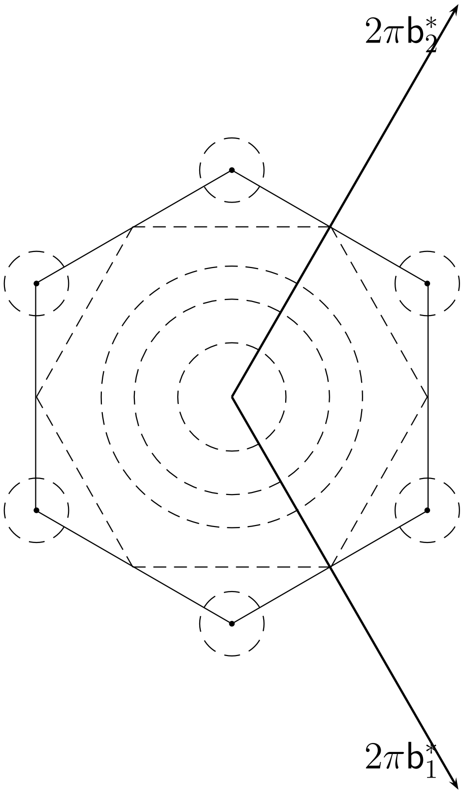


Figure 8.15 Some energy contours in the filled zone (schematic)

The outer hexagon in Figure 8.15 shows the boundary (in k-space) of the lowest-energy Brillouin zone, which contains G^2 1-electron states (see text). With two Carbons per unit cell, these are filled with the $2G^2$ π-electrons they provide. Beyond the boundary, there begins the next zone – containing orbitals that are normally empty. The energy contours are indicated by broken lines and the corner-points (K-points) are marked with bold dots.

Notice that around the centre of the filled zone, where the energy has the absolute minimum value $\epsilon = \alpha + 3\beta$, the contours are almost perfect circles; but when the energy approaches $\epsilon = \alpha + \beta$ the contour becomes a perfect hexagon, whose sides join the mid-points (the M-points) of the hexagonal boundary of the filled zone, and here the surface becomes 'flat', *all* points on the hexagon having the same energy as at the M-point. After that, the energy approaches the value $\epsilon = \alpha$, the highest energy level in the filled zone, but this is found only at the K-points and close to them – where the contours again become roughly circular. At these points, something very unusual happens: the energy surface is just *touched* by the lowest-energy points of the next energy surface, whose orbitals have energies going from $\epsilon = \alpha$ up to the maximum $\epsilon = \alpha - \beta$. At all other points there is a gap between the lower and upper surfaces.

It is this strange fact that gives graphene its unique properties.

The π electrons serve mainly to 'stiffen' the sigma-bonded framework of Carbon atoms and to give the material the unique properties that arise from the touching of the two energy surfaces. The Carbon-Carbon bonds in general can be difficult to break, especially when they form a 3-dimensional network that can't be pulled apart in any direction without breaking very many bonds. This is the case in crystals of diamond, where every Carbon forms tetrahedral bonds with its four nearest neighbours, as in Figure 7.7. (Remember that diamonds – which contain only Carbon atoms – are used in cutting steel!) But in graphite the Carbons have the rare property of forming separate layers, held together only by very weak bonds – which allow them to slide over one another, or to be 'peeled off' as sheets of graphene.

The great strength of graphene sheets is often called the "Cat's Cradle" property, because a single sheet – *one atom thick* and weighing almost nothing! – would support the weight of a sleeping cat!

More useful properties arise from the limited contact (in k-space) between the filled and empty electronic bands. When the lowest-energy band is filled and separated from the next band above it by an energy gap greater than $(3/2)kT$ (which is the average energy of a particle in equilibrium with its surroundings at temperature T° K – as you may remember from Book 5) an electron with energy at the top of the filled band is unable to jump across the gap into an orbital of the empty band, where it will be able to move freely. But at the K-points in graphene the energy gap is zero and some electrons will be found in the **conduction band** where they are free to conduct electricity. In fact, graphene is a perfect **semiconductor**, whose conductivity starts at zero, when it is cold, but rises rapidly as the temperature increases. You know how valuable semiconductors have become nowadays, when they form the vital parts of so many electronic devices such as radios and computers.

Such properties are revolutionizing not only whole fields of experimental Physics and Technology, but also large parts of Chemistry and Biology. Tiny sheets of graphene can be wound into ‘tubes’ so small that they can carry single atoms from one place to another, opening up new fields of ‘molecular engineering’.

“Looking back – ” and “Index” to follow (10 May 2014)