Walter Thirring

A Course in Mathematical Physics

3

Quantum Mechanics of Atoms and Molecules

Translated by Evans M. Harrell

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Preface

In this third volume of *A Course in Mathematical Physics* I have attempted not simply to introduce axioms and derive quantum mechanics from them, but also to progress to relevant applications. Reading the axiomatic literature often gives one the impression that it largely consists of making refined axioms, thereby freeing physics from any trace of down-to-earth residue and cutting it off from simpler ways of thinking. The goal pursued here, however, is to come up with concrete results that can be compared with experimental facts. Everything else should be regarded only as a side issue, and has been chosen for pragmatic reasons. It is precisely with this in mind that I feel it appropriate to draw upon the most modern mathematical methods. Only by their means can the logical fabric of quantum theory be woven with a smooth structure; in their absence, rough spots would inevitably appear, especially in the theory of unbounded operators, where the details are too intricate to be comprehended easily. Great care has been taken to build up this mathematical weaponry as completely as possible, as it is also the basic arsenal of the next volume. This means that many proofs have been tucked away in the exercises. My greatest concern was to replace the ordinary calculations of uncertain accuracy with better ones having error bounds, in order to raise the crude manners of theoretical physics to the more cultivated level of experimental physics.

The previous volumes are cited in the text as I and II; most of the mathematical terminology was introduced in volume I. It has been possible to make only sporadic reference to the huge literature on the subject of this volume—the reader with more interest in its history is advised to consult the compendious work of Reed and Simon [3].

Of the many colleagues to whom I owe thanks for their help with the German edition, let me mention F. Gesztesy, H. Grosse, P. Hertel, M. and T.

Hoffmann-Ostenhof, H. Narnhofer, L. Pittner, A. Wehrl, E. Weimar, and, last but not least, F. Wagner, who has transformed illegible scrawls into a calligraphic masterpiece. The English translation has greatly benefited from the careful reading and many suggestions of H. Grosse, H. Narnhofer, and particularly B. Simon.

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Symbols Defined in the Text

p, q	momentum and position coordinates	
ψ	Schrödinger wave function	
$\hbar$	Planck's constant	
$\mathbf{L}$	orbital angular momentum	
l	angular momentum quantum number	
Z	nuclear charge	
r_b	Bohr radius	(1.2.3)
Ry	Rydberg	(1.2.4)
$\mathbb{E}$	vector space	(2.1.1)
$\mathbb{C}$	set of complex numbers	(2.1.1)
$\| \ \|$	norm	(2.1.4)
$\| \ \|_p$	p-norm	(2.1.5; 6)
$L^p(K, \mu)$	space of p-integrable functions on K	(2.1.5; 6)
l^p	sequence space	(2.1.6; 2)
$\langle \mid \rangle$	scalar product	(2.1.7)
e_ν	basis vector	(2.1.12; 3)
$\mathbb{E}'$	dual space to $\mathbb{E}$	(2.1.16)
$\mathscr{L}(\mathbb{E}, \mathbb{F})$	space of continuous, linear mappings from $\mathbb{E}$ to $\mathbb{F}$	(2.1.24)
$\mathscr{B}(\mathbb{E})$	space of bounded operators on $\mathbb{E}$	(2.1.24)
a^*	adjoint operator for a	(2.1.26; 3)
w-lim, $\rightarrow$	weak limit	(2.1.27)
s-lim, $\rightarrow$	strong limit	(2.1.27)
lim, $\Rightarrow$	norm limit	(2.1.27)
l^0	sequence space	(2.2.2)
$\mathrm{Sp}(a)$	spectrum of a	(2.2.13)
$a \geq b$	partial ordering of operators	(2.2.16)
$X(\mathscr{A})$	set of characters	(2.2.25)
$(\Delta_w(a))^2$ $= (\Delta a)^2$ $= \Delta a^2$	mean-square deviation	(2.2.33; 3)

$\mathscr{P}$	propositional calculus	(2.2.35)
$p_1 \wedge p_2$	intersection of propositions	(2.2.35(i))
$p_1 \vee p_2$	union of propositions	(2.2.35(ii))
$\sigma_x, \sigma_y, \sigma_z$	spin matrices	(2.2.37)
π	representation	(2.3.1)
$\mathscr{M}'$	commutant of $\mathscr{M}$	(2.3.4)
$\mathscr{Z}$	center	(2.3.4)
$\theta(x)$	step function	(2.3.14)
$\sigma_p(a)$	point spectrum	(2.3.16)
σ_{ac}	absolutely continuous spectrum	(2.3.16)
$\sigma_s(a)$	singular spectrum	(2.3.16)
σ_{ess}	essential spectrum	(2.3.18; 4)
Tr m	trace of m	(2.3.19)
$\mathscr{C}_1$	trace-class operators	(2.3.21)
$\mathscr{C}_2$	Hilbert–Schmidt operators	(2.3.21)
$\mathscr{C}$	compact operators	(2.3.21)
$\mathbf{T}$	time-ordering	(2.4.10; 3)
$D(a)$	domain of definition of a	(2.4.12)
Ran(a)	range of a	(2.4.12)
$\Gamma(a)$	graph of a	(2.4.15)
$a \supset b$	a extends b	(2.5.1)
$Q(q)$	quadratic-form domain	(2.5.17)
$\mathscr{W}$	Weyl algebra	(3.1.1)
$(z\|z')$	scalar product	(3.1.2; 1)
$\|l, m\rangle$	angular momentum eigenvectors	(3.2.13)
$L_\pm$	circular components of $\mathbf{L}$	(3.2.13)
$\mathrm{ad}_H^n(a)$	(derivation)^n	(3.3.1)
P_{ac}	projection onto the absolutely continuous eigenspace	(3.4.4)
$\mathscr{A}$	algebra of asymptotic constants	(3.4.6)
$a_\pm$	limit of an asymptotic constant	(3.4.6)
$\tau_\pm$	homomorphism $\mathscr{A} \to \mathscr{A}_\pm$	(3.4.6)
$\Omega_\pm$	Møller operators	(3.4.7; 4)
P_α	projection for the channel with H_α	(3.4.17)
$Q_{\alpha\pm}$	channel decomposition of P_{ac}	(3.4.17)
$S_{\alpha\beta}$	S matrix in the interaction representation	(3.4.23)
$R(\alpha, z)$	resolvent	
$P_k(\alpha)$	projection operator for the perturbed Hamiltonian $H(\alpha)$	(3.5.1)
$t(k)$	t matrix	
$f(k; \mathbf{n}', \mathbf{n})$	angular dependence of the outgoing spherical wave	(3.6.10;3)
D	delay operator	(3.6.17)
$\sigma(\mathbf{k}, \mathbf{k}_0)$	differential scattering cross-section	(3.6.19)
σ_t	total scattering cross-section	(3.6.19)
a	scattering length	(3.6.23; 5)
$\mathbf{F}$	Runge–Lenz vector	(4.1.7)
A_k, B_k	generators of O(4)	(4.1.8)

Introduction 1

1.1 The Structure of Quantum Theory

The structure of quantum mechanics differs startlingly from that of the classical theory. In volume I we learned that in classical mechanics the observables form an algebra of functions on phase space (p and q), and states are probability measures on phase space. The time-evolution is determined by a Hamiltonian vector field. It would be reasonable to expect that atomic physics would distort the vector field somewhat, or even destroy its Hamiltonian structure; but in fact the break it makes with classical concepts is much more drastic. The algebra of observables is no longer commutative. Instead, position and momentum satisfy the famous **commutation relations**,

$$qp - pq = i\hbar. \tag{1.1.1}$$

Since matrix algebras are not generally commutative, one of the early names for quantum theory was matrix mechanics. It became apparent in short order, however, that the commutator (1.1.1) of finite-dimensional matrices can never be proportional to the identity (take the trace of both sides), so attempts were then made to treat p and q as infinite-dimensional matrices. This proved to be a false scent, since infinite-dimensional matrices do not provide an ideal mathematical framework. The right way to proceed was pointed out by J. von Neumann, and the theory of C^* and W^* algebras today puts tools for quantum theory at our disposal, which are polished and comparatively easy to understand. There do remain a few technical complications connected with unbounded operators, for which reason the **Weyl relation**

$$e^{i\alpha q}e^{i\beta p}e^{-i\alpha q} = e^{i\beta(p-\alpha)} \tag{1.1.2}$$

(setting $\hbar = 1$) is a better characterization of the noncommutativity.

Admittedly, Schrödinger historically first steered quantum mechanics in a different direction. The equation that bears his name treats p and q as differentiation and multiplication operators acting on the **Schrödinger wave-function** ψ, which has the interpretation of a **probability amplitude**: It is complex-valued, and $|\psi|^2$ is the probability distribution in the state specified by ψ. Superposition of the solutions of the equation causes **probability interference effects**, a phenomenon that can not be understood classically at all. Later, ψ was characterized axiomatically as a vector in Hilbert space, but the peculiar fact remained that one worked with a complex Hilbert space and came up with real probabilities.

At long last the origin of the Hilbert space was uncovered. A state would normally be required to be represented as a **positive linear functional**, where positivity means that the expectation value $\langle a^2 \rangle$ of the square of any real observable a must always be nonnegative. It turns out that to each state there corresponds a representation of the observables as linear operators on some Hilbert space. (It is at first unsettling to learn that each state brings with it its own representation of the algebra characterized by (1.1.2), but it also turns out that they are all equivalent.) The schema of quantum theory thus adds no new postulates to the classical ones, but rather omits the postulate that the algebra is commutative. As a consequence, quantum mechanically there are no states for which the expectation values of all products are equal to the products of the expectation values. Such a state would provide an algebraic isomorphism to the ordinary numbers, which is possible only for very special noncommutative algebras. The occurrence of nonzero fluctuations $(\bar{\Delta}a)^2 \equiv \langle a^2 \rangle - \langle a \rangle^2$ is in general unavoidable, and gives rise to the indeterministic features of the theory. The extremely good experimental confirmation of quantum mechanics shows that the numerous paradoxes it involves are owing more to the inadequacy of the understanding of minds raised in a classical environment than to the theory.

Quantum theory shows us where classical logic goes awry; the logical maxim *tertium non datur* is not valid. Consider the famous double-slit experiment. Classical logic would reason that if the only and mutually exclusive possibilities are "the particle passes through slit 1" and "the particle passes through slit 2," then it follows that "the particle passes through slit 1 and then arrives at the detector" and "the particle passes through slit 2 and then arrives at the detector" are likewise the only and mutually exclusive possibilities. **Quantum logic** contests this conclusion by pointing to the irreparable change caused in the state by preparing the system to test the new propositions. The rules of quantum logic can be formulated just as consistently as those of classical logic. Nonetheless, the world of quantum physics strikes us as highly counterintuitive, more so even than the theory of relativity. It requires radically new ways of thinking.

The mathematical difficulties caused by the noncommutativity have all been overcome. Indeed, the fluctuations it causes often simplify problems. For example, the fluctuations of the kinetic energy, the **zero-point energy**,

have the effect of weakening the singularity of the Coulomb potential and eliminating the problem of the collision trajectories, which are so troublesome in classical mechanics. Quantum theory guarantees that the time evolution can be continued uniquely from $t = -\infty$ to $t = +\infty$ for (non-relativistic) systems with $1/r$ potentials. In a certain sense this potential energy is only a small perturbation of the kinetic energy, and free particles can be used as a basis of comparison. Calculations are sometimes much easier to do in quantum theory than in classical physics; it is possible, for instance, to evaluate the energy levels of helium with fantastic precision, whereas only relatively crude estimates can be made for the corresponding classical problem.

1.2 The Orders of Magnitude of Atomic Systems

One can come to a rough understanding of the characteristics of quantum-mechanical systems by grafting discreteness and fluctuations of various observables onto classical mechanics. Their magnitudes depend on **Planck's constant** $\hbar$, which is best thought of as a quantum of angular momentum, since quantum-mechanically the orbital angular momentum L takes on only the values $l\hbar$, $l = 0, 1, 2, \ldots$. Suppose an electron moves in the Coulomb field of a nucleus of charge Z; then the energy is

$$E = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} - \frac{Ze^2}{r}. \tag{1.2.1}$$

For circular orbits ($p_r = 0$), quantization of the angular momentum means that

$$E(r) = \frac{l^2\hbar^2}{2mr^2} - \frac{Ze^2}{r}. \tag{1.2.2}$$

At the radius

$$r = \frac{l^2\hbar^2}{mZe^2} \equiv \frac{l^2 r_b}{Z}, \tag{1.2.3}$$

where r_b is known as the **Bohr radius**, the energy is minimized, with the value

$$E = -\frac{(Ze^2)^2}{2}\frac{m}{l^2\hbar^2} = \frac{-Z^2}{l^2}\frac{e^2}{2r_b} \equiv -\frac{Z^2}{l^2}\,(\text{Rydberg} \equiv \text{Ry}) \tag{1.2.4}$$

(**Balmer's formula**). If $l = 0$, then we would find $r = 0$ and $E = -\infty$, except that the stability of the system is saved by the inequality for the fluctuations $\Delta p\,\Delta q \geq \hbar/2$, the **indeterminacy relation**, which follows from (1.1.1). This makes $\langle p_r^2 \rangle \geq (\Delta p_r)^2 \approx \hbar^2/r^2$, the **zero-point energy**, and hence this part of

the kinetic energy contributes as much as a centrifugal term with $l = 1$. This argument actually gives the correct ground-state energy. The reasoning is of course not a mathematically rigorous deduction from the indeterminacy relation, as the average of $1/r$ could conceivably be large without Δr being small. We shall later derive generalizations of the inequality $\Delta p\, \Delta q \geq \hbar/2$, which will justify the argument.

The virial theorem states that the velocity v of an electron is given classically by

$$\frac{mv^2}{2} = -E = \frac{Z^2 e^4 m}{2l^2\hbar^2} \Rightarrow v = \frac{Z}{l}\frac{e^2}{\hbar}.$$

The universal speed $e^2/\hbar$ is about 1/137 times the speed of light. As Z increases, the nonrelativistic theory rapidly loses its accuracy. Relativistic corrections, entering through the increase of the mass and magnetic interactions, are $\sim v^2/c^2 \approx 10^{-5}Z^2$. For small Z they show up as fine structure of the spectral lines, but their effect becomes pronounced for heavy nuclei, and when Z is sufficiently greater than 137 the system is not even stable anymore. The relativistic kinetic energy is $\sqrt{m^2c^4 + p^2c^2} - mc^2$, which for large momenta grows only as $cp \approx c\hbar/r$. Equation (1.2.2) is accordingly changed to

$$E(r) \approx \frac{c\hbar}{r} - \frac{Ze^2}{r} = \frac{c\hbar}{r}\left(1 - \frac{Z}{137}\right), \tag{1.2.5}$$

which is no longer bounded below when $Z > 137$. The question of what happens for such large Z can only be answered in the relativistic quantum theory, and lies beyond the scope of this book.

If a second electron is introduced to form a helium-like atom, then the repulsion of the electrons makes it impossible to solve the problem analytically. To orient ourselves and to understand the effect of the repulsion, let us provisionally make some simplifying assumptions. Since an electron can not be localized well, we can suppose that its charge fills a ball of radius R homogeneously. Such an electronic cloud would produce an electrostatic potential

$$V(r) = \begin{cases} -\dfrac{3e}{2R} + \dfrac{e}{2R}\left(\dfrac{r}{R}\right)^2, & r \leq R \\ -\dfrac{e}{r}, & r \geq R \end{cases} \tag{1.2.6}$$

(Figure 1). The potential energy of one electron and the nucleus is consequently $ZeV(0) = -3Ze^2/2R$. We can gauge the kinetic energy by reference to the hydrogen atom, for which the following rule of thumb leads to the correct ground-state energy: An electron cloud having potential energy $-Ze^2/r_b$ requires a kinetic energy $\hbar^2/2mr_b^2$. We set the kinetic energy equal to $9\hbar^2/8mR^2$, since $R = 3r_b/2$ provides the same amount of potential energy.

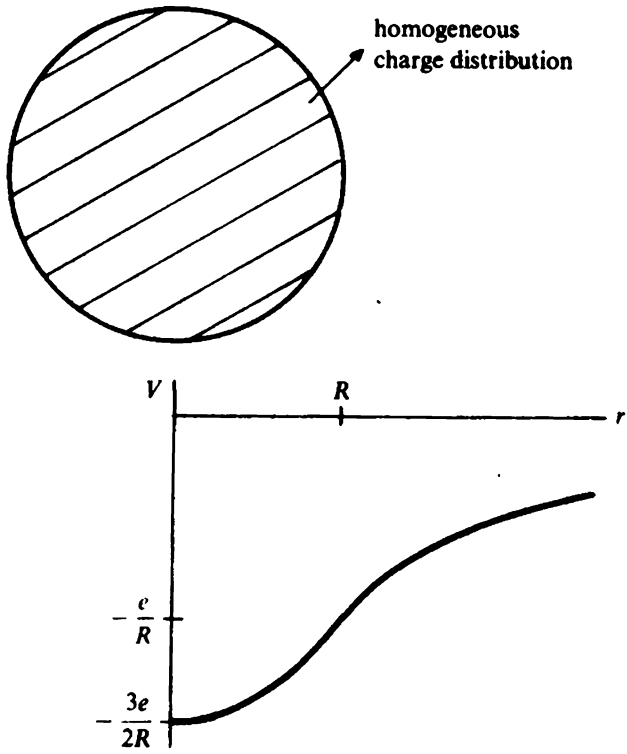


Figure 1 The potential of a homogeneous charge distribution.

If the second electron is also a homogeneously charged sphere coinciding with the first one, then the electronic repulsion is

$$-\frac{3}{4\pi R^3}\,4\pi e^2\int_0^R r^2\,dr\,V(r)=\frac{6e^2}{5R}. \tag{1.2.7}$$

Therefore we obtain the ratio

$$\frac{|\text{Attraction of the electrons to the nucleus}|}{\text{Repulsion of the electrons}}=\frac{2\cdot(3Ze^2/2R)}{6e^2/5R}=\frac{5Z}{2}, \tag{1.2.8}$$

and thus the total energy is

$$\begin{aligned}E(R)&=\text{kinetic energy}+\text{nuclear attraction}+\text{electronic repulsion}\\&=2\cdot\frac{9\hbar^2}{8mR^2}-2\cdot\frac{3Ze^2}{2R}\left(1-\frac{2}{5Z}\right).\end{aligned} \tag{1.2.9}$$

This has its minimum at the value $R=R_{\min}=R_H/(Z-\frac{2}{5})$, where

$$E(R_{\min})=-Ry\cdot 2Z^2\left(1-\frac{2}{5Z}\right)^2. \tag{1.2.10}$$

If $Z=2$, then $R_{\min}=5R_H/8$, and the energy has the value $-2Ry\cdot\frac{64}{25}=-2Ry\cdot 2.56$. For such a primitive estimate, this comes impressively near to

the experimentally measured $-2Ry \cdot 2.9$, and a helium atom is indeed only about half as large as a hydrogen atom. Actually, however, even if $Z = 1$ (H^-) the energy lies somewhat below $-Ry$ while (1.2.10) gives only $-\frac{16}{25}Ry$. In this case the picture of two equal spheres is not very apt, since the outer electron will travel out to large distances. Nevertheless, nonrelativistic quantum mechanics describes these systems very well.

If there are more than two electrons, then some of them must have spins in parallel, and **Pauli's exclusion principle** is of primary importance for the spatial configuration of atoms; it says that no two electrons may have the same position, spin, etc. An atom with N electrons and radius R has a volume of about R^3/N per particle. Electrons insist on private living quarters of this volume, so Δq will be on the order of the distance to the nearest neighbor, which is $R/N^{1/3}$. This makes the zero-point energy of an electron $\approx \hbar^2 N^{2/3}/2mR^2$, as a rough approximation, and its potential energy $\approx -e^2 Z/R$. The minimum energy is attained at $R_{\min} = \hbar^2 N^{2/3}/me^2 Z$, making the total energy of all the electrons

$$E(R_{\min}) = -\frac{e^4 Z^2 m}{2\hbar^2} N^{1/3}. \tag{1.2.11}$$

The value $R_{\min}$ is an average radius, which goes as $N^{-1/3}$ for $N = Z$, making $E \sim N^{7/3}$. Yet the outermost electrons, which are the important ones for chemistry, see a screened nuclear charge, and the radii of their orbitals are $\approx \hbar^2/me^2$. Strangely enough, it is not yet known whether the Schrödinger equation predicts that these radii expand, contract, or remain constant as $Z \to \infty$. Their contribution of about 10 eV to the total energy (1.2.11), on the order of MeV for $Z \sim 100$, is rather slight, however.

Chemical forces also arise from an energetically optimal compromise between electrostatic and zero-point energies. History has saddled us with a misleading phrase for this, **exchange forces**. Let us now consider the simplest molecule, H_2^+, that is, a system of two protons and one electron. There is clearly a negative potential energy if the electron sits right in the middle of the line between the two protons. But is it possible for the electron's potential energy to be sufficiently negative to make the total energy less than that of H, or would its wave-function be too narrow, giving it an excessive zero-point energy? To be more quantitative about this question, let us again imagine that the electron is a homogeneously charged sphere with the potential (1.2.6). The radius R is chosen the same as for H, so there is no difference between this zero-point energy and that of hydrogen. If, as with H, we put one proton at the center of the cloud (Figure 2a), the potential energy is eV(0). Taking the Coulombic repulsion of the protons into account, we note that the second proton feels no potential as long as it is outside the cloud, but when it comes to within a distance $r < R$ its energy increases, because

$$V(0) + V(r) + \frac{e^2}{r} \geq V(0). \tag{1.2.12}$$

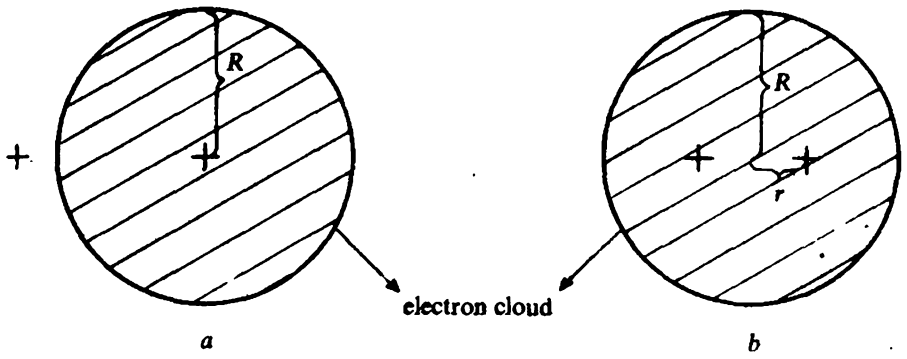


Figure 2 Two electron distributions assumed for H_2^+.

Hence there is no binding. However, if the two protons are placed diametrically across the center of the electron cloud, at radius r (Figure 2b), then the total potential energy

$$2V(r) + \frac{e^2}{2r} = -\frac{3e^2}{R} + \left(\frac{e^2}{R}\right)\left(\frac{r}{R}\right)^2 + \frac{e^2}{2r} \tag{1.2.13}$$

has the minimum

$$-\frac{3e^2}{2R}[2 - 2^{-1/3}] = -\frac{3e^2}{2R} \cdot 1.2 \tag{1.2.14}$$

at $r = 2^{-2/3} \cdot R$. This is more negative than $V(0)$, the energy with one proton outside the sphere, by a factor 1.2, and so we expect H_2^+ to be bound. If the total energy is now minimized with respect to R, then $R_{\min} = R_H/1.2$ and $E(R_{\min}) = -(1.2)^2 Ry$. The separation $2r$ of the protons at the minimum is $2^{1/3}R_{\min} = 1.57r_b$, which is significantly smaller than the experimental value $2r_b$. The binding energy $((1.2)^2 - 1)Ry$ also amounts to more than twice the measured value, so the simple picture is not very accurate.

Finally, consider the molecule H_2, again assuming that the H atoms are spheres. If they do not overlap, then the electrostatic energy is twice that of a single H atom, and the two separate atoms exert no force on each other. As the spheres are pushed together, the energy first decreases, since the repulsion of the electrons is reduced (the energy of two uniformly charged spheres at a distance $r < 2R$ is less than e^2/r), while the other contributions to the energy remain unchanged. In order to find out how much energy can be gained by making the spheres overlap, let us superpose them and place the protons diametrically across their center at a distance r. As with the helium atom, the electronic repulsion is $6e^2/5r$, and hence the total potential energy is

$$V_{H_2}(r) = -\frac{6e^2}{R} + 2\frac{e^2r^2}{R^3} + \frac{e^2}{2r} + \frac{6e^2}{5R}. \tag{1.2.15}$$

The minimum at $r = R/2$ can now be compared with $2V(0)$:

$$V_{H_2}\left(\frac{R}{2}\right) = -2\frac{3e^2}{2R} \cdot 1.1. \tag{1.2.16}$$

The minimum in R is now attained at $R_H/1.1$, and the corresponding interprotonic distance $3r_b/2 \cdot 1.1 = 1.36r_b$ is in excellent agreement with the actual distance. The resultant binding energy $2\ Ry((1.1)^2 - 1) \simeq 5.7$ eV is consequently also fairly close to the measured energy of dissociation 4.74 eV. Of course, it is necessary for the electrons in H_2 to have antiparallel spins, as otherwise the exclusion principle would restrict the room they have to move about in.

One lesson of these rough arguments is that delicate questions like that of stability depend on small energy differences. It will require highly polished calculational techniques to reach definitive conclusions.

The Mathematical Formulation of Quantum Mechanics

2

2.1 Linear Spaces

There are many surprising aspects to the infinitely many directions in an infinite-dimensional space. For this reason it is necessary to investigate carefully which of the familiar properties of finite-dimensional spaces carry over unchanged and which do not.

We begin by recollecting the basic definitions and theorems:

Definition (2.1.1)

A **linear**, or **vector, space** $\mathbb{E} \ni v_i$ over the complex numbers $\mathbb{C} \ni \alpha_i$ is a set on which sums $\mathbb{E} \times \mathbb{E} \to \mathbb{E}: (v, u) \to v + u = u + v$ and products with scalars $\mathbb{E} \times \mathbb{C} \to \mathbb{E}: (v, \alpha) \to \alpha v$ are defined so that $\alpha_1(\alpha_2 v) = (\alpha_1\alpha_2)v$, $\alpha(v + u) = \alpha v + \alpha u$, $1 \cdot v = v$, and $(\alpha_1 + \alpha_2)v = \alpha_1 v + \alpha_2 v$.

Examples (2.1.2)

1. Vectors in $\mathbb{C}^n$.
2. Complex $n \times n$ matrices.
3. Polynomials in n complex variables.
4. $C^r \equiv$ the r-times continuously differentiable functions.
5. Analytic functions.

Etc. Sums and products with α are defined in the usual way.

Remark (2.1.3)

A subset $\mathbb{E}_1 \subset \mathbb{E}$ that is also a vector space is called a **subspace** of $\mathbb{E}$. For example, (2.1.2; 5) is a subspace of 4, and 3 is a subspace of 5. The **quotient space** $\mathbb{E}/\mathbb{E}_1$ consists of equivalence classes of vectors whose differences are elements of $\mathbb{E}_1$. In the absence of a scalar product there is no uniquely defined decomposition of vectors $v \in \mathbb{E}$ such that $v = v_1 + v_2$ with $v_1 \in \mathbb{E}_1$. However, if an $\mathbb{E}_2$ is also specified so that $\mathbb{E}_1 + \mathbb{E}_2 = \mathbb{E}$ and $\mathbb{E}_1 \cap \mathbb{E}_2 = \{0\}$, then there is such a decomposition with a unique $v_2 \in \mathbb{E}_2$; $\mathbb{E}$ is then the **sum** of $\mathbb{E}_1$ and $\mathbb{E}_2$, and $\mathbb{E}_2$ is a **complement** of $\mathbb{E}_1$. General sums of linear spaces can be defined in the same manner. According to the axiom of choice, it is always possible, by an inductive argument, to find a **Hamel basis** $\{e_\gamma\}$, $\gamma \in \mathbb{I}$, such that every vector can be written uniquely as

$$v = \sum_{\text{finite}} \alpha_i e_{\gamma_i}, \qquad \alpha_i \in \mathbb{C}.$$

Unfortunately, for infinite-dimensional spaces the set $\mathbb{I}$ is usually uncountable, and the Hamel basis is of little practical significance. The cardinality of $\mathbb{I}$ is known as the **algebraic dimension of the space**.

Definition (2.1.4)

A **normal** linear space is a vector space on which there is defined a **norm** mapping $\mathbb{E} \to \mathbb{R}^+$, $v \to \|v\|$, such that $\|\alpha v\| = |\alpha|\,\|v\|$, $\|v + u\| \leq \|v\| + \|u\|$, and $\|v\| = 0$ iff $v = 0$.

Examples (2.1.5)

1. $\mathbb{E} = \mathbb{C}^n \ni v = (v_1, v_2, \ldots, v_n)$, $\|v\|_p = [\sum_{i=1}^n |v_i|^p]^{1/p}$, $1 \leq p < \infty$, $\|v\|_\infty = \max_i |v_i|$.
2. $\mathbb{E} = n \times n$ matrices, $m = (m_{ij})$, $\|m\| = (\sum_{i,j} |m_{ij}|^2)^{1/2} = (\mathrm{Tr}\, mm^*)^{1/2}$.
3. $\mathbb{E} = n \times n$ matrices, $\|m\|^2 = \sup_{\sum_i |v_i|^2 = 1} \sum_i |\sum_k m_{ik} v_k|^2$.
4. Polynomials $P(z_i)$ for $z = (z_1, \ldots, z_n)$ in a compact set $K \subset \mathbb{C}^n$, $\|P\| = \sup_{z \in K} |P(z_i)|$.
5. The r-times continuously differentiable functions $f(z_i)$ on K, $\|f\| = \sup_{z \in K} |f(z_i)|$.
6. Given a measure μ on K, it defines a norm $\|f\|_p = [\int d\mu |f|^p]^{1/p}$, $1 \leq p < \infty$. (We use the word **measure** to mean **positive measure**.) $L^p(K, \mu) \equiv \{f : \|f\|_p < \infty\}$.

Remarks (2.1.6)

1. As $p \to \infty$, the norm $\|f\|_p$ approaches the norm of Example 5, which is denoted by $\|f\|_\infty$.
2. If μ is a sum of n point masses, then the space of Example 6 is the same as that of Example 1. If n is infinite, it is denoted by l^p.

3. As we see, different norms can be given to the same space, while, on the other hand, a space must sometimes be restricted for a norm to be finite on all of it.

Definition (2.1.7)

If a norm on $\mathbb{E}$ satisfies the **parallelogram law** $\|u + v\|^2 + \|u - v\|^2 = 2\|u\|^2 + 2\|v\|^2$, then $\mathbb{E}$ is a **pre-Hilbert space**. In that case there exists a **scalar product**

$$\mathbb{E} \times \mathbb{E} \to \mathbb{C}: (u, v) \to \langle u|v\rangle$$
$$\equiv \tfrac{1}{4}(\|u + v\|^2 - \|u - v\|^2 - i\|u + iv\|^2 + i\|u - iv\|^2),$$

which has the properties

$$\|v\|^2 = \langle v|v\rangle, \langle v|u\rangle = \langle u|v\rangle^*, \langle v|\alpha u\rangle$$
$$= \alpha\langle v|u\rangle, \langle u|v + w\rangle = \langle u|v\rangle + \langle u|w\rangle,$$

and $\langle v|v\rangle = 0$ iff $v = 0$.

Examples (2.1.8)

Of Examples (2.1.5), the only pre-Hilbert spaces (for $n > 1$) are Example 1 with $p = 2$, Example 2, and Example 6 with $p = 2$.

Remarks (2.1.9)

1. Only the length of a vector is defined on a general normed linear space; on a pre-Hilbert space it is also known when two vectors are orthogonal. Pre-Hilbert spaces therefore conform better to our geometric intuition; by Problem 10,

   (i) $|\langle u|v\rangle| \leq \|u\|\,\|v\|$ (the **Cauchy–Schwarz inequality**);
   (ii) $\langle u|v\rangle = 0 \Leftrightarrow \|u + v\|^2 = \|u\|^2 + \|v\|^2$ (**Pythagoras's law**).

2. If $\mathbb{E}_1$ and $\mathbb{E}_2$ are two pre-Hilbert spaces, then $\mathbb{E} \equiv \mathbb{E}_1 \oplus \mathbb{E}_2$ can be made into a pre-Hilbert space, the **Hilbert sum**, by setting $\langle (u_1, u_2)|(v_1, v_2)\rangle = \langle u_1|v_1\rangle + \langle u_2|v_2\rangle$. The vectors of $\mathbb{E}_1$ become orthogonal to those of $\mathbb{E}_2$ in the new space. Conversely, given a subspace $\mathbb{E}_1 \subset \mathbb{E}$ and defining $\mathbb{E}_1^\perp \equiv \{v \in \mathbb{E}: \langle v|u\rangle = 0 \text{ for all } u \in \mathbb{E}_1\}$, it follows that $\mathbb{E}_1 \cap \mathbb{E}_1^\perp = \{0\}$. It is tempting to single $\mathbb{E}_1^\perp$ out as the complement of $\mathbb{E}_1$. However, it can happen for infinite-dimensional spaces that $\mathbb{E}_1 \oplus \mathbb{E}_1^\perp \neq \mathbb{E}$: Let $\mathbb{E}_1 \subset l^2$ consist of the vectors having only finite many nonzero components; then $\mathbb{E}_1^\perp = \{0\}$ but $\mathbb{E}_1 \neq l^2$. This is related to the fact, which we shall return to shortly, that in infinitely many dimensions not every linear subspace is topologically closed.

3. The tensor product $\mathbb{E}_1 \otimes \mathbb{E}_2$ and the antisymmetric tensor product $\mathbb{E}_1 \wedge \mathbb{E}_2$ can be defined as for finite-dimensional spaces (*I*: §2.4), and the scalar product in these constructions is multiplicative: $\langle v_1 \otimes v_2 | u_1 \otimes u_2 \rangle = \langle v_1 | u_1 \rangle \langle v_2 | u_2 \rangle$.
4. If two norms satisfy $\|\cdot\|_1 \leq a\|\cdot\|_2 \leq b\|\cdot\|_1$ for $a > 0, b > 1$, then they are said to be **equivalent**. They clearly produce the same topology (see below). Remarkably, all norms on finite-dimensional spaces are equivalent.
5. A mapping $a: \mathbb{E} \to \mathbb{F}$ satisfying $\|ax\| = \|x\|$ for all $x \in \mathbb{E}$ is called an **isometry**. We shall reserve the term **isomorphism** of normed spaces for a linear, isometric bijection.
6. Conversely, a scalar product $\langle u | v \rangle$ with the properties (2.1.7) defines a norm $\|x\|^2 = \langle x | x \rangle$ that obeys the parallelogram law.

Although the dimension of the space has only played a secondary role in the algebraic rules discussed above, infinite dimensionality disrupts the topological properties. These properties can be studied by using the norm (2.1.4), which induces a metric topology on a vector space with the distance function $d(u, v)$ defined as $\|u - v\|$. The neighborhood bases of vectors $v \in \mathbb{E}$ are $\{v' \in \mathbb{E}: \|v - v'\| \leq \varepsilon\}$. Definition (2.1.4) guarantees that addition and multiplication are continuous in this topology (Problem 3), i.e., the limit of sums or products equals the sum or product of the limits. There remains one obstacle to the use of the methods of classical analysis, in that not every **Cauchy sequence** v_n (i.e., for all $\varepsilon \to 0$ there exists an N such that $\|v_n - v_m\| \leq \varepsilon$ for all $n, m > N$) converges. In Example (2.1.5; 4), any continuous function is a limit of a Cauchy sequence of polynomials. Thus there are Cauchy sequences that do not converge in this space. In order to exclude such difficulties with limits, we make

Definition (2.1.10)

A normed space is **complete** iff every Cauchy sequence converges. A complete, normed, linear space (resp. pre-Hilbert space) is a **Banach** (resp. **Hilbert**) **space**.

Examples (2.1.11)

Of Examples (2.1.5), only 1, 2, 3, 5 with $r = 0$, and 6 are complete.

Remarks (2.1.12)

1. It is crucial that the limit exists as an element of the space in question. One can always complete spaces by appending all the limiting elements, but this can occasionally force one to deal with queer objects. For instance,

if the polynomials (2.1.5; 4) are completed in the norm of (2.1.5; 6), then the resulting space $L^p(K, \mu)$ has elements that are not functions, but equivalence classes of functions differing on null sets.

2. One does not naturally have a good intuition about the concept of completeness, since finite-dimensional spaces are automatically complete. It should be distinguished from the notion of closure: Like every topological space, even an incomplete space is closed. It merely fails to be closed as a subspace of its completion, which is then its closure; in other words, it is dense in its completion.
3. Since convergent infinite sums are now defined and their limits exist, it is possible to introduce smaller bases than the Hamel basis. A set of vectors e_γ, $\gamma \in \mathfrak{I}$ is said to be **total** provided that the set of its finite linear combinations is dense in $\mathfrak{E}$. If $\mathfrak{I}$ is countable, then $\mathfrak{E}$ is **separable** (as a topological space).
4. By the axiom of choice, the e_γ can even be chosen orthonormal in a Hilbert space. If this has been done and $v = \sum_{\gamma \in \mathfrak{I}} c_\gamma e_\gamma$, $c_\gamma = \langle e_\gamma | v \rangle$, then $\|v\|^2 = \sum_{\gamma \in \mathfrak{I}} |c_\gamma|^2$, and the Hilbert space can be considered as $L^2(\mathfrak{I}, \mu)$, where μ assigns every element of $\mathfrak{I}$ the measure 1. If $\mathfrak{I}$ is countable, then the Hilbert space is isomorphic to an l^2 space. If $\mathfrak{I}$ is uncountable, then the countable sets and their complements constitute the measurable sets, and the resulting Hilbert space is not separable.
5. Every vector of a Hilbert space can be written in an orthogonal basis as a convergent infinite sum, $v = \sum_\gamma e_\gamma \langle e_\gamma | v \rangle$, and accordingly the sum (2.1.9; 2) of Hilbert spaces can easily be extended to infinite sums (though more care must be taken with the construction of infinite tensor products—see volume IV). However, if one approximates a vector v with an arbitrary total set $\{e_j\}$, say $v_n = \sum_{j=1}^{n} c_j e_j$, $\|v - v_n\| \leq 1/n$, then it may be necessary to keep changing some of the c's substantially as $n \to \infty$, and the expansion $v = \sum_{j=1}^{\infty} c_j e_j$ may not exist. For instance, in l^2 the vectors

$$e_n = \Big(1, \frac{1}{2^2}, \ldots, \underbrace{\frac{1}{n^2}}_{n\text{-th position}}, 0, 0, \ldots\Big)$$

are total. If we expand $v = \lim_{n \to \infty} v_n \equiv (1, \frac{1}{2}, \ldots, 1/n, 0, 0, \ldots)$ then $v_n = -e_1 - e_2 - \cdots - e_{n-1} + n e_n$. Thus v can be approximated arbitrarily well by the e's, while the formal limit $v = -e_1 - e_2 - \cdots + \infty e_\infty$ does not make sense. In a general Banach space, where there is not an orthogonal basis at one's disposal, it is therefore unclear whether there exists a basis in which every vector can be written as a convergent sum. If there is a set of vectors in terms of which any vector can be written as a convergent sum, we shall call it **complete**. These distinctions may be somewhat unfamiliar, since for n vectors of $\mathbb{C}^n$, linearly independent $\Leftrightarrow$ total $\Leftrightarrow$ complete. In an infinite-dimensional space the implications go only one way; an infinite set of linearly independent vectors need not be total, and a total set need not be complete. For instance, $\{e^{inx}, n \in \mathbb{Z}\}$

is total and complete in $L^2((0, 2\pi), dx)$, but total and incomplete in the Banach space of continuous, periodic functions on $(0, 2\pi)$ with the sup-norm.

Definition (2.1.13)

A **linear functional** w on a vector space $\mathbb{E}$ is a mapping $\mathbb{E} \to \mathbb{C}: v \to (w|v)$ such that $(w|v_1 + v_2) = (w|v_1) + (w|v_2)$ and $(w|\alpha v) = \alpha(w|v)$, for $a \in \mathbb{C}$.

Examples (2.1.14)

In Examples (2.1.2) the linear functionals are

1. Scalar products with a vector.
2. Traces of the product of a matrix with some other matrix.

Linear functionals on the other examples include integrals of the functions by distributions and many other things. (See (2.2.19; 3).)

Remarks (2.1.15)

1. The space of linear functionals on a vector space is called its **algebraic dual space**. It has a natural linear structure, $(w_1 + w_2|v) = (w_1|v) + (w_2|v)$ and $(\alpha w|v) = \alpha^*(w|v)$. The dual space of $\mathbb{R}^n$ can be identified with $\mathbb{R}^n$. However, infinite-dimensional spaces are not algebraically self-dual, and for that reason we introduce the abstract definition (2.1.13).
2. The concept defined in (2.1.13) is somewhat too general for our purposes, since the mapping $v \to (w|v)$ is automatically continuous only for finite-dimensional spaces (Examples 1 and 2). For example, consider $l^1 \equiv \{v = (v_1, v_2, v_3, \ldots): \|v\| \equiv \sum_i |v_i| < \infty\}$ with Hamel basis

$$\{e_i = (0, 0, \ldots, \overbrace{1}^{i\text{-th position}}, 0, \ldots, 0)\},$$

augmented with some other vectors $\bar{e}_\gamma$ to take care of vectors with infinitely many components. Every vector can be written as a finite sum, $v = \sum_{i,\,\text{finite}} c_i e_i + \sum_{\gamma,\,\text{finite}} \bar{c}_\gamma \bar{e}_\gamma$. If we define $(w|v) = \sum_{i=1}^{\infty} i c_i$, which converges because only finitely many c_i are nonzero, then w is obviously a linear functional, but it is not continuous. In fact, it is not even **closed**, i.e., there exists a sequence $v_n \to 0$ such that $(w|v_n) \to 1 \neq (w|0) = 0$; e.g., take

$$v_n = (0, 0, \ldots, \overbrace{1/n}^{n\text{-th position}}, 0, \ldots).$$

This phenomenon can be understood as meaning that the steepness of w in the i-th direction is i; as i gets larger, it corresponds to a more nearly vertical plane. The formal reason for it is again that infinite-dimensional

spaces can have nonclosed linear subspaces. The **kernel** of w, defined as $\{v : (w|v) = 0\}$, is a subspace, and if w were continuous, it would be closed, since it is the inverse image of the point zero. In this case, however, it contains all finite linear combinations of the vectors

$$v_{nm} = (0, \ldots, 0, \overbrace{1}^{n\text{-th position}}, 0, \ldots, \overbrace{-n/m}^{m\text{-th position}}, 0, \ldots),$$

and it is thus dense in l^1. It is desirable to exclude such pathologies, which is the motivation for

Definition (2.1.16)

The linear space $\mathbb{E}'$ of the *continuous* linear functionals of a Banach space $\mathbb{E}$ is called its **dual space**.

Examples (2.1.17)

As mentioned above, $\mathbb{C}^n$ and the space of the $n \times n$ matrices are their own duals. More generally, all Hilbert spaces are self-dual; by a theorem of Riesz and Fréchet [3] any continuous linear functional on $\mathscr{H}$ can be written as a scalar product $v \to \langle w|v\rangle$ with a unique $w = \sum e_\gamma (w|e_\gamma) \in \mathscr{H}$. Generalizing further, $(L^p(M, \mu))' = L^q(M, \mu)$ for $1/p + 1/q = 1$, $1 < p < \infty$; and $(L^1)' = L^\infty$, though, for infinite-dimensional spaces $(L^\infty)'$ is actually larger than L^1. The dual space of the continuous functions on a compact set, with the norm $\sup_{z \in K} |f(z)|$ consists of the (not necessarily positive) measures on K.

Remark (2.1.18)

These statements depend critically on the completeness of the spaces. If we consider, for instance, the pre-Hilbert space $\mathbb{E}$ of the vectors of l^2 having finitely many nonzero components, then $(v_i) \to \sum_{i=1}^{\infty} v_i/i$ is a continuous linear functional that can not be written as $\langle w|v\rangle$ for $w \in \mathbb{E}$, since

$$(1, \tfrac{1}{2}, \tfrac{1}{3}, \ldots) \notin \mathbb{E}.$$

The dual space $\mathbb{E}'$ is also a linear space, so the next task is to topologize it.

Definition (2.1.19)

The neighborhood bases of vectors $w \in \mathbb{E}'$ will be defined alternatively by

$$U_{v,\varepsilon}(w) = \{w' \in \mathbb{E}' : |(w - w'|v)| < \varepsilon\}, \qquad v \in \mathbb{E}, \varepsilon \in \mathbb{R}^+,$$

and by

$$U_\varepsilon(w) = \bigcap_{\|v\| = 1} U_{v,\varepsilon}(w) \tag{2.1.20}$$

These produce respectively the weak * and the strong topology; the latter is equivalent to the topology given by the norm

$$\|w\| = \sup_{\|v\|=1} |(w|v)|, \tag{2.1.21}$$

which makes $\mathbb{E}'$ a Banach space (Problem 4). Its dual space is denoted $\mathbb{E}''$, and $\mathbb{E}'' \supset \mathbb{E}$. If $\mathbb{E}'' = \mathbb{E}$ (identifying elements of $\mathbb{E}''$ with those of $\mathbb{E}$ under the natural injection), then $\mathbb{E}$ is said to be **reflexive**.

Examples (2.1.22)

Spaces with $\mathbb{E}' = \mathbb{E}$, such as Hilbert spaces, are clearly reflexive. As shown in Example (2.1.17), L^p is reflexive if $1 < p < \infty$, but not if $p = 1$ or ∞, since $\mathbb{E}$ can not be reflexive unless $\mathbb{E}'$ is.

Remarks (2.1.23)

1. It is also possible to topologize $\mathbb{E}$ weakly, by taking

$$U_{w,\varepsilon}(v) = \{v' \in \mathbb{E}: |(w|v - v')| < \varepsilon, w \in \mathbb{E}', \varepsilon \in \mathbb{R}^+\}.$$

   It is a corollary of the Hahn–Banach theorem that this is a Hausdorff topology. It is compatible with linearity in the sense that sums of vectors and multiplication by scalars are continuous mappings.
2. As its name suggests, the weak topology is weaker than the strong topology; in the weak topology the mapping $w \to \|w\|$ is not continuous, but only lower semicontinuous, as the supremum of continuous mappings. The weakening of the topology produces additional compact sets: in an infinite-dimensional Banach space the unit ball $\{v: \|v\| \leq 1\}$ fails to be norm-compact, but it is weak-* compact with respect to the space of which it is the dual (if this predual exists). Hence, if the Banach space is reflective, its unit ball is weak-* compact (cf. Problem 7).
3. The weak topologies do not have countable neighborhood bases, and they can not be specified in terms of sequences; they require instead nets or filters. This means that the concepts of completeness and sequential completeness, and compactness and sequential compactness, are not identical. Hilbert spaces are weakly sequentially complete, but not weakly complete. Another inconvenience is that not every point of accumulation is attainable as the limit of a convergent sequence (Problem 8). Fortunately, the **bounded sets**, i.e., $\{v: \|v\| \leq M\}$ in a Banach space with a separable dual space are a metrizable space when weakly topologized. For metric spaces the above notions coincide, and if only bounded sets are considered, these complications can be ignored.

Linear functionals are a special case of linear operators:

Definition (2.1.24)

We let $\mathscr{L}(\mathbb{E}, \mathbb{F})$ denote the **space of continuous linear mappings** of the Banach space $\mathbb{E}$ into the Banach space $\mathbb{F}$. If $\mathbb{E} = \mathbb{F}$, define $\mathscr{B}(\mathbb{E}) \equiv \mathscr{L}(\mathbb{E}, \mathbb{E})$. The elements $a \in \mathscr{L}(E, F)$ are also called **operators**.

Examples (2.1.25)

1. $\mathscr{L}(\mathbb{E}, \mathbb{C}) = \mathbb{E}'$.
2. $\mathscr{L}(\mathbb{C}^n, \mathbb{C}^m)$ consists of the $n \times m$ matrices.

Remarks (2.1.26)

1. $\mathscr{L}(\mathbb{E}, \mathbb{F})$ is a vector space, as $(\sum \alpha_i a_i)x \equiv \sum \alpha_i a_i x$ for all $\alpha_i \in \mathbb{C}$ and $a_i \in \mathscr{L}(\mathbb{E}, \mathbb{F})$.
2. A linear mapping a is **bounded** iff it sends bounded sets to bounded sets, and thus $\|a\| \equiv \sup_{\|x\|=1} \|ax\|_{\mathbb{F}} < \infty$. For linear mappings the properties
   (i) continuous,
   (ii) continuous at the origin,
   (iii) bounded
   are all equivalent (Problem 11).
3. The transpose of a real, finite-dimensional matrix has an infinite-dimensional generalization: $a \in \mathscr{L}(\mathbb{E}, \mathbb{F})$ induces a mapping $a^*: \mathbb{F}' \to \mathbb{E}'$, known as the **adjoint operator**, since for $y' \in \mathbb{F}'$ the mapping $\mathbb{E} \to \mathbb{C}$ by $x \to (y'|ax)$ is continuous and linear, and consequently it guarantees the existence of exactly one $x' \in \mathbb{E}'$ such that $(y'|ax) = (x'|x)$. Now define $x' \equiv a^* y'$. It is trivial to verify that the operator a^* is linear, and it is continuous in the norm topology (Problem 5).

There are several ways to topologize $\mathscr{L}(\mathbb{E}, \mathbb{F})$.

Definition (2.1.27)

The neighborhood bases of elements $a \in \mathscr{L}(\mathbb{E}, \mathbb{F})$ can be taken alternatively as

$$U_{y', x, \varepsilon}(a) = \{a' : |(y'|(a - a')x)| < \varepsilon\}$$

or

$$U_{x, \varepsilon}(a) = \{a' : \|(a - a')x\|_{\mathbb{F}} < \varepsilon\} = \bigcap_{\|y'\|=1} U_{y', x, \varepsilon}(a)$$

or

$$U_{\varepsilon}(a) = \bigcap_{\|x\|=1} U_{x, \varepsilon}(a).$$

The topologies are respectively called **weak**, **strong**, and **uniform**, and the associated kinds of convergence will be denoted by $\rightharpoonup$, $\to$, and $\Rightarrow$ (elsewhere often by *w*-lim, *s*-lim, and lim).

Remarks (2.1.28)

1. The uniform topology corresponds to the norm $\|a\| = \sup_{\|x\|=1} \|ax\|_{\mathbb{F}}$, which makes $\mathscr{L}(\mathbb{E}, \mathbb{F})$ a Banach space (Problem 4).
2. Even though $\mathbb{E}$ and $\mathbb{F}$ are metrizable, the strong and weak topologies do not have countable neighborhood bases (cf. Problem 9), and only their restrictions to norm-bounded sets are metrizable. They are compatible with linearity, but not with the algebraic structure; multiplication is not necessarily a continuous mapping $\mathscr{L} \times \mathscr{L} \to \mathscr{L}$. However, it is sequentially continuous in the topologies $\mathscr{B}(\mathbb{E})$ (weak) $\times$ $\mathscr{B}(\mathbb{E})$ (strong) $\to$ $\mathscr{B}(\mathbb{E})$ (weak) and $\mathscr{B}(\mathbb{E})$ (strong) $\times$ $\mathscr{B}(\mathbb{E})$ (strong) $\to$ $\mathscr{B}(\mathbb{E})$ (strong). Of course, multiplication in one factor alone is continuous in all topologies.
3. For reflexive Banach spaces $\mathbb{E}$ and $\mathbb{F}$ the adjoint operation (2.1.26; 3) $\mathscr{L}(\mathbb{E}, \mathbb{F}) \to \mathscr{L}(\mathbb{F}', \mathbb{E}')$: $a \to a^*$ is a continuous mapping in the norm topology because $\|a\| = \|a^*\|$, and it is obviously continuous in the weak topology; yet it is not continuous in the strong topology. We shall later become acquainted with examples for which $\Omega_n \to \Omega$ but only $\Omega_n^* \rightharpoonup \Omega^*$.
4. The origin of many of the technical complications of quantum mechanics is that the norm topology of operators is too restrictive; one is often interested in a limiting operator of a sequence or family of operators that is not convergent in the norm topology. While weaker limits exist more frequently, the algebraic operations are not always continuous in the weaker topologies, so great care must be taken in passing to a limit.
5. If $x_n \in$ a Hilbert space $\mathscr{H}$ converges weakly to $x \in \mathscr{H}$ and $\lim_{n\to\infty} \|x_n\| = \|x\|$, then the sequence is also strongly convergent: $\langle x_n - x | x_n - x\rangle = \|x_n\|^2 + \|x\|^2 - 2\,\mathrm{Re}\langle x_n | x\rangle \to 0$. Hence the strong and weak topologies are equivalent for unitary operators. If unitary operators converge weakly but not strongly, the limit will not be unitary.

Problems (2.1.29)

1. Show that the space l^∞ is not separable. (Hint: There exists an uncountable set of elements v_i, $i \in \mathbb{I}$, such that $\|v_i\| = 1$ and $\|v_i - v_j\| \geq 1$ whenever $i \neq j$.)

2. Show that the usual operator norm for operators on a Hilbert space satisfies the triangle inequality.

3. Prove the triangle inequality for the spaces L^p, $p \geq 1$. (Hint: the inequality $xy \leq x^p/p + y^q\,q$ for $x, y \geq 0$ and $1/p + 1/q = 1$ implies **Hölders inequality**, $|\int fg\,d\mu| \leq \int |fg|d\mu \leq |f|_p |g|_q$, where $|f|_p \equiv (\int |f|^p\,d\mu)^{1/p}$. Next show that $|f|_p = \sup_{q\,|g|_q=1} \int |fg|d\mu$ and conclude that $|f+g|_p \leq |f|_p + |g|_p$, which is known as **Minkowski's inequality**.

4. Let $\mathbb{E}$ and $\mathbb{F}$ be two Banach spaces. Show that the space of continuous linear mappings $\mathbb{E} \to \mathbb{F}$ (with the uniform topology) is also a Banach space. Moreover, show that if $\mathbb{F}$ is a normed space but not complete, then $\mathscr{L}(\mathbb{E}, \mathbb{F})$ is likewise not complete.

5. Let $a: \mathbb{E} \to \mathbb{F}$ be a continuous linear mapping of two Hilbert spaces. Show that $a^*: \mathbb{F} \to \mathbb{E}$ is also continuous.

6. Prove that on a Hilbert space $\mathbb{E}$ $\|ax\| = \|a^*x\| = \|x\|$ for all $x \in \mathbb{E}$ iff $aa^* = a^*a = \mathbf{1}$.

7. Show that the unit ball in a separable Hilbert space $\mathscr{H}$ is weakly sequentially compact. Conclude that the Hilbert cube $\subset l^2$: $\{v = (v_n): |v_n| \leq 1/n\}$ is even strongly ($\equiv$ norm) compact.

8. Show that an infinite-dimensional Hilbert space is not metrizable in the weak topology. (Hint: Consider the vectors $x_n = (0, 0, \ldots, \sqrt{n}, 0, \ldots)$ in l^2. This set has a point of accumulation at 0, but it contains no convergent subsequences, which is impossible in a metric topological space.)

9. Show that in the weak topology, compactness does not imply sequential compactness (except when the Hilbert space is separable).

10. Prove the Cauchy-Schwarz inequality $|\langle v_1 | v_2 \rangle| \leq \|v_1\| \, \|v_2\|$, and show that $|\langle v_1 | v_2 \rangle| = \|v_1\| \, \|v_2\|$ iff $v_1 = zv_2$ for some $z \in \mathbb{C}$ (and $v_i \neq 0$).

11. Show the equivalence of the properties of (2.1.26; 2).

Solutions (2.1.30)

1. Let v_i be the vectors of the form $(c_1, c_2, \ldots, c_n, \ldots)$ with $c_n = 1$ or 0. This set has the power of the continuum, and $\|v_i\| = \sup|c_n| = 1$ (unless $v_i \equiv 0$) and $\|v_i - v_j\| \geq 1$, unless all the coefficients of v_i and v_j are equal. If there existed a countable dense set $A \subset l^\infty$, then for all v_i there would be an $a_i \in A$ with $\|v_i - a_i\| \leq \frac{1}{3}$. Since $\|v_i - v_j\| \geq 1$, the mapping $v_i \to a_i$ would be one-to-one, and the set of v_i would have only the cardinality of a subset of A.

2. $\|a + b\| = \sup_{\|x\| = 1} \|ax + bx\| \leq \sup_{\|x\| = 1} \|ax\| + \sup_{\|x\| = 1} \|bx\| = \|a\| + \|b\|$.

3. The inequality is trivial for $p = 1$, so assume $p > 1$. For $t \geq 0$, $t \leq t^p/p + 1/q$ (proof: find the minimum of the function $\varphi(t) = t^p/p - t$), and if $t = x/y^{q/p}$ this reads $xy \leq x^p/p + y^q/q$. Let f and g be two functions such that

$$\int |f|^p \, d\mu = \int |g|^q \, d\mu = 1.$$

Since

$$\left| \int fg \, d\mu \right| \leq \int |fg| \, d\mu \quad \text{and} \quad \int |fg| \, d\mu \leq \frac{1}{p} \int |f|^p \, d\mu + \frac{1}{q} \int |g|^q \, d\mu = 1,$$

Hölder's inequality is proven in this special case. The general case follows by considering $f/\|f\|_p$ and $g/\|g\|_q$ in place of f and g. Furthermore,

$$\|f\|_p = \int |fg| \, d\mu \quad \text{with} \quad g = \frac{|f|^{p-1}}{\|f\|_p^{p-q}},$$

since

$$\int |fg|\,d\mu = \frac{\|f\|_p^p}{\|f\|_p^{p/q}} = \|f\|_p,\ \|g\|_q^q = \|f\|_p^{-p}\|f\|_p^p = 1.$$

Hence

$$\|f+g\|_p = \sup_{\|h\|_q=1} \int |(f+g)h|\,d\mu \le \sup_h \int |fh|\,d\mu + \sup_h \int |gh|\,d\mu = \|f\|_p + \|g\|_p.$$

4. The vector-space properties are trivial. As for the norm, let $a: \mathbf{E} \to \mathbf{F}$,

$$\|a\| = \sup_{x\in\mathbf{E}} \frac{\|ax\|}{\|x\|}.$$

Then $\|\lambda a\| = |\lambda|\,\|a\|$ and $\|a+b\| \le \|a\| + \|b\|$ as in Problem 2. Finally, $\|a\| = 0 \Rightarrow \|ax\| = 0$ for all $x \in \mathbf{E} \Rightarrow ax = 0 \Rightarrow a = 0$. As for completeness, let a_n be a Cauchy sequence; then $a_n x$ is also a Cauchy sequence in $\mathbf{F}$ for all $x \in \mathbf{E}$, and thus there exists a limit $\lim a_n x = ax \in \mathbf{E}$. This mapping is linear and bounded (since $\|a_n\| \le C < \infty$ for all n, $\|a_n x\| \le C\|x\|$, which implies $\|ax\| \le C\|x\|$), and $\|a - a_n\| = \sup\|ax - a_n x\|/\|x\| \to 0$. The proof depends in an essential way on the completeness of $\mathbf{F}$. Remark: The Hahn–Banach theorem prevents $\mathscr{L}(\mathbf{E}, \mathbf{F})$ from being the trivial space $\{0\}$.

5. $$\|a\| = \sup_{\substack{\|x\|=1\\ x\in\mathbf{E}}} \|ax\| = \sup_{\substack{\|x\|=1,\,x\in\mathbf{E}\\ \|y\|=1,\,y\in\mathbf{F}}} |\langle y|ax\rangle| = \sup|\langle a^*y|x\rangle| = \|a^*\|.$$

(This is also true when $\mathbf{E}$ and $\mathbf{F}$ are only assumed to be Banach spaces.)

6. $aa^* = a^*a = 1 \Rightarrow \langle x|aa^*x\rangle = \|a^*x\|^2 = \langle x|a^*ax\rangle = \|ax\|^2 = \|x\|^2.$

$$\|ax\| = \|x\| \Rightarrow \langle x|a^*ax\rangle = \langle x|x\rangle \Rightarrow a^*a = 1,$$

and likewise

$$\|a^*x\| = \|x\| \Rightarrow aa^* = 1.$$

$$\begin{aligned}(4\langle y|ax\rangle = &\langle x+y|a(x+y)\rangle - \langle x-y|a(x-y)\rangle\\ &+ i\langle x+iy|a(x+iy)\rangle - i\langle x-iy|a(x-iy)\rangle;\end{aligned}$$

it therefore follows from $\langle x|ax\rangle = 0$ for all x that $\langle y|ax\rangle = 0$ for all x and y, which implies that $a = 0$.)

7. Let $\{x_n\}$ be a total orthonormal set. Since the matrix elements $(x_n|a_k x_m)$ of a sequence $a_k \in \mathscr{B}(\mathscr{H})$ are bounded in absolute value by $\|x_n\|\,\|x_m\|\sup_k \|a_k\|$, for every n and m there is a point of accumulation a_{nm}. Let us define $a \in \mathscr{B}(\mathscr{H})$ by $ax_m = \sum_n a_{nm}x_n$ and note that $a_k \rightharpoonup a$, i.e., $(y|a_k x) \to (y|ax)$ for all $y, x \in \mathscr{H}$; this is because for all $\varepsilon > 0$, x and y can be written as $\sum_{\text{finite}} c_n x_n + \eta$ with $\|\eta\| < \varepsilon$, and the convergence of the finite sum follows by definition, so the convergence of general matrix elements is shown to within arbitrary accuracy, since $\sup_n \|a_n\| < \infty$. We next show that the strong and weak topologies are equivalent on the Hilbert cube: Let $v^{(n)} \rightharpoonup v$, and for any given ε choose r and N such that $\sum_{j=r+1}^{\infty} 1/j^2 < \varepsilon$ and if $n > N$ then

$$\sum_{j=1}^{r} |v_j^{(n)} - v_j|^2 < \varepsilon.$$

$\sum_{j=1}^{\infty} |v_j^{(n)} - v_j|^2 < 5\varepsilon$, and therefore $v^{(n)} \to v$. The Hilbert cube is thus strongly

sequentially compact and, since the strong topology on a Hilbert space is a metric topology, also strongly compact.

8. A weak neighborhood of 0 has the form $U = \{x: |\langle v^{(1)}|x\rangle| + |\langle v^{(2)}|x\rangle| + \cdots + |\langle v^{(l)}|x\rangle| \leq \varepsilon\}$. A neighborhood U necessarily contains some x_n, as otherwise $|\langle v^{(1)}|x_n\rangle| + \cdots + |\langle v^{(l)}|x_n\rangle| > \varepsilon$ for all n, which would mean that $|v_n^{(1)}| + \cdots + |v_n^{(l)}| > \varepsilon/\sqrt{n}$ and $\sum_{n=1}^{\infty} |v_n^{(1)}|^2 + \cdots + |v_n^{(l)}|^2 = \infty$, while, on the other hand, this sum $\leq l(\sum_n |v_n^{(1)}|^2 + \cdots + \sum_n |v_n^{(l)}|^2) < \infty$. However, it is not true that there is an N such that $x_n \in U$ for all $n > N$. Despite the foregoing, there can not be a weakly convergent subsequence of x_{n_k} of x_n; for consider the vector v whose n_{10^r}-th component is r and whose other components are all 0. Then $\langle v|x_{n_k}\rangle = \sqrt{n_k}(1/r)$ if $k = 10^r$, and otherwise 0; but $n_k \geq k = 10^r$.

9. General theorems guarantee that the unit ball is always compact in the weak operator topology. Let us now investigate the nonseparable Hilbert space $\mathscr{H} = L^2([0, 1], \mu)$, where μ is the measure assigning every point the measure 1. All of the multiplication operators multiplying any function in $\mathscr{H}$ by a function φ_n, a "sawtooth" function going linearly from 0 to 1 in each interval $[k/10^n, (k+1)/10^n]$, $k \in \mathbb{Z} \cap [0, 10^n)$, have norm 1. But, even so, for each subsequence φ_{n_m} there exists a point x at which $\varphi_{n_m}(x)$ diverges, and consequently the sequence of operators is not weakly sequentially compact.

10. Let $v_2' = v_2 \exp(-i \arg\langle v_1|v_2\rangle)$. Then $|\langle v_1|v_2\rangle| = \langle v_1|v_2'\rangle$, and it follows from

$$\|\|v_1\|v_2' - \|v_2'\|v_1\|^2 = 2\|v_1\|^2\|v_2'\|^2 - 2\|v_1\|\,\|v_2'\|\langle v_1|v_2'\rangle \geq 0$$

that $\langle v_1|v_2'\rangle \leq \|v_1\|\,\|v_2'\| = \|v_1\|\,\|v_2\|$. There can be equality only if $\|v_1\|v_2' - \|v_2'\|v_1 = 0$, i.e., $v_1 = zv_2$ with $z = (\|v_1\|/\|v_2\|)\exp(-i \arg\langle v_1|v_2\rangle)$.

11. (ii) $\Rightarrow$ (iii): Property (ii) implies that for all δ there exists ε such that $\|x\| < \varepsilon \Rightarrow \|ax\| < \delta$, which implies $\|a\| = \sup_{\|x\|=r} \|ax\|/\|x\| < \delta/\varepsilon$, which $\Rightarrow$ (iii).
(iii) $\Rightarrow$ (i): For all δ $\exists$ $\varepsilon = \delta/\|a\|$ such that for all $x' \in \mathbb{E}$,

$$\|x - x'\| < \varepsilon \Rightarrow \|ax - ax'\| \leq \|a\| \cdot \|x - x'\| \leq \delta.$$

(i) $\Rightarrow$ (ii) is trivial.

2.2 Algebras

C^* and W^* algebras are generalizations of algebras of matrices and functions. Their axioms are the basic algebraic and topological properties of these familiar algebras.

Definition (2.2.1)

An **algebra** $\mathscr{A}$ is a vector space on which there is a mapping $\mathscr{A} \times \mathscr{A} \to \mathscr{A}$, called **multiplication**, having the properties

$$a(b_1 + b_2) = ab_1 + ab_2, \qquad a(bc) = (ab)c,$$
$$a(\alpha b) = \alpha ab, \qquad a, b, b_i \in \mathscr{A}, \qquad \alpha \in \mathbb{C}.$$

Additionally, we assume the existence of a **unit**, or **identity**, element 1 such that $a\,1 = 1\,a = a$ for all $a \in \mathscr{A}$; if this element should ever be lacking, we shall refer to $\mathscr{A}$ as an **algebra without a unit**. If $ab = ba$ for all a and $b \in \mathscr{A}$, then $\mathscr{A}$ is **Abelian**.

Examples (2.2.2)

All of Examples (2.1.2) are algebras when multiplication is defined componentwise for vectors, pointwise for functions, and in the usual way for matrices. These multiplication rules make all of them Abelian except for the matrices. The spaces L^p, $p < \infty$, are not generally algebras; for examples, $x^{-1/2} \in L^1([0, 1], dx)$ but $x^{-1} \notin L^1([0, 1], dx)$. The spaces l^p are algebras, but they have no unit if $p < \infty$. The space $l^0 \equiv \{(v_1, v_2, \ldots) \in l^\infty : \lim_i |v_i| = 0\}$ is a subalgebra of l^∞ without a unit.

Remark (2.2.3)

Every subspace of a vector space is the kernel of a homomorphism π, i.e., it is $\pi^{-1}(0)$. The kernels of homomorphisms of an algebra are only its **two-sided ideals**, i.e., subalgebras $\mathscr{B} \subset \mathscr{A}$ for which $a\mathscr{B} \subset \mathscr{B}$ and $\mathscr{B}a \subset \mathscr{B}$ for all, $a \in \mathscr{A}$. The quotient space with respect to a two-sided ideal is another algebra, known as the **quotient algebra**.

Since we work with the field of the complex numbers, there is another operation to axiomatize, complex conjugation:

Definition (2.2.4)

A * **algebra** is an algebra on which there is a mapping $^* : \mathscr{A} \to \mathscr{A}$, called **conjugation**, having the properties $(ab)^* = b^*a^*$; $(a + b)^* = a^* + b^*$; $(\alpha a)^* = \alpha^* a^*$ for $\alpha \in \mathbb{C}$; and $a^{**} = a$. The element a^* is known as the **adjoint** of a.

Examples (2.2.5)

If * is complex conjugation or, in the case of matrices, Hermitian conjugation, then all of Examples (2.1.2) except for the analytic functions are * algebras.

Remark (2.2.6)

It is at this point that complex numbers first become important. Anyone having philosophical objections to the occurrence of complex numbers in what ultimately pertains only to real physical measurements can just as well represent i, the square root of -1, as the real matrix

$$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

or else postulate the existence of an abstract element $\mathbf{I} \in \mathscr{A}$ with the properties $\mathbf{I}^2 = -\mathbf{1}$, $\mathbf{I}^* = -\mathbf{I}$, and $\mathbf{I}a = a\mathbf{I}$ for all a.

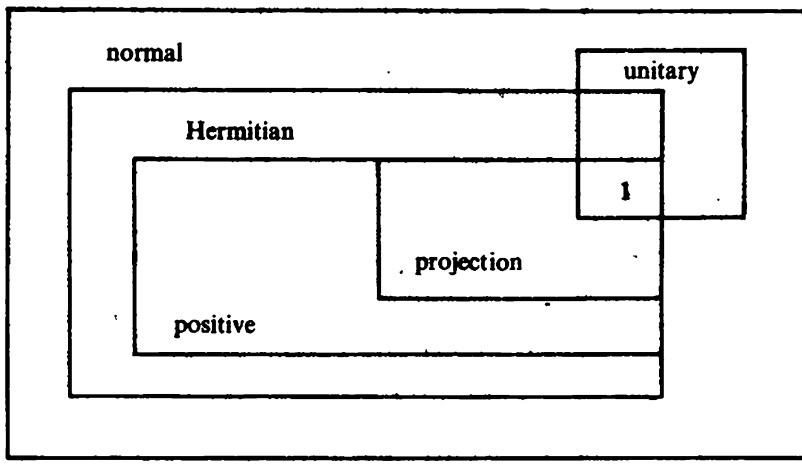
Since matrices are the prototype of a * algebra, its elements are often referred to as operators, and the terminology follows that of matrices:

Definition (2.2.7)

a is **normal** iff $aa^* = a^*a$
a is **Hermitian** iff $a = a^*$
a is **unitary** iff $aa^* = a^*a = \mathbf{1}$
a is a **projection**† iff $a = a^* = a^2$
a is **positive** iff $a = bb^*$ for some b
a is the **inverse** of b iff $ab = ba = \mathbf{1}$.

Remarks (2.2.8)

1. The relationships among these sets of operators are depicted in the diagram below:



2. Although in a finite-dimensional space $ab = \mathbf{1}$ implies $ba = \mathbf{1}$, this is not true in general. A counterexample is given by the infinite matrix

$$a = \begin{vmatrix} 0 & 1 & 0 & 0 & 0 & \dots \\ 0 & 0 & 1 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 1 & 0 & \dots \\ & & & \dots & & \end{vmatrix} \quad \text{and} \quad b = a^*$$

Hence the property $ab = \mathbf{1}$ is not sufficient to make a the inverse of b. The Definitions (2.2.7) easily imply the

† In this book the word "projection" will be understood as meaning "orthogonal projection."

Propositions (2.2.9)

1. $(a^{-1})^{-1} = a$
2. $(ab)^{-1} = b^{-1}a^{-1}$
3. $(a^*)^{-1} = (a^{-1})^*$
4. *The unitary elements form a subgroup of the group of invertible elements.*

The next subject is the topology of the algebra, which must conform with the algebraic properties discussed above. This will allow us to generalize the analytic rules we are familiar with for matrices.

Definition (2.2.10)

A C^* **algebra** is at the same time a * algebra and a Banach space, the norm of which satisfies

(i) $\|ab\| \leq \|a\| \|b\|$
(ii) $\|a^*\| = \|a\|$
(iii) $\|aa^*\| = \|a\| \|a^*\|$
(iv) $\|\mathbf{1}\| = 1$.

Examples (2.2.11)

Recall Examples (2.1.5):

1. This is a C^* algebra only if $p = \infty$, because (iii) is violated for smaller p.
2. This is not a C^* algebra. For instance, if

$$a = \begin{pmatrix} 1 & i \\ 0 & 1 \end{pmatrix}, \qquad aa^* = \begin{pmatrix} 2 & i \\ -i & 1 \end{pmatrix}, \qquad aa^*aa^* = \begin{pmatrix} 5 & 3i \\ -3i & 2 \end{pmatrix},$$

   then $\|aa^*\|^2 = \operatorname{Tr} aa^*aa^* = 7 \neq \|a\|^2\|a^*\|^2 = (\operatorname{Tr} aa^*)^2 = 9$.
3. This is a C^* algebra, as in fact is the more general $\mathscr{B}(\mathscr{H})$ (2.1.24), $\mathscr{H}$ a Hilbert space, and with the norm of (2.1.28; 1), because

$$\|a^*a\| = \sup_{\|x\| = 1 = \|y\|} |\langle y|a^*ax\rangle| = \sup_{\|x\| = 1} \langle x|a^*ax\rangle$$
$$= \sup_{\|x\| = 1} \|ax\|^2 = \|a\|^2,$$

   along with (i) and (ii), implies (iii).
4. The space of this example is not complete.
5. In this example the space is complete only if $r = 0$, in which case it is a C^* algebra.
6. L^p is not an algebra for $p < \infty$. If $p = \infty$, it is a C^* algebra.

Remarks (2.2.12)

1. Properties (i) and (ii) guarantee that multiplication and conjugation are continuous (Problem 3). Property (iii) roots the topology so deeply in the algebraic structure that (algebraic) homomorphisms of C^* algebras are automatically continuous (Problem 2). Property (iv) is just a convenient normalization.
2. It may happen that Property (iii) is satisfied by one norm and violated by another, although both norms produce the same topology. This occurs in Examples (2.2.11; 2) and (2.2.11; 3) as well as for the continuous functions on [0, 1] with the norms $\|f\| = \sup_{x\in[0,1]} |f(x)|$ and

$$\|f\|_e = \sup_{x\in[0,1]} e^{-x}|f(x)|,$$

which are related by $\|\cdot\| \geq \|\cdot\|_e \geq e^{-1}\|\cdot\|$. The norm $\|\cdot\|$ yields a C^* algebra, but $\|\cdot\|_e$ does not, since $\|(e^x - 1)\|_e^2 = (1 - 1/e)^2 \leq \|(e^x - 1)^2\|_e = e + 1/e - 2$. In such situations we shall always choose the norm that satisfies (2.2.10)
3. $\mathbb{C}\backslash\{0\}$ is an open set, and $\{z \in \mathbb{C}: |z| = 1\}$ and $\{z \in \mathbb{C}: \operatorname{Im} z = 0\}$ are closed. Because both conjugation (*) and multiplication are continuous, these statements have the generalizations that the set of invertible elements of a C^* algebra is open, and that the unitary and the Hermitian elements form closed sets (Problem 4). Similarly, the sets of normal, positive, and projection operators are closed, and hence norm-limits of these types of operators are of the same types.

Given an operator a, it is always possible to get an invertible operator by adding some multiple of the identity $\mathbf{1}$ to it.

Definition (2.2.13)

The **resolvent set** of $a \in \mathcal{A}$ is $\{z \in \mathbb{C}: (a - z)^{-1} \text{ exists}\}$, and its complement $\mathrm{Sp}(a)$ is known as the **spectrum**.

Examples (2.2.14)

The spectrum of a matrix consists of its eigenvalues, and the spectrum of an ordinary function is its range.

Remarks (2.2.15)

1. In (2.2.13) it is essential that $(a - z)^{-1}$ exist as an element of $\mathcal{A}$, and not in some other sense. Moreover, if $\mathcal{A}$ is a subalgebra of some other algebra $\mathcal{B}$, then one must specify whether $(a - z)^{-1}$ is to exist in $\mathcal{A}$ or $\mathcal{B}$. Fortunately,

if $\mathscr{A}$ is a C^* algebra, then the inverse of $a - z$ belongs to the C^* algebra generated by a (that is, the norm-closure of the polynomials in a and a^*), and so one need not specify which algebra the inverse belongs to.

2. If $|z| > \|a\|$, then $(z - a)^{-1}$ can be expanded as a convergent series $z^{-1} \sum_{n=0}^{\infty} (a/z)^n$, and therefore $\mathrm{Sp}(a) \subset \{z \in \mathbb{C} : |z| \leq \|a\|\}$. In particular, all elements such that $\|a - \mathbf{1}\| < 1$ are invertible. The mapping $\mathbb{C} \to \mathscr{A} : z \to (a - z)^{-1}$ is actually analytic on the resolvent set, which is always open, by Problem 7.
3. It is easy to show that $\mathrm{Sp}(a^*) = \mathrm{Sp}(a)^*$ and $\mathrm{Sp}(P(a)) = P(\mathrm{Sp}(a))$ for any polynomial P and $a \in \mathscr{A}$. This implies (Problem 5) that the spectra of the unitary, Hermitian, positive, and projection operators lie respectively on the unit circle, the real axis, the positive real axis, and the set $\{0, 1\}$. If the operator is normal, the fact that the spectrum belongs to one of these sets implies that the operator belongs to the appropriate class (2.2.7) (Problem 5).
4. As the term "spectrum" suggests, the spectral values of an element represent the values it can attain in a certain sense; we shall see in (2.2.31; 2) that the convex combinations of the spectral values are all the possible expectation values of the element (2.2.18).

Positivity is a useful property in analysis, and it provides an algebra with an additional associative structure:

Definition (2.2.16)

The algebra $\mathscr{A}$ has a **partial ordering** $a \geq b$ defined as meaning that $a - b$ is positive.

Remarks (2.2.17)

1. As remarked in (2.2.15; 3), positivity is synonymous with having a positive spectrum. According to (2.2.15; 4) the sum of two positive elements is positive, since expectation values are additive. Hence if $a \geq b$ and $b \geq c$, then $a \geq c$. If $a \geq 0$ and $-a \geq 0$, then $a = 0$, since 0 is the only Hermitian element a with $\mathrm{sp}(a) = \{0\}$. Thus $a \geq b$ and $b \geq a$ implies $a = b$. Since it is also true that $a \geq a$, the relationship $\geq$ is a partial ordering. Since positive operators are Hermitian, one might hope to extend the definition of $\geq$ to all Hermitian elements, but it fails to be a total ordering on this set: Consider

$$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

which do not stand in this ordering relationship to each other.

2. Although it is true that $\geq$ is compatible with the linear structure of $\mathcal{A}$ in the sense that $a_i \geq b_i \Rightarrow \sum_i a_i \geq \sum_i b_i$, difficulties arise with products because the product of two Hermitian elements is not generally Hermitian. But even if it is, there remains the inconvenience that inequalities can not be multiplied, $a \geq b \not\Rightarrow a^2 \geq b^2$ (Problem 10). Yet inverses of ordered positive operators have a definite ordering, $a \geq b > 0 \Rightarrow b^{-1} \geq a^{-1} > 0$, and as a consequence it is possible to show monotonicity of certain functions of operators with respect to the ordering $\geq$ (Problem 11). Finally, note that $a \geq b$ clearly implies $c^*ac \geq c^*bc$ for any c.
3. The partial ordering is compatible with the topological structure; it commutes with the taking of limits.
4. Positivity is preserved by homomorphisms $\pi: \mathcal{A} \to \mathcal{B}$ of C^* algebras: $\pi(a^*a) = \pi(a)^*\pi(a) \geq 0$, and therefore $a \geq b \Rightarrow \pi(a) \geq \pi(b)$. Linear mappings of C^* algebras do not generally preserve positivity.

Definition (2.2.18)

A linear functional f is **positive** iff $f(aa^*) \geq 0$ for all $a \in \mathcal{A}$. If, moreover, $f(\mathbf{1}) = 1$, then f is called a **state**, and $f(a)$ is the **expectation value** of a in the state f.

Examples (2.2.19)

1. Positive measures on function algebras are positive linear functionals. Probability measures are states.
2. The mapping $m \to \operatorname{Tr} \rho m$ on $n \times n$ matrices m is positive iff ρ is positive in the sense that all of its eigenvalues are positive. If in addition $\operatorname{Tr} \rho = 1$, then it is a state.
3. On the C^* subalgebra $\{v \in l^\infty : \lim_{i\to\infty} v_i \text{ exists}\}$ of l^∞, the functional $f(v) = \lim_{i\to\infty} v_i$ is a state.

Remarks (2.2.20)

1. Definition (2.2.18) does not require continuity, i.e., the statement that there exists $M \in \mathbb{R}^+$ such that $|f(a)| < M\|a\|$ for all $a \in \mathcal{A}$, because it follows automatically. It is even true that $|f(b^*ab)| \leq \|a\| f(b^*b)$ and, as a generalization of the Cauchy–Schwarz inequality,
$$|f(b^*a)|^2 \leq f(b^*b) f(a^*a)$$
(Problem 8). It is consequently always possible to normalize a positive linear functional to be a state, for which $\|f\| = \sup_{a\in\mathcal{A}} |f(a)|/\|a\| = 1$.
2. Convex combinations of states are states. States that can not be written as convex combinations of other states are called **extremal**, or **pure**. In Examples (2.2.19), integrals with delta functions and traces with one-dimensional projections are pure states. A theorem of Krein and Milman

[1, 12.15] says that our naive idea of convex, compact sets is valid for states; there must exist extremal points, and their convex combinations are dense in the space of states. Choquet's theorem allows any state to be written as an integral over pure states, though the measure used is unique only if the algebra is Abelian. For example, the state $m \to (1/n)\mathrm{Tr}\, m$ of $n \times n$ matrices can be written as $(1/n)\sum_{k=1}^{n} \langle e_k | m e_k \rangle$, where the e_k are any orthonormal system. The state $m \to \langle e_k | m e_k \rangle$ (no sum) is pure, so there are many ways to write $(1/n)\mathrm{Tr}$ as a convex combination of pure states. If the space of states is pictured as a ball, then the pure states will constitute its surface. For Abelian algebras this ball becomes instead a simplex, only the corners of which are extremal. The extremal points of infinite-dimensional simplices may form a connected, closed set, like the surface of a ball. For instance, consider the Abelian C^* algebra of continuous functions on a compact set. The states are probability measures, and the extremal states are Dirac δ functions. They form a weak-* connected, closed set (see (2.2.28)), though their convex combinations are weak-* dense in the set of states.

3. There exist pure states for which the inequality $|f(a)| \leq \|a\|$ of Remark 1 becomes an equality. This can be seen as follows: Given any $a \in \mathcal{A}$, one can construct a state for which $f(a^*a) = \|a\|^2$, by setting $f(\alpha + \beta a^*a) = \alpha + \beta\|a\|^2$ on the subspace spanned by 1 and a^*a. It is easy to convince oneself that this is a positive functional with $f(1) = 1$ and $f(a^*a) = \|a\|^2$. According to theorems of Hahn and Banach and of Krein, the functional can be extended to all of $\mathcal{A}$ (but not necessarily uniquely, of course). Now let Z_a be the convex set of states such that $f(a^*a) = \|a\|^2$. The extremal points of Z_a are pure, since if $f_e = \lambda f_1 + (1 - \lambda) f_2$, $0 < \lambda < 1$, then we would find $\|a\|^2 = \lambda f_1(a^*a) + (1 - \lambda) f_2(a^*a)$, which implies that $f_i(a^*a) = \|a\|^2$, and f_e would not be extremal.
4. Another blemish afflicting positive linear functionals is that the supremum of linear functionals over many elements may not be the same as the linear functional of the maximal element using the partial ordering $\geq$. For example, if

$$v^{(n)} = (\overbrace{1, 1, \ldots, 1}^{n\text{-th position}}, 0, 0, \ldots) \in l^\infty,$$

then with the state of Example (2.2.19; 3), $f(v^{(n)}) = 0$, but with $v \equiv \sup_n v^{(n)} = (1, 1, 1, \ldots)$, $f(v) = 1$. (Of course, $v^{(n)} \not\to v$.)

The states suffering these afflictions can be set aside by a

Definition (2.2.21)

An **ascending filter** F is a norm-bounded subset of $\mathcal{A}$ in which any two elements are both exceeded (in the sense of $\geq$) by some element. The **supremum** sup F is the smallest element of $\mathcal{A}$ with $a \leq \sup F$ for all $a \in F$. A state f is **normal** iff $\sup_{a \in F} f(a) = f(\sup F)$ for every ascending filter F.

If the supremum always exists in $\mathscr{A}$, and there are also sufficiently many normal states at hand, then the algebra has such nice properties that it merits a special name.

Definition (2.2.22)

A W^* **algebra** is a C^* algebra in which

(i) every ascending filter achieves its supremum in $\mathscr{A}$; and
(ii) for all nonzero elements $a \in \mathscr{A}$, there exists a normal state f with $f(a) \neq 0$.

Examples (2.2.23)

Matrices are W^* algebras, while the continuous functions on a compact set $\subset \mathbb{C}^n$ are not, because their supremum need not be continuous. The set of bounded, measurable functions $L^\infty(K, d^n x)$ is a W^* algebra. We saw earlier that it is a C^* algebra, and (i) is satisfied since monotonic, bounded sequences converge in L^∞. As for (ii), positive, normalized functions in $L^1 \subset (L^\infty)'$ provide the required normal states.

Remarks (2.2.24)

1. Although the W^* property is defined with reference only to the ordering structure of the algebra, it will have both algebraic and topological consequences.
2. Integration theory relies on classes of functions that allow the taking of suprema. The permutability with integration is a fundamental characteristic of measures, distinguishing them from such things as abstract averages. With W^* algebras much of measure theory can be generalized to the noncommutative case.
3. In atomic physics we shall primarily be concerned with the W^* algebra $\mathscr{B}(\mathscr{H})$, and the reader interested only in these problems need not worry much about the distinctions mentioned above. It is not until the fourth volume, *Quantum Mechanics of Large Systems*, that these notions will become important in the limit of infinite systems.

Because $\mathbb{C}$ is such a trivial space, the homomorphisms of C^* algebras into it are particularly simple. They are only of interest for Abelian C^* algebras, for which they completely determine the algebra's structure.

Definition (2.2.25)

An algebraic *-homomorphism χ (i.e., $\chi(\alpha a + \beta b) = \alpha\chi(a) + \beta\chi(b)$, $\chi(ab) = \chi(a)\chi(b)$, and $\chi(a^*) = \chi(a)^*$ for all $a, b \in \mathscr{A}$ and $\alpha, \beta \in \mathbb{C}$) of an Abelian C^* algebra into $\mathbb{C}$ is called a **character**. The set of characters of $\mathscr{A}$ is denoted $X(\mathscr{A})$.

Examples (2.2.26)

1. The characters of the algebra of $n \times n$ diagonal matrices are the maps $\chi_m: a \to a_{mm}$, $1 \leq m \leq n$; but the state $a \to \langle e|ae\rangle$ over this algebra is not necessarily a character for an arbitrary unit vector e.
2. The characters of the algebra $C(K)$ of continuous functions on a compact set $K \subset \mathbb{C}^n$ are of the form $\chi_z: f \to f(z)$, $z \in K$.

Remarks (2.2.27)

1. Since the algebraic relationships are preserved by χ, the existence of $(a - z)^{-1}$ implies that of $(\chi(a) - z)^{-1}$. Hence, for all $\chi \in X(\mathscr{A})$, $\chi(a) \in \mathrm{Sp}(a)$, and thus $|\chi(a)| \leq \|a\|$.
2. Since $\chi(a^*a) = \chi(a)^*\chi(a) = |\chi(a)|^2 \geq 0$ and $\chi(1) = 1$, every character is a state, which automatically makes the mapping $\chi: \mathscr{A} \to \mathbb{C}$ continuous. Indeed, every χ is a pure state, since no convex combination $\alpha_1\chi_1 + \alpha_2\chi_2$, $0 < \alpha_i < 1$, $\alpha_1 + \alpha_2 = 1$, can be multiplicative: $(\alpha_1\chi_1 + \alpha_2\chi_2)(a^2)$ is at the same time $(\alpha_1\chi_1(a) + \alpha_2\chi_2(a))^2$ and $\alpha_1\chi_1(a^2) + \alpha_2\chi_2(a^2)$. This can only be true for all $a \in \mathscr{A}$ if one $\alpha_i\chi_i$ vanishes. This shows that $X(\mathscr{A})$ does not have a linear structure, but consists of the extremal points of a convex set. The results of the following section will imply that $X(\mathscr{A})$ contains all pure states; they provide irreducible representations of $\mathscr{A}$, which are one-dimensional if the algebra is Abelian, and therefore characters.
3. The kernel $\{a \in \mathscr{A}: \chi(a) = 0\}$ is a closed, two-sided ideal of $\mathscr{A}$. Since $\mathbb{C}$ has no proper ideals, the kernel is maximal in the sense that there are no larger proper ideals containing it. The converse of this statement is also true: to every maximal ideal there corresponds a character. Thus characters, pure states, and maximal ideals are bijectively related.
4. The set of characters $X(\mathscr{A})$ has the weak-* topology as a subset of $\mathscr{A}'$. Weak-* limits clearly preserve the algebraic characterization of $X(\mathscr{A})$ (for instance, $\chi_n(a) \to \chi(a)$ and $\chi_n(b) \to \chi(b) \Rightarrow \chi_n(ab) = \chi_n(a)\chi_n(b) \to \chi(a)\chi(b)$). Therefore $X(\mathscr{A})$ is a weak-* closed subset of the unit ball of $\mathscr{A}'$ and thus, according to Remark (2.1.23; 2), weak-* compact. By definition the mappings $X(\mathscr{A}) \to \mathbb{C}: \chi \to \chi(a)$ are weak-* continuous.

Since $\mathscr{A}$ is a subset of $\mathscr{A}''$, the elements $a \in \mathscr{A}$ can be considered as functions on $X(\mathscr{A})$, by setting $a(\chi) \equiv \chi(a)$. There is in fact a complete correspondence:

The Gel'fand Isomorphism (2.2.28)

Any Abelian C^* algebra $\mathscr{A}$ is isomorphic to the C^* algebra of the continuous functions $C(X(\mathscr{A}))$: $X(\mathscr{A})$ (with the weak- topology) $\to \mathbb{C}$.*

Proof

The mapping $\mathscr{A} \to C(X(\mathscr{A})): a \to a(\chi)$ preserves all the algebraic properties such as $a_1 a_2(\chi) = \chi(a_1 a_2) = \chi(a_1)\chi(a_2) = a_1(\chi)a_2(\chi)$. Since $X(\mathscr{A})$ contains the pure states, Remark (2.2.20; 3) states that $\|a\| = \sup_{\chi \in X(\mathscr{A})} |a(\chi)|$, so the norms of $\mathscr{A}$ and $C(X(\mathscr{A}))$ are the same. It also follows from this that $a(\chi) = 0$ for all $\chi \Rightarrow a = 0$, and it only remains to show that $\mathscr{A}$ contains all the continuous functions on $X(\mathscr{A})$: A theorem of Weierstrass states that the polynomials in $z \in$ any compact set $\subset \mathbb{C}$ are dense in the continuous functions in the supremum topology. Stone [1, 7.3] generalized this to the statement that the norm-closure of any algebra of complex-valued functions with a unit and such that for all $\chi_1 \neq \chi_2$ there is an f with $f(\chi_1) \neq f(\chi_2)$ contains all continuous functions, and the $a(\chi)$ satisfy this requirement. Consequently $a \to a(\chi)$ is a bijection, preserving the algebraic and topological structure. □

Examples (2.2.29)

1. In Example (2.2.26; 1), $X(\mathscr{A}) = \{\chi_1, \chi_2, \ldots, \chi_n\}$ (with the discrete topology), and $C(X(\mathscr{A})) = \{a_{mm} \in \mathbb{C}, m = 1, 2, \ldots, n: X_m \to a_{mm} X_m\}$ is the set of diagonal matrices.
2. In Example (2.2.26; 2), we already have a bijection between K and $X(C(K))$, $z \to \chi_z$. According to (2.2.28) the bijection is in fact a homeomorphism if $X(C(K))$ is equipped with the weak-* topology.

Remarks (2.2.30)

1. The dual space of the continuous functions F is the space $M(F)$ of (not necessarily positive) measures. The following collection of continuous mappings into $\mathbb{C}$ summarizes the various identifications:

$$\mathscr{A} \xrightarrow{\mathscr{A}' \supset X(\mathscr{A})} \mathbb{C}$$

$$X(\mathscr{A}) \xrightarrow{C(X(\mathscr{A})) \equiv \mathscr{A}} \mathbb{C}$$

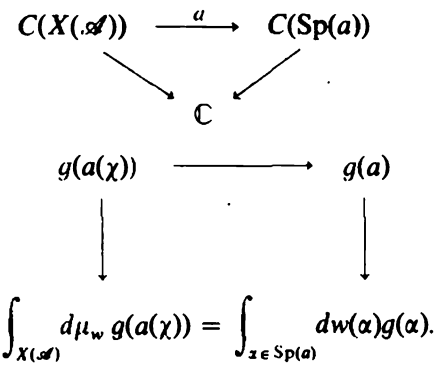
$$C(X(\mathscr{A})) \xrightarrow{M(C(X(\mathscr{A}))) \equiv \mathscr{A}'} \mathbb{C}.$$

2. These results for Abelian C^* algebras provide convenient representations of the normal elements a of any C^* algebra, when one simply considers the algebra generated by 1, a, and a^*.
3. Theorem (2.2.28) holds a fortiori for Abelian W^* algebras, which can also be represented as L^∞ functions on suitable measure spaces.

Since algebras of functions are easy to manipulate, (2.2.28) has a number of

Corollaries (2.2.31)

1. The power series of $z \to (a(\chi) - z)^{-1}$ converges for all $\chi \in X(A)$ provided that $z > \sup_{\chi \in X(A)} |a(\chi)| = \|a\|$. As we see, if a is a normal element of a C^* algebra, then the radius of convergence of the series for $(a - z)^{-1}$ is exactly $\|a\|$. (This may be false if a is not normal: $\left(\begin{smallmatrix} z & 1 \\ 0 & z \end{smallmatrix}\right)$ is invertible for all $z \neq 0$, but $\left\|\left(\begin{smallmatrix} 0 & 1 \\ 0 & 0 \end{smallmatrix}\right)\right\| = 1$.) The spectrum of a is precisely the image of $X(A)$ under a.
2. Continuous functions $f(a)$ are defined on the range of the Gel'fand isomorphism as $f(a(\chi))$, and they exist for all normal a in any C^* algebra. More specifically, a Hermitian element can be decomposed into a positive and a negative part, and unique square roots can be taken of positive elements. In a W^* algebra, all the spectral projections $\theta(a - \alpha)$, $\alpha \in \mathbb{R}$, exist for every Hermitian element, since a step function is the supremum of continuous functions. It is always true that $\|f(a)\| = \sup_\chi |f(a(\chi))| = \sup_{\alpha \in \mathrm{Sp}(a)} |f(\alpha)|$.
3. Hermitian elements can be characterized by $-1 \leq a/\|a\| \leq 1$, and positive elements by $\|\mathbf{1} - a/\|a\|\| \leq 1$.
4. According the Remark (2.2.30; 1), the Gel'fand isomorphism maps a state w to a probability measure $d\mu_w$ on $C(X(\mathscr{A}))$: $w(a) = \int_{X(\mathscr{A})} d\mu_w(\chi) a(\chi)$ for a normal. The pure states are the point measures $d\mu_w(\chi) = \delta(\chi - \chi_0)$. $\chi_0 \in X(\mathscr{A})$, which $\Rightarrow w(a) = a(\chi_0)$. We again note that
$$\|a\| = \sup_{\chi \in X(\mathscr{A})} |a(\chi)| = \sup_{w \text{ pure}} |w(a)|.$$
5. Since a maps the compact set $X(\mathscr{A})$ continuously into the compact set $\mathrm{Sp}(a)$, $a(\chi)$ can be introduced as a variable of integration as in Corollary 4, the integral being over the image measure $dw = a(d\mu_f)$:



Thus every state w furnishes a probability measure on the spectrum of a normal element a, such that $f(a) = \int_{\alpha \in \mathrm{Sp}(a)} dw(\alpha)\alpha$. For Hermitian or unitary elements this becomes a measure on the real axis or, respectively, the unit circle in $\mathbb{C}$.

The mathematical framework that we have developed will now allow us to formulate the conceptual schema of quantum theory.

The Basic Assumption of Quantum Theory (2.2.32)

The observables and states of a system are described by Hermitian elements a of a C^* algebra $\mathcal{A}$ and by states on $\mathcal{A}$. The possible outcomes of a measurement of a are $\in \mathrm{Sp}(a)$, and their probability distribution in a state w is dw, the probability measure induced on $\mathrm{Sp}(a)$ by w.

Remarks (2.2.33)

1. Since physical measurements are always real numbers, observables are Hermitian operators, but they constitute a subalgebra (over the real numbers) only if $\mathcal{A}$ is Abelian.
2. In classical mechanics the observables were a real function algebra, and the spectrum of a function was its range. Assumption (2.2.32) generalizes the classical schema only by not requiring commutativity.
3. In this volume the C^*-algebra of observables will nsually be $\mathcal{B}(\mathcal{H})$, and we will need to consider only the normal states over $\mathcal{B}(\mathcal{H})$.
4. For Abelian algebras we learned that maximal ideal = character = pure state = point probability measure. These states are nondispersive for all observables, i.e., the **mean-square deviation** $(\Delta_w(a))^2 \equiv w(a^2) - w(a)^2$ vanishes. If the algebra is noncommutative, nondispersive states do not normally exist, since the operator inequality
$$\left(\frac{a - w(a)}{\Delta_w(a)} + i\frac{b - w(b)}{\Delta_w(b)}\right)\left(\frac{a - w(a)}{\Delta_w(a)} - i\frac{b - w(b)}{\Delta_w(b)}\right) \geq 0$$
for an arbitrary state w implies the **indeterminacy**, or **uncertainty, relationship** (by taking w of the inequality above):
$$\left| w\left(\frac{ab - ba}{2i}\right)\right| \leq \Delta_w(a)\,\Delta_w(b).$$
A state that had no dispersion on any observable would yield zero for any commutator $[a, b] \equiv ab - ba$. The algebra of interest here will be $\mathcal{A} \equiv \mathcal{B}(\mathcal{H})$, on which that is not possible for normal states; there are increasing sequences of projection operators having $\mathbf{1}$ for supremum, but for which each one can be written as the commutator of two Hermitian operators (Problem 9).
5. Although it is obvious how a function of one observable is to be measured—take the function of the measured value of the observable—it is less clear how to measure the sum or product of noncommuting observables. The spectrum is certainly not just the sum or product of the original spectra; we shall see that the spectra of xp_y and yp_x are both $\mathbb{R}$, while their difference, the angular momentum, has spectrum $\mathbb{Z}$. That is, the only possible measured

values of the angular momentum are integers, whereas measurements of x, y, p_x, and p_y, or of the products xp_y and yp_x can yield any real numbers whatsoever. This makes the algebraic structure of the observables rather problematic, for which reason there have been attempts to find alternative and more economically phrased axioms. Some of these will be discussed shortly, and we shall see that they eventually lead back to the schema of (2.2.32), which is our justification for imbedding the observables in a C^* algebra.

It will not be possible here to unfurl the whole subject of the theory of measurement, so we shall merely describe the bare mathematical structures that have been proposed for the formulation of quantum theory.

Jordan Algebras (2.2.34)

If one tries to invent an algebra containing nothing but observables, then one is confronted by the problem that, while sums of Hermitian elements are Hermitian, the same is not true of products. The symmetric product $a \circ b \equiv (a + b)^2 - a^2 - b^2$ results in a new Hermitian element, and can be used as an alternative binary relationship on an algebra of observables over $\mathbb{R}$. Abstracting from that the commutative and distributive laws for $\circ$, one can formulate the rules of a nonassociative algebra. It turns out that modulo a few topological assumptions, which are more or less convincing on physical grounds, these **Jordan algebras** can be imbedded in $\mathscr{B}(\mathscr{H})$, whereby $a \circ b = ab + ba$.

Propositional Calculi (2.2.35)

In a propositional calculus the only observables are known as the **propositions** $p_i \in \mathscr{P}$, which correspond to statements like "The particle is in region G," and can be tested by experiments having only *yes* and *no* as possible outcomes. The algebraic formulation represents the propositions as projection operators or, as above, the characteristic function of G for the statement just mentioned. Algebraic operations are avoided in favor of lattice-theoretical operations, which correspond to logical relationships and seem less burdened with the problematics of measurement. Next one postulates a partial ordering for $\mathscr{P}$ with a maximal element $\mathbf{1}$ and a minimal element $\mathbf{0}$. In addition, there are assumed to exist

(i) $\inf\{p_1, p_2, \ldots, p_n\} \equiv p_1 \wedge p_2 \wedge \cdots \wedge p_n$,
(ii) $\sup\{p_1, p_2, \ldots, p_n\} \equiv p_1 \vee p_2 \vee \cdots \vee p_n$, and
(iii) a complementation$'$: $\mathscr{P} \to \mathscr{P}$ such that $p \wedge p' = \mathbf{0}$, $p'' = p'$, and $p_1 \geq p_2 \Leftrightarrow p_1' \leq p_2'$.

From this it follows that $(p_1 \wedge p_2)' = p_1' \vee p_2'$, and thus $p \vee p' = \mathbf{1}$. The connection with logic is that a larger proposition makes a weaker statement,

i.e., $p_1 \leq p_2$ means that $p_1 \Rightarrow p_2$; and the proposition **1** is always true and **0** always false. Thus $p_1 \wedge p_2$ (respectively $p_1 \vee p_2$) is the weakest (strongest) proposition that implies (is implied by) both p_1 and p_2. The proposition $p \wedge p' = \mathbf{0}$ means that there are no true propositions that imply both p and p'; a proposition can not be true at the same time as its complement. In classical logic p' is the negation of p, $p_1 \wedge p_2$ means both p_1 and p_2, and $p_1 \vee p_2$ means either p_1 or p_2 (or both).

From the algebraic point of view, $\mathscr{P}$ is the set of projections with the ordering (2.2.16) and $p' = \mathbf{1} - p$. Classically, p_i are the characteristic functions of sets G_i in phase-space (in which case p_1' corresponds to the complementary set CG_1, $p_1 \wedge p_2$ to the intersection, and $p_1 \vee p_2$ to the union, of G_1 and G_2). These facts can, of course, also be expressed in terms of algebraic operations, and in the noncommutative case the product of characteristic functions generalizes to $p_1 \wedge p_2 = \lim_{n\to\infty} p_1(p_2p_1)^n$.

On Hilbert space $\mathscr{H}$, the p_i are projections onto subspaces $\mathscr{H}_i$, and p_i' are projections onto the orthogonal subspaces $\mathscr{H}_i^\perp$, $p_1 \wedge p_2$ onto $\mathscr{H}_1 \cap \mathscr{H}_2$, and $p_1 \vee p_2$ onto the subspaces spanned by $\mathscr{H}_1$ and $\mathscr{H}_2$.

Remarks (2.2.36)

1. The algebraic realization of the propositional calculus will require the W^* property to make the lattice-theoretical operators properly definable. All the projections then exist, as does the limit of the positive, decreasing sequence $p_1(p_2p_1)^n$, $n \to \infty$.
2. Characteristic functions χ_I: $\mathbb{R} \supset I \to 1$, $CI \to 0$, of observables are projections. $\chi_I(A)$ corresponds to the statement that some spectral value $a \in I$ has been measured, and $\chi_I(A)'$ means that the measured value is in CI.
3. In the commutative case the p_i are realizable as characteristic functions χ_I, and the distributive law $p_1 \wedge (p_2 \vee p_3) = (p_1 \wedge p_2) \vee (p_1 \wedge p_3)$ follows from the correspondence with the set-theoretical operations. They are algebraically realized as follows: $p_1 \wedge p_2 \leftrightarrow \chi_1 \cdot \chi_2$, $p_1 \vee p_2 \leftrightarrow \chi_1 + \chi_2 - \chi_1 \cdot \chi_2$, and the distributive law states that $\chi_1 \cdot (\chi_2 + \chi_3 - \chi_2 \cdot \chi_3) = \chi_1\chi_2 + \chi_1\chi_3 - \chi_1 \cdot \chi_2 \cdot \chi_1 \cdot \chi_3$. If $p_1 > p_2$ for $p_i \in \mathscr{B}(\mathscr{H})$, then p_1 and p_2 commute, and the distributive law holds on the propositional subcalculus constructed from p_1, p_2, p_1', and p_2'. However, it does not hold in general.

Example (2.2.37)

With the Pauli spin matrices

$$(\sigma_x, \sigma_y, \sigma_z) = \left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right)$$

on $\mathscr{H} = \mathbb{C}^2$, we form the one-dimensional projections

$$p_{\mathbf{n}} = \frac{1 + \boldsymbol{\sigma} \cdot \mathbf{n}}{2}, \qquad \mathbf{n} \in \mathbb{R}^3, \qquad |\mathbf{n}|^2 = 1.$$

Their physical interpretation is the statement, "A measurement of $\boldsymbol{\sigma}$ in the direction $\mathbf{n}$ definitely has the value 1." For all $\mathbf{n}_1 \neq \mathbf{n}_2$, $p_{\mathbf{n}_1} \wedge p_{\mathbf{n}_2} = 0$. Hence for different $\mathbf{n}_i$,

$$p_{\mathbf{n}_1} \wedge (p_{\mathbf{n}_2} \vee p_{\mathbf{n}_3}) = p_{\mathbf{n}_1} \wedge \mathbf{1} = p_{\mathbf{n}_1},$$

but

$$(p_{\mathbf{n}_1} \wedge p_{\mathbf{n}_2}) \vee (p_{\mathbf{n}_1} \wedge p_{\mathbf{n}_3}) = \mathbf{0} \vee \mathbf{0} = \mathbf{0}.$$

Hence, the classical conclusion: If the particle is in region G_1 and either in G_2 or G_3 then it is either in G_1 and G_2 or in G_1 and G_3, is invalid for non-commuting observables. The proposition "The spin points in the direction $\mathbf{n}_2$ as well as in $\mathbf{n}_3$" is certainly false ($p_{\mathbf{n}_2} \wedge p_{\mathbf{n}_3} = \mathbf{0}$). The complementary statement is the tautology "The spin points in some direction," and is the most restrictive statement implied by both $p_{\mathbf{n}_2}$ and $p_{\mathbf{n}_3}$ ($p_{\mathbf{n}_2} \vee p_{\mathbf{n}_3} = \mathbf{1}$). It does not imply that one of the measurements of $\boldsymbol{\sigma} \cdot \mathbf{n}_2$ or $\boldsymbol{\sigma} \cdot \mathbf{n}_3$ yields the value 1 with certainty, and thus $p_{\mathbf{n}_1} \wedge (p_{\mathbf{n}_2} \vee p_{\mathbf{n}_3})$ is to be read neither as "The spin has the direction $\mathbf{n}_1$ and $\mathbf{n}_2$ or $\mathbf{n}_3$" nor as "The spin has the direction $\mathbf{n}_1$ and $\mathbf{n}_2$ or $\mathbf{n}_1$ and $\mathbf{n}_3$." Therefore the classical distributive law fails in quantum mechanics.

It turns out that, up to technical assumptions, any propositional calculus in which the distributive law holds on (p_1, p_2, p_1', p_2') for $p_1 \geq p_2$ can be represented as a calculus of projections on Hilbert space, and for this reason the algebraic framework we have chosen seems to be the most appropriate one for quantum mechanics.

Problems (2.2.38)

1. Show that the statement of (2.2.15; 2) is true.
2. Show that a *-homomorphism π of a C^* algebra is continuous.
3. Show that multiplication is continuous (in both factors simultaneously) in a C^* algebra.
4. Prove (2.2.12; 3).
5. Show that the statement of (2.2.15; 3) is true.
6. Consider a mixture of two states: Show that if $w = \alpha w_1 + (1 - \alpha)w_2$, $0 < \alpha < 1$, then $(\Delta_w a)^2 \geq \alpha(\Delta_{w_1} a)^2 + (1 - \alpha)(\Delta_{w_2} a)^2$, and that equality holds iff $w_1(a) = w_2(a)$.
7. Show that the resolvent set is open and that the spectrum is not empty.
8. Prove the inequality of (2.2.20; 1).
9. Write the projection P_n onto the subspace of l^2 spanned by the first n basis vectors as i times the commutator of two Hermitian elements of $\mathcal{B}(l^2)$.
10. Find an example of 2×2 matrices for which $0 \leq a \leq b \not\Rightarrow a^2 \leq b^2$. (Hint: $a \geq 0$ iff $a = a^*$, $\mathrm{Tr}\, a \geq 0$, and $\mathrm{Det}\, a \geq 0$.)

11. Let $0 \le a \le b$. Show that (i) if a^{-1} exists, then $b^{-1} \le a^{-1}$; (ii) if $\ln a$ exists, then $\ln a \le \ln b$; and (iii) $a^\gamma \le b^\gamma$ for $0 \le \gamma \le 1$. (Hint: Use

$$b \ge a \ge 0 \Rightarrow \int_0^\infty d\lambda\, \sigma(\lambda)(a+\lambda)^{-1} \ge \int_0^\infty d\lambda\, \sigma(\lambda)(b+\lambda)^{-1} \quad \text{for} \quad \sigma \ge 0.$$

It can even be shown that all functions f for which $b \ge a \ge 0$ implies $f(b) \le f(a)$ are of this form.)

Solutions (2.2.39)

1. $(a-z)^{-1} = -(1/z)\sum_{n=0}^\infty (a/z)^n$, and the radius of convergence of this series is exactly $|z| = \lim \|a^n\|^{1/n} \equiv \operatorname{spr} a$ (the **spectral radius**). It is always true that $\operatorname{spr} a \le \|a\|$, and for normal a, $\operatorname{spr} a = \|a\|$ because $\|a^2\| = \|a\|^2$, etc. (cf. Corollaries (2.2.31; 1) and (2.2.31; 2)).

2. If $(a-z)^{-1}$ exists, then so does $(\pi(a)-z)^{-1}$, and consequently, by Problem 1, $\|\pi(a)\| \le \|a\|$ for Hermitian a, and in general $\|\pi(a)\|^2 = \|\pi(a^*a)\| \le \|a^*a\| = \|a\|^2$. With the aid of Remark (2.2.17; 4), one can also argue as follows:

$$a^*a \le \|a\|^2 \cdot \mathbf{1} \Rightarrow \pi(a^*a) \le \|a\|^2 \pi(\mathbf{1}) \Rightarrow \|\pi(a)\|^2 \le \|a\|^2.$$

3. $\|(a+\delta a)(b+\delta b) - ab\| < \varepsilon$ for

$$\|\delta a\| \quad \text{and} \quad \|\delta b\| < (\varepsilon + ((\|a\| + \|b\|)/2)^2)^{1/2} - (\|a\| + \|b\|)/2.$$

4. $(a-\delta)^{-1} = a^{-1}(1-\delta\cdot a^{-1})^{-1} = a^{-1}\sum(\delta\cdot a^{-1})^n$; this series converges for all δ with $\|\delta\| < \|a^{-1}\|^{-1}$. The mappings $a \to a^*a - aa^*$, $a \to a - a^*$, $a \to aa^* - \mathbf{1}$, $a \to a^*a - \mathbf{1}$, and $a \to a^2 - a$ are continuous, and hence the inverse image of $\mathbf{0}$ is closed in every case. The Gel'fand isomorphism allows positivity to be characterized by $\|a\| - \|\,\|a\| - a\| \ge 0$ for Hermitian a (2.2.31; 3). This function is continuous and thus the inverse image of $[0, \infty)$ is likewise closed.

5. It is trivial to see that $\operatorname{Sp}(a^*) = \operatorname{Sp}(a)^*$. Now suppose that $P(a) - \lambda = \alpha\prod_i (a - \lambda_i)$ for λ, λ_i and $\alpha \in \mathbb{C}$. Then $\lambda \in \operatorname{Sp}(a) \Leftrightarrow (P(a)-\lambda)^{-1}$ does not exist $\Leftrightarrow$ some $\lambda_i \in \operatorname{Sp}(a)$ $\Leftrightarrow \lambda = P(\lambda_i) \in P(\operatorname{Sp}(a))$.

$$aa^* = a^*a = \mathbf{1} \Rightarrow \|a\| = \|a^{-1}\| = 1 \Rightarrow \operatorname{Sp}(a) \subset \{z \in \mathbb{C} : |z| = 1\}.$$

$$a = a^* : \alpha + i\beta \in \operatorname{Sp}(a) \Leftrightarrow \alpha + i(\beta+\lambda) \in \operatorname{Sp}(a + i\lambda) \Rightarrow \alpha^2 + (\beta+\lambda)^2$$

$$\le \|a + i\lambda\|^2 = \|a^*a + \lambda^2\| \le \|a\|^2 + \lambda^2 \quad \text{for all} \quad \lambda \in \mathbb{R} \Rightarrow \beta = 0.$$

$$a^2 - a = 0,\ a = a^* : \operatorname{Sp}(a^2 - a) = (\operatorname{Sp} a)^2 - (\operatorname{Sp} a) = 0,\ \operatorname{Sp}(a) \subset \{0, 1\}.$$

If $a = b^*b$, then the proof of the positivity of the spectrum is a bit more involved, but it can be shown that it is possible to restrict to Hermitian b, for which positivity follows from $\operatorname{Sp} b^2 = (\operatorname{Sp} b)^2$. It follows from the Gel'fand isomorphism (2.2.28) that the spectral properties of normal operators satisfy the various operator relationships, since the corresponding facts for function algebras are obvious.

6. $(\Delta_w a)^2 - \alpha(\Delta_{w_1} a)^2 - (1-\alpha)(\Delta_{w_2} a)^2 = (\alpha - \alpha^2)[w_1(a) - w_2(a)]^2$.

7. The resolvent set is open because of the convergence of

$$(a - z)^{-1} = (a - z_0)^{-1} \sum_{n=0}^{\infty} (a - z_0)^{-n}(z - z_0)^n$$

$$\text{for} \quad |z - z_0| < \|(a - z_0)^{-1}\|^{-1}.$$

If the resolvent set were all of $\mathbb{C}$, then $(a - z)^{-1}$ would be an operator-valued, entire, bounded function, which would have to be constant by Liouville's theorem (cf. [7], IX.11).

8. With the method of (2.1.29; 10) it can be shown that $|f(a^*b)|^2 \leq f(a^*a)f(b^*b)$. If $a \geq 0$, then by (2.2.17; 2) and (2.2.31; 3) $b^*ab \leq \|a\|b^*b$ and $f(b^*ab) \leq \|a\| f(b^*b)$. For arbitrary a, $|f(bab^*)|^2 \leq f(baa^*b^*)f(bb^*) \leq \|aa^*\| f(bb^*)^2 = \|a\|^2 f(bb^*)^2$.

9. Let

$$S_n = \begin{pmatrix} 0 & 0 & \ldots & 0 & \underbrace{1}_{n\text{-th position}} & 0 & 0 & \ldots \\ 0 & 0 & \ldots & 0 & 0 & 1 & 0 & \ldots \\ 0 & 0 & \ldots & 0 & 0 & 0 & 1 & \ldots \end{pmatrix}.$$

Then $P_n = [S_n, S_n^\dagger] = (i/2)[S_n + S_n^\dagger, i(S_n - S_n^\dagger)]$.

10. $a \geq 0 \Leftrightarrow$ both eigenvalues $\geq 0 \Leftrightarrow$ the sum and product of the two eigenvalues ≥ 0, i.e., $\operatorname{Tr} a \geq 0$ and $\operatorname{Det} a \geq 0$. Now let

$$0 \leq a = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \leq \begin{pmatrix} \lambda & 1 \\ 1 & 1 \end{pmatrix} = b, \qquad \lambda \geq 1.$$

$$\operatorname{Det}(b^2 - a^2) = \begin{vmatrix} \lambda^2 - 1 & \lambda - 1 \\ \lambda - 1 & 0 \end{vmatrix} = -(\lambda - 1)^2 < 0 \Rightarrow b^2 - a^2 \not\geq 0.$$

11. (i) $0 < a \leq b \Rightarrow 0 < b^{-1/2}ab^{-1/2} \leq \mathbf{1} \Rightarrow \mathbf{1} \leq b^{1/2}a^{-1}b^{1/2} \Rightarrow b^{-1} \leq a^{-1}$.
(ii) $\ln b - \ln a = \int_0^\infty d\lambda[(\lambda + a)^{-1} - (\lambda + b)^{-1}]$.
(iii) $\int_0^\infty d\lambda\, \lambda^{-\gamma}(a + \gamma)^{-1} = \text{const.} \cdot a^{-\gamma}$ for $0 < \gamma < 1 \Rightarrow a^{-\gamma} \geq b^{-\gamma} \Rightarrow a^\gamma \leq b^\gamma$.

2.3 Representations on Hilbert Space

Algebras of matrices are typical C^* algebras, because any C^* algebra can be represented as an algebra of bounded operators on a Hilbert space.

The concepts of linear functional and character are generalized in

Definition (2.3.1)

A **representation** π of a C^* algebra $\mathcal{A}$ is a *-homomorphism from $\mathcal{A}$ into $\mathcal{B}(\mathcal{H})$, that is, $\pi(\lambda_1 a_1 + \lambda_2 a_2) = \lambda_1\pi(a_1) + \lambda_2\pi(a_2)$, $\pi(a_1a_2) = \pi(a_1)\pi(a_2)$, and $\pi(a^*) = \pi(a)^*$ for all $a_i \in \mathcal{A}$ and $\lambda_i \in \mathbb{C}$. If $\pi(a) \neq 0$ whenever $a \neq 0$,

then π is said to be **faithful**. Two representations π_1 and π_2 on $\mathscr{H}_1$ and $\mathscr{H}_2$ are **equivalent** iff there exists an isomorphism $U: \mathscr{H}_1 \to \mathscr{H}_2$ such that $\pi_2(a) = U\pi_1(a)U^{-1}$ for all $a \in \mathscr{A}$.

Examples (2.3.2)

1. Matrix algebras represent themselves.
2. The continuous functions on a compact set K represent themselves as multiplication operators on $L^2(K, d\mu)$ if one defines $(\pi(a)\varphi)(x) = a(x)\varphi(x)$ for all $a \in \mathscr{A}$, $\varphi \in L^2$, and $x \in K$. ($\|\pi(a)\varphi\| \leq \|a\| \, \|\varphi\|$).

Remarks (2.3.3)

1. It need not be required that π be continuous; it is automatically continuous because of positivity (2.2.17; 4): $0 \leq a^*a \leq \|a\|^2 \cdot \mathbf{1} \Rightarrow 0 \leq \pi(a^*)\pi(a) \leq \|a\|^2 \cdot \mathbf{1} \Rightarrow \|\pi(a)\| \leq \|a\|$. Note that $\|\pi(\mathbf{1})\| = 0$ or 1, since $\|\pi(\mathbf{1})\| = \|\pi(\mathbf{1})^*\pi(\mathbf{1})\| = \|\pi(\mathbf{1})\|^2$.
2. The kernel $\mathscr{K} = \pi^{-1}(0)$ is a closed, two-sided ideal of $\mathscr{A}$. Faithfulness of π means that $\mathscr{K} = \{0\}$, i.e., π is injective. The positivity argument of Remark 1 then also works for $\pi^{-1}: \pi(\mathscr{A}) \to \mathscr{A}$, and therefore π is faithful iff $\|\pi(a)\| = \|a\|$ for all $a \in \mathscr{A}$. If $\mathscr{A}$ has no proper two-sided ideals, it is said to be a **simple algebra**, and every nontrivial representation is faithful. More generally, π is always a faithful representation of the quotient algebra $\mathscr{A}/\mathscr{K}$. When topologized with the quotient norm, defined as $\inf\|a + b\|$ for $b \in \mathscr{K}$, the representation of the quotient algebra is faithful and forms a C^* algebra [Bratelli and Robinson]. At any rate, $\pi(\mathscr{A})$ is itself a C^* algebra, and hence it is a norm-closed subalgebra of $\mathscr{B}(\mathscr{H})$.

Since π may fail to be either injective or surjective, the following terminology for subalgebras of $\mathscr{B}(\mathscr{H})$ is convenient:

Definition (2.3.4)

Let $\mathscr{M}$ be a *-subalgebra of $\mathscr{B}(\mathscr{H})$. Then the *-subalgebra

$$\mathscr{M}' \equiv \{b \in \mathscr{B}(\mathscr{H}): ba = ab \text{ for all } a \in \mathscr{M}\}$$

is its **commutant**.

$\mathscr{M}' \cap \mathscr{M} \equiv \mathscr{Z}$ is its **center**.
If $\mathscr{M} \subset \mathscr{M}'$, then $\mathscr{M}$ is **Abelian**.
If $\mathscr{M} = \mathscr{M}'$, then $\mathscr{M}$ is **maximally Abelian**.
If $\mathscr{M} = \mathscr{M}''$, then $\mathscr{M}$ is a **von Neumann algebra**.
If $\mathscr{M}' = \{\lambda \cdot \mathbf{1}\}$, then $\mathscr{M}$ is **irreducible**.
If $\mathscr{Z} = \{\lambda \cdot \mathbf{1}\}$, then $\mathscr{M}''$ is a **factor**.

If $\mathscr{T}$ is a subspace of $\mathscr{H}$, then if $\mathscr{M} \cdot \mathscr{T} \subset \mathscr{T}$, $\mathscr{T}$ is an **invariant subspace**; if $\mathscr{M} \cdot \mathscr{T}$ is dense in $\mathscr{H}$, $\mathscr{T}$ is a **totalizer**. If the totalizer $\mathscr{T}$ is one-dimensional, then its vectors are said to be **cyclic** (with respect to $\mathscr{M}$).

Examples (2.3.5)

1. Letting α and β take values in $\mathbf{C}$ or $\mathbf{C}^3$, some examples can be constructed with the Pauli spin matrices (2.2.37):
   (i) $\mathscr{M} = \{\alpha \cdot \mathbf{1} + \boldsymbol{\beta} \cdot \boldsymbol{\sigma}\} = \mathscr{M}''$; $\mathscr{M}' = \mathscr{Z} = \{\alpha \cdot \mathbf{1}\}$. This is irreducible, a factor, and non-Abelian. Every vector is cyclic, and there are no invariant proper subspaces.
   (ii) $\mathscr{M} = \{\alpha \cdot \mathbf{1} + \beta\sigma_z\} = \mathscr{M}''$, $\mathscr{M}' = \mathscr{M} = \mathscr{Z}$. This is reducible, not a factor, and maximally Abelian. $\binom{a}{b}$ is cyclic only if a and b are both different from zero, while $\binom{a}{0}$ and $\binom{0}{b}$ are invariant subspaces.
   (iii) $\mathscr{M} = \{\alpha \cdot \mathbf{1}\} = \mathscr{Z} = \mathscr{M}''$, $\mathscr{M}' = \{\alpha \cdot \mathbf{1} + \boldsymbol{\beta} \cdot \boldsymbol{\sigma}\}$. This is reducible, a factor, and Abelian. There are no cyclic vectors, and every subspace is invariant.
2. $L^\infty(\mathbf{R}, dx)$, considered as multiplication operators on $L^2(\mathbf{R}, dx)$, is maximally Abelian. Every function in L^2 that is nonzero a.e. is a cyclic vector. Functions that vanish on some interval $I \subset \mathbf{R}$ are invariant subspaces. L^∞ is reducible, and not a factor.

Remarks (2.3.6)

1. The following three conditions for irreducibility are equivalent (Problem 1):
   (i) $\mathscr{M}' = \lambda \cdot \mathbf{1}$.
   (ii) Every nonzero vector is cyclic.
   (iii) There are no invariant proper subspaces.
2. The direct sum $\pi_1 \oplus \pi_2$ and tensor product $\pi_1 \otimes \pi_2$ of two representations π_1 and π_2 are defined as for finite-dimensional spaces: If $x \equiv x_1 \oplus x_2 \in \mathscr{H}_1 \oplus \mathscr{H}_2 \equiv \mathscr{H}$ (respectively $x_1 \otimes x_2 \in \mathscr{H}_1 \otimes \mathscr{H}_2 \equiv \mathscr{H}$), then
   $$\pi(a)x = \pi_1(a)x_1 \oplus \pi_2(a)x_2 \qquad \text{(respectively } \pi_1(a)x_1 \otimes \pi_2(a)x_2\text{)}.$$
   Sums of representations are reducible, and the $\mathscr{H}_i$ are invariant subspaces.
3. The commutant obviously has the properties:
   (i) $\mathscr{N} \supset \mathscr{M} \Rightarrow \mathscr{N}' \subset \mathscr{M}'$;
   (ii) $\mathscr{M}'' \supset \mathscr{M}$;
   (iii) $(\mathscr{M} \cap \mathscr{N})' \supset \mathscr{M}' \cup \mathscr{N}'$, $(\mathscr{M} \cup \mathscr{N})' \supset \mathscr{M}' \cap \mathscr{N}'$.

   These imply that $\mathscr{M}''' = \mathscr{M}'$, since $(\mathscr{M}'')' \subset \mathscr{M}' \subset (\mathscr{M}')''$. It turns out that $\mathscr{M}''$ is the closure of $\mathscr{M}$ in both the strong and the weak topology (Problem 4). Strongly closed *-subalgebras of $\mathscr{B}(\mathscr{H})$ are the von Neumann algebras, and a theorem of Vigier (Problem 11) states that they have the properties of

Definition (2.2.22), i.e., they are W^* algebras. Note that $\mathcal{M} \cap \mathcal{M}' = \lambda \cdot \mathbf{1} \Rightarrow \mathcal{M}' \cup \mathcal{M}'' = \{\lambda \cdot \mathbf{1}\}' \Rightarrow \mathcal{M}' \cap \mathcal{M}'' = \{\lambda \cdot \mathbf{1}\}'' = \lambda \cdot \mathbf{1}$, so that for a factor the center of $\mathcal{M}''$ is trivial.

4. For finite-dimensional spaces, $\mathcal{M} = \mathcal{M}''$, and $\mathcal{M}$ is

   irreducible iff $= \mathcal{B}(\mathbb{C}^n)$;

   a factor iff $= \mathcal{B}(\mathbb{C}^n) \otimes \mathbf{1}$;

   Abelian iff all $a \in \mathcal{A}$ are simultaneously diagonal; and

   maximally Abelian iff to each pair of diagonal positions in the diagonal representation there exist elements with different eigenvalues.
5. If $\mathcal{M}$ contains a maximally Abelian subalgebra $\mathcal{N}$, then $\mathcal{M}' \subset \mathcal{N}' = \mathcal{N} \subset \mathcal{M}$, so $\mathcal{Z} = \mathcal{M}'$. In this case, being a factor is equivalent to being irreducible, though in general irreducibility implies being a factor but not vice versa.
6. $\mathcal{M}$ Abelian implies $\mathcal{M} = \mathcal{Z}$, so Abelian factors have the trivial form $\lambda \cdot \mathbf{1}$.
7. If $\pi(\mathcal{A})$ is reducible, then $s = s^* \in \pi(\mathcal{A})'$, $s \neq \lambda \cdot \mathbf{1}$ is said to induce a superselection rule. The Hilbert space decomposes into subspaces that are not connected by observables, and there exists a Hermitian operator s that assigns different quantum numbers to the various invariant subspaces. If $\pi(\mathcal{A})$ is a factor, then s does not belong to $\pi(\mathcal{A})$, and it is consequently not an observable, but rather a kind of hidden variable. There is no maximally Abelian subalgebra of $\pi(\mathcal{A})$, because s could always be added to any subalgebra.

In any representation π, every vector $x \in \mathcal{H}$, $\|x\| = 1$, produces a state $a \to \langle x | \pi(a) x \rangle$, $a \in \mathcal{A}$. We shall next show that, conversely, for every state there is a representation in which it is of this form. Since algebras have a linear structure, any $a \in \mathcal{A}$ can be represented as an operator on a linear space, namely the algebra itself, by $b \to ab$, $b \in \mathcal{A}$. For a C^* algebra, this linear space will only be a Banach space, but a state provides the scalar product needed to make the space a Hilbert space.

Lemma (2.3.7)

If w is a state, then $\mathcal{N} \equiv \{a \in \mathcal{A} : w(a^*a) = 0\}$ is a closed, left ideal. The scalar product $\langle b | a \rangle = w(b^*a)$ makes the quotient space $\mathcal{A}/\mathcal{N}$ a pre-Hilbert space, and the canonical mapping $\mathcal{A} \to \mathcal{A}/\mathcal{N}$ is a continuous linear mapping of $\mathcal{A}$ (as a Banach space) onto $\mathcal{A}/\mathcal{N}$ (as a pre-Hilbert space).

Proof

That $\mathcal{N}$ is a left ideal follows from (2.2.20; 1), as $w(a^*b^*ba) \leq \|b^*b\| w(a^*a)$, and closure follows from continuity. The scalar product $\langle | \rangle$ on $\mathcal{A}/\mathcal{N}$ satisfies Postulates (2.1.7), and $|\langle b | a \rangle| = |w(b^*a)| \leq \|b\| \|a\|$ guarantees that the mapping is continuous. □

Remarks (2.3.8)

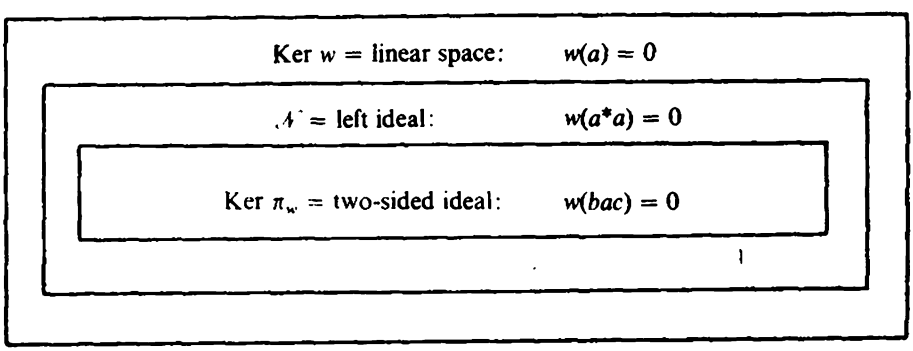
1. Since $|w(a)|^2 \leq w(a^*a)$, the ideal $\mathcal{N} \subset \text{Ker } w = \{a \in \mathcal{A}: w(a) = 0\}$. Thus, in Example (2.3.5; 1) with $w(\cdot) = (\begin{smallmatrix}1\\0\end{smallmatrix})(\cdot)(\begin{smallmatrix}1\\0\end{smallmatrix})$, $\mathcal{N} = \{(\begin{smallmatrix}0 & \alpha\\0 & \beta\end{smallmatrix})\}$ and Ker $w = \{(\begin{smallmatrix}0 & \alpha\\\beta & \gamma\end{smallmatrix})\}$, $\alpha, \beta, \gamma \in \mathbb{C}$.
2. Despite the norm-completeness of $\mathcal{A}$, the quotient $\mathcal{A}/\mathcal{N}$ may fail to be a Hilbert space. For example, let $\mathcal{A}$ be the continuous functions in $x \in [0, 1]$ and $w(a) = \int_0^1 dx\, a(x)$; then $\mathcal{N} = \{0\}$, but $\mathcal{A}$ is strictly smaller than its completion $L^2([0, 1], dx)$.
3. Given the product of two algebras $\mathcal{A}$ and $\mathcal{B}$, i.e., each element of the product algebra is a linear combination of $a_i b_j = b_j a_i$, $a_i \in \mathcal{A}$, $b_j \in \mathcal{B}$, the Hilbert space constructed from a product state is the tensor product of the two Hilbert spaces gotten from $\mathcal{A}$ and $\mathcal{B}$.

Definition (2.3.9)

The **Gel'fand–Naimark–Segal (GNS) representation** π_w of $\mathcal{A}$ on $\mathcal{B}(\mathcal{H})$, where $\mathcal{H}$ is the completion of $\mathcal{A}/\mathcal{N}$, corresponding to any state w is defined as the continuous extension of $\pi_w(a)$: $b \to ab$, $a \in \mathcal{A}$, $b \in \mathcal{A}/\mathcal{N}$ to all of $\mathcal{H}$.

Remarks (2.3.10)

1. The elements of $\mathcal{A}/\mathcal{N}$ are equivalence classes of objects of the form $b + n$, $n \in \mathcal{N}$, though the mapping $\pi_w(a)$ is independent of the representative b, since $\mathcal{N}$ is a left ideal ($an \in \mathcal{N}$).
2. The general fact about continuity (2.2.20; 1) can be seen directly: $\|\pi_w(a)\| = \sup_{w(b^*b)=1} (w(b^*a^*ab))^{1/2} \leq \|a^*a\|^{1/2} = \|a\|$. Hence $\pi_w(a)$ is a continuous operator on $\mathcal{A}/\mathcal{N}$, and has a unique extension to $\mathcal{H}$.
3. Ker $\pi_w = \{a \in \mathcal{A}: w(b^*ac) = 0 \text{ for all } b, c \in \mathcal{A}\}$ is a closed, two-sided ideal contained in $\mathcal{N}$. It reduces to $\{0\}$ in the example of (2.3.8; 1), which shows that the GNS representation may be faithful even if $\mathcal{N} \neq \{0\}$. The logical interrelationships are depicted below:



4. The vector corresponding to $\mathbf{1} \in \mathscr{A}/\mathscr{N}$ is cyclic.
5. π_w is irreducible iff w is pure (Problem 2).
6. If, conversely, we have a representation π with a cyclic vector Ω, then it defines a state $w(a) = (\Omega|\pi(a)\Omega)$, and π_w is then equivalent to π. By the axiom of choice, every representation is a sum of representations with a cyclic vector.
7. Since for all $a \in \mathscr{A}$ there is a state such that $w(a^*a) = \|a\|^2$, it is always possible to construct a faithful representation of any C^* algebra, by taking the sum of the representations for all possible w.
8. As we have seen, each vector Ω in the Hilbert space corresponds to a pure state, which corresponds to a ray in Hilbert space, i.e., $\{e^{i\alpha}\Omega, \alpha \in \mathbb{R}\}$. In wave-mechanics, this fact shows up as the **principle of superposition**, which states that the vector $\Omega = \alpha_1\Omega_1 + \alpha_2\Omega_2$, $|\alpha_1|^2 + |\alpha_2|^2 = 1$ describes the quantum-mechanical superposition of the states Ω_1 and Ω_2. Yet Ω contains information not contained in Ω_1 and Ω_2 taken separately, namely the relative phase of the vectors Ω_1 and Ω_2.

In order to study the form of the representation of Hermitian element a in more detail, consider the restriction to the C^* algebra generated by a. By the axiom of choice, we can choose $b_i \in \mathscr{H}$ such that $\mathscr{H}_i \equiv$ the completions of the sets of linear combinations of $a^n b_i$, $n = 0, 1, \ldots$ span all of $\mathscr{H}$. Each $\mathscr{H}_i$ provides a representation of the (Abelian) C^* algebra generated by a, and has b_i as a cyclic vector. By Corollary (2.2.31; 5), to the state

$$w_i: w_i(a^n) = \langle b_i | a^n b_i \rangle$$

there corresponds a measure μ_i on $\mathrm{Sp}(a)$ such that $w_i(\varphi(a)) = \int d\mu_i(\alpha)\varphi(\alpha)$. Taking the norm-closure of the polynomials next extends this to all continuous functions $\varphi \in C(\mathrm{Sp}(a))$; then the completion with the w_i norm extends this to $\mathscr{H}_i = L^2(\mathrm{Sp}(a), d\mu)$, on which $\pi(a)$ acts as the multiplication operator $\varphi(\alpha) \to \alpha\varphi(\alpha)$, $\alpha \in \mathrm{Sp}(a)$, $\varphi \in L^2(\mathrm{Sp}(a), d\mu)$. The use of this notation yields

The Spectral Theorem (2.3.11)

For any given Hermitian element $a \in \mathscr{A}$, every representation of $\mathscr{A}$ is equivalent to a representation $\mathscr{H} = \oplus \mathscr{H}_i$, for which $\mathscr{H}_i = L^2(\mathrm{Sp}(a), d\mu_i)$ and $\pi(a)_{|\mathscr{H}_i}$: $\varphi(\alpha) \to \alpha\varphi(\alpha)$. In this representation, a acts as a ***multiplication operator.***

Remarks (2.3.12)

1. Theorem (2.3.11) generalizes the statement that any finite-dimensional Hermitian matrix is diagonable with a unitary transformation. Of course, not all Hermitian elements of $\mathscr{A}$ are multiplication operators in this representation unless $\mathscr{A}$ is Abelian.

2. Although we made use of the GNS representation, by Remark (2.3.10; 6), the argument leading to (2.3.11) works just as well with any specified representation.
3. Theorem (2.3.11) shows that any Hermitian operator of $\mathscr{B}(\mathscr{H})$ can be transformed unitarily into a multiplication operator.
4. The scaling $\varphi \to 2^{n/2}\varphi$ is an isomorphism $L^2(\mathrm{Sp}(a), d\mu_n) \to L^2(\mathrm{Sp}(a), 2^{-n}\, d\mu_n)$; and hence $\mathscr{H}$ is also isomorphic to $\bigoplus_{n=1}^{\infty} L^2(\mathrm{Sp}(a), 2^{-n}\, d\mu_n)$ (assuming $\mathscr{H}$ is separable). Furthermore, since the μ_n are probability measures, $\mathscr{H}$ is also isomorphic to L^2 of a finite measure space. Incidentally, this shows that the μ_n are not in any way fixed uniquely.
5. The only fact that has been used so far is that the algebra generated by a and a^* is commutative, so all the same statements can be made for normal operators, except that $\mathrm{Sp}(a)$ would not be real, but just some subset of $\mathbb{C}$. If there are m mutually commuting operators $a_j = a_j^*$, then they can be represented simultaneously as multiplication operators on $L^2(\mathbb{R}^m, d\mu)$.

Examples (2.3.13)

1. A Hermitian $n \times n$ matrix a with eigenvalues α_i. The space $\mathbb{C}^n$ is isometric to $L^2(\mathbb{R}, d\mu)$ with $d\mu(\alpha) = \sum_{i=1}^{n} \delta(\alpha - \alpha_i)d\alpha$, $\langle w|v\rangle = \sum_{i=1}^{n} w_{\alpha_i}^* v_{\alpha_i}$,

$$\langle w|av\rangle = \sum_{i=1}^{n} w_{\alpha_i}^* \alpha_i v_{\alpha_i}.$$

2. $l^2(-\infty, \infty) = \{(v_n): -\infty < n < \infty\}$, where $(av)_n = v_{n+1} + v_{n-1}$ is a Hermitian operator $\in \mathscr{B}(l^2)$. In order to rewrite it as a multiplication operator, map $l^2(-\infty, \infty)$ onto $L^2([-\pi, \pi], dx)$ by $(v_n) \to \sum_{n=-\infty}^{\infty} v_n e^{inx}$; then a becomes multiplication by $e^{ix} + e^{-ix} = 2\cos x$. Next write

$$L^2([-\pi, \pi], dx) = L^2([-\pi, 0], dx) \oplus L^2([0, \pi], dx)$$

and introduce the new variable $\eta = 2\cos x$, to make this isomorphic to $L^2([-2, 2], d\eta/\sqrt{4 - \eta^2}) \oplus L^2([-2, 2], d\eta/\sqrt{4 - \eta^2})$. On this space a has become the multiplication operator η.

We have found a representation on $L^2(\mathrm{Sp}(a), d\mu)$ of the C^* algebra generated by a, for which each element of the algebra corresponds to multiplication by a continuous function on $\mathrm{Sp}(a)$. The algebra does not, however, account for all multiplication operators on $L^2(\mathrm{Sp}(a), d\mu)$, as they constitute the much larger space $L^\infty(\mathrm{Sp}(a), d\mu)$ (Problem 5). Problem 4 shows that this space is obtained by strong closure and also has a purely algebraic characterization, as the bicommutant $\pi(a)''$. By taking strong limits one obtains a representation in which it is possible to describe the operator $f(a)$ for $f \in L^\infty$ more explicitly.

Once we know all the integrable functions of a Hermitian operator, and in particular the characteristic functions, the explicit form of the operator $f(a)$ can be written down in terms of the

Spectral Family (2.3.14)

An element $a = a^* \in \mathcal{A}$ can be written as

$$a = \int_{-\infty}^{\infty} dP_a(\alpha)\alpha, \qquad P_a(\alpha) = \Theta(\alpha - a), \qquad \Theta(x) = \begin{cases} 1, & \text{if } x > 0 \\ 0, & \text{otherwise,} \end{cases}$$

and given any $f \in L^\infty$,

$$f(a) = \int_{-\infty}^{\infty} dP_a(\alpha) f(\alpha).$$

*The set of projection operators $P_a(\alpha)$ is known as the **spectral family** of a.*

Remark (2.3.15)

The construction of (2.3.14) is a generalization of the Stieltjes integral to the case of operators. Just as for functions, it is defined as the limit of the sums

$$a = \lim_{N \to \infty} \sum_{j=1}^{2^N} \|a\| \left\{ \frac{j-1}{2^N} \left[\Theta\left(a - \frac{\|a\|}{2^N} j\right) - \Theta\left(a - \frac{\|a\|}{2^N}(j-1)\right) \right] \right.$$
$$\left. - \frac{j}{2^N} \left[\Theta\left(a + \frac{\|a\|}{2^N} j\right) - \Theta\left(a + \frac{\|a\|}{2^N}(j-1)\right) \right] \right\}.$$

Vigier's theorem (Problem 11) guarantees the existence of the strong limit, since the sums are a bounded, increasing sequence of operators.

There are many different ways to classify the spectra of Hermitian operators. The classification we shall make uses the Lebesgue decomposition of a measure on $\mathbb{R}$; any measure is the sum of a part $d\mu_{ac} = f(\alpha)d\alpha, f \geq 0$ and locally integrable, which is absolutely continuous with respect to Lebesgue measure $d\alpha$; a part $d\mu_p$ concentrated on some separate points, $d\mu_p = d\alpha \sum_n c_n \delta(\alpha - \alpha_n)$, $\alpha_n \in \mathbb{R}$; and a remainder $d\mu_s$, the singular spectrum [2]. This last part is somewhat pathological (Problem 7) and will not occur in any of our applications (though there exist one-electron band models with $d\mu_s$). Each of the three pieces of the measure is concentrated on null sets with respect to the others, and there is an orthogonal decomposition of $L^2(\mathbb{R}, d\mu)$ as

$$L^2(\mathbb{R}, d\mu) = L^2(\mathbb{R}, d\mu_p) \oplus L^2(\mathbb{R}, d\mu_{ac}) \oplus L^2(\mathbb{R}, d\mu_s)$$

(Problem 6). By making the same decomposition of all the $d\mu_i$ of (2.3.11), one can decompose the space $\mathcal{H}$ according to the properties of any normal operator a into orthogonal subspaces invariant under a:

Definition (2.3.16)

If the Hilbert space is decomposed as

$$\mathscr{H} = \mathscr{H}_p \oplus \mathscr{H}_{ac} \oplus \mathscr{H}_s,$$

as in Remark (2.3.15) for some normal a, then the **point spectrum**, **absolutely continuous spectrum**, and **singular spectrum** of a are defined by the restrictions of a to the subspaces,

$$\sigma_p(a) = \mathrm{Sp}(a_{|\mathscr{H}_p}), \qquad \sigma_{ac}(a) = \mathrm{Sp}(a_{|\mathscr{H}_{ac}})$$

and

$$\sigma_s(a) = \mathrm{Sp}(a_{|\mathscr{H}_s}).$$

Examples (2.3.17)

1. For the finite matrices (2.3.13; 1), $d\mu$ is a pure point measure, and $\mathscr{H}_{ac} = \mathscr{H}_s = \{0\}$, $\mathrm{Sp}(a) = \sigma_p(a)$.
2. Let a be multiplication by α on $L^2([0, 1], d\alpha)$. Then $\mathscr{H}_p = \mathscr{H}_s = \{0\}$, and $\mathrm{Sp}(a) = \sigma_{ac}(a)$.

Remarks (2.3.18)

1. $\mathscr{H}_p$ is the space spanned by the eigenvectors. To see this, consider $\psi_n \in L^2(\mathbb{R}, d\mu_p)$ as above, so that $\psi_n(\alpha_n) = 1$, but $\psi_n(\alpha) = 0$ for other α. In $\mathscr{H}_p$, $\|\psi_n\| = 1$, but single-point sets have measure zero with respect to $d\mu_{ac}$ and $d\mu_s$, $\int d\mu_{ac}|\psi_n|^2 = \int d\mu_s|\psi_n|^2 = 0$. Therefore $\psi_n \in \mathscr{H}_p$, and $a\psi_n = \alpha_n\psi_n$. The vectors ψ_n form a basis for $\mathscr{H}_p$.
2. It is a natural question whether the decomposition of (2.3.16) depends on the choice of μ_i in (2.3.11). In fact the μ_i are unique up to the equivalence relation $\mu_i \to \mu_i f(\alpha)$, f > 0 and locally integrable, and equivalent measures effect the same decomposition of $\mathscr{H}$.
3. The sets σ_p, σ_{ac}, σ_s are closed, though they need not be disjoint, nor does the Lebesgue measure of σ_p or of σ_s have to be zero. Suppose, for example, that α_n is a numbering of the rational numbers between 0 and 1, and $\mathscr{H} = L^2([0, 1], d\alpha \sum_n \delta(\alpha - \alpha_n))$, and let a be the operator of multiplication by α. Then $\mathscr{H} = \mathscr{H}_p$ and $\sigma_p = [0, 1]$, because the spectrum is closed, but almost no point of σ_p is an eigenvalue. (I.e., the irrational points vastly outnumber the rationals.) Many authors define σ_p as just as the set of eigenvalues, which case $\sigma_p \cup a_{ac} \cup \sigma_s$ may be different from $\mathrm{Sp}(a)$.
4. The **essential spectrum** σ_{css} comprises all points of $\mathrm{Sp}(a)$ other than isolated points of finite multiplicity, that is, having a finite-dimensional eigenspace. There is no essential spectrum on a finite-dimensional space, but in the infinite case every bounded Hermitian element has an essential spectrum.

5. Although there may not exist eigenvectors for every point α of σ_{ess}, the spectral representation contains sequences of functions that are more and more spectrally concentrated near α. This idea can be used to prove the following theorem: *For all* $a = a^*$ *and* $\alpha \in \mathrm{Sp}(a)$, *there exists a sequence* $\{\psi_n\}_{n=1}^{\infty}$, $\|\psi_n\| = 1$, *such that* $\lim_{n\to\infty} \|(a - \alpha)\psi_n\| = 0$. $\alpha \in \sigma_{ess}(a) \Leftrightarrow$ *there exists such a set of orthogonal vectors, or, equivalently, a set of* ψ_n *that* $\to 0$.

The sum of the eigenvalues of a diagonable $n \times n$ matrix m is given by the trace

$$\mathrm{Tr}\, m = \sum_{i=1}^{n} \langle e_i | m e_i \rangle, \qquad \langle e_i | e_j \rangle = \delta_{ij}.$$

The trace is a unitary invariant, and hence independent of the basis $\{e_i\}$. If one attempts to define the trace of an element $a \in \mathscr{A}$ in some representation, the essential spectrum causes trouble. If the space is infinite-dimensional, then the question of whether $\sum_i$ converges must first be grappled with. One problem is that convergence in one basis does not necessarily imply convergence in another, even if the eigenvalues tend to zero. For example, if $a \in \mathscr{B}(l^2)$ is

$$a = \begin{bmatrix} 0 & 1 & & & & & & \\ 1 & 0 & & & & & & \\ & & 0 & \frac{1}{2} & & & & \\ & & \frac{1}{2} & 0 & & & & \\ & & & & 0 & \frac{1}{3} & & \\ & & & & \frac{1}{3} & 0 & & \\ & & & & & & \ddots & \end{bmatrix},$$

then it has the absolutely convergent trace $\sum_{i=1}^{\infty} |a_{ii}| = 0$. Yet in a different basis a has the form

$$a = \begin{bmatrix} 1 & 0 & & & & & & \\ 0 & -1 & & & & & & \\ & & \frac{1}{2} & 0 & & & & \\ & & 0 & -\frac{1}{2} & & & & \\ & & & & \frac{1}{3} & 0 & & \\ & & & & 0 & -\frac{1}{3} & & \\ & & & & & & \ddots & \end{bmatrix},$$

and $\sum_i a_{ii}$ is only conditionally convergent, which means that it can be rearranged (equivalent to a change of basis) so as to sum to any value whatsoever, or to diverge. This lack of definition is avoided if the operator

is positive. In that case the worst possibility is divergence, but aside from that the sum has all the ordinary

Properties of the Trace (2.3.19)

The mapping $m \to \operatorname{Tr} m = \sum_i \langle e_i | m e_i \rangle$, *for* $\langle e_i | e_j \rangle = \delta_{ij}$, *sends the positive operators to* $\overline{\mathbb{R}^+}$, *and for* $m_i \geq 0$,

(i) $\operatorname{Tr}(\alpha_1 m_1 + \alpha_2 m_2) = \alpha_1 \operatorname{Tr} m_1 + \alpha_2 \operatorname{Tr} m_2, \alpha_i \in \mathbb{R}^+$,
(ii) $\operatorname{Tr} U^{-1} m U = \operatorname{Tr} m$, U *unitary*,
(iii) $m_1 \leq m_2 \Rightarrow \operatorname{Tr} m_1 \leq \operatorname{Tr} m_2$.

If m_i *is not necessarily positive, but* $\operatorname{Tr} |m_i| < \infty$, *where* $|m| \equiv (m^* m)^{1/2}$, *then* (i) *and* (ii) *are still true, and moreover*

(iv) $\operatorname{Tr}|m_1 + m_2| \leq \operatorname{Tr}|m_1| + \operatorname{Tr}|m_2|$,
(v) $(\operatorname{Tr}|m_1 m_2|)^2 \leq \operatorname{Tr}|m_1|^2 \operatorname{Tr}|m_2|^2$,
(vi) $\operatorname{Tr} ma = \operatorname{Tr} am$ *for all* $a \in \mathcal{B}(\mathcal{H})$.

Proof

Properties (i) and (iii) are trivial. For the others, see Problem 10. □

Remarks (2.3.20)

1. The unitary invariance (ii) implies that the definition is independent of the choice of basis provided that $\operatorname{Tr}|m| < \infty$.
2. On an infinite-dimensional space, the trace is an unbounded, positive linear functional. This does not contradict Remark (2.2.20; 1), since the trace is not finite on a whole C^* algebra; for instance, $\operatorname{Tr} \mathbf{1} = \infty$.
3. For Property (iv) it was not necessary to assume that $\operatorname{Tr}|a| < \infty$, since $|\operatorname{Tr} am| \leq \|a\| \operatorname{Tr}|m|$. This can be shown most conveniently with a **polar decomposition** $m = V|m|$ (see [3], VIII.9), where

$$V^* V = |m|^{-1} |m|^2 |m|^{-1}$$

is the projection onto the space perpendicular to the null space of $|m|$, so $\|Vx\| \leq \|x\|$ for all $x \in \mathcal{H}$, and

$$|\operatorname{Tr} am| = \left| \sum_i \langle |m|^{1/2} e_i | aV |m|^{1/2} e_i \rangle \right|$$
$$\leq \sum_i \|a\| \, \| |m|^{1/2} e_i \|^2 = \|a\| \operatorname{Tr}|m|.$$

4. Most trace inequalities valid for finite-dimensional matrices can be carried over to general Hilbert spaces, as will be discussed in the fourth volume.†

† Quantum Mechanics of Large Systems.

5. The trace has several technical advantages over the operator norm, which is only easy to work with in the spectral representation. Suppose $K \in L^2(\mathbb{R}^n \times \mathbb{R}^n, d^n x\, d^n x')$ is the kernel of a bounded integral operator on $L^2(\mathbb{R}^n, d^n x)$, $\psi(x) \to \int K(x, x')\psi(x')d^n x'$. Its norm is difficult to compute, while $\operatorname{Tr} K^*K = \int d^n x\, d^n x'\, K^*(x, x')K(x', x)$, as can be seen by writing the operator in a basis,

$$K(x, x') = \sum_{ij} K_{ij} e_i^*(x) e_j(x'),$$

$$\operatorname{Tr} K^*K = \sum_{ij} K_{ij}^* K_{ji} = \int d^n x\, d^n x'\, K^*(x, x')K(x', x).$$

Since $\operatorname{Tr}|m|$ has the properties of a norm (2.1.4) by Property (2.3.19(iv)), it is interesting to set the operators of finite trace aside in a separate category. They bear a close resemblance to finite matrices.

Definition (2.3.21)

Let $\mathscr{F} \subset \mathscr{B}(\mathscr{H})$ be the space of operators of finite rank, i.e., which map $\mathscr{H}$ to a finite-dimensional space. The completions of $\mathscr{F}$ in the norms $\|a\|_1 \equiv \operatorname{Tr}|a|$, $\|a\|_2^2 \equiv \operatorname{Tr} a^*a$, and $\|a\|_\infty \equiv \|a\|$ are denoted $\mathscr{C}_1$, the **trace class** operators; $\mathscr{C}_2$, the **Hilbert–Schmidt operators**; and $\mathscr{C}$, the **compact**, or **completely continuous**, **operators**.

Examples (2.3.22)

In $\mathscr{B}(l^2)$, the matrices with only finitely many nonzero rows or columns belong to $\mathscr{F}$. Diagonal matrices with eigenvalues α_i belong to $\mathscr{C}_1$ provided that $\sum_i |\alpha_i| < \infty$; to $\mathscr{C}_2$ provided that $\sum_i |\alpha_i|^2 < \infty$; and to $\mathscr{C}$ provided that $\lim_{i\to\infty} \alpha_i = 0$.

Remarks (2.3.23)

1. It follows from (2.3.19) that the $\| \ \|_p$ are norms. By Remark (2.3.18; 5), it is necessary to have $\sigma_{\text{ess}} = \{0\}$ for the trace to be finite, so the spectrum is purely discrete. If $\alpha_i > 0$ are the eigenvalues of $(a^*a)^{1/2}$, then we conclude from $\sum_i \alpha_i^2 < \sum_i \alpha_i \sum_j \alpha_j$ that $\| \ \|_p \le \| \ \|_q$ for $p \ge q$, $p, q = 1, 2, \infty$. Hence a Cauchy sequence in $\| \ \|_q$ is also one in $\| \ \|_p$ for $p \ge q$, so we have the inclusions

$$\mathscr{F} \subset \mathscr{C}_1 \subset \mathscr{C}_2 \subset \mathscr{C} \subset \mathscr{B}(\mathscr{H}).$$

2. Let a be an operator such that $\|a\|_1 < \infty$ (resp. $\|a\|_2 < \infty$) and α_i are the eigenvalues of $(a^*a)^{1/2}$. The truncated operators $a_N \equiv P_N a P_N$, where P_N is the projection onto the first N basis vectors, obviously belong to $\mathscr{F}$

and converge to a in the $\| \ \|_1$ (resp. $\| \ \|_2$) norm. Hence the sets $\mathscr{C}_1$ and $\mathscr{C}_2$ contain all operators with finite $\| \ \|_1$ and respectively $\| \ \|_2$ norm. However, $\mathscr{C}$ is not all of $\mathscr{B}(\mathscr{H})$: $\|a\|$ is equal to $\sup_i|\alpha_i|$, and in this norm it does not generally suffice to have $\|a\| < \infty$ for a_N to converge in norm to a. (A simple counterexample is $a = \mathbf{1}$.) The correspondence with the l^p spaces is: $l^0 \leftrightarrow \mathscr{C}$; $l^1 \leftrightarrow \mathscr{C}_1$; $l^2 \leftrightarrow \mathscr{C}_2$; $l^\infty \leftrightarrow \mathscr{B}(\mathscr{H})$.

3. $\mathscr{E}$ is a two-sided ideal of $\mathscr{B}(\mathscr{H})$, and this is also a property of its completions $\mathscr{C}_p$, since $\|ab\|_p \leq \min(\|a\| \, \|b\|_p, \|b\| \, \|a\|_p)$, $p = 1, 2, \infty$.
4. The essential spectrum of any operator of $\mathscr{E}$ is $\{0\}$. This property carries over to all of $\mathscr{C}$, and is a distinguishing characteristic of self-adjoint, compact operators (Problem 9).
5. An operator $a \in \mathscr{E}$ sends a bounded set $\mathscr{G} \in \mathscr{H}$ to a finite-dimensional, bounded set, which is necessarily relatively compact. The image of a bounded set remains relatively compact when one passes to the norm-completion: any $c \in \mathscr{C}$ can be written as $a + \delta$, where $a \in \mathscr{E}$ and for any $\varepsilon > 0$, $\|\delta\| \leq \varepsilon / \sup_{v \in \mathscr{G}} \|v\|$, and $c\mathscr{G}$ is the relatively compact set $a\mathscr{G}$ added to a set of diameter less than ε. Relative compactness means that for any ε there exists a finite convering with balls of diameter less than ε, and this is also true of the image of $\mathscr{G}$ under $c \in \mathscr{C}$. This fact is the origin of the nomenclature for $\mathscr{C}$: compact operators carry bounded sets into relatively compact sets.
6. Completion of $\mathscr{E}$ in the strong topology yields all of $\mathscr{B}(\mathscr{H})$ (Problem 8), but the strong topology is not strong enough for Properties (iv) and (v) to carry over to $\mathscr{B}(\mathscr{H})$.
7. $\mathscr{B}(\mathscr{H})$, in the strong topology, is not a separable topological space (see (2.1.29; 1)) while $\mathscr{C}$ is separable when $\mathscr{H}$ is a separable Hilbert space.
8. The sets $\mathscr{C}_p$ can be defined for

$$1 \leq p < \infty \quad \text{as} \quad \{a \in \mathscr{C} : \|a\|_p = (\mathrm{Tr}(a^* a)^{p/2})^{1/p} < \infty\}.$$

The $\mathscr{C}_p$ are complete, normed algebras with $\| \ \|_p$, but are not C^* algebras (see (2.2.11; 2)). $\mathscr{C}$ is one, and $\mathscr{B}(\mathscr{H})$ is even a W^*-algebra.

Problems (2.3.24)

1. Show that the three conditions of Remark (2.3.6; 1) are equivalent under the restriction that in Condition (iii) the word "subspace" should be understood as "closed subspace."

2. Show that w is pure iff π_w is irreducible. (Hints: (i) w is pure iff for every positive linear functional w_1 such that $w_1 \leq w$, $w_1 = \lambda w$ for some $\lambda \in (0, 1]$; and (ii) if $w_1 \leq w$, then there exists a positive operator $t_0 \in \pi_w(\mathscr{A})'$, with $0 \leq t_0 \leq 1$, such that $w(b^* a) = \langle \pi_w(b)\Omega | t_0 \pi_w(a)\Omega \rangle$.)

3. Show that $\mathrm{Ker}\, \pi_w = \{a : w(b^* a^* a b) = 0 \text{ for all } b \in \mathscr{A}\}$.

4. Let $\mathscr{A}(\ni \mathbf{1})$ be a C^* algebra of operators in $\mathscr{B}(\mathscr{H})$. Show that $\mathscr{A}''$ is both the weak and the strong closure of $\mathscr{A}$. This is known as von Neumann's density theorem. (The argument for why $\mathscr{A}''$ is contained in the strong closure of $\mathscr{A}$ proceeds by the following steps:

   (i) Let $x \in \mathscr{H}$. The projection P onto the closure of $\{ax: a \in \mathscr{A}\}$ belongs to $\mathscr{A}'$.
   (ii) Let $b \in \mathscr{A}''$. Then $P\mathscr{H}$ is stable under b, and thus for all $\varepsilon > 0$ there exists an $a \in \mathscr{A}$ such that $\|bx - ax\| < \varepsilon$.
   (iii) It remains to be shown that finite intersections of neighborhoods of b of the kind considered in step (ii) with various x_i also contain elements of the strong closure of $\mathscr{A}$. To do this, take n nonzero vectors $x_1, x_2, \ldots, x_n$, and consider the representation π of $\mathscr{A}$ on $\mathscr{H} \oplus \mathscr{H} \oplus \cdots \oplus \mathscr{H}$; For any a, $\pi(a) = a \oplus a \oplus \cdots \oplus a$, which is known as the amplification of a. $\pi(b) \in \{\pi(a)\}''$, and the same argument as before, with $x = x_1 \oplus x_2 \oplus \cdots \oplus x_n$, shows that there exists an $a \in \mathscr{A}$ such that $\sum_{i=1}^{n} \|(b - a)x_i\|^2 < \varepsilon^2$.)

5. Show that the strong closure of the operators acting on $L^2(\mathbb{R}^n, d^n x)$ by multiplication by continuous functions is L^∞. (Hint: If $f \in L^\infty$, consider the continuous functions $(\rho * f)(x) \equiv \int d^n x' \, \rho(x - x') f(x')$ for ρ continuous and $\int \rho \, d^n x = 1$, and then let ρ approach a delta function.)

6. Show that the sum in (2.3.16) is orthogonal.

7. Construct an operator with a purely singular continuous spectrum.

8. Show that $\mathscr{E}$ is strongly dense in $\mathscr{B}(\mathscr{H})$. (Use the fact that every vector is cyclic for $\mathscr{E}$.)

9. Show that compactness of a Hermitian operator on an infinite-dimensional Hilbert space is equivalent to: $\sigma_{ac} = \sigma_s = \varnothing$ and $\sigma_{ess} = \{0\}$.

10. Prove Properties (2.3.19).

11. Prove Vigier's Theorem: *Every bounded, increasing filter F of operators has a supremum s, i.e., there exists an operator s such that $a \leq s$ for all $a \in F$, and $a \leq s'$ for all $a \in F \Rightarrow s \leq s'$. The supremum s is unique and belongs to the strong closure of F.*

Solutions (2.3.25)

1. (iii) $\Rightarrow$ (ii): Suppose $x \neq 0$. The closed subspace spanned by $\pi(a)x$, for $a \in \mathscr{A}$, is stable for all $\pi(a)$, and therefore identical to all of $\mathscr{H}$.
   (ii) $\Rightarrow$ (iii): Let $\mathscr{H}'$ be a nontrivial, closed, invariant subspace of $\mathscr{H}$ and let $x \in \mathscr{H}'$. Since $\pi(a)x \in \mathscr{H}'$ for all $a \in \mathscr{A}$, $\mathscr{H}'$ must be dense, so $\mathscr{H}' = \mathscr{H}$.
   (i) $\Rightarrow$ (iii): Let $\mathscr{H}' \subset \mathscr{H}$ be stable and P be the projection onto $\mathscr{H}'$. Then $P\pi(a)P = \pi(a)P$ for all $a \in \mathscr{A}$, so $P\pi(a^*)P = \pi(a^*)P$ for all $a \in \mathscr{A}$, which implies $P\pi(a) = \pi(a)P$, since $\pi(a^*) = \pi(a)^*$. But then $P = \mathbf{0}$ or $\mathbf{1}$.
   (iii) $\Rightarrow$ (i): If $a \in \pi(\mathscr{A})'$, then $a^* \in \pi(\mathscr{A})'$, and likewise for $b = a + a^*$ and $c = i(a - a^*)$. Hence all the spectral projections of b and c also belong to $\pi(\mathscr{A})'$. This means that a is a multiple of the identity, since every projection in $\pi(\mathscr{A})'$ defines a stable, closed subspace.
   Remark: It is also possible to show that for C^* algebras conditions (i)-(iii) are equivalent to algebraic irreducibility: The only invariant, closed *or unclosed* subspaces are $\{0\}$ and $\mathscr{H}$.

2. Proof of Lemma (i): *w is pure iff every $w_1 \leq w$ is of the form λw.*
$\Rightarrow$: $w = (w_1/w_1(1))w_1(1) + ((w - w_1)/(1 - w_1(1)))(1 - w_1(1))$ is a convex combination of two states unless $w_1 = \lambda w$.
$\Leftarrow$: w is not pure iff $w = \alpha w_1 + (1 - \alpha)w_2$, $\lambda w \neq w_1 \leq w$.
Proof of Lemma (ii): *The mapping $(\pi_w(b)\Omega, \pi_w(a)) \to w_1(b^*a)$ has a unique continuous extension to a positive bilinear form on $\mathscr{H} \times \mathscr{H}$, bounded by* 1. Hence there exists an operator t_0, $0 \leq t_0 \leq 1$, such that $w_1(b^*a) = \langle \pi_w(b)\Omega | t_0 \pi_w(a)\Omega \rangle$. (This is a direct corollary of the Riesz–Frêchet theorem (2.1.17), and is often referred to as the Lax–Milgram theorem). The substitution $a \to ca$ yields

$$\langle \pi_w(b)\Omega | t_0 \pi_w(c)\pi_w(a)\Omega \rangle = w_1(b^*ca) = w_1((c^*b)^*a)$$
$$= \langle \pi_w(c)^*\pi_w(b)\Omega | t_0 \pi_w(a)\Omega \rangle = \langle \pi_w(b)\Omega | \pi_w(c)^* t_0 \pi_w(a)\Omega \rangle \text{ for all } a, b \in \mathscr{A}$$
$$\Rightarrow [t_0, \pi_w(c)] = 0 \text{ for all } c \in \mathscr{A} \Rightarrow t_0 \in \pi(\mathscr{A})'.$$

Proof of the theorem:
$\Rightarrow$: Let P be a projection operator $\in \pi_w(\mathscr{A})'$. The mapping $a \to \langle P\Omega | \pi_w(a)P\Omega \rangle$ is a positive linear functional $\leq w$, so $\langle P\Omega | \pi_w(a)P\Omega \rangle = \lambda \langle \Omega | \pi_w(a)\Omega \rangle$, and if a is replaced with b^*a, then $\langle P\pi_w(b)\Omega | \pi_w(a)\Omega \rangle = \langle \lambda \pi_w(b)\Omega | \pi_w(a)\Omega \rangle$, which implies that $P = \lambda \cdot \mathbf{1}$, since Ω is cyclic, and thus $P = \mathbf{0}$ or $\mathbf{1}$.
$\Leftarrow$: Suppose $0 \leq w_1 \leq w$. Then $w_1(a) = \langle \Omega | t_0 \pi_w(a)\Omega \rangle = \lambda \langle \Omega | \pi_w(a)\Omega \rangle$, since $\pi_w(\mathscr{A})'$ consists only of scalars.

3. $w(b^*ac) = 0$ for all $b, c \in \mathscr{A} \Rightarrow w(b^*a^*ab) = 0$ for all b, using the substitution $b^* \to b^*a^*, c \to b$. Conversely, $w(b^*a^*ab) = 0$ for all $b \Rightarrow |w(b^*ac)|^2 \leq w(b^*b) \cdot w(c^*a^*ac)$, so $w(b^*ac) = 0$.

4. Since multiplication is continuous in one factor in any topology, it is easy to see that the strong closure of $\mathscr{A}$, which is contained in the weak closure of $\mathscr{A}$, is contained in $\mathscr{A}''$. Thus it suffices to show that $\mathscr{A}'' \subset$ the strong closure of $\mathscr{A}$.

   (i) Let $\mathscr{K} = \{ax : a = a^* \in \mathscr{A}\}$. $a\mathscr{K} \subset \mathscr{K} \Rightarrow a\overline{\mathscr{K}} \subset \overline{\mathscr{K}}$, where $\overline{\mathscr{K}}$ is the closure of $\mathscr{K}$. For any $\bar{x} \in \mathscr{H}$, $PaP\bar{x} = aP\bar{x} \Rightarrow aP = PaP = (PaP)^* = Pa \Rightarrow [a, P] = 0$.
   (ii) $bPh = bP = Pb \Rightarrow b\overline{\mathscr{K}} \subset \overline{\mathscr{K}} \Rightarrow bx \in \overline{\mathscr{K}}$.
   (iii) Operators t on $\mathscr{H} \oplus \cdots \oplus \mathscr{H}$ can be considered as matrices (t_{ik}) the entries of which belong to $\mathscr{B}(\mathscr{H})$, in which case $(\pi(a))_{ik} = a\delta_{ik}$. $([t, \pi(a)])_{ik} = t_{ik}a - at_{ik}$, i.e., $\{\pi(a)\}'$ consists of all t such that $t_{ik} \in \mathscr{A}'$, and therefore $\pi(b) \in \{\pi(a)\}''$.

5. Since f and ρ^*f are bounded, it suffices to show that $\|(f - \rho^*f)\varphi\|_2 \to 0$ for the dense set of $\varphi \in L^\infty$ and of compact support K. On K, f is also $\in L^2$, and

$$\|(f - \rho^*f)\varphi\|_2 \leq \|\varphi\|_\infty \|f - \rho^*f\|_2.$$

In Fourier-transformed space, $\|f - \rho^*f\|_2^2 = \int d^n k |\tilde{f}(k)|^2 |1 - \tilde{\rho}(k)|^2 \to 0$ if $\tilde{\rho}(k)$ tends monotonically to 1.

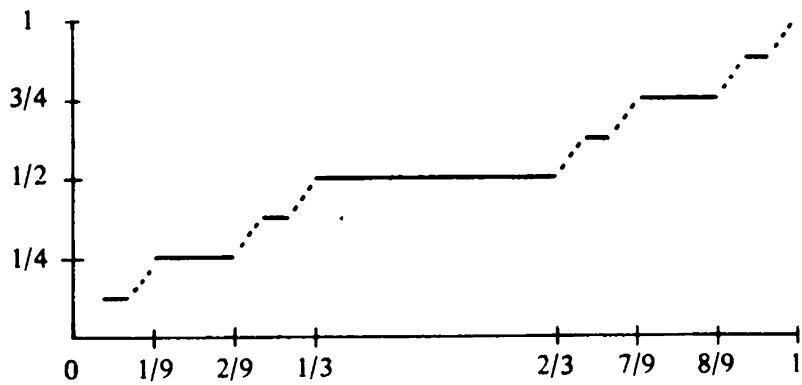
6. Let $a = \int dP_a(\alpha)\alpha$. To each vector x we can associate a measure $d\mu_x = d\langle x | P_a(\alpha)x \rangle$ and construct $\mathscr{H}_{ac} = \{x : d\mu_x$ is absolutely continuous with respect to $d\alpha\}$ and $\mathscr{H}_s' = \{x : d\mu_x$ is singular with respect to $d\alpha\}$. These two subspaces are orthogonal: Suppose $x \in \mathscr{H}_{ac}$ and $y \in \mathscr{H}_s'$; then there is a set M of Lebesgue measure zero on which $d\mu_y$ is concentrated. With the notation $P(M) = \int_M dP_a(\alpha)$, $(\mathbf{1} - P(M))y = 0$, and so $\langle x | y \rangle = \langle x | P(M)y \rangle = \langle P(M)x | y \rangle = 0$. Now consider arbitrary $x \in \mathscr{H}$; $d\mu_x$ can be decomposed into a singular and an absolutely continuous part: $d\mu_x = d\mu_x' + d\mu_x''$. (**Lebesgue decomposition**; see [1, 13.18.7].) Therefore there exists another

set M of Lebesgue measure zero, on which $d\mu_x^x$ is concentrated, and thus $P(M)x \in \mathscr{H}'_s$ and $(\mathbf{1} - P(M))x \in \mathscr{H}_{ac}$. Since $\mathscr{H}'_s \perp \mathscr{H}_{ac}$ and $\mathscr{H}'_s + \mathscr{H}_{ac} = \mathscr{H}$, $\mathscr{H} = \mathscr{H}'_s \oplus \mathscr{H}_{ac}$. It is obvious that $\mathscr{H}_p \subset \mathscr{H}'_s$ and $\mathscr{H}_s \subset \mathscr{H}'_s$. On the other hand, if $x \in \mathscr{H}'_s \ominus \mathscr{H}_p$, then $x \in \mathscr{H}_s$, and the same argument as before shows that $\mathscr{H}'_s = \mathscr{H}_p \oplus \mathscr{H}_s$.

7. Let f be the **Cantor function**, defined as follows: The **Cantor set** $\mathscr{C}$ in $[0, 1]$ is the complement of $(\frac{1}{3}, \frac{2}{3}) \cup (\frac{1}{9}, \frac{2}{9}) \cup (\frac{7}{9}, \frac{8}{9}) \cup (\frac{1}{27}, \frac{2}{27}) \cup \cdots$. It is a closed set of Lebesgue measure zero. Now let $f = \frac{1}{2}$ on $(\frac{1}{3}, \frac{2}{3})$, $\frac{1}{4}$ on $(\frac{1}{9}, \frac{2}{9})$, $\frac{3}{4}$ on $(\frac{7}{9}, \frac{8}{9})$, etc. (see figure below). The function f increases monotonically and has a unique extension to a continuous function. Let a be the multiplication operator on $\mathscr{H} = L^2([0, 1], df)$ defined by $\varphi(x) \to x\varphi(x)$. Then $P_a(\alpha)\mathscr{H} = \{\varphi: \varphi(x) = 0 \text{ for } x > \alpha\}$, and if $M \subset [0, 1]$, then

$$\|P(M)\varphi\|^2 = \int_M |\varphi(x)|^2 \, df.$$

In particular, $\|P(\mathscr{C})\varphi\|^2 = \|\varphi\|^2$, and hence $\mathscr{H}_{ac} = \{0\}$. The point spectrum is empty, since f has no discontinuities, so $\int_{\{\lambda\}} |\varphi(x)|^2 \, df = 0$ when the integral is over any one-point set $\{\lambda\}$.



8. Let x and $y \in \mathscr{H}$. The operator $a: v \to \langle x|v\rangle y$, which maps x to y, is of finite rank and therefore compact. Thus every vector is cyclic for the compact operators. Consequently, the compact operators form an irreducible C^* algebra and are strongly dense in $\mathscr{B}(\mathscr{H})$ by von Neumann's density theorem.

9. $\sigma_{ac} \subset \sigma_{ess}$ and $\sigma_s \subset \sigma_{ess}$. It is not possible for each set to consist of one isolated point, so $\sigma_{ess} = \{0\}$ implies $\sigma_{ac} = \sigma_s = \varnothing$. Now let a be compact and $\lambda \in \sigma_{ess}(a)$. There exists an orthonormal system $\{\psi_n\}$ such that $\|(a - \lambda)\psi_n\| \to 0$. The operator a sends the bounded set $\{\psi_n\}$ to a compact set, and hence $\{a\psi_n\}$ contains a strongly convergent subsequence $\{a\psi_{n_k}\}$. This implies that $\lambda = 0$, since no subsequence of $\{\psi_n\}$ is strongly convergent.

$\sigma_{ess}(a) = \{0\}$: Let $P_\varepsilon = P_a(\varepsilon) - P_a(-\varepsilon)$. Then $\dim(\mathbf{1} - P_\varepsilon)$ is finite for all $\varepsilon > 0$, so $a_n = \int_{-\infty}^{-1/n} dP_a(\alpha)\alpha + \int_{1/n}^{\infty} dP_a(\alpha)\alpha$ is of finite rank, and a fortiori compact. Since $\|a - a_n\| \leq 1/n$, a is compact.

10. (ii) $\operatorname{Tr} a = \sum_i \langle e_i|ae_i\rangle = \sum_i \|a^{1/2}e_i\|^2 = \sum_i \sum_k \langle Ue_k|a^{1/2}e_i\rangle^2 = \sum_k \sum_i |\langle Ue_k|a^{1/2}e_i\rangle|^2$

(since all summands are nonnegative), which $= \sum_k \|a^{1/2}Ue_k\|^2 = \operatorname{Tr} U^*aU$.

(iv) With the polar decompositions,

$$m_1 + m_2 = U|m_1 + m_2|, \qquad m_1 = V|m_1|, \qquad m_2 = W|m_2|,$$

$$\mathrm{Tr}|m_1 + m_2| = \sum_k \langle e_k|U^*(m_1 + m_2)e_k\rangle \le \sum_k (|\langle e_k|U^*V|m_1|e_k\rangle| + |\langle e_k|U^*W|m_2|e_k\rangle|) \le \mathrm{Tr}|m_1| + \mathrm{Tr}|m_2|.$$

For the final step, choose the e_k as the eigenvectors of $|m_1|$ and $|m_2|$, and observe that $\|V^*Ue_k\| \le 1$.

(v) The trace is a positive linear functional on the $n \times n$ matrices, and (v) holds for matrices by (2.2.20; 1). Since each $m_i \in \mathscr{C}_2$ can be written as a finite matrix plus something of arbitrarily small $\| \ \|_2$ norm, (v) holds for all of $\mathscr{C}_2$ by Remark (2.3.20; 3): It can first be extended to $m_1 \in \mathscr{A}$ and $m_2 \in \mathscr{C}_2$, and then to both $m_{1,2} \in \mathscr{C}_2$.

(vi) This follows from (ii), because any $a \in \mathscr{B}(\mathscr{H})$ is a linear combination of two Hermitian elements, each of which is in turn a linear combination of the positive elements $|a| \pm a$ or of the unitary elements $\|a\|^{-1}[a \pm i(\|a\|^2 - a^2)^{1/2}]$.

11. F is weakly relatively compact, and hence the set $\bigcap_{a \in F} \overline{\{b \in F: b \ge a\}}^{\text{weak}}$ is not empty, but must contain at least one element s. This $s \ge a$ for all $a \in F^{\text{weak}}$, since the weak topology can be defined with the seminorm $\langle x|\cdot x\rangle$, and thus the weak closure preserves the ordering. If the set $\bigcap_a \cdots$ contained two elements $s_1 \ne s_2$, then there would exist some $x \in \mathscr{H}$ such that $|(x|s_1x) - (x|s_2x)| = \varepsilon > 0$, as well as $a_1, a_2 \in F$ such that $|(x|s_ix) - (x|a_ix)| < \varepsilon/2$, $i = 1, 2$. But then there would exist some $c \in F: c \ge a_1$ and $c \ge a_2$, so that $\varepsilon = |(x|s_1x) - (x|s_2x)| \le |(x|s_1x) - (x|cx)| + |(x|s_2x) - (x|cx)| < \varepsilon/2 + \varepsilon/2 = \varepsilon$, which leads to a contradiction. The ... rimum $s \in F^{\text{strong}}$ by the inequality

$$((b-a)x|(b-a)x) = ((b-a)^{1/2}x|(b-a)^{3/2}x) \le (x|(b-a)x)^{1/2} \cdot \|x\| \, \|b\|^{3/2},$$

for all $b \ge a \ge 0$. $s' \ge a$ for all $a \in F \Rightarrow s' \ge a'$ for all $a' \in F^{\text{weak}}$, which $\Rightarrow s' \ge s$.

2.4 One-Parameter Groups

Just as in classical mechanics, quantum-mechanical time-evolution is a one-parameter group. The group has a weaker sort of continuity than norm-continuity, which shows up in the unboundedness of the generators.

The dynamics of a closed system can be described quantum-mechanically by an equation of the form

$$\frac{d}{dt} f = af, \tag{2.4.1}$$

where a is a time-independent operator. In this section we investigate the circumstances under which the formal solution,

$$f(t) = U_t f(0), \qquad U_t = \exp(at), \tag{2.4.2}$$

can be made sense of. In the applications f will be an element of a Banach space on which a acts linearly. From (2.4.2) we can abstract certain desiderata for an actual solution:

Definition (2.4.3)

A mapping $\mathbb{R}^+ \to \mathscr{B}(\mathbb{E}): t \to U_t$, is a **one-parameter semigroup** of operators on the Banach space $\mathbb{E}$ iff

(i) $U_{t_1+t_2} = U_{t_1} \cdot U_{t_2}$ for all $t_1, t_2 \geq 0$,
(ii) $U_0 = \mathbf{1}$.

If $\|U_t\| \leq 1$ (respectively $\|U_t\| = 1$), then we speak of **semigroups of contractions** (respectively **isometries**). If (i) and (ii) hold for all $t \in \mathbb{R}$ for a mapping $\mathbb{R} \to \mathscr{B}(\mathbb{E})$, then the semigroup is a group.

Remarks (2.4.4)

1. Since $U_{t_1}U_{t_2} = U_{t_1+t_2} = U_{t_2}U_{t_1}$, all operators of a semigroup commute.
2. Groups of contractions are groups of isometries, since by definition $\|U_t\| \leq 1$ for all $t \in \mathbb{R}$, while $1 = \|U_tU_{-t}\| \leq \|U_t\| \cdot \|U_{-t}\| \Rightarrow \|U_t\| \geq 1$, so $\|U_t\| = 1$. On a Hilbert space, isometric groups are unitary groups. since for all $x \in \mathscr{H}$,
$$\|x\| = \|U^{-1}Ux\| \leq \|Ux\| \leq \|x\|,$$
so U and U^{-1} are both isometric $\Leftrightarrow$ U is unitary.
3. It is advisable to impose some continuity requirement on the mapping $\mathbb{R}^+ \to \mathscr{B}(\mathbb{E})$, as some crazy functions $\mathbb{R} \to \mathbb{R}$ are known which are linear but discontinuous. It only takes the weak topology on $\mathscr{B}(\mathbb{E})$ to guarantee that the norms are uniformly bounded on an interval (Problem 1): $\sup_{0 \leq t \leq \delta} \|U_t\| = M < \infty$. It then follows from the group property that
$$\|U_t\| \leq M^{t/\delta} \text{ for all } t \geq 0,$$
so we may restrict ourselves to the study of the contractions $U_t M^{-t/\delta}$.

The strongest continuity property to require is that of the norm topology on $\mathscr{B}(\mathbb{E})$. It in fact implies analyticity.

Theorem (2.4.5)

For a semigroup, the following are equivalent:
(i) U_t *is norm-continuous*;
(ii) $\lim_{t \to 0} \|U_t - \mathbf{1}\| = 0$;
(iii) $\exists a \in \mathscr{B}(\mathbb{E})$, *such that* $\lim_{t \to 0} \|(1/t)(U_t - \mathbf{1}) - a\| = 0$;
(iv) $U_t = \sum_{n=0}^{\infty} a^n(t^n/n!)$.

Because of (iv), *we write* $U_t = \exp(at)$. *The semigroup can be extended to a group, in which case* $\|U_t\| \leq \exp(\|a\|\,|t|)$ *for all* $t \in \mathbb{R}$.

Proof

It is obvious that (iv) $\Rightarrow$ (i) $\Rightarrow$ (ii) $\Leftarrow$ (iii) $\Leftarrow$ (iv), so it only remains to show that (ii) $\Rightarrow$ (iv). It follows from $U(0) = \mathbf{1}$ and norm-continuity at $t = 0$ that

$$\frac{1}{\tau}\int_0^\tau dt\, U_t$$

is close to the identity operator for small enough τ, and hence invertible. Therefore

$$a_\tau = \frac{U_\tau - 1}{\tau}\,\frac{1}{(1/\tau)\int_0^\tau dt\, U_t}$$

is well defined for small enough τ. This a_τ does not actually depend on τ, because

$$a_{n\tau} = \frac{U_\tau^n - 1}{\int_0^{n\tau} dt\, U_t} = \frac{(U_\tau - 1)(1 + U_\tau + \cdots + U_\tau^{n-1})}{\int_0^\tau dt\, U_t(1 + U_\tau + \cdots + U_\tau^{n-1})} = a_\tau.$$

Consequently, $a_{\tau'} = a_\tau$ whenever τ' is a rational multiple of τ and, by continuity, for all τ'. Since it is a constant, we may rename it a, and write

$$U_t = 1 + a\int_0^t ds\, U_s,$$

which leads to (iv) by iteration. Property (iv) implies the estimate $\|U_t\| \leq \exp(\|a\|\,|t|)$. □

Remarks (2.4.6)

1. The exponential boundedness is the quantum version of a classical statement (I: 3.2.3; 6) for flows of bounded vector fields. Any faster growth, as for example for particles reaching infinity in a finite time, would violate the group structure.
2. It is of course possible for U_t to grow more slowly (e.g., for $a = \left(\begin{smallmatrix}0 & 1\\ 0 & 0\end{smallmatrix}\right)$, $\exp(at) = 1 + at$) or even not at all ($a = i\left(\begin{smallmatrix}0 & 1\\ 1 & 0\end{smallmatrix}\right)$, $\exp(at) = \cos t + a \sin t$).

We have seen that to each $a \in \mathscr{B}(\mathbb{E})$ there corresponds a U_t and vice versa. Now let us apply the methods of perturbation theory (I: §3.5) to the situation confronting us to evaluate the change in U_t if $a_0 \to a_0 + a_1$.

Theorem (2.4.7)

Let $U_t = \exp(a_0 t)$, $V_t = \exp((a_0 + a_1)t)$, $a_i \in \mathscr{B}(\mathbb{E})$. *Then*

(i) $\|U_t - V_t\| \leq |t| \|a_1\| \exp(|t|(2\|a_0\| + \|a_1\|))$;
and, on the other hand, for all $\lambda \geq \|a_0\| + \|a_1\|$,

(ii) $\|a_1\| \leq (\|a_0\| + \lambda)(\|a_0 + a_1\| + \lambda) \int_0^\infty dt\, e^{-\lambda t} \|U_t - V_t\|$.

Remarks (2.4.8)

1. Statement (i) is the precise analogue of the classical bound (I: 3.5.4), and (ii) says that any perturbation has a noticeable effect after a rather short time.
2. Perturbation theory becomes quite inaccurate at large times, so it is not well suited as a tool for the study of the limit $t \to \infty$.

Proof

(i) If we integrate

$$\frac{d}{d\lambda} \exp(a_0 t\lambda)\exp((a_0 + a_1)t(1 - \lambda))$$

$$= t\exp(a_0 t\lambda) a_1 \exp((a_0 + a_1)t(1 - \lambda))$$

between 0 and 1, we obtain

$$U_t - V_t = t \int_0^1 d\lambda\, U_{\lambda t} a_1 V_{t(1-\lambda)}.$$

With Theorem (2.4.5) this gives the bound (i).

(ii) This follows from the identity

$$a_1 = (a_0 - \lambda) \int_0^\infty dt\, e^{-\lambda t}(U_t - V_t)(\lambda - a_0 - a_1),$$

in which we have assumed that $\lambda \geq \|a_0\| + \|a_1\| \geq \max\{\|a_0\|, \|a_0 + a_1\|\}$ so as to be certain that the integral exists. □

There are many ways to construct V_t from U_t and a_1. These constructions are subject to the complications typical of noncommuting operators.

Theorem (2.4.9)

Let $a_1(t) \equiv \exp(-a_0 t) a_1 \exp(a_0 t)$. *Then*

(i) $\exp((a_0 + a_1)t) = \exp(a_0 t)(1 + \sum_{n=1}^\infty \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n\, a_1(t_1) \cdots a_1(t_n))$
(the Dyson expansion).

(ii) $\exp((a_0 + a_1)t) = \lim_{n \to \infty} (\exp(a_0 t/n)\exp(a_1 t/n))^n$
(the Trotter product formula).

Remarks (2.4.10)

1. The sum and limit as $n \to \infty$ converge in the norm topology.
2. The Dyson expansion is identical to the classical formula (I: 3.5.7), and (ii) also has a formulation for flows.
3. With the time-ordering symbol T, defined by

$$\mathrm{T}(a(t_1)a(t_2)\cdots a(t_n)) \equiv a(t_{i_1})a(t_{i_2})\cdots a(t_{i_n}),$$

where $t_{i_1} \geq t_{i_2} \geq t_{i_3} \geq \cdots \geq t_{i_n}$, Formula (i) can be written as

$$\exp(-a_0 t)\exp((a_0 + a_1)t) = \mathrm{T}\exp\left(\int_0^t dt' a_1(t')\right)$$

Proof

(i) $$\frac{d}{dt}\exp(-a_0 t)\exp((a_0 + a_1)t) = a_1(t)\exp(-a_0 t)\exp((a_0 + a_1)t)$$

$$\Rightarrow \exp((a_0 + a_1)t) = \exp(a_0 t)\left[1 + \int_0^t dt_1\, a_1(t_1)\exp(-a_0 t_1)\right.$$

$$\left.\times \exp((a_0 + a_1)t_1)\right],$$

from which (i) follows by iteration.

(ii) Let

$$S_n = \exp((a_0 + a_1)/n), \qquad T_n = \exp(a_0/n)\exp(a_1/n)$$

$$S_n^n - T_n^n = \sum_{m=0}^{n-1} S_n^m (S_n - T_n) T_n^{n-m-1}.$$

Since for all $k \leq n$, both $\|S_n^k\|$ and $\|T_n^k\| \leq \exp(\|a_0\| + \|a_1\|)$,

$$\|S_n^n - T_n^n\| \leq n\|S_n - T_n\|\exp(\|a_0\| + \|a_1\|).$$

However,

$$\|S_n - T_n\| = \left\| \sum_{m=0}^{\infty} \frac{1}{m!}\left(\frac{a_0 + a_1}{n}\right)^m - \left(\sum_{m=0}^{\infty} \frac{1}{m!}\left(\frac{a_0}{n}\right)^m\right)\right.$$

$$\left.\times \left(\sum_{m=0}^{\infty} \frac{1}{m!}\left(\frac{a_1}{n}\right)^m\right)\right\| \leq \frac{c}{n^2},$$

so

$$\|S_n^n - T_n^n\| \to 0.$$

□

Example (2.4.11)

Perturbation of the Larmor precession of a spin. Let $a_0 = i\sigma_x$ and $a_1 = ig\sigma_y$, with the σ's from (2.2.37). Since $(\mathbf{b}\cdot\boldsymbol{\sigma}) = |\mathbf{b}|^2$, it follows that

$$\exp((a_0 + a_1)t) = \cos t\sqrt{1+g^2} + i(\sigma_x + g\sigma_y)\frac{1}{\sqrt{1+g^2}}\sin t\sqrt{1+g^2}.$$

This is an entire function of g for all $t \in \mathbb{R}$, and (2.4.9(i)) is its Taylor series. The latter is rather cumbersome, because the t dependence is greatly affected by g as it varies in $\mathbb{C}$. It is oscillatory if g is real, linear if $g = \pm i$, and otherwise it grows exponentially.

We must next confront the physically important case where U_t is only strongly continuous. The integral $(1/\tau)\int_0^\tau dt\, U_t$ will not converge uniformly to the operator $\mathbf{1}$, and might not be invertible even for very small τ. If we simply formally adopt the expression derived above for the generator

$$a = \frac{U_\tau - 1}{\tau}\left[\frac{1}{\tau}\int_0^\tau dt\, U_t\right]^{-1},$$

we find that it is not an element of $\mathscr{B}(\mathbb{E})$, but at least it is still true that a is defined on a dense set of $\varphi \in \mathbb{E}$: The inverse must certainly exist on vectors $\in \mathbb{E}$ of the form

$$\psi = \frac{1}{\tau}\int_0^\tau dt\, U_t\cdot\varphi, \qquad \varphi \in \mathbb{E}, \qquad \tau > 0 \quad \text{and} \quad a\psi = \frac{U_\tau - 1}{\tau}\varphi.$$

Since strong continuity means that $(1/\tau)\int_0^\tau dt\, U_t\varphi$ converges to φ as $\tau \to 0$, every vector φ of $\mathbb{E}$ can be approximated arbitrarily well by such a ψ. On ψ it is also true that

$$a\psi = \lim_{h\to 0}\frac{U_h - 1}{h}\psi,$$

because

$$(U_h - 1)\int_0^\tau dt\, U_t = \int_\tau^{\tau+h} dt\, U_t - \int_0^\tau dt\, U_t = (U_\tau - 1)\int_0^h dt\, U_t,$$

so

$$\frac{U_h - 1}{h} = \frac{U_\tau - 1}{\tau}\left[\int_0^\tau \frac{dt}{\tau}\, U_t\right]^{-1}\frac{1}{h}\int_0^h ds\, U_s.$$

Since the last factor converges strongly to $\mathbf{1}$ as $h \to 0$, we make

Definition (2.4.12)

The **generator** a of a strongly continuous semigroup U_t is a linear mapping $D(a) \to \mathbb{E}$ for which the **domain of definition**

$$D(a) = \left\{ \psi \in \mathbb{E} \colon \exists \lim_{h \to 0} \frac{U_h - 1}{h} \psi \equiv a\psi \right\}$$

is dense in $\mathbb{E}$. The image of $D(a)$ is the **range** of a, $\mathrm{Ran}(a) \equiv aD(a) \subset \mathbb{E}$.

Example (2.4.13)

$\mathbb{E} = l^2, \psi = (v_1, v_2, \ldots, v_n, \ldots), U_t\psi = (e^{it}v_1, e^{2it}v_2, \ldots, e^{nit}v_n, \ldots)$ is strongly but not uniformly (=norm) continuous, $a\psi = i(v_1, 2v_2, \ldots, nv_n, \ldots)$.

$$D(a) = \left\{ \psi \in l^2 \colon \sum_{n=1}^{\infty} |nv_n|^2 < \infty \right\}$$

is dense in l^2 but not equal to all of l^2.

Remarks (2.4.14)

1. The condition of strong continuity may be weakened to weak continuity; as for instance the strong and weak topologies are the same for unitary operators on Hilbert space.
2. Furthermore, even weak measurability (i.e., $t \to \langle \psi | U_t \varphi \rangle$ is measurable for all φ and $\psi \in \mathscr{H}$) is equivalent to strong continuity for unitary groups on separable Hilbert spaces $\mathscr{H}$. This is not true for nonseparable Hilbert spaces: Let $\mathscr{H} = \bigoplus_x \mathscr{H}_x$, $\mathscr{H}_x = \mathscr{C}$ for all $x \in \mathbb{R}$, where the uncountable sum is to be understood in the sense that only countably many of the components ψ_x of a vector ψ are nonzero, and

$$\|\psi\|^2 = \sum_x |\psi_x|^2.$$

   If $(U_t\psi)_x = \psi_{x+t}$, then $t \to U_t$ is a unitary group that is weakly measurable but not weakly continuous: $\langle \psi | U_t \psi \rangle = \|\psi\|^2$ for $t = 0$ and is otherwise nonzero for only countably many t's. In this example, there exists no generator of any kind.
3. In order for $t \to U_t$ to be strongly differentiable, it is necessary for a to be $\in \mathscr{B}(\mathbb{E})$ and $D(a) = \mathbb{E}$. But then $t \to U_t$ is in fact analytic and strong differentiability is equivalent to the conditions of Theorem (2.4.5).
4. If a unitary group acts on a Hilbert space, ia must be Hermitian:

$$\langle ia\psi | \varphi \rangle = \langle \psi | ia\varphi \rangle \quad \text{for} \quad \text{all } \psi, \varphi \in D(a).$$

This can be seen just as for finite matrices,

$$\langle a\psi|\varphi\rangle = \lim_{h\to 0}\left\langle \frac{U_h - 1}{h}\psi|\varphi\right\rangle = \lim_{h\to 0}\left\langle \psi\left|\frac{U_{-h}-1}{h}\varphi\right.\right\rangle = -\langle\psi|a\varphi\rangle,$$

the only additional complication being to worry about the domains. Unitary semigroups can obviously be extended to unitary groups, even if only strongly continuous.

If U_t is only strongly continuous, then although $D(a)$ is dense in $\mathscr{H}$, it is not all of $\mathscr{H}$, that is, there are sequences $\varphi_n \in D(a)$ which converge, $\varphi_n \to \varphi$, but the limit $\varphi \notin D(a)$. Yet if $a\varphi_n$ converges to some $\psi \in \mathscr{H}$, then $\varphi \in D(a)$ and $\psi = a\varphi$ (Problem 2). This property will be important later on, for which reason we make the

Definition (2.4.15)

The **graph** Γ of an operator $a: D \to \mathbb{E}$ is $\Gamma(a) \equiv \{(\psi, \varphi) \in D \times \mathbb{E}: \varphi = a\psi\}$. If $\Gamma(a)$ is a closed subspace of $\mathbb{E} \times \mathbb{E}$, a is said to be **closed**.

Examples (2.4.16)

1. $\mathbb{E} = L^2([0, 1], d\alpha)$, $(a\psi)(\alpha) = (1/\alpha)\psi(\alpha)$ with the domain
$$D_1(a) = \{\psi \in \mathbb{E}: \psi = 0 \text{ on some neighborhood of } 0\}.$$
The operator a is not closed, for consider $\psi_n = \alpha$ when $\alpha > 1/n$ and otherwise $\psi_n = 0$; then $\psi_n \to \psi(\alpha) = \alpha$ and $a\psi_n \to 1$, but $\psi \notin D(a)$.
2. Let a and $\mathbb{E}$ be as in Example 1, but take
$$D_2(a) = \left\{\psi \in \mathbb{E}: \int_0^1 \left|\frac{1}{\alpha}\psi(\alpha)\right|^2 d\alpha < \infty\right\}.$$
Since D_2 contains all ψ for which $a\psi \in \mathbb{E}$, a is closed on D_2.
3. Let $a\varphi = 1 \cdot \varphi(\frac{1}{2})$, $D(a) = \{\varphi \in L^2([0, 1] \equiv \mathscr{H}, d\alpha), \varphi \text{ continuous}\}$. This operator is not closed, since $\varphi_n \equiv \exp(-(\alpha - \frac{1}{2})^2 n^2) \to 0$ because $\|\varphi_n\| = 0(1/n)$, but $a\varphi_n = 1 \not\to 0$.

Remarks (2.4.17)

1. Note that Γ is required to be closed in $\mathbb{E} \times \mathbb{E}$ and not in $D \times \mathbb{E}$. By this definition with $\mathbb{E} = [0, \infty)$, the mapping $x \to 1/x$, $D = (0, \infty)$, is closed, while $x \to x$, $D = (0, \infty)$ is not.
2. Since the graph of a continuous mapping is always closed (Problem 4) Γ is closed in $D \times \mathbb{E}$ whenever a is continuous. Hence a is closed iff D is closed (and therefore equal to $\mathbb{E}$).

3. Definition (2.4.15) is equivalent to the statement that $D \ni \psi_n \to \psi$, $a\psi_n \to \varphi \Rightarrow \psi \in D$, $\varphi = a\psi$, and to the statement that D is complete in the norm $\|\psi\|_a = \|\psi\| + \|a\psi\|$ (Problem 3).
4. If $aD(a)$ is dense in $\mathbb{E}$, then a^{-1} is a densely defined operator, and it is closed whenever a is, since $\Gamma(a^{-1}) = J\Gamma(a)$, where $J(x, y) = (y, x)$.
5. It might be imagined that whenever an operator is not closed, the domain has merely been chosen too small, and that by taking the closure $\bar{\Gamma}$ of Γ in $\mathbb{E} \times \mathbb{E}$ one would get a closed operator. This does not always work, as $\bar{\Gamma}$ might not be the graph of an operator. The trouble can be understood with $\theta(x) = 1$ for $x > 0$ and 0 for $x < 0$; the closure of the graph assigns the two values 0 and 1 to the point $x = 0$. It is also clear in Example (2.4.16; 3) that making $D(a)$ larger will not produce a closed operator.

The operator a: $D(a) \to \mathbb{E}$ of (2.4.12) is a discontinuous mapping. Continuity of a linear operator is equivalent to continuity at any single point and to boundedness. All of these conditions imply that there exists an $M \in \mathbb{R}^+$ such that $\|a\psi\| \leq M\|\psi\|$ for all $\psi \in D(a)$. The connection between the notion of continuity and the notions of closure and domain of definition is:

Theorem (2.4.18)

Any two of the three properties
(i) $D(a) = \mathbb{E}$;
(ii) *a is continuous; and*
(iii) *a is closed*
imply the third.

Proof

(i) $\wedge$ (ii) $\Rightarrow$ (iii): Every graph of a continuous mapping is closed.
(ii) $\wedge$ (iii) $\Rightarrow$ (i): This was explained in (2.4.17; 2).
(i) $\wedge$ (iii) $\Rightarrow$ (ii): This follows from the closed-graph theorem [1, (12.16.1)], which is rather profound and cannot be proved here. □

Corollaries (2.4.19)

1. If an operator is closed but not continuous, it can not be defined everywhere.
2. If an operator is defined on all vectors and is discontinuous, then it is not closed (cf. (2.1.15; 2)).
3. If an operator is continuous, then it can be extended to all of $\mathbb{E}$, and it is thus closeable.

Since the difficulties attendant on the definition of a have to do with the inversion of an operator, a reasonable expectation would be that the resolvent $R_z \equiv (a - z)^{-1}$ of the operator a ought to belong to $\mathscr{B}(\mathbb{E})$. If we write formally that $U_t = \exp(at)$, then

$$R_z = -\int_0^\infty dt\, e^{-tz} U_t.$$

In fact, for this formula there is a

Theorem (2.4.20)

Let U_t be a strongly continuous contractive semigroup, with generator a. Then for all $z \in \mathbb{C}$ with Re $z > 0$,

$$R_z = -\int_0^\infty dt\, e^{-tz} U_t$$

maps $\mathbb{E}$ into $D(a)$. The resolvent satisfies $(a - z)R_z = \mathbf{1}$ and $\|R_z\| \leq (\text{Re } z)^{-1}$.

Proof

The statement about the norm follows from $\|U_t\| \leq 1$. If a operates after R_z, then

$$aR_z = \lim_{h \to 0} \frac{U_h - 1}{h} R_z = \lim_{h \to 0} \frac{1 - e^{hz}}{h} \int_0^\infty dt\, e^{-zt} U_t + \frac{e^{zh}}{h} \int_0^h dt\, e^{-zt} U_t.$$

The first term converges uniformly to zR_z, and the second term converges strongly to $\mathbf{1}$. □

The problems that arise in physics usually go the other way: a is given and one tries to find U_t. It might be supposed that U_t could be defined as $\sum_{n=0}^\infty (t^n/n!)a^n$, but this often leads to disasters.

Example (2.4.21)

Let $\mathbb{E} = L^2((0, 1), dx)$. Let us try to write the group of translations $\exp(itp)$ as a unitary family of operators by using the generator $p = -i(d/dx)$. So that all powers of id/dx will be well defined and Hermitian, we choose $D(p) = C_0^\infty(0, 1)$. These functions are supported within (0, 1), so

$$\left\langle \frac{d^n}{dx^n} \psi \middle| \varphi \right\rangle = (-1)^n \left\langle \psi \middle| \frac{d^n}{dx^n} \varphi \right\rangle \quad \text{for all } \psi, \varphi \in D\left(\frac{d}{dx}\right),$$

and $\sum_{n=0}^\infty (t^n/n!)(d^n/dx^n)$ is formally unitary. Unfortunately, the analytic functions on a complex neighborhood of (0, 1) for which this sum has a

finite radius of convergence for all $x \in (0, 1)$ are not included in $D(-i\,d/dx)$. Moreover, it is impossible to construct a unitary, finite translation this way, since it would have to translate part of the function out of (0, 1), and the missing part would affect the normalization integral:

$$\int_0^1 dx|\psi(x+t)|^2 = \int_t^1 dx|\psi(x)|^2 + \text{something unknown},$$

since $\psi(x)$ is not defined for $1 < x < 1 + t$ (see Figure 3).

Likewise, the attempt to write $U_t = \lim_{n\to\infty}(1 + at/n)^n$ opens the question of what $D(a^n)$ are for all $n \in \mathbb{Z}$. However, the use of the resolvent integral works without such difficulties, because it involves bounded operators only. It turns out that the properties we have found of a characterize the generators of semigroups; every such a determines a unique U_t.

The Hille–Yosida Theorem (2.4.22)

Let a be a densely defined operator such that $(a - x)^{-1}: \mathbb{E} \to D(a)$ is bounded in norm as $\|(a - x)^{-1}\| \leq |x^{-1}|$ for all $x > 0$. Then there exists a unique contractive semigroup U_t satisfying

$$\lim_{h\to 0} \frac{U_h - 1}{h}\varphi = a\varphi \quad \text{for all} \quad \varphi \in D(a).$$

Remarks (2.4.23)

1. It then follows from (2.4.20) that $(a - z)^{-1}$ exists for all z with $\operatorname{Re} z > 0$, and is bounded in norm by $(\operatorname{Re} z)^{-1}$.
2. Since $(a - x)^{-1}$ is defined on all of $\mathbb{E}$ and bounded, it is closed by Theorem (2.4.18). According to Remark (2.4.17; 4), $a - x$ and a are then also closed.
3. If $(a - x)^{-1}$ is defined only on a dense subspace, but is bounded there by $|x^{-1}|$, then it has a unique extension to all of $\mathbb{E}$, and Theorem (2.4.22) is still valid.
4. In the proof below we try to recover a from the resolvent by taking the limit $\lim_{x\to\infty}(-x - x^2(a - x)^{-1})$. It is also possible to work with $\exp(at) = \lim_{n\to\infty}(1 - at/n)^{-n}$.

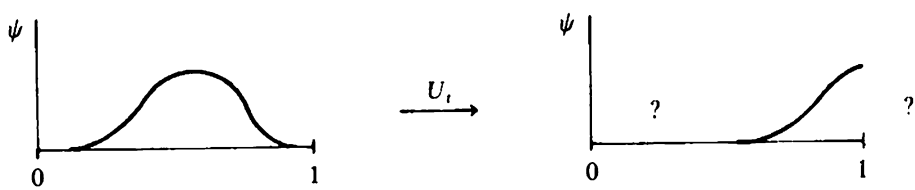


Figure 3 Unitary representation of the translation on [0, 1].

5. Vectors φ on which $a^n\varphi$ is defined for all n and $\sum_n t^n\|a^n\varphi\|/n!$ converges for $|t| < t_0 > 0$ are called **analytic vectors**, or **entire vectors** if $t_0 = \infty$. The semigroup $\exp(at)$ is uniquely defined if a has a dense set of analytic vectors.

Proof

Let $a_x = -x - x^2(a - x)^{-1}$. For all $\varphi \in D(a)$, $a_x\varphi \to a\varphi$ as $x \to \infty$ (Problem 5). Consider the semigroup generated by $a_x \in \mathscr{B}(\mathbf{E})$. By Theorem (2.4.7), since the semigroups generated by a_{x_1} and a_{x_2} commute, for all x_1 and $x_2 > 0$ and $\varphi \in D(a)$,

$$\|(\exp(ta_{x_1}) - \exp(ta_{x_2}))\varphi\| \leq c\|(a_{x_1} - a_{x_2})\varphi\|.$$

Because the vectors $a_x\varphi$ converge as $x \to \infty$, the vectors $\exp(ta_x)\varphi$ form a Cauchy sequence, which must always have a limit in a Banach space $\mathbf{E}$. Call the limit $U_t\varphi$. The operator U_t can be extended uniquely to $\mathbf{E}$, as the $\exp(ta_x)$ are uniformly bounded in x. To see that a is the generator of U_t, take the limit $x \to \infty$ of

$$\exp(a_x t)\varphi = \varphi + \int_0^t ds \exp(a_x s)a_x\varphi \text{ for } \varphi \in D(a).$$

Uniqueness follows from

$$\langle\psi|(a - x)^{-1}\varphi\rangle = -\int_0^\infty dt \exp(-xt)\langle\psi|U_t\varphi\rangle$$

and the fact that the Laplace transformation is injective on the continuous functions.

Corollary (Stone's Theorem) (2.4.24)

The operator ia is the generator of a unitary group on a Hilbert space $\mathscr{H}$ iff
(i) $\langle\psi|a\varphi\rangle = \langle a\psi|\varphi\rangle$ for all $\psi, \varphi \in D(a)$, *and*
(ii) $(a \pm i)D(a) = \mathscr{H}$.

Proof

It only needs to be shown that $(a - z)D(a) = \mathscr{H}$ for all z with $\operatorname{Im} z \neq 0$ when this holds for $z = \pm i$ and that $\|(a - z)^{-1}\| \leq |\operatorname{Im} z|^{-1}$. This is done in Problem 6. □

Examples (2.4.25)

1. The a of example (2.4.13) obviously satisfies (i). It also satisfies (ii), since for any $\psi = (v_1, v_2, \ldots) \in l^2$ and $z \notin \mathbb{N}$,

$$\varphi = (a - z)^{-1}\psi = \left(\frac{v_1}{1 - z}, \frac{v_2}{2 - z}, \ldots, \frac{v_n}{n - z} \ldots\right) \in D(a)$$

and $(a - z)\varphi = \psi$.

2. In the troublesome Example (2.4.21), (i) is satisfied, as a never sends a vector out of $D(a)$. Since $C_0^\infty(0, 1)$ is not all of $L^2((0, 1), dx)$, (ii) is violated. $(-i(d/dx) - z)C_0^\infty(0, 1)$ is not even dense in $L^2(0, 1)$, since $\psi = e^{izx}$ is orthogonal to it: $\int_0^1 dx\, e^{-izx}(-i(d/dx) - z)\varphi(x) = 0$ for all $\varphi \in C_0^\infty(0, 1)$.

In later sections we shall consider under what circumstances formal expressions for a can be interpreted so that the Hille–Yosida Theorem (2.4.22) applies, and whether the perturbation-theoretic formulas (2.4.7) and (2.4.9) also make some sense for only strongly continuous semigroups.

Problems (2.4.26)

1. Show that the norms $\|U_t\|$ of a weakly continuous semigroup U_t are bounded for t in some interval $[0, \delta]$. Hint: argue as with the uniform boundedness principle.

2. Verify that if U_t is strongly continuous, then (cf. (2.4.12))

$$a = \frac{dU}{dt}, \qquad D(a) = \left\{\varphi \in \mathbb{E}: \lim_{h \to 0} \frac{U_h - 1}{h} \varphi \text{ exists}\right\},$$

is a closed operator.

3. Show that an operator a on D is closed if D is complete in the norm $\|\psi\|_a = \|\psi\| + \|a\psi\|$.

4. Why is the graph of a continuous mapping $\mathbb{E} \to \mathbb{E}$ closed in $\mathbb{E} \times \mathbb{E}$?

5. Investigate the convergence of a_x from the proof of (2.4.22).

6. Let a be a Hermitian operator. Show that the existence of $(a \pm i)^{-1}$ implies that of $(a - z)^{-1}$ for all z with $\operatorname{Im} z \neq 0$, and that $\|(a - z)^{-1}\| \leq |\operatorname{Im} z|^{-1}$.

Solutions (2.4.27)

1. Let $p(\varphi) = \sup_{0 \leq t \leq \delta} |\langle \psi | U_t \varphi \rangle|$, fixing ψ for the moment. For any such ψ and $\varphi \in \mathbb{E}$, $p(\varphi)$ is the supremum of a continuous function on a compact set and consequently finite, and the mapping $\varphi \to p(\varphi)$ is lower semicontinuous in the norm topology. Moreover, $p(\varphi_1 + \varphi_2) \leq p(\varphi_1) + p(\varphi_2)$ and $p(\alpha\varphi) = |\alpha| p(\varphi)$. If p is bounded on any closed ball, then it is bounded everywhere, because

$$p(\varphi_0 - \varphi) < M \text{ for all } \|\varphi\| \leq \varepsilon \Rightarrow p(\varphi) = \frac{\|\varphi\|}{\varepsilon} p\left(\frac{\varepsilon\varphi}{\|\varphi\|}\right) \leq \|\varphi\| \frac{p(\varphi_0) + M}{\varepsilon}.$$

Unboundedness of p on every ball would contradict lower semicontinuity: If p were unbounded on the ball K_{n-1}, then there would be $\varphi_n \in K_{n-1}$ with $p(\varphi_n) > n$. Since p is lower semicontinuous, there must exist a ball $K_n \subset K_{n-1}$ containing φ_n and such that $p(\varphi) > n$ for all $\varphi \in K_n$. Since p must also be unbounded on the ball K_n, K_n must contain a φ_{n+1} such that $p(\varphi_{n+1}) > n + 1$ and another ball $K_{n+1} \subset K_n$ such that $p(\varphi) > n + 1$ for all $\varphi \in K_{n+1}$. The closed balls $K_1 \supset K_2 \supset \cdots$ are weakly compact, so there must exist some $\varphi \in \bigcap_n K_n$. Then $p(\varphi)$ would be greater than any n, which would contradict the finiteness of $p(\varphi)$ for all φ. Thus we conclude that $p(\varphi) < M_1\|\varphi\|$, and, using the same argument for ψ, that

$$\sup_{0\le t\le\delta}\|U_t\| = \sup_{\substack{\|\psi\|=1\\ \|\varphi\|=1}} \sup_{0\le t\le\delta} |\langle\psi|U_t\varphi\rangle| \le M.$$

2. Let $\varphi_n \to \varphi$, $a\varphi_n \to \psi$:

$$\lim_{h\to 0}\frac{U_h - 1}{h}\varphi = \lim_{h\to 0}\lim_{n\to\infty}\frac{U_h - 1}{h}\varphi_n = \lim_{h\to 0}\lim_{n\to\infty}\frac{1}{h}\int_0^h U_h a\varphi_n$$

$$= \lim_{h\to 0}\frac{1}{h}\int_0^h U_h\psi = \psi \Rightarrow \varphi \in D(a),\ a\varphi = \psi.$$

3. A set (φ, ψ) in $\mathscr{H} \times \mathscr{H}$ is closed provided that it is complete in the norm $\|\varphi\| + \|\psi\|$. For a graph this norm is $\|\varphi\|_a = \|\varphi\| + \|a\varphi\|$.

4. Since $\|a\varphi\| \le \|a\|\,\|\varphi\|$, the norm $\|\varphi\| + \|a\varphi\|$ is equivalent to $\|\varphi\|$, and the graph is closed if $D(a)$ is closed.

5. For all $\varphi \in D(a)$,

$$\lim_{x\to\infty}(1 + x(a - x)^{-1})\varphi = \lim_{x\to\infty}(a - x)^{-1}a\varphi = 0.$$

But if the bounded operators $-x/(a - x)$ converge on a dense set to 1, then they converge to 1 on the whole space, so

$$\lim_{x\to\infty}(-x(a - x)^{-1}a\varphi) = \lim_{x\to\infty} a_x\varphi = a\varphi$$

for all $\varphi \in D(a)$.

6. If a is Hermitian and $\mathrm{Ran}(a + i) = \mathscr{H}$, then $\|(a + i)^{-1}\| \le 1$, since $(a + i)^{-1}x = y \Rightarrow \|x\|^2 = \|ay\|^2 + \|y\|^2$, and

$$\sup_x \frac{\|y\|^2}{\|x\|^2} = \sup_y \frac{\|y\|^2}{\|x\|^2} \le 1.$$

Hence

$$(a + i + z)^{-1} = (a + i)^{-1}\sum_n (z(a + i)^{-1})^n$$

has radius of convergence 1. The operators $a \pm 3i/2$, $a \pm 2i$, etc., have the same properties, and expansions around these points also converge up to the real axis, so the open half-planes can eventually be covered by such discs. For the second part, note that $(a + u + iv)^{-1}x = y$, $u, v \in \mathbb{R}$, $\Rightarrow \|x\|^2 = \|(a + u)y\|^2 + v^2\|y\|^2 \Rightarrow \|y\|^2/\|x\|^2 \le 1/v^2$.

2.5 Unbounded Operators and Quadratic Forms

The generators of strongly continuous unitary groups are self-adjoint operators. Under the right circumstances, the domain of a formally Hermitian expression can be chosen so as to make it self-adjoint.

Typically, a physicist is confronted with an unbounded Hermitian operator, and an important question is in what sense does such an operator generate a one-parameter group as the time-evolution. Since it is not always possible in classical mechanics to generate a satisfactory time-evolution—vector fields may fail to be complete, and a particle may reach infinity in a finite time—one must be prepared for trouble when doing quantum mechanics. Yet we shall discover later that the situation with $1/r$ potentials is much better quantum-theoretically than classically, and that the rather annoying question of the existence of collision trajectories in the classical three-body problem will cause no difficulty in quantum mechanics.

Our first task is to generalize the definition of the adjoint of an operator (2.1.26; 3) to cover unbounded operators, so as to ensure that all self-adjoint operators on Hilbert space generate unitary groups.

Definition (2.5.1)

The **adjoint operator** a^* of an unbounded operator a having a dense domain $D(a)$ in $\mathscr{H}$ is defined on the domain

$$D(a^*) = \left\{ \varphi \in \mathscr{H} : \sup_{\psi \in D(a)} |\langle \varphi | a\psi \rangle| \, \|\psi\|^{-1} < \infty \right\}$$

by the formula $\langle \varphi | a\psi \rangle = \langle a^*\varphi | \psi \rangle$ for all $\psi \in D(a)$, $\varphi \in D(a^*)$.

If $a = a^*$, then a is said to be **self adjoint**;
if $a^* = a^{**}$, then a is **essentially self adjoint**;
if $a^* \supset a$, then a is **Hermitian**.

The symbol $b \supset a$ means that b is an extension of a: $D(b) \supset D(a)$ and $b_{|D(a)} = a$.

Remarks (2.5.2)

1. Since it is assumed that $D(a)$ is dense, (2.5.1) defines a^* uniquely.
2. The choice of the domain D for a fixes the domain of a^*; if $a^*\varphi \in \mathscr{H}$, then $\psi \to (a^*\varphi | \psi)$ is a continuous functional. $D(a^*)$ consists of all φ for which $\psi \to \langle \varphi | a\psi \rangle$ is a continuous functional $D \to \mathbb{C}$: it is thus the biggest possible domain.
3. If $D(a^*)$ is dense, then a^{**} is defined uniquely, and $a^{**} \supset a$. This is the case for Hermitian operators, since $D(a^*) \supset D(a)$, but in general $D(a^*)$ need be no larger than $\{0\}$.

4. If a is continuous, then $D(a^*) = \mathscr{H}$. This accords with Remark (2.1.26; 3), by which $a: D \to \mathscr{H}$ induces the mapping $a^*: \mathscr{H}^* = \mathscr{H} \to D^* = \mathscr{H}$. If, in addition, $D(a) = \mathscr{H}$, then the concepts of Hermitian and self-adjoint become synonymous.
5. $a \subset b \Rightarrow a^* \supset b^*$. In particular, a is Hermitian iff $a^* \supset a$, which implies that $a \subset a^{**} \subset a^*$; and a^* is Hermitian iff $a^{**} \supset a^*$. Therefore, if a and a^* are Hermitian, then a^* is self adjoint and a is essentially self-adjoint. Moreover, if b is a Hermitian extension of a, $a \subset b \subset b^* \subset a^*$; then b is determined by its domain, on which it must have the same action as a^*.
6. If a is essentially self-adjoint, then $a^* = a^{**} \supset a$ is the unique self-adjoint extension of a. $a \subset b = b^* \Rightarrow a^* \supset b^* = b^{**} \supset a^{**} = a^*$. The advantage of speaking of essential self-adjointness is the flexibility it allows in the choice of $D(a)$; a change in the domain $D(a)$ can leave a essentially self-adjoint, but it necessarily alters the statement that $a = a^*$.
7. The graph $\Gamma(a^*)$ (see (2.4.15)) can be described as follows: Let J be the unitary operator $(x, y) \to (y, -x)$ on $\mathscr{H} \oplus \mathscr{H}$. Then $\Gamma(a^*) = (J\Gamma(a))^\perp$ (Problem 3). Any subspace defined by orthogonality is closed, so a^* is always a closed operator. If a is Hermitian, then its closure is a^{**}, since $J^2 = -1$ and $(J(J\Gamma^\perp))^\perp = \bar{\Gamma}$. Hence Hermitian operators are always closeable, and we may assume them closed without loss of generality.

Examples (2.5.3)

1. Let us recall Examples (2.4.16; 1) and (2.4.16; 2). Define $a_{1,2} \equiv a$ with the domains D_1 and D_2. The operator a_1 is not self-adjoint, since it is not closed. What is a_1^*? Its domain consists of all φ such that

$$\sup_{\psi \in D_1} \int_0^1 d\alpha \frac{1}{\alpha} \varphi^*(\alpha)\psi(\alpha) \left| \int_0^1 d\alpha |\psi(\alpha)|^2 \right|^{-1/2} < \infty,$$

so $(1/\alpha)\varphi^*(\alpha)$ must belong to $L^2([0, 1], d\alpha)$. Consequently $D((a_1)^*) = D_2$, $a_1^* = a_2 \supset a_1$, and we see that a_1 is Hermitian. It is also easy to see that a_2 is Hermitian and thus, according to (2.5.2; 5), self-adjoint: $a_2 \subset a_2^* \subset a_1^* = a_2$. This means that a_1 is essentially self-adjoint.
2. In Example (2.4.16; 3), $D(a^*)$ would be

$$\left\{\varphi \in L^2([0, 1], dx): \sup_{\psi \text{ continuous}} \int dx\, \varphi(x) \frac{\psi(\frac{1}{2})}{\|\psi\|} < \infty\right\}.$$

Since $\psi(\frac{1}{2})/\|\psi\|$ can be arbitrarily large, $D(a^*)$ is the subspace orthogonal to the constant function, and is not dense.
3. Let $a_1: \psi(\alpha) \to i(d/d\alpha)\psi(\alpha) = i\psi'$, with $D(a_1) = \{\psi \in \mathscr{H} = L^2([0, 1], d\alpha): \psi$ is absolutely continuous, $\psi' \in \mathscr{H}$, and $\psi(0) = \psi(1) = 0\}$. **Absolutely continuous** functions are of the form

$$\psi(\alpha) = \int_0^\alpha d\alpha'\, g(\alpha') + \psi(0), \text{ with } g \text{ integrable.}$$

For such functions, $\psi' = g$ a.e., so

$$\psi(\alpha) - \psi(0) = \int_0^\alpha d\alpha'\, \psi'(\alpha');$$

they are the functions for which integration by parts is justified. It is not restrictive enough to have merely functions that are continuous and have derivatives a.e. which are in L^2; there are continuous, strictly monotonic functions ψ for which ψ' vanishes almost everywhere (cf. (2.3.25; 7)). The boundary conditions ensure that a is Hermitian, for

$$\langle\varphi|a\psi\rangle = i\int_0^1 d\alpha\, \varphi^*(\alpha)\frac{d}{d\alpha}\psi(\alpha)$$

$$= i\left|\varphi^*(\alpha)\psi(\alpha)\right|_0^1 + \int_0^1 d\alpha\left(i\frac{d}{d\alpha}\varphi(\alpha)\right)^*\psi(\alpha) = \langle a\varphi|\psi\rangle$$

for all $\varphi, \psi \in \mathrm{D}$. (2.5.4)

They are too strong for self-adjointness, however, since (2.5.4) is also valid without the requirement that $\psi(0) = \psi(1) = 0$. The other conditions are clearly necessary, so $D(a^*) = \{\varphi \in \mathscr{H}: \varphi$ is absolutely continuous and $\varphi' \in \mathscr{H}\}$. If we now calculate a^{**}, we are again led to (2.5.4), though this time it is necessary to reimpose the condition $\psi(0) = \psi(1) = 0$ to make $|\ldots|_0^1$ vanish. Therefore $a^{**} = a$, so a must be closed. The adjoint a^* is a proper extension of a and thus definitely not Hermitian, as $a^{**} \subset a^*$.

4. Consider again $a: \psi(\alpha) \to i(d/d\alpha)\psi(\alpha)$, $D(a) = \{\psi \in \mathscr{H} = L^2([0, 1], d\alpha): \psi$ is absolutely continuous, $\psi' \in \mathscr{H}$, and $\psi(0) = \psi(1)e^{i\gamma}, \gamma \in \mathbb{R}\}$. It follows as in (2.5.4) that a is again Hermitian, but now $|\varphi^*(\alpha)\varphi(\alpha)|_0^1 = 0$ requires that $\varphi(0) = \varphi(1)e^{i\gamma}$. Therefore $D(a) = D(a^*)$, and a is self-adjoint. This a is an extension of the a of Example 3 for any $\gamma \in \mathbb{R}$, so there is a one-parameter family of extensions of that a, and in fact it contains all possible self-adjoint extensions. (See (2.5.12).)
5. $a: \psi(\alpha) \to i(d/d\alpha)\psi(\alpha)$, $D(a) = \{\psi \in \mathscr{H} = L^2([0, \infty), d\alpha): \psi$ is absolutely continuous, $\psi' \in \mathscr{H}$, and $\psi(0) = 0\}$. This operator is also Hermitian, as it is easy to see that the upper limit contributes nothing upon integration by parts (Problem 4), and the equation

$$\langle\varphi|a\psi\rangle = \int_0^\infty d\alpha\, i\varphi^*\psi' = i\varphi^*(0)\psi(0) + \int_0^\infty d\alpha(i\varphi')^*\psi \stackrel{?}{=} \langle a\varphi|\psi\rangle$$

will hold provided that either $\varphi^*(0) = 0$ or $\psi(0) = 0$. This means that $D(a^*)$ lacks the condition $\psi(0) = 0$, and that $a^{**} = a$. It is not possible in this case to weaken the boundary condition to make $a^* = a$.
6. $a: \psi(\alpha) \to i(d/d\alpha)\psi(\alpha), D(a) = \{\psi \in \mathscr{H} = L^2((-\infty, \infty)\, d\alpha): \psi$ is absolutely continuous, and $\psi' \in \mathscr{H}\}$. The operator is Hermitian since, as in Example 5, there is no contribution from $\pm\infty$ to the boundary term of the partial integration. In fact the operator is self-adjoint; there is no way to weaken the boundary conditions for $D(a^*)$. It is clear on reflection that the

difficulties in Example (2.4.21) or with a unitary translation on $L^2(0, \infty)$ can not arise on $L^2(-\infty, \infty)$, and nothing prevents $i(d/d\alpha)$ from being self-adjoint. Moreover, a^n is self-adjoint in this case on

$$D(a^n) = \left\{\psi \in \mathscr{H} : \psi, \ldots, \frac{d^{n-1}}{d^{n-1}\alpha}\psi \text{ absolutely continuous}, \frac{d^{n-1}}{d^{n-1}\alpha}\psi \in D(a)\right\}.$$

If a is Hermitian but not self-adjoint, then it may have any finite number of self-adjoint extensions, or an infinite number, or none at all. The adjoint a^* will not be Hermitian, and indeed it has complex eigenvalues. Returning to Example 3 (respectively 5), $\exp(-i\alpha z)$, $z \in \mathbb{C}$ (resp. $\operatorname{Im} z < 0$), is an eigenfunction of a^* with eigenvalue z. In these cases every point of $\mathbb{C}$ (resp. the lower half-plane) belongs to the point spectrum of a^*. This behavior is typical, as is shown by:

Theorem (2.5.5)

Let a be a closed, Hermitian operator. Then

(i) $F_z = (a - z)D(a) = (\operatorname{Ker}(a^* - z^*))^{\perp} (z = x + iy,\ y \neq 0)$ *is a closed subspace of $\mathscr{H}$, and $(a - z)^{-1} : F_z \to D(a)$ is a continuous bijection;*

(ii) $V : F_{-i} \to F_i : \psi \to (a - i)(a + i)^{-1}\psi$ *is unitary, and $1 - V = 2i(a + i)^{-1} : F_{-i} \to D(a)$ is bijective, so that $a\psi = i(1 + V)(1 - V)^{-1}\psi$ for all $\psi \in D(a)$;*

(iii) $D(a^*) = D(a) + F_z^{\perp} + F_{z^*}^{\perp}$ *for all $z \in \mathbb{C}$, $\operatorname{Im} z \neq 0$;*

(iv) *if a is self-adjoint, then $F_z = \mathscr{H}$ for all $z \in \mathbb{C}$, $\operatorname{Im} z \neq 0$; and a is self-adjoint if $F_z = \mathscr{H}$ for some $z \in \mathbb{C}$ with $\operatorname{Im} z > 0$ and for some z with $\operatorname{Im} z < 0$.*

Remarks (2.5.6)

1. Since all Hermitian operators are closeable, we have considered only closed operators a. If the assumption of closure were dropped, then Propositions (i)–(iv) would hold for the closure a^{**}. As a consequence, the resolvent $(a - z)^{-1}$ of an essentially self-adjoint operator a is densely defined, and, since it is bounded, it has a unique extension $(a^{**} - z)^{-1}$ as a bounded operator defined on all of $\mathscr{H}$. (Recall Remarks (2.4.23).)
2. V is known as the **Cayley transform** of a.
3. These propositions are depicted schematically in Figure 4.

Proof

(i) Because $\|(a - x - iy)\psi\|^2 = \|(a - x)\psi\|^2 + \|y\psi\|^2 \geq y^2\|\psi\|^2$, the resolvent $(a - z)^{-1}$ is bounded, and by assumption $\Gamma(a - z)$ and thus also $\Gamma((a - z)^{-1})$ are closed, so it follows from Theorem (2.4.18) that $D((a - z)^{-1}) = F_z$ is a Hilbert space, and thus a closed subspace of $\mathscr{H}$.

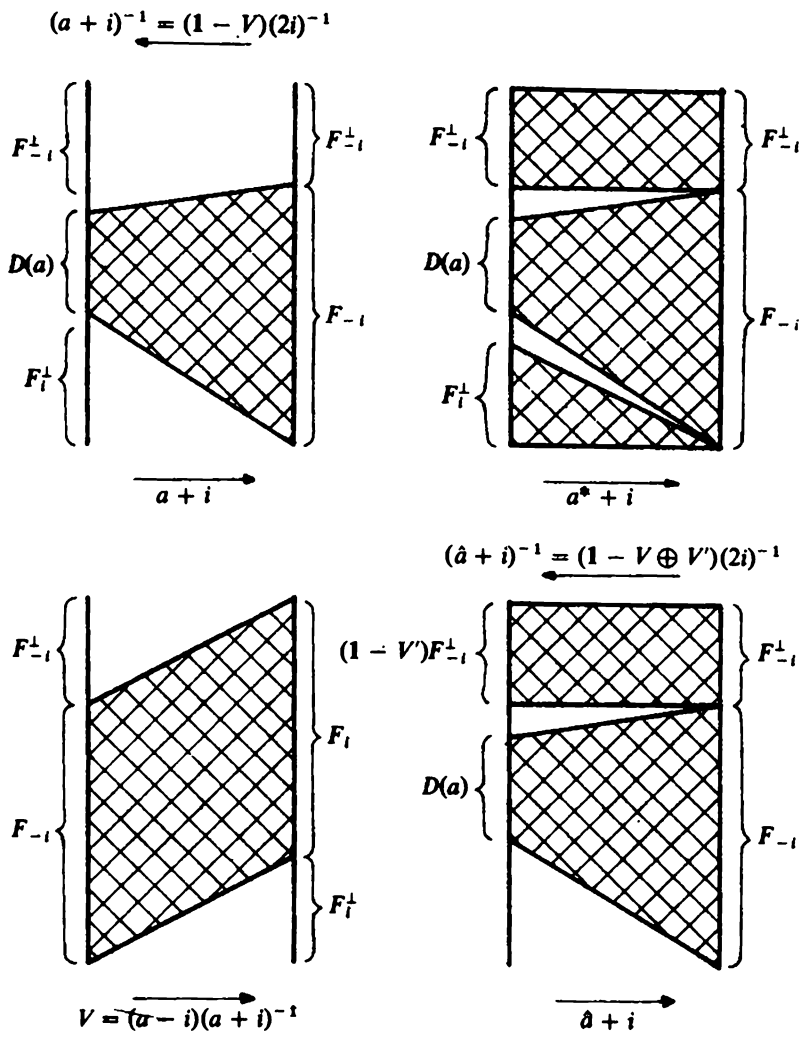


Figure 4 In the top two figures, the decomposition on the left is not assumed orthogonal. Although $D(a) \cap F_{\pm i}^{\perp} = \{0\}$, $D(a) \not\subset F_{\pm i}$. The extension $\hat{a}$, $a \subset \hat{a} \subset a^*$ and V' are defined in (2.5.11).

Since $\langle\varphi|(a-z)\psi\rangle = \langle(a^*-z^*)\varphi|\psi\rangle$ for all $\varphi \in D(a^*)$, $\psi \in D(a)$, F_z is orthogonal to the eigenvectors of a^* of eigenvalue z^*. As a Hermitian operator, a can not have any complex eigenvalues. Hence $a - z$ is injective and, by definition, surjective as a mapping $D(a) \to F_z$.

(ii) $\psi \in F_{-i} \Leftrightarrow \psi = (a+i)\varphi$, $\varphi \in D(a)$, and because $\|(a+i)\varphi\| = \|(a-i)\varphi\|$, the operators V and $V^{-1} = (a+i)(a-i)^{-1}$ are isometric. From $\varphi = (\psi - V\psi)/2i$ and $a\varphi = (\psi + V\psi)/2$, we conclude that $(1-V)\psi = 0$, and so $(1+V)\psi = 0$ and $\psi = 0$. Therefore $1 - V$ is invertible on F_{-i}, and $a = i(1+V)(1-V)^{-1}$.

(iii) Let $\psi \in D(a^*)$ and write $(a^* + i)\psi$ as a sum of vectors of F_{-i} and $F_{-i}^{\perp}$: $(a^* + i)\psi = (a + i)\eta + 2i\chi$, $\eta \in D(a)$, $\chi \in F_{-i}^{\perp} = \mathrm{Ker}(a^* - i)$. Hence $2i\chi = (a^* + i)\chi \Rightarrow (a^* + i)(\psi - \eta - \chi) = 0$, because $a^* \supset a \Rightarrow a\eta = a^*\eta$. Therefore $\psi = \eta + \chi + \varphi, \varphi \in F_i^{\perp}$ is the required decomposition of any vector ψ of $D(a^*)$.

(iv) This follows from (iii), because if (2.4.27; 6) is generalized to unbounded operators, we see that $F_{z_0} = \mathscr{H} \Rightarrow F_z = \mathscr{H}$ for all z with $\mathrm{Im}\, z/\mathrm{Im}\, z_0 > 0$. □

Example (2.5.7)

$a = i(d/d\alpha)$, $D(a)$ as in (2.5.3; 3) $\ni \varphi$; $F_{-i} \ni \psi(\alpha) = i(d/d\alpha + 1)\varphi(\alpha)$ is orthogonal to $\mathrm{Ker}(a^* - i) = \{ce^{\alpha}\}$, since

$$\int_0^1 d\alpha\, e^{\alpha}\left(\frac{d}{d\alpha} + 1\right)\varphi(\alpha) = e\varphi(1) - \varphi(0) = 0,$$

$$\varphi(\alpha) = -i\int_0^{\alpha} d\alpha'\, e^{\alpha' - \alpha}\psi(\alpha'),$$

so $\psi \to (a + i)^{-1}\psi$ is continuous, and

$$(V\psi)(\alpha) = \left(i\left(\frac{d}{d\alpha} - 1\right)\varphi(\alpha) = \int_0^1 d\alpha'[\delta(\alpha - \alpha') - 2\Theta(\alpha - \alpha')e^{\alpha' - \alpha}]\psi(\alpha')\right.$$

$$\left. \equiv \int_0^1 d\alpha' V(\alpha, \alpha')\psi(\alpha')\right).$$

V is isometric on F_{-i}, since $\int_0^1 d\alpha'\, V^*(\alpha, \alpha')V(\alpha', \alpha'') = \delta(\alpha - \alpha'') - 2e^{\alpha + \alpha''}$.

Remarks (2.5.8)

1. If a is not self-adjoint, then $a - z: D(a) \to \mathscr{H}$ with $\mathrm{Im}\, z \neq 0$ is still injective, but it is not surjective, while $a^* - z: D(a^*) \to \mathscr{H}$ is surjective but not injective. Consequently, $\mathrm{Sp}(a)$ and $\mathrm{Sp}(a^*)$ each contain at least a half-plane, if Definition (2.2.13) is carried over for the spectrum of unbounded operators.
2. If a is self-adjoint, then $V: \mathscr{H} \to \mathscr{H}$ is unitary, so the spectral theorem extends to cover a. If $d\mu(\theta)$, $0 \leq \theta < 2\pi$, is one of the spectral measures (2.3.14) for $V: \mathrm{Sp}(V) \doteq \{e^{i\theta}\}$, $(V\psi)(\theta) = e^{i\theta}\psi(\theta)$, then the multiplication operator equivalent to a is $a: \psi(\theta) \to i(1 + e^{i\theta})/(1 - e^{i\theta})\psi(\theta)$. We saw earlier that V does not have the eigenvalue 1, so the measure of the point $\theta = 0$ is zero, and a is multiplication by an a.e. finite function. This form of the spectral theorem for unbounded self-adjoint operators is as general as possible. If $\lambda = \cot\theta/2$ is introduced as a new variable, then $L^2([0, 2\pi], d\mu(\theta))$ is mapped to $L^2((-\infty, \infty), d\mu(\lambda))$, and a becomes multiplication by

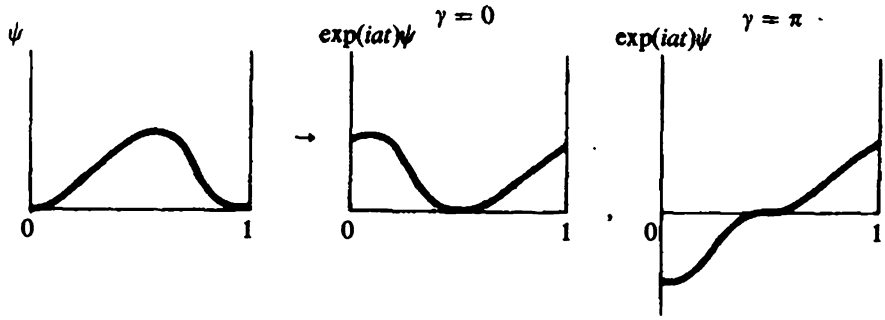


Figure 5 Two unitary representations of the translation on [0, 1].

λ. In analogy with (2.3.14), a may then be written as $\int_{-\infty}^{\infty} \lambda \, dP_\lambda$, which extends Theorem (2.3.14) to unbounded self-adjoint operators.

3. We shall understand convergence of a sequence of self-adjoint operators $a_n \to a$ to mean that all sequences of bounded functions f of the a_n converge: $f(a_n) \to f(a)$. It suffices to have convergence for either of the two classes of functions $f(a) = \exp(iat)$ for all $t \in \mathbb{R}$ and $f(a) = (a - z)^{-1}$ for all z with $\operatorname{Im} z \neq 0$.
4. By Stone's Theorem (2.4.24), the self-adjoint operators are exactly the class of Hermitian operators that generate unitary groups. For instance, the a of Example (2.5.3; 4) generates the group of translations

$$(\exp(iat)\psi)(x) = \psi(x - t)$$

and answers the question that arose in (2.4.21) about the effect of the periodic boundary conditions: whatever is pushed past one end of the interval reappears at the other end with some constant change of phase (see Figure 5):

5. A converse of Theorem (2.5.5) can also be proved (Problem 7): If V is an isomorphism of a closed subspace F_- onto a subspace, such that $\mathbf{1} - V$ is a bijection of F_- onto a dense subspace of $\mathscr{H}$, then $i(\mathbf{1} + V)(\mathbf{1} - V)^{-1}$ is a Hermitian operator.
6. The part of $D(a^*)$ not contained in $D(a)$ consists only of eigenvectors of a^* with complex eigenvalues. The sum in (iii) of (2.5.5) is of course not orthogonal.

Because of these facts, the most important criterion for self-adjointness is the absence of complex eigenvalues of a^*. To pursue this subject further, we make

Definition (2.5.9)

$(m, n) \equiv \dim(\operatorname{Ker}(a^* \mp i)) = \dim(F_{\pm i}(a))^\perp$ are the **deficiency indices** of a.

Examples (2.5.10)

1. a is essentially self-adjoint iff $(m, n) = (0, 0)$.
2. In Example (2.5.3; 3), $(m, \ ) = (1, 1)$.
3. In Example (2.5.3; 5), $(m, n) = (0, 1)$.

If one wishes to extend a Hermitian operator $a = i(1 + V)(1 - V)^{-1}$ to a self-adjoint operator $\hat{a} = i(1 + U)(1 - U)^{-1} \supset a$, then U must be a unitary extension of $V: F_{-i} \to F_{+i}$. It is clear that the extension must map the orthogonal complements $\mathrm{Ker}(a^* \mp i)$ unitarily onto each other, so U has to be an orthogonal sum $V \oplus V'$ for some V' acting on the orthogonal complements. This is possible only if $F^{\perp}_{\pm i}$ have the same dimension:

Theorem (2.5.11)

A Hermitian operator a can be extended to a self-adjoint operator $\hat{a}$ iff the deficiency indices are equal. In that case, for every unitary mapping V': $\mathrm{Ker}(a^* - i) \to \mathrm{Ker}(a^* + i)$ there exists a distinct extension

$$\hat{a} = i(1 + V \oplus V')(1 - V \oplus V')^{-1}.$$

Example (2.5.12)

Let us return to (2.5.7), which has $(m, n) = (1, 1)$: $U(1, \mathbb{C})$ is multiplication by a phase factor, so there exists a one-parameter family $\{a_\beta\}$ of self-adjoint extensions of a. If $V'e^{\alpha} = e^{1-\alpha}e^{i\beta}$, then $U = V \oplus V'$ is defined on all of $\mathscr{H}$. With the procedure we have described above, $\varphi \in D(a)$ is written in the form

$$\begin{aligned}
\varphi(\alpha) &= ((U - 1)\psi)(\alpha) \\
&= (U - 1)\left(\psi(\alpha) - e^{\alpha}c\int_0^1 d\alpha'\, e^{\alpha'}\psi(\alpha') + e^{\alpha}c\int_0^1 d\alpha'\, e^{\alpha'}\psi(\alpha')\right) \\
&= -2\int_0^{\alpha} d\alpha'\, e^{\alpha'-\alpha}\left(\psi(\alpha') - e^{\alpha'}c\int_0^1 d\alpha''\, e^{\alpha''}\psi(\alpha'')\right) \\
&\quad + (e^{1-\alpha}e^{i\beta} - e^{\alpha})c\int_0^1 d\alpha'\, e^{\alpha'}\psi(\alpha'),
\end{aligned}$$

where $c\int_0^1 d\alpha\, e^{2\alpha} = 1$, so φ satisfies the boundary conditions

$$\begin{aligned}
\frac{\varphi(0)}{\varphi(1)} &= \frac{e^{i\beta+1} - 1}{e^{i\beta} - e} = \left(\frac{e^{1-i\beta} - 1}{e^{-i\beta} - e}\right)^* = \left(\frac{e - e^{i\beta}}{1 - e^{i\beta+1}}\right)^* \\
&= \left(\frac{\varphi(1)}{\varphi(0)}\right)^* \Rightarrow |\varphi(0)| = |\varphi(1)|,
\end{aligned}$$

which makes a_β identical to the a of (2.5.3; 4).

Remarks (2.5.13)

1. Theorem (2.5.11) reveals why it was not possible to weaken the boundary conditions in (2.5.3; 5) to make a self-adjoint. In that example, $m \neq n$.
2. Although the deficiency indices and extensions were defined with the special values $z = \pm i$, any other pair of complex conjugates z, z^*, $\operatorname{Im} z \neq 0$, would have produced an equivalent definition.
3. If either m or n is zero, then the operator is maximal, i.e., it has no Hermitian extensions. If $m = n < \infty$, then every maximal Hermitian extension is self-adjoint, and if $m = n = \infty$, then there are maximal Hermitian extensions that are not self-adjoint.
4. If a Hermitian operator is real (see (3.3.19; 5)), that is, invariant under $i \to -i$, then $m = n$, and it always has a self-adjoint extension.

The delicate attribute of self-adjointness is not even preserved by the formation of linear combinations of operators. If a and b are self-adjoint, then $a + b$ (and $ab + ba$) may fail to be self-adjoint. The sum $a + b$ is a priori defined only on $D(a) \cap D(b)$, and $ab + ba$ only on $D(a) \cap D(b) \cap aD(a) \cap bD(b)$, and these sets might not be dense. Even if the intersection of the domains is dense in $\mathscr{H}$, it might be too small for the sum to be self-adjoint.

Example (2.5.14)

A $1/r^2$ potential. Let $H = K + V$, $K: \psi(r) \to -(d^2/dr^2)\psi(r)$: $D(K) = \{\psi \in \mathscr{H}: \psi'$ is absolutely continuous, $\psi'' \in \mathscr{H}$, and $\psi(0) = 0\}$, where $\mathscr{H} = L^2([0, \infty), dr)$; $V: \psi(r) \to (\gamma/r^2)\psi(r)$, $\gamma \in \mathbb{R}$: $D(V) = \{\psi \in \mathscr{H}: (1/r^2)\psi \in \mathscr{H}\}$. With the a of Example (2.5.3; 5), $K = a^*a$, which is always self-adjoint. As in Example (2.5.3; 1), V is likewise self-adjoint. However, $D(H) = D(K) \cap D(V) = \{\psi \in \mathscr{H}: \psi'$ is absolutely continuous and $\in \mathscr{H}$, $\psi'' \in \mathscr{H}$, and $\psi(0) = \psi'(0) = 0\}$, and as in (2.5.4) the boundary condition does not show up in $D(H^*)$: $D(H^*) = \{\psi \in \mathscr{H}: \psi'$ is absolutely continuous and $\in \mathscr{H}$, and $(-\psi'' + \gamma\psi/r^2) \in \mathscr{H}\}$. It is possible for $D(H)$ to be a proper subset of $D(H^*)$, provided that neither ψ'' nor $\gamma\psi/r^2$ is in $\mathscr{H}$, but that their difference is, because of a cancellation of the singularities at 0. In order to understand when this happens, let us examine the solutions of the equation $\psi''_\pm = (\gamma/r^2 \pm i)\psi_\pm$. The solutions that decrease when $r \to \infty$ as $\psi_\pm \sim \exp(-r(1 \pm i)/\sqrt{2})$ are linear combinations of $r^{\pm\nu + 1/2}$, $\nu = \sqrt{\gamma + 1/4}$, in the limit $r \to 0$. These functions are square-integrable only if $\nu < 1 \Leftrightarrow \gamma < \frac{3}{4}$, so if $\gamma \geq \frac{3}{4}$, then the deficiency indices are (0, 0), and if $\gamma < \frac{3}{4}$, then they are (1, 1). In the latter case there is a one-parameter family of self-adjoint extensions, which append $\psi_+ - \exp(2i\delta)\psi_-$, $\delta \in \mathbb{R}$, to $D(H)$ so that $H(\psi_+ - \exp(2i\delta)\psi_-) = i(\psi_+ + \exp(2i\delta)\psi_-)$. Even

if $\gamma = 0$, $D(H)$ gets expanded by the inclusion of $\exp(-r(1+i)/\sqrt{2}) - \exp(2i\delta - r(1-i)/\sqrt{2})$, i.e., it can be characterized by the boundary condition $\psi(0)/\psi'(0) = \sqrt{2}/(\cot(\delta) - 1)$. Since $\varphi_\cdot \equiv \psi/r$ in three-dimensional polar coordinates, $-\Delta\varphi$ becomes $\delta^3(x)\psi(0)/4\pi$, so this extension corresponds physically to the addition of a delta-function potential at the origin.

However, if b is small in comparison with a in a certain sense, then the addition of b to a does not affect its self-adjointness.

The Kato–Rellich Theorem (2.5.15)

Let $a^* = a$, $b^* \supset b$, and $D(b) \supset D(a)$, and suppose that there exist constants $0 \le \alpha < 1$ and $\beta \ge 0$ such that $\|b\psi\| \le \alpha\|a\psi\| + \beta\|\psi\|$ for all $\psi \in D(a)$. Then $a + b$ is self-adjoint on $D(a)$. If a is essentially self-adjoint on $D \subset D(a)$, then so is $a + b$.

Proof

In the spectral representation of a (see (2.5.8; 2)) we discover that

$$\|(a \pm i\eta)^{-1}\| \le \eta^{-1} \qquad \text{and} \qquad \|a(a \pm i\eta)^{-1}\| \le 1.$$

If η is large enough, then it follows that $\|b(a \pm i\eta)^{-1}\| \le \alpha + \beta\eta^{-1} < 1$, so $1 + b(a + i\eta)^{-1}$ is a bijection of $\mathscr{H}$. Consequently $(a + b \pm i\eta)D(a) = (1 + b(a \pm i\eta)^{-1})(a \pm i\eta)D(a)$ is either all of $\mathscr{H}$ or dense in $\mathscr{H}$, depending on whether $(a \pm i\eta)D(a)$ is all of $\mathscr{H}$ or only dense. □

Remarks (2.5.16)

1. If b is bounded, then it is a fortiori relatively bounded, and $a + b$ is self-adjoint or essentially self-adjoint on $D(a)$ whenever a is.
2. Since $\sqrt{\alpha^2(1+\varepsilon) + \beta^2(1 + 1/\varepsilon)} \ge \alpha + \beta$ for all $\alpha, \beta, \varepsilon > 0$, Criterion (2.5.15) is equivalent to $\|b\psi\|^2 \le \alpha^2\|a\psi\|^2 + \beta^2\|\psi\|^2$, or to $b^2 \le \alpha^2 a^2 + \beta^2$.
3. For the statement about essential self-adjointness, α may be allowed to be 1.
4. For the physical systems that will concern us, b = a Coulomb potential is bounded relative to a = the kinetic energy. The Kato–Rellich Theorem is thus sufficient for our purposes to guarantee existence and uniqueness of the time-evolution.

It sometimes happens that formal Hamiltonians are not even strictly speaking operators, because they send every vector of $\mathscr{H}$ out of $\mathscr{H}$. However, knowledge of enough matrix elements is frequently sufficient to determine the time evolution, even in the absence of a well-defined operator.

Definition (2.5.17)

A **quadratic form** q is a mapping $Q(q) \times Q(q) \to \mathbb{C}: (\varphi, \psi) \to \langle \varphi | q | \psi \rangle$, where $Q(q)$ is a dense subspace of $\mathscr{H}$ known as the **form domain**, such that $\langle \varphi | q | \psi \rangle$ is linear in ψ and conjugate-linear in φ. If $\langle \psi | q | \varphi \rangle^* = \langle \varphi | q | \psi \rangle$, then q is said to be **Hermitian**, and if $\langle \varphi | q | \varphi \rangle \geq 0$, it is **positive**. A positive quadratic form q is said to be **closed** iff $Q(q)$ is complete in the form norm $\|\varphi\|_q^2 = \langle \varphi | q | \varphi \rangle + \|\varphi\|^2$.

Gloss

Conjugate-linearity means that $\langle \lambda\varphi | q | \psi \rangle = \lambda^* \langle \varphi | q | \psi \rangle$. If $\langle \varphi | q | \varphi \rangle \geq -M\|\varphi\|^2$, then q is **semibounded**; equivalently, the form $\langle \varphi | q_1 | \psi \rangle \equiv \langle \varphi | q | \psi \rangle + M \langle \varphi | \psi \rangle$ is positive.

Examples (2.5.18)

1. Let a be a (densely defined, linear) operator. Then $(\varphi, \psi) \to \langle \varphi | a\psi \rangle$ is a quadratic form, and is Hermitian or positive iff a is.
2. Suppose a self-adjoint operator a has been written in a spectral representation on $\bigoplus_n L^2(\mathbb{R}, d\mu_n)$. Then $\langle \varphi | q | \psi \rangle = \sum_n \int_{-\infty}^{\infty} d\mu_n(\alpha) \alpha \varphi_n^*(\alpha) \psi_n(\alpha)$ for $\varphi, \psi \in Q(a) = \{\zeta \in \mathscr{H}: \sum_n \int_{-\infty}^{\infty} d\mu_n(\alpha) |\alpha| |\zeta_n(\alpha)|^2 < \infty\}$ is a Hermitian form, which is closed if $a \geq 0$. Observe that $Q(a)$ is different from $D(a) = \{\zeta \in \mathscr{H}: \sum_n \int_{-\infty}^{\infty} d\mu_n(\alpha) |\alpha|^2 |\zeta_n(\alpha)|^2 < \infty\}$, but that rather $Q(a) = D(\sqrt{|a|})$.
3. For $\mathscr{H} = L^2(\mathbb{R}, d\alpha) \supset Q(q) = \{\psi \in \mathscr{H}: \psi \text{ is continuous at } 0\}$, the "delta operator" $\langle \varphi | q | \psi \rangle = \varphi^*(0)\psi(0)$ is positive but not closed. The sequence $\psi_n = \exp(-n\alpha^2) \to 0$ in $\mathscr{H}$ is also a Cauchy sequence in the form norm, but without a limit in $Q(q)$: since the topology coming from $\| \ \|_q$ is finer than the one coming from $\| \ \|$, and the sequence tends to 0 in the latter topology, the only possible limit in $Q(q)$ would be 0. However, because $\langle \psi_n | q | \psi_n \rangle = 1$, the sequence does not tend to 0 in the $\| \ \|_q$ topology, and this fact is not changed by an enlargement of $Q(q)$. Hence q is not closed, and in fact not even closeable.

Thus Hermitian forms, in contradistinction to Hermitian operators, need not be closeable. However, if they are closeable, then they are always the quadratic form of some self-adjoint operator.

Theorem (2.5.19)

If the form q is positive and closed, then it is the form of a unique self-adjoint, positive operator.

Proof

Consider $Q(q) \subset \mathscr{H}$ as a Hilbert space with the scalar product $\langle\varphi|\psi\rangle_q \equiv \langle\varphi|\psi\rangle + \langle\varphi|q|\psi\rangle$. The resulting topology is finer than that coming from $\langle|\rangle$, so the mapping $Q(q) \to \mathbf{C}: \psi \to \langle\varphi|\psi\rangle$ is continuous for all $\varphi \in \mathscr{H}$. As in (2.1.17), there exists a unique $\chi \in Q(q)$ such that $\langle\varphi|\psi\rangle = \langle\chi|\psi\rangle_q$. This defines an injection $c: \mathscr{H} \to Q(q): \varphi \to \chi \equiv c\varphi$. If we consider c as a mapping $\mathscr{H} \to \mathscr{H}$, then it is Hermitian and bounded:

$$\langle\varphi|c\psi\rangle = \langle c\varphi|c\psi\rangle_q = \langle c\psi|c\varphi\rangle_q^* = \langle\psi|c\varphi\rangle^* = \langle c\varphi|\psi\rangle,$$

$$\|c\| = \sup_{\|\psi\|=1} \|c\psi\| \le \sup_{\|\psi\|=1} \|c\psi\|_q = \sup_{\substack{\|\psi\|=1 \\ \|\varphi\|_q=1}} |\langle c\psi|\varphi\rangle_q| = \sup_{\substack{\|\psi\|=1 \\ \|\varphi\|_q=1}} |\langle\psi|\varphi\rangle| \le 1.$$

Note that $c\mathscr{H}$ is dense in $Q(q)$ in the $\|\ \|_q$ norm (i.e., $\langle c\varphi|\psi\rangle_q = \langle\varphi|\psi\rangle = 0$ for all $\varphi \in \mathscr{H} \Rightarrow \psi = 0$), and hence it is also dense in $\mathscr{H}$ in the norm $\|\ \|$. Therefore c^{-1} is densely defined, and since c, being a bounded, Hermitian operator, is self-adjoint, c^{-1} is also self-adjoint on $c\mathscr{H}$ (Problem 10). The operator $c^{-1} - 1$ has the required property $\langle(c^{-1} - 1)\varphi|\psi\rangle = \langle\varphi|q|\psi\rangle$ on the domain $c\mathscr{H} \subset Q(q)$. For uniqueness, see Problem 8. □

Example (2.5.20)

We attempt to make sense of $d^2/dx^2 + V(x)$ with $V(x) = \lambda\delta(x)$ by extending the operator $H = -d^2/dx^2$ on $D(H) = \{\psi \in L^2((-\infty, \infty), dx): \psi'$ is absolutely continuous, $\psi''(0) \in L^2$, and $\psi(0) = 0\}$. The Fourier transformation makes H a multiplication operator:

$$(H\psi)(k) = k^2\psi(k),\ D(H) = \left\{\psi \in L^2\left((-\infty, \infty), \frac{dk}{2\pi}\right): \int_{-\infty}^{\infty} dk\,|k^2\psi(k)|^2 < \infty,\ \int_{-\infty}^{\infty} dk\,\psi(k) = 0\right\}.$$

It is closed since the graph norm (2.4.17; 3) is equivalent to $\|\psi\|_\Gamma^2 \equiv \langle\psi|\psi\rangle_\Gamma \equiv \int_{-\infty}^{\infty} (dk/2\pi)|\psi(k)|^2(1 + k^4)$, and

$$D(H) = \left\{\psi \in \mathscr{H}: \|\psi\|_\Gamma < \infty, \left\langle\psi\middle|\frac{1}{1 + k^4}\right\rangle = 0\right\}$$

and $\|1/(1 + k^4)\|_\Gamma < \infty$. Clearly,

$$(F_z)^\perp = \frac{1}{k^2 - z} \Rightarrow D(H^*) = D(H) + \left\{\frac{1}{k^2 - z}\right\}, \qquad z \in \mathbf{C} - \mathbf{R}^+,$$

$$H^* \frac{1}{k^2 - z} = z\frac{1}{k^2 - z}.$$

Therefore the deficiency indices are (1, 1), and there is a one-parameter family of self-adjoint extensions. The domain $D(H)$ is not complete in the appropriate q-norm

$$\|\psi\|_q^2 = \int_{-\infty}^{\infty} \frac{dk}{2\pi} |\psi(k)|^2(1 + k^2) = \langle \psi | 1 + q | \psi \rangle;$$

its completion contains ψ's which decrease only like $|k|^{-1-\varepsilon}$ as $k \to \infty$:

$$Q(q) = \left\{ \psi \in L^2 : \|\psi\|_q < \infty, \int_{-\infty}^{\infty} dk\, \psi(k) = 0 \right\}.$$

This is a subspace of $\{\psi : \|\psi\|_q < \infty\}$ closed in the norm $\| \ \|_q$, because

$$\int_{-\infty}^{\infty} dk\, \psi(k) = \left\langle \psi \left| \frac{1}{1 + k^2} \right. \right\rangle_q \quad \text{and} \quad \left\| \frac{1}{1 + k^2} \right\|_q = \frac{1}{\sqrt{2}};$$

therefore $\int_{-\infty}^{\infty} dk \psi(k)$ is a continuous linear functional on $Q(q)$ with the $\| \ \|_q$ norm (unlike the $\| \ \|$ norm). The injection c for the form $q = k^2$ with domain $Q(q)$ is determined by

$$\int_{-\infty}^{\infty} dk\, \varphi^*(k)\psi(k) = \int_{-\infty}^{\infty} dk (c\varphi(k))^* \psi(k)(1 + k^2)$$

for all $\psi \in Q(q)$, $\varphi \in \mathscr{H}$, $c\varphi \in Q(q)$, which implies that

$$c : \varphi(k) \to \frac{\varphi(k)}{1 + k^2} - \frac{1}{1 + k^2} \int_{-\infty}^{\infty} \frac{dk'}{\pi} \frac{\varphi(k')}{1 + k'^2}.$$

Hence c sends $(1/(1 + k^2))^{\perp} = \{\varphi : \langle \varphi | 1/(1 + k^2) \rangle = 0\}$ to $D(H)$ and $1/(1 + k^2)$ to $1/(1 + k^2)^2 - 1/2(1 + k^2) \equiv \chi(k) \notin D(H)$, which means that $c^{-1}_{|D(H)} = 1 + k^2$ and $c^{-1}\chi = 1/(1 + k^2)$. The domain of H is enlarged by the inclusion of χ, on which the extension does not act as k^2 (see Figure 6).

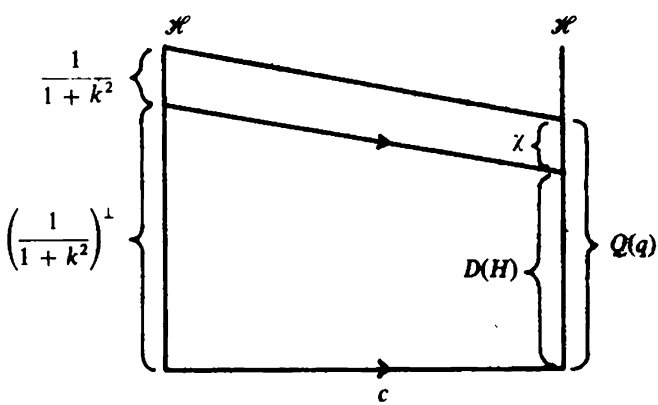


Figure 6 The domains involved in the extension of a quadratic form.

Since the deficiency indices are (1, 1), the domain of any self-adjoint extension is $D(H)$ + some one-dimensional space, so $D(H) + \{\chi\}$ is large enough to be $D(c^{-1})$. The operator $c^{-1} - 1$ is called the **Friedrichs extension** of H.

Remarks (2.5.21)

1. If we choose $Q(\hat{q}) = \{\psi: \|\psi\|_q < \infty\} \supset Q(q)$, then
$$D(\hat{c}^{-1}) = \left\{\psi: \int dk |\psi(k)(1 + k^2)|^2 < \infty\right\} \subset Q(\hat{q})$$
and $\hat{c}^{-1}$ is just multiplication by $1 + k^2$, and thus different from c^{-1}, even though $\hat{q}_{|Q(q)} = q$ and both q and $\hat{q}$ are closed. In contrast, for self-adjoint operators, $a \subset \hat{a}$ necessarily implies $a = \hat{a}$.
2. If q arises from a positive operator a, $\langle\varphi|q|\psi\rangle = \langle\varphi|a\psi\rangle$, then q is always closeable to some $\hat{q}$ with $Q(\hat{q})$ the completion of $D(a)$ in the norm $\| \ \|_q$: If $\{\psi_n\}$ is a Cauchy sequence with $\| \ \|_q$, then it is also one with $\| \ \|$ and converges to some $\psi \in \mathscr{H}$. To show that $\psi \in Q(\hat{q})$ and $\psi_n \xrightarrow{\| \ \|_q} \psi$, note that $\langle\varphi|\psi_n\rangle_q = \langle(a + 1)\varphi|\psi_n\rangle \to \langle(a + 1)\varphi|\psi\rangle = \langle\varphi|\psi\rangle_q$ for all $\varphi \in D(a)$. Since $Q(\hat{q})$ is complete, it must follow that $\psi_n \xrightarrow{\| \ \|_q}$ some $\psi' \in Q(q)$, and we see that $\langle\varphi|\psi - \psi'\rangle_q = 0$ for all $\varphi \in D(a)$. Since $D(a)$ is dense in $Q(q)$, ψ must be the same as ψ'. This shows that every semibounded operator has such a self-adjoint extension, known as the **Friedrichs extension**.
3. In x-space the functions $(F_{\pm i})^{\perp}$ are of the form $\exp(-|x|(1 \pm i)/\sqrt{2})$ The self-adjoint extensions append the functions $\psi = \exp(-|x|(1+i)/\sqrt{2}) - \exp(2i\delta - |x|(1 - i)/\sqrt{2})$ to $D(H)$ (Problem 5). The functions ψ satisfy $\lim_{\varepsilon \downarrow 0} \psi'(\varepsilon) - \psi'(-\varepsilon) = \lambda\psi(0)$, $\lambda = (\cot(\delta) - 1)\sqrt{2}$, and so at $x = 0$,
$$\left(-\frac{d^2}{dx^2} + \lambda\delta(x)\right)\psi(x) = 0.$$
The form q defines the extension with $\lambda = \infty$, since χ has a discontinuous derivative at $x = 0$, but it vanishes at that point ($\int dk\, \chi(k) = 0$).
4. Since the norm on $Q(q)$ is weaker than the graph norm (2.4.17; 3) of H, the closure in $Q(q)$ produces an extension of the operator H, which is closed in its graph norm.
5. $Q(q)$ is closed with $\| \ \|_q$, but it is not all of $\{\psi \in \mathscr{H}: \|\psi\|_q < \infty\}$.
6. Whereas $\delta(x)$ of Example (2.5.18; 3) is not an operator, since its quadratic form is not closeable, $-d^2/dx^2 + \lambda\delta(x)$ is an operator.

Problems (2.5.22)

1. Show that $a_{|D_2}$ of (2.4.16; 2) is closed.
2. Find an example of an operator on l^2 with $D(a^*) = \{\varphi: |\langle\varphi|a\psi\rangle| < c$ for all $\psi \in D(a), \|\psi\| = 1\} = 0$.

3. Show that $\Gamma(a^*) = (J\Gamma(a))^\perp$.
4. Show that $a \subset a^*$ for the a of (2.5.3; 5).
5. What are the other self-adjoint extensions of H in (2.5.20)?
6. Determine the Friedrichs extension of H in (2.5.14).
7. Prove the claim made in (2.5.8; 5).
8. Show that the operator defined in (2.5.19) is unique.
9. Carry out the intermediate steps in the calculations of Examples (2.5.7) and (2.5.12).
10. Use the graph $\Gamma(a)$ to show that the inverse of a self-adjoint operator is self-adjoint whenever it exists.

Solutions (2.5.23)

1.

$$\psi_n \to \psi, \frac{1}{\alpha}\psi_n \to \varphi \Rightarrow \int_\varepsilon^1 \left|\frac{1}{\alpha}\psi - \varphi\right|^2 d\alpha = 0,$$

since it is

$$\leq \int_\varepsilon^1 \left|\frac{1}{\alpha}\psi - \frac{1}{\alpha}\psi_n\right|^2 d\alpha + \int_\varepsilon^1 \left|\frac{1}{\alpha}\psi_n - \varphi\right|^2 d\alpha$$

for all $n \Rightarrow \int_\varepsilon^1 (1/\alpha^2)|\psi|^2\, d\alpha \leq \|\varphi\|^2$, i.e., $\psi \in D_2$ and $\|(1/\alpha)\psi - \varphi\| = 0$. Remark: The same argument works for any multiplication operator $\psi(\alpha) \to f(\alpha)\psi(\alpha)$, which is closed on the domain

$$\{\psi \in L^2 : f\psi \in L^2\}.$$

2. Let a be given in a matrix representation as $a_{in} = (1/n)\mathrm{i}$, and let $D(a)$ be

$$\{\psi = (\psi_1, \psi_2, \ldots) : \text{only finitely many } \psi_i \text{ are nonzero}\}.$$

Then

$$\sup_{\|\psi\| \leq 1} |\langle \varphi | a\psi \rangle| = \sup_{\|\psi\| \leq 1} \sum_n \varphi_n \frac{1}{n} \sum_i i\psi_i = \infty \quad \text{for all} \quad \varphi \in l^2 \Rightarrow D(a^*) \neq 0.$$

3. y is contained in the domain of a^* if there exists a $y^* \in \mathscr{H}$ such that $\langle y|ax\rangle = \langle y^*|x\rangle$ for all $x \in D(a)$, and if there is such a y^*, then $a^*y = y^*$. The equation $\langle y|ax\rangle = \langle y^*|x\rangle$ can be rewritten as $\langle (y, y^*)|(ax, -x)\rangle = \langle (y, y^*)|J(x, ax)\rangle = 0$, i.e., $\Gamma(a^*) = (J\Gamma(a))^\perp$.

4. It only needs to be shown that the upper limit contributes nothing to the integration by parts, that is, $\varphi^*(\alpha)\psi(\alpha) \to 0$ as $\alpha \to \infty$. Since

$$\varphi^*(\beta)\psi(\beta) - \varphi^*(\alpha)\psi(\alpha) = \int_\alpha^\beta [\varphi^*(\alpha')\psi'(\alpha') + \varphi^{*\prime}(\alpha')\psi(\alpha')]d\alpha'$$

and because $[\ldots] \in L^1$, it follows first that $\varphi^*(\alpha)\psi(\alpha)$ is a Cauchy sequence and hence convergent, and secondly, because $\int_{-\infty}^{\infty} d\alpha |\varphi^*(\alpha)\psi(\alpha)| < \infty$, that the limit is 0.

5. Theorems (2.5.5) and (2.5.11) imply that every self-adjoint extension is of the form $\hat{H}$: $D(\hat{H}) = \{\psi = \eta + \varphi - V'\varphi, \eta \in D(H), \varphi \in F_i^{\perp}, V'$ an isometry $F_i^{\perp} \to F_{-i}^{\perp}\}, \hat{H}\psi = H\eta - i\varphi + iV'\varphi$. In our case, $\varphi = 1/(k^2 + i)$, and the most general V' acts by $V'\varphi = e^{2i\delta}/(k^2 - i)$.

6. The form domain $Q(H)$ of $\langle\varphi|H|\varphi\rangle = \int_0^{\infty} dr(\varphi'^2 + \gamma\varphi^2/r^2)$ contains the operator domain $D_F(H)$ of the Friedrichs extension. The functions φ of $Q(H)$ must go to 0 faster than $r^{1/2}$ as $r \to 0$, so that $\int_0^{\infty} dr|\varphi|^2/r^2 < \infty$. Since functions of $D(H^*) \supset D_F(H)$ approach linear combinations of $r^{\pm\nu+1/2}$ in this limit, only $r^{+\nu+1/2}$ is possible, and that only if ν is real, i.e., $\gamma > -1/4$. Thus the Friedrichs extension amounts to appending the linear combination $\psi_+ - e^{2i\delta}\psi_-$, which behaves like $r^{\nu+1/2}$ as $r \to 0$. H is in fact a positive form only until the point $\gamma = -1/4$, since, by integration by parts,

$$\frac{1}{2}\int_0^{\infty} dr\,\frac{\varphi^2}{r^2} = \int_0^{\infty} dr\,\frac{\varphi'\varphi}{r} \le \left[\int_0^{\infty} dr\,\varphi'^2\right]^{1/2}\left[\int_0^{\infty} dr\,\frac{\varphi^2}{r^2}\right]^{1/2}$$

$$\Rightarrow \int_0^{\infty} dr\,\frac{\varphi^2}{r^2} \le 4\int_0^{\infty} dr\,\varphi'^2.$$

Equality holds for $\varphi' =$ constant, which means $\varphi =$ (const.)r, though at large r, φ must somehow go to 0. The large-r dependence can be arranged so that when $\gamma < -\frac{1}{4}$, the form H is no longer positive. For the other extension H_δ with $D(H_\delta) \not\subset Q(H)$ we have $\langle\varphi|H_\delta\varphi\rangle \ne \langle\varphi|H|\varphi\rangle = \infty$ for all $\varphi \in D(H_\delta)$, $\varphi \notin Q(H)$.

7. V sends F_- to the dense subspace D, and the association given by

$$a: f = i(1 - V)g \to (1 + V)g$$

is linear. As to whether the operator is Hermitian: It is necessary to show that $\langle f'|af\rangle = \langle af'|f\rangle$ for f and $f' \in D$, i.e.,

$$\langle +i(1 - V)g'|(1 + V)g\rangle = \langle(1 + V)g'|i(1 - V)g\rangle.$$

This is true because V is an isometry.

8. $\langle(c^{-1} - 1)\varphi|\psi\rangle = \langle\varphi|q|\psi\rangle = \langle a\varphi|\psi\rangle$ for all φ, $\psi \in Q(q) \Rightarrow a \supset c^{-1} - 1 \Rightarrow a = c^{-1} - 1$, since the latter operator is self-adjoint, and consequently can not have any proper, Hermitian extensions.

9. Simple integration by parts.

10. Let $\bar{\mathscr{H}} = \mathscr{H} \oplus \mathscr{H} \supset \Gamma(a) = (J\Gamma(a))^{\perp}$, and let $U: \bar{\mathscr{H}} \to \bar{\mathscr{H}}, (x, y) \to (y, x)$.

$\Gamma(a^{-1}) = U\Gamma(a) \Rightarrow \Gamma((a^{-1})^*) = (J\Gamma(a^{-1}))^{\perp} = (JU\Gamma(a))^{\perp} = U(J\Gamma(a))^{\perp} = U\Gamma(a)$,

i.e.,

$$\Gamma((a^{-1})^*) = \Gamma(a^{-1}), (a^{-1})^* = a^{-1}.$$

3 Quantum Dynamics

3.1 The Weyl System

Phase space is the arena of classical mechanics. The algebra of observables in quantum mechanics is likewise constructed with position and momentum, so this section covers the properties of those operators.

In classical mechanics, every function F on phase space generates a one-parameter group of diffeomorphisms $\exp(tL_{X_F})$ ($t \in \mathbb{R}$ and L_{X_F} is the Lie derivative with respect to the Hamiltonian vector field corresponding to F). Similarly, we learned in §2.4 that in quantum theory every observable a is associated with a one-parameter group of automorphisms $b \to \exp(iat)b \exp(-iat)$. One of the basic postulates of quantum theory is that, in units with $\hbar = 1$, the groups generated by the Cartesian position and momentum coordinates $\mathbf{x}_j$ and $\mathbf{p}_j$ of n particles ($j = 1, \ldots, n$) are the same as classically, i.e., displacements respectively in the momenta and positions. Since $\mathbf{x}_j$ and $\mathbf{p}_j$ do not have bounded spectra, and hence can not be represented by bounded operators, it is convenient to consider instead the bounded functions

$$\exp\left(i \sum_{j=1}^{n} \mathbf{x}_j \cdot \mathbf{s}_j\right) \quad \text{and} \quad \exp\left(i \sum_{j=1}^{n} \mathbf{p}_j \cdot \mathbf{r}_j\right), \qquad \mathbf{s}_j, \mathbf{r}_j \in \mathbb{R}^3,$$

so as not to have domain questions to worry about. The group of automorphisms can be written in terms of them as follows:

The Weyl Algebra (3.1.1)

The operators

$$\exp\left(i\sum_{j=1}^{n}\mathbf{x}_j\cdot\mathbf{s}_j\right) \quad \text{and} \quad \exp\left(i\sum_{j=1}^{n}\mathbf{p}_j\cdot\mathbf{r}_j\right)$$

generate the **Weyl algebra** $\mathscr{W}$ with the multiplication law

$$\exp\left(i\sum_{j=1}^{n}\mathbf{p}_j\cdot\mathbf{r}_j\right)\exp\left(i\sum_{j=1}^{n}\mathbf{x}_j\cdot\mathbf{s}_j\right)\exp\left(-i\sum_{j=1}^{n}\mathbf{r}_j\cdot\mathbf{p}_j\right)$$
$$=\exp\left(i\sum_{j=1}^{n}(\mathbf{x}_j+\mathbf{r}_j)\cdot\mathbf{s}_j\right)\text{ for all }\mathbf{s}_j,\mathbf{r}_j\in\mathbb{R}^3.$$

Remarks (3.1.2)

1. To simplify the notation, we consider $\mathbf{z}_j\equiv\mathbf{r}_j+i\mathbf{s}_j$ as a single vector in the Hilbert space $\mathbb{C}^{3n}$, with scalar product $(z|z')\equiv\sum_{j=1}^{n}\mathbf{z}_j^*\cdot\mathbf{z}_j'$ and volume element $dz=d^3r_1\cdots d^3r_n\,d^3s_1\cdots d^3s_n$. Then we define the **Weyl operators** by

$$W(z)\equiv\exp\left(-\frac{i}{2}\sum_{j=1}^{n}\mathbf{r}_j\cdot\mathbf{s}_j\right)\exp\left(i\sum_{j=1}^{n}\mathbf{r}_j\cdot\mathbf{p}_j\right)\exp\left(i\sum_j\mathbf{s}_j\cdot\mathbf{x}_j\right)$$
$$=W^*(-z)=W^{-1}(-z).$$

   The multiplication law (3.1.1) can then be written compactly as

$$W(z)W(z')=\exp\left(\frac{i}{2}\operatorname{Im}(z|z')\right)W(z+z').$$

   This shows that products of $W(z)$ can be written linearly in $W(z)$, so the algebra $\mathscr{W}$ consists of linear combinations of the $W(z)$.
2. We shall only be interested in representations for which $z\to W(z)$ is strongly continuous, so that we can recover $\mathbf{x}$ and $\mathbf{p}$ from knowledge of $W(z)$. In the representations we shall use, $\|W(z)-W(z')\|=2$ whenever $z\neq z'$. Norm continuity is impossible, as $\mathbf{x}$ and $\mathbf{p}$ are always unbounded.
3. The C^* algebra gotten by taking the norm closure of $\mathscr{W}$ is too small for many purposes. In order to include all L^∞ functions of $\mathbf{x}$ and $\mathbf{p}$, it is necessary to take the strong closure $\bar{\mathscr{W}}$. The question then arises whether the isomorphism mentioned above, of the canonical and unitary transformations, can be extended to other coordinate systems involving L^∞ functions of $\mathbf{x}$ and $\mathbf{p}$. One cause for concern is that because of the noncommutativity of observables, a classical function $f(p,x)$ does not have a uniquely determined quantum mechanical version: Is the classical function p^2x^3 to be px^3p or $(p^2x^3+x^3p^2)$, which by formal manipulation of (1.1.1) equals $-3x+px^3p$? It can even happen that the product of operators simply fails to be

defined because of the lack of a domain of definition (cf. (3.1.10; 5)). We shall not generally be able to settle the question of the proper quantum mechanical operators associated with all classical observables and find what groups they generate but shall instead consider successively more complicated special cases.

For a better understanding of the possible representations of $\mathscr{W}$, we consider the

Mapping of $L^1(\mathbb{C}^{3n})$ into $\overline{\mathscr{W}}$ (3.1.3)

Given a strongly continuous representation of $\mathscr{W}$,

$$W_f \equiv \int dz\, f(z)W(z) \in \overline{\mathscr{W}}$$

is well-defined for all $f \in L^1(\mathbb{C}^{3n})$, and:

(i) $W_{f+g} = W_f + W_g$;
(ii) $W_f^* = W_{\bar{f}}$, $\bar{f}(z) = f^*(-z)$;
(iii) $W_{f*g} = W_f \cdot W_g$, $(f * g)(z) = \int dz'\, f(z - z')g(z')\exp((i/2)\mathrm{Im}(z|z'))$;
(iv) $W_{f_0}W(z)W_{f_0} = W_{f_0}\exp(-\frac{1}{4}(z|z))$ for all $z \in \mathbb{C}^{3n}$,
$f_0(z) = (2\pi)^{-3n}\exp(-((z|z)/4))$;
(v) *The mapping $L^1 \to \mathscr{B}(\mathscr{H})$: $f \to W_f$ is injective*;
(vi) $\|W_f\| \leq \|f\|_1$.

Proof

Since $W(z)$ is strongly continuous, the integral is defined as a strong limit, but will not necessarily be in the norm closure of $\mathscr{W}$.

(i) and (ii) are obvious.
(iii) follows from (3.1.2; 1).
(iv) follows from (3.1.2; 1) and a Gaussian integral (Problem 5).
(v) If $W_f = 0$, then for all $z' \in \mathbb{C}^{3n}$ and $g, h \in \mathscr{H}$,

$$0 = \int dz\, f(z)\langle g|W(-z')W(z)W(z')h\rangle$$

$$= \int dz\, f(z)\exp(i\,\mathrm{Im}(z|z'))\langle g|W(z)h\rangle.$$

Now choose $h = W(z)^{-1}g$ and observe that the Fourier transform of f vanishes, and therefore so does f itself as an element of L^1.

(vi) Since $W(z)$ is unitary, $\|W(z)\| = 1$ for all $z \in \mathbb{C}^{3n}$, and

$$\left\| \int dz\, f(z) W(z) \right\| \leq \int dz |f(z)| \|W(z)\|. \qquad \square$$

Consequences (3.1.4)

Property (iv) implies that $W_{f_0} = W_{f_0}^*$ is a projection, and that $\mathscr{W} W_{f_0} \mathscr{H}$ is all of $\mathscr{H}$: The space orthogonal to it would be invariant under $\mathscr{W}$ and such that W_{f_0} would vanish on it, as $\langle y | W_{f_0} x \rangle = \langle W_{f_0} y | x \rangle = 0$ for all $x \in \mathscr{H} \Rightarrow W_{f_0} y = 0$. Thus in this subspace we would have a representation of $\mathscr{W}$ with $W_{f_0} = 0$, which is impossible by Property (v). Therefore the subspace $W_{f_0} \mathscr{H}$ is a totalizer for $\mathscr{W}$, and in an orthogonal basis $\{u_j\}$ of $W_{f_0} \mathscr{H}$ with $W_{f_0} u_j = u_j$, the representation has the form:

$$\begin{aligned} \langle u_j | W(z) u_k \rangle &= \langle u_j | W_{f_0} W(z) W_{f_0} u_k \rangle \\ &= \langle u_j | W_{f_0} u_k \rangle \exp\left(-\frac{(z|z)}{4} \right) = \delta_{jk} \exp\left(-\frac{(z|z)}{4} \right). \end{aligned}$$

This argument proves

The Uniqueness Theorem of Representations of W (3.1.5)

Every strongly continuous representation of $\mathscr{W}$ is equivalent to a sum of cyclic representations with

$$\langle u | W(z) u \rangle = \exp\left(-\frac{(z|z)}{4} \right).$$

Remarks (3.1.6)

1. If $\mathscr{H}$ is separable, then the sum is countable.
2. In the spectral representation of $\mathbf{x}$, the operator W_{f_0} projects onto

$$u(\mathbf{x}) = \pi^{-3n/4} \exp\left(-\sum_j \frac{x_j^2}{2} \right),$$

and

$$(W(z)u)(\mathbf{x}) = \exp\left(i \sum_{j=1}^{3n} s_j \left(x_j + \frac{r_j}{2} \right) \right) u(x_j + r_j)$$

(Problem 2).

3. If the assumption of strong continuity is left out, then there are more representations. Suppose $\mathscr{H}$ is as in (2.4.14; 2), and that, as before, $(W(z)\psi)_x = \exp(is(x + r/2))\psi_{x+r}$. This constitutes another representation of $\mathscr{W}$, on a nonseparable $\mathscr{H}$. It is definitely not equivalent to (3.1.5), since $\exp(ixs)$ has a purely discrete spectrum, every $z \in \mathbb{C}: |z| = 1$ is an eigenvalue. In this example the operator p does not even exist.
4. There are inequivalent representations of $\mathscr{W}$ for infinite systems ($n = \infty$), in fact uncountably many of them, even on separable Hilbert spaces. (See volume IV.)
5. If x-space is not infinite, but rather a torus (I: 2.1.7; 2), then there are infinitely many inequivalent representations of the Weyl relations. In that case $\exp(i\sum_{j=1}^{n} \mathbf{x}_j \cdot \mathbf{s}_j)$ is an observable only if $s_j \in (2\pi\mathbb{Z})^3$, and (3.1.1) is valid only for these s_j. The operator p is again formally the derivative $-i(d/dx)$, but, according to (2.5.3; 4) this has a one-parameter family of self-adjoint extensions corresponding to the boundary conditions $\psi(1) = e^{-ij}\psi(0), 0 \leq j \leq 2\pi$, for $\psi \in L^2(0, 1) \cong L^2(T^1)$. Then $-(d/dx)$ has the eigenfunctions e^{ikx} with eigenvalues $k = 2\pi\mu - j, \mu \in \mathbb{Z}$. The representations are clearly inequivalent for different j and inequivalent to the representation (3.1.5), where the spectrum is absolutely continuous rather than pure point.
6. Theorem (3.1.5) gives what is known as a **ray representation** of $\mathbb{R}^{6n}$, which means that $W(z)W(z')$ equals $W(z + z')$ up to a phase factor. It may seem peculiar that the representation of $\mathscr{W}$ is essentially unique, even though every subgroup of $\mathbb{R}^{6n}$ is an invariant subgroup (a normal divisor), and a representation of any factor group is also a representation of $\mathbb{R}^{6n}$. The state of affairs can be understood as follows: for any $r \in \mathbb{R}$, the integral multiples $\{nr\}$, $n \in \mathbb{Z}$, constitute a normal divisor of $\mathbb{R}$, and $t \to \exp(2\pi it/r)$ is the unique faithful representation of the factor group $\mathbb{R}/\{nr\}$. Hence there exists a one-parameter family of unfaithful representations of $\mathbb{R}$, and every (strongly continuous) representation is a sum or integral of them. However, the Weyl algebra is simple—it contains no nontrivial subideal—so that only the trivial representation fails to be faithful, and the irreducible faithful representations are all equivalent.

The self-adjoint generators $\mathbf{x}_j$ and $\mathbf{p}_j$ can be recovered from $W(z)$ by differentiation. Yet the problem remains of being precise about the commutation relations (1.1.1), since unbounded operators do not form an algebra. However, the fact that two operators commute can easily be interpreted in a mathematically reasonable way:

Definition (3.1.7)

The statement that two unbounded, self-adjoint operators a and b **commute** will mean that $f(a)g(b) - g(b)f(a) \equiv [f(a), g(b)] = 0$ for all f and $g \in L^\infty$. We shall write this for simplicity as $[a, b] = 0$.

Remarks (3.1.8)

1. For $[a, b]$ to equal 0, it suffices that $[\exp(iat), \exp(ibs)] = 0$ for all $t, s \in \mathbb{R}$, or that $[(a - z)^{-1}, (b - z')^{-1}] = 0$ for all $z, z' \in \mathbb{C}\backslash\mathbb{R}$ (Problem 6). A consequence of (3.1.1) is thus that $[\mathbf{x}_k, \mathbf{x}_j] = [\mathbf{p}_k, \mathbf{p}_j] = 0$ for all k, j, and $[\mathbf{x}_k, \mathbf{p}_j] = 0$ for $k \neq j$.
2. The Gel'fand isomorphism (2.2.28) is still applicable to the C^* algebra generated by the bounded, continuous functions of such a and b, and it provides a spectral representation in which both a and b are multiplication operators. This is a generalization of the simultaneous diagonability of commuting Hermitian matrices.
3. It is tempting to conjecture that $[a, b] = 0$ whenever

   (i) there exists a dense domain D invariant under a and b;
   (ii) a and b are essentially self-adjoint on D; and
   (iii) $ab\psi = ba\psi$ for all $\psi \in D$.

   This is false; see the counterexample of Problem 4.

To make sense of $[x_k, p_j]$ for $k = j$, we need to find a $D \subset D(x_k) \cap D(p_i)$ such that $x_k D \subset D(p_j)$ and $p_j D \subset D(x_k)$. One such domain consists of the vectors that belong to $\mathscr{S}$ in the x-representation, where $\mathscr{S}$ is the space of C^∞ functions that decrease at infinity along with all their derivatives faster than any negative power of x. This space equals its Fourier transform $\hat{\mathscr{S}}$, and on $\mathscr{S}$, $x: f(x) \to xf(x)$, $p: f(x) \to -i(\partial/\partial x)f(x)$, while on $\hat{\mathscr{S}}$, $x: f(p) \to i(\partial/\partial p)f(p)$ and $p: f(p) \to pf(p)$. On $\mathscr{S}$ we can write

The Heisenberg Commutation Relations (3.1.9)

$$(x_k p_j - p_j x_k)\psi = i\delta_{kj}\psi \text{ for all } \psi \in \mathscr{S}.$$

Remarks (3.1.10)

1. The operators x and p are clearly Hermitian on $\mathscr{S}$ with deficiency indices $(0, 0)$, and thus essentially self-adjoint.
2. It is a natural question whether all representations of $[x_k, p_j] = i\delta_{kj}$ on dense domains D of essential self-adjointness lead to the Weyl relations (3.1.1). The answer is no. Additional assumptions are needed, such as that $\sum_{k=1}^{3n} x_k^2 + \sum_{k=1}^{3n} p_k^2$ be essentially self-adjoint on D. Otherwise, a variant of Problem 4 would provide a counterexample. Another possible condition is that $\prod_k (x_k + i)(p_k + i)D$ be dense in $\mathscr{H}$.
3. It has already been noted that finite matrices can not satisfy (3.1.9). It is likewise impossible to represent p and x with bounded operators of any kind. Equation (3.1.9) also requires that $x^n p - px^n = inx^{n-1}$, so $n\|x^{n-1}\| = \|x^n p - px^n\| \leq 2\|x^n\| \cdot \|p\|$, and thus $\|x\| \cdot \|p\| \geq n/2$ for all n.

4. There are many inequivalent representations of x and p if we allow matrices that satisfy $xp - px = i$ on some dense domain by formal manipulation; for instance,

$$x = \begin{bmatrix} 0 & & & & \\ & 1 & & & \\ & & 2 & & \\ & & & 3 & \\ & & & & 4 \end{bmatrix}, \quad p = -i \begin{bmatrix} 0 & -1 & -\frac{1}{2} & -\frac{1}{3} & \cdots \\ 1 & 0 & -1 & -\frac{1}{2} & \cdots \\ \frac{1}{2} & 1 & 0 & -1 & \cdots \\ \frac{1}{3} & \frac{1}{2} & 1 & 0 & \cdots \end{bmatrix}$$

$$[x, p] = -i \begin{bmatrix} 0 & 1 & 1 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & 1 & 1 & 1 \\ 1 & 1 & 1 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 & 0 & 1 \end{bmatrix}.$$

On $D = \{(v) \in l^2 : \sum_i v_i = 0$, with only finitely many $v_i \neq 0\}$, with these matrices, $[x, p] = i$. This representation is not equivalent to the Weyl representation: $\mathrm{Sp}(x) = \mathbb{Z}^+$. The eigenvectors e_k of x do not belong to D, as otherwise there would be a contradiction, $(e_k | [x, p] e_k) = 0 = i(e_k | e_k)$.

5. One might hope that the Poisson bracket $\{\ \}$ of classical mechanics goes over to the commutator in quantum mechanics not just for the Cartesian coordinates p and x, but also for generalized coordinates (cf. (3.1.2; 3)). Unfortunately, it does not. Consider p and x on the one-dimensional torus (circle) T^1; while x, $0 \leq x < 1$, is not a global coordinate, the equation $\{x, p\} = 1$ holds locally. Suppose that the quantum-mechanical Hilbert space is $\mathscr{H} = L^2(T^1, dx)$. Then the formal equation $[x, p] = i$ makes no sense as an operator equation, since p is defined only on the absolutely continuous functions on T^1 (which implies that $\psi(0) = \psi(1)$), while x maps functions out of this subspace. If the matrix elements are calculated with respect to the eigenfunctions $\psi_n = \exp(2\pi i n x)$, $n \in \mathbb{Z}$, then

$$\langle n | p | m \rangle = n\delta_{nm}, \qquad \langle n | x | m \rangle = \frac{i(-1)^{n-m}}{2\pi(n-m)}(1 - \delta_{nm}) + \tfrac{1}{2}\delta_{nm},$$

and if these matrices are multiplied, one finds (Problem 8) that $[x, p] \neq i$. Hence (3.1.9) is not even valid in the sense of quadratic forms, so the representations (3.1.6; 5) can not strictly speaking be characterized by (3.1.9).

Following Remark (2.2.33; 3), the commutation relations (3.1.9) have as a consequence the

Indeterminacy Relations (3.1.11)

$$\Delta x_i \, \Delta p_k \geq \tfrac{1}{2}\delta_{ik}.$$

Remarks (3.1.12)

1. There are, of course, some domain questions to answer when Remark (2.2.33; 3) is extended to unbounded operators; but assuming that there is no real difficulty, (3.1.4) applies equally to all states, so there is no need for an index on Δ.
2. A natural question is whether there can be equality in (3.1.11), and, if so, for which states. The inequality of (2.2.33; 4) is of the form $\langle (a^* - \alpha^*)(a - \alpha)\rangle \geq 0$ for pure states, where we have let $a = x + 2ip(\Delta x)^2$ and $\alpha = \langle x\rangle + 2i\langle p\rangle(\Delta x)^2$. Equality would require that the state $|\,\rangle$ be an eigenvector of the (nonnormal) operator a with complex eigenvalue α. The operators a are the annihilation operators that are so important in the theory of many-particle physics.

In an x-representation ($p = (1/i)(\partial/\partial x$, $|\,\rangle = \psi(x) \in L^2(\mathbb{R}, dx)$), the a's can be used according to (3.1.12; 2) to construct

States of Minimal Uncertainty, or Coherent States (3.1.13)

The equation

$$\Delta p = \frac{1}{2\Delta x}$$

holds only for the states

$$\psi(x) = \exp\left[- \frac{(x - \langle x\rangle - 2i\langle p\rangle(\Delta x)^2)^2}{4(\Delta x)^2} \right].$$

Remarks (3.1.14)

1. If $\Delta x = \frac{1}{2}$, then we get the states $W(z)|u\rangle$ of (3.1.6; 2) with $z = \langle x\rangle + i\langle p\rangle$, which appeared in the GNS construction for the Weyl algebra. It follows that linear combinations of states of minimal uncertainty are dense in $\mathscr{H}$. The additional parameter Δx occurring here provides a standard of comparison between x and p, and was fixed earlier in the choice of f_0. States with different z are not orthogonal, even with the same Δx. There is, however, an analogue of the representation of the identity operator in an orthonormal system:

$$\mathbf{1} = \int \frac{dz}{2\pi} W(z)|\,\rangle\langle\,|W(-z)$$

This equation in fact holds for any normalized vector $|\,\rangle \in L^1 \cap L^\infty$ (Problem 7). The states $W(z)|\,\rangle$ are thus not only total, but moreover every vector can be written as an integral over them.

2. There is a strict inequality $(\Delta x)^2(\Delta p)^2 > \frac{1}{4}$ for impure states. Problem (2.2.38; 6) showed that $(\Delta x)^2$ and $(\Delta p)^2$ for a convex combination of two states are greater than or equal to the convex combinations of the two $(\Delta x)^2$ and the two $(\Delta p)^2$ of the constituent states, and equality holds only if the expectation values are the same in the two states. Since $\langle p\rangle$, $\langle x\rangle$, and $\Delta x = 1/2\Delta p$ determine a unique coherent state, any genuine mixture of states will have $\Delta x\,\Delta p > \frac{1}{2}$: If states are averaged with a weight $\rho(\lambda) \geq 0$,

$$\int_0^1 d\lambda\, \rho(\lambda) = 1, \qquad W(a) = \int d\lambda\, \rho(\lambda)\langle a\rangle_\lambda,$$

then

$$(\Delta_W x)^2(\Delta_W p)^2 \geq \int_0^1 d\lambda (\Delta_\lambda x)^2 \rho(\lambda) \int_0^1 d\lambda' (\Delta_{\lambda'} p)^2 \rho(\lambda')$$
$$\geq \left(\int d\lambda\, \rho(\lambda)\Delta_\lambda x \Delta_\lambda p\right)^2 \geq \tfrac{1}{4}.$$

The last inequality is an equality only if $\Delta_\lambda x\,\Delta_\lambda p = \frac{1}{2}$, and the second one is an equality only if $\Delta_\lambda x = c\,\Delta_\lambda p$, so $\Delta_\lambda x = 1/2\Delta_\lambda p$ is independent of λ. But the first one is an equality only if all $\langle x\rangle_\lambda$ and $\langle p\rangle_\lambda$ are the same; so no genuine mixture makes all three equalities.

The Classical Limit (3.1.15)

Until now, we have taken the microscopic standpoint and set $\hbar = 1$. In order to see how the operators turn into ordinary numbers in the classical limit $\hbar \to 0$, let

$$x_\hbar = x\sqrt{\hbar}, \qquad p_\hbar = p\sqrt{\hbar}, \qquad [x_\hbar, p_\hbar] = i\hbar.$$

If we used $W(z/\sqrt{\hbar})$ to cause a displacement by $r/\sqrt{\hbar}$ (respectively $s/\sqrt{\hbar}$) on $L^2(\mathbb{R}, dx)$ (resp. $L^2(\mathbb{R}, dp)$) at the same time as we let $\hbar \to 0$, then we would expect $x_\hbar$(resp. $p_\hbar$) to converge to $r\cdot\mathbf{1}$ (resp. $s\cdot\mathbf{1}$). Indeed, the equation

$$W(z\hbar^{-1/2})\exp(is(x_\hbar - r))W(-z\hbar^{-1/2}) = \exp(isx_\hbar)$$

can be derived from (3.1.2; 1). As $\hbar \to 0$, $\exp(isx_\hbar) = (\exp(isx))^{\sqrt{\hbar}} \to 1$, so

$$W(z\hbar^{-1/2})\exp(isx_\hbar)W(-z\hbar^{-1/2}) \to \exp(isr),$$

and analogously for $\exp(itp_\hbar)$. In the sense of (2.5.8; 3), the operators $Wx_\hbar W^{-1}$ and $Wp_\hbar W^{-1}$ converge strongly to r and respectively s; the dilatation by $\hbar$ suppresses the fluctuations, and W translates the operators back to the proper positions.

If the particles are indistinguishable, then only the algebra $\mathcal{N}_s$ of symmetric functions of the $\mathbf{x}_i$ and $\mathbf{p}_i$ is observable. This algebra has a reducible

representation on $\mathscr{W} \cdot u$: the unitary operator Π, permuting the indices $(1, 2, \ldots, n)$ to $(\pi_1, \pi_2, \ldots, \pi_n)$, $\Pi \mathbf{x}_i \Pi^{-1} = \mathbf{x}_{\pi_i}$, $\Pi \mathbf{p}_i \Pi^{-1} = \mathbf{p}_{\pi_i}$, then commutes with all observables. The set of permutations forms a representation of the symmetric group S_n. If it is decomposed into its irreducible parts, then $\mathscr{N}_s$ maps each part into itself, and there is a superselection rule (cf. (2.3.6; 7)). Unless we restrict ourselves to the identical or alternating representation of S_n, the algebra $\mathscr{N}_s$ contains no maximal Abelian subalgebra, and the Π become the hidden parameters mentioned in (2.3.6; 7). By definition they can never be observed, but they decompose the Hilbert space since they do not simply multiply by ± 1. These superselection rules apparently do not exist in Nature.

The identical (respectively alternating) representation of S_n is obtained by restricting the tensor product of the Hilbert spaces belonging to individual particles to the symmetric (antisymmetric) subspace (cf. (I: 2.4.28)). As is well known, the symmetrization or antisymmetrization of ψ in the particle coordinates leads to Bose–Einstein or respectively Fermi–Dirac statistics. Relativistic quantum theory correlates these statistics with the spin of the particle, but in the framework of nonrelativistic quantum mechanics it appears as a special postulate:

The Connection between Spin and Statistics (3.1.16)

For a system of indistinguishable particles with integral (respectively half-odd integral) spin, the representation must be restricted to the subspace of the identical (resp. alternating) representation of S_n.

Problems (3.1.17)

1. Let $\mathscr{A} = \mathscr{B}(\mathbb{C}^2) \otimes \mathscr{B}(\mathbb{C}^2) = \{\sigma_1 \otimes \sigma_2\}''$. Construct a P such that $P\sigma_1 P = \sigma_2$ and $P = P^* = P^{-1}$.
2. Verify the x-representation of u (3.1.6; 2).
3. According to (2.4.23; 5), a dense set of analytic vectors determines $\exp(iat)$ uniquely, and thus a Hermitian operator a defined on such a set is essentially self-adjoint. Show that the analytic vectors for $a = -i\, d/dx$ on the space $L^2((-\infty, \infty), dx)$ are (complex-valued) real-analytic functions.
4. Let M be the Riemann surface of $\sqrt{z}$ and $\mathscr{H} = L^2(M, dz = dx\, dy)$. Moreover, let the operators $a = -i\, \partial/\partial x$ and $b = -i\, \partial/\partial y$ be defined on $D = \{C^\infty$ functions with compact support not including $0\}$. Show that
   (i) a and b are essentially self-adjoint;
   (ii) D is mapped into itself by a and b;
   (iii) $ab\psi = ba\psi$ for all $\psi \in D$;
   but for the closures $\bar{a} = a^{**}$ and $\bar{b} = b^{**}$,
   (iv) $\exp(i\bar{a}t)\exp(i\bar{b}t) \neq \exp(i\bar{b}t)\exp(i\bar{a}t)$.

5. Verify (3.1.3(iv)).

6. Show that a sufficient condition for two operators to commute is that their exponentials or resolvents commute.

7. Verify (3.1.14; 1).

Solutions (3.1.18)

1. $P = (1 + \sigma_1 \cdot \sigma_2)/2$.

2. $$W_{f_0} u = \int \frac{d^{3n}r\, d^{3n}s}{(2\pi)^{3n}} \exp\Big(-\sum_j (|\mathbf{r}_j|^2 + |\mathbf{s}_j|^2)/4\Big)\exp\Big(i\sum_j \mathbf{s}_j \cdot (\mathbf{x}_j + \mathbf{r}_j/2)\Big)$$
$$\times \exp\Big(-\sum_j |\mathbf{x}_j + \mathbf{r}_j|^2/2\Big)\pi^{-3n/4} = u.$$

3. If $\psi \in L^2$ is an analytic vector, then $\psi \in \bigcap_n D(a^n) \subset C^\infty$.
$$e^{iat}\psi(x) = \psi(x + t) = \sum \frac{(it)^n}{n!} a^n \psi(x).$$
The sum converges iff ψ is analytic.

4. Propositions (ii) and (iii) are obvious, as are $a \subset a^*$ and $b \subset b^*$. As for essential self-adjointness: Let $D_x \subset D$ be the set of all functions the support of which never contains the x-axis on any sheet of the Riemann surface of $\sqrt{z}$. D_x is dense. The operators $U(t)$: $\psi(x, y) \to \psi(x + t, y)$ are isometric and have dense ranges, so they have unique unitary extensions, which are strongly continuous in t. $U(t)$ is differentiable on D_x, and $dU(t)/dt = ia_{|D_x}$, so $a_{|D_x}$ is essentially self-adjoint (cf. Problem 3), and therefore so is a. The argument for b is similar; $ib_{|D_y} = dV(t)/dt$, $V(t)$: $\psi(x, y) \to \psi(x, y + t)$, and $D_y \subset D$ is the set of functions the support of which never contains the y-axis on any sheet.
(iv): Let ψ be a function supported in the circle centered at $(-\frac{1}{2}, -\frac{1}{2})$ on the first sheet and having some radius less than $\frac{1}{2}$. Then $U(1)V(1)\psi$ has its support on the first sheet and $V(1)U(1)\psi$ has its support on the second sheet, so $U(1)V(1) \neq V(1)U(1)$.

5. This calculation of a Gaussian integral will be entrusted to the reader.

6. The von Neumann algebra $\mathcal{A} = \{f(a): f \in L^\infty\}$ is generated by

(i) the exponential functions $\exp(iat)$: If $f \in L^1$, then the Fourier transform
$$\int f(t)\exp(iat)dt \in \mathcal{A}.$$
But the Fourier transformation is a bijection $L^1 \cap L^\infty \to L^1 \cap L^\infty$, and $L^1 \cap L^\infty$ is weakly dense in L^∞.

(ii) the resolvents $(a + x + iy)^{-1}$:
$$(a + x + iy)^{-1} + (a + x - iy)^{-1} = 2(a + x)((a + x)^2 + y^2)^{-1}$$
and
$$(a + x + iy)^{-1} - (a + x - iy)^{-1} = -2iy((a + x)^2 + y^2)^{-1},$$

and by the Stone–Weierstrass theorem, these functions generate all continuous functions vanishing at infinity, which is also a weakly dense set in L^∞. If there are two algebras $\mathscr{A}_0$ and $\mathscr{B}_0$ such that $\mathscr{A}_0'' = \mathscr{A}$ and $\mathscr{B}_0'' = \mathscr{B}$, and for which $[\mathscr{A}_0, \mathscr{B}_0] = 0$, then $[\mathscr{A}, \mathscr{B}]$ also $= 0$.

7. Let $\psi(x)$ be $|\rangle$ in the x-representation. Then $W(z)|\rangle$ becomes $e^{ixs}\psi(x + r)$ and $\int (dz/2\pi)W(z)|\rangle\langle|W^*(z)\varphi$ is

$$\int \frac{ds\,dr}{2\pi} e^{ixs}\psi(x + r)\psi^*(x' + r)e^{-ix's}\varphi(x')dx' = \int dr|\psi(x + r)|^2\varphi(x) = \varphi(x).$$

This formal manipulation can easily be justified for instance if $\psi \in L^1 \cap L^\infty$.

3.2 Angular Momentum

In quantum physics, just as in classical physics, the angular momentum **L** *is the generator of the group of rotations. This group is compact, so all of its irreducible representations are finite-dimensional. It is possible, however, for* **L** *to be unbounded in a reducible representation.*

In the earlier sections it was postulated that the group of canonical transformations in classical mechanics generated by p and x was represented in quantum theory by $\exp(irp)$ and respectively $\exp(isx)$. The next most simple group of transformations to study is the one generated by the angular momentum $\mathbf{L} = [\mathbf{x} \times \mathbf{p}]$. Classically, **L** generates the point transformations

$$\mathbf{x} \to M\mathbf{x}, \qquad MM^t = \mathbf{1}. \tag{3.2.1}$$

We consider here a single particle and use matrix notation; everything factorizes for systems of many particles. In quantum theory it is more convenient to work with the bounded Weyl operators, so we wish to find a unitary transformation U for which

$$U^{-1}W(z)U = W(Mz) \tag{3.2.2}$$

(cf. (3.1.2; 1)). Such a transformation must exist, since the operators $W(Mz)$ also satisfy (3.1.2; 1), and all irreducible representations of those relationships are equivalent. Following (3.1.6; 2) we can write (3.2.2) in the

Schrödinger Representation for the Rotations (3.2.3)

The unitary transformation

$$(U\psi)(x) = \psi(Mx)$$

produces the automorphism (3.2.2) of the Weyl algebra.

Remark (3.2.4)

The operator U is not fixed uniquely by (3.2.3); $e^{i\alpha}U$ would do just as well for any $\alpha \in \mathbb{R}$. This, however, is the extent of the arbitrariness in an irreducible representation of $W(z)$, as U is determined up to a unitary element of the commutant. Hence at this stage the U's only constitute a ray representation of $O(3)$ [cf. (3.1.6; 5)]. Yet it is possible to show that every strongly continuous ray representation of a compact group is derived from a representation of the universal covering group (see Problem 5). The universal covering group of $O(3)$ is $SU(2)$, which will be discussed in more detail later. The compactness is essential: The Weyl system (3.1.1) provides a ray representation of $\mathbb{R}^{6n}$, which is its universal covering group, but it is not a representation in the ordinary sense.

The generators of the one-parameter subgroups of rotations about the coordinate axes will be denoted $\mathbf{L}$, as a vector operator. We begin the study of the generators by determining a

Domain of Essential Self-Adjointness for $\mathbf{L}$ (3.2.5)

The operator $\mathbf{L}$ *is essentially self-adjoint on the linear hull* D *of the vectors*

$$\psi_k = \exp\left(-\frac{|x|^2}{2}\right) x_1^{k_1} x_2^{k_2} x_3^{k_3}, \qquad k_i = 0, 1, 2, \ldots .$$

Proof

D is dense (Problem 2) and obviously invariant under rotations. It is convenient to change to polar coordinates about the z-axis = the axis of rotation to check the differentiability of U on D. It is then a question of showing that

$$\lim_{\delta \to 0} \delta^{-2} \int_0^{2\pi} d\varphi \, |P(\sin(\varphi + \delta), \cos(\varphi + \delta)) - P(\sin\varphi, \cos\varphi) - \delta P'(\cos\varphi, -\sin\varphi)|^2 = 0,$$

where P is a polynomial and P' is its derivative. Since the integral is over a compact set, its existence poses no difficulties. Taylor's formula allows the difference to be estimated with P'', which remains bounded in $[0, 2\pi]$. Since the integrand converges pointwise, differentiability follows from Lebesgue's dominated convergence theorem. Thus D is contained in the domain of the generators. It remains to be shown that it is large enough for essential self-adjointness. To this end, consider the finite-dimensional subspace D_k generated by $\{\psi_k \in D: k_1 + k_2 + k_3 \leq k\}$, which is invariant under rotations and therefore represents the L's by finite matrices. All vectors are entire for finite matrices, so D is a dense set of entire vectors. According to (2.4.23; 5), it determines U uniquely, which means that $\mathbf{L}$ is essentially self-adjoint on D.

The connection between U and L can be written explicitly as

$$U_{\delta e} = \exp(i\delta \mathbf{L} \cdot \mathbf{e}),$$

where $\mathbf{e}$ is a unit vector in the direction of the axis of rotation. In polar coordinates it is apparent that $-i(x\,\partial/\partial y - y\,\partial/\partial x) = -i\,\partial/\partial\varphi$ has the same action as L_z on ψ_k, so on D,

$$\mathbf{L} = [\mathbf{x} \times \mathbf{p}]. \qquad \square$$

Remarks (3.2.6)

1. U is not strongly differentiable on all of $L^2(\mathbb{R}^3)$—e.g., not on $\exp(-|\mathbf{x}|^2/2)\,\Theta(|\varphi| - \alpha), 0 < \alpha < \pi$. Hence $\mathbf{L}$ is unbounded in the representation (3.2.3).
2. Furthermore, D is invariant under x_j and p_j, which are essentially self-adjoint on it (Problem 3). It is contained in the intersection of the three distinct domains on which $\mathbf{x}$, $\mathbf{p}$, and $\mathbf{L}$ are self-adjoint.
3. The sets D_k also consist of entire vectors for the operator $|\mathbf{L}|^2 = L_1^2 + L_2^2 + L_3^2$, since there is no question that

$$\sum_{n=0}^{\infty} (|\mathbf{L}_{|D_k}|^2)^n \frac{t^n}{n!}$$

converges for all $t \in \mathbb{C}$. According to (2.4.23; 5), this means that $|\mathbf{L}|^2$ is essentially self-adjoint on D.

The Commutation Relations of L (3.2.7)

Since $\mathbf{L}$ is the generator of the rotations, its commutators with other operators tell how much they change under infinitesimal rotations. Thus, on D,

$$[L_m, V_r] = i\varepsilon_{mrs} V_s. \text{ for } \mathbf{V} = \mathbf{L}, \mathbf{x}, \text{ or } \mathbf{p}. \tag{3.2.8}$$

These relations can be derived by differentiating (3.2.2) or directly from (3.1.9). The operator $|\mathbf{L}|^2$, as a scalar, commutes with $\mathbf{L}$:

$$[L_m, |\mathbf{L}|^2] = 0, \qquad m = 1, 2, 3. \tag{3.2.9}$$

These relationships are all initially valid on vectors of D, and can then be extended to exponential functions in the sense of (3.1.7), since the vectors of D are entire for $\mathbf{L}$, $|\mathbf{L}|^2$, $\mathbf{x}$, and $\mathbf{p}$. In this extended sense, it is also true that $[\mathbf{L}, |\mathbf{x}|^2] = [\mathbf{L}, |\mathbf{p}|^2] = 0$.

Parity (3.2.10)

The group $O(3)$ has two separate parts, depending on whether $\text{Det } M = \pm 1$. The matrix $M = -\mathbf{1}$ belongs to the component not connected with $\mathbf{1}$, and can not be attained by letting one-parameter, continuous subgroups act on $\mathbf{1}$.

The division of the group in two parts corresponds to the **parity operator** P such that

$$P^{-1}W(z)P = W(-z).$$

The phase factor is fixed by the condition that

$$(P\psi)(\mathbf{x}) = \psi(-\mathbf{x}), \qquad \psi \in L^2(\mathbb{R}^3),$$

so that we have $P^2 = \mathbf{1}$ and $P^{-1} = P^* = P$. The parity operator changes the sign of both $\mathbf{x}$ and $\mathbf{p}$, and thus commutes with $\mathbf{L}$:

$$P\mathbf{L}P^{-1} = \mathbf{L}.$$

Remark (3.2.11)

Just as with $\mathbf{L}$, P can be constructed out of $\mathbf{x}$ and $\mathbf{p}$ (Problem 1). This is different from classical mechanics, where although every one-parameter group of canonical transformations has a function of $\mathbf{x}$ and $\mathbf{p}$ as its generator, the finite canonical transformation $\mathbf{x} \to -\mathbf{x}$, $\mathbf{p} \to -\mathbf{p}$, has no infinitesimal generator; it can not be reached by a continuous path from the identity.

The Spectrum of L (3.2.12)

Let us consider one of the components of $\mathbf{L}$, say L_3, and the Abelian C^* algebra $\mathscr{L}_3$ generated by $\exp(i\delta L_3)$. Because of the Gel'fand isomorphism (2.2.28), every point of the spectrum corresponds to a character on $\mathscr{L}_3$. Since, from (3.2.3), $\exp(2\pi i L_3) = \mathbf{1}$, every character is of the form $\exp(i\delta L_3) \to \exp(im\delta)$, $m \in \mathbb{Z}$, and so the only possible spectral values of L_3 (or the component of $\mathbf{L}$ in any other direction) are whole numbers. The construction given below will show that all these possible values actually occur.

The Eigenvectors of L (3.2.13)

Different components of $\mathbf{L}$ do not commute with one another, so their only common eigenvectors ψ must be eigenvectors of their commutators with eigenvalue 0. Since the commutator of any two orthogonal components of $\mathbf{L}$ is always the third component, $\mathbf{L}\psi$ must equal 0, and ψ is invariant under rotations ($\psi(x) = \psi(r)$).

However, $[|\mathbf{L}|^2, \mathbf{L}] = 0$ when acting on any vector, so it is possible to have common vectors $|l, m\rangle$ of $|\mathbf{L}|^2$ and L_3:

$$L_3|l, m\rangle = m|l, m\rangle, \qquad |\mathbf{L}|^2|l, m\rangle = l(l+1)|l, m\rangle.$$

(letting the eigenvalues of $|\mathbf{L}|^2$ be $l(l+1)$, with the benefit of hindsight). In order to discover the possible values of the new eigenvalue $l \geq 0$ and its relationship to m, note that $l(l+1)$ must always be $\geq m^2$, because $\langle l, m||\mathbf{L}|^2|l, m\rangle = m^2 + \langle l, m|L_1^2|l, m\rangle + \langle l, m|L_2^2|l, m\rangle = l(l+1) \geq m^2$.

As already remarked, equality can only hold for $\mathbf{L}|l, m\rangle = 0$, i.e., $l = m = 0$. Now, (3.2.7) may be rewritten as

$$[L_3, L_\pm] = \pm L_\pm, \qquad L_\pm = L_1 \pm iL_2,$$

so

$$L_3 L_\pm |l, m\rangle = (m \pm 1) L_\pm |l, m\rangle,$$
$$|\mathbf{L}|^2 L_\pm |l, m\rangle = l(l+1) L_\pm |l, m\rangle.$$

Consequently $L_\pm |l, m\rangle$ is a simultaneous eigenvector of L_3 and $|\mathbf{L}|^2$ whenever $|l, m\rangle$ is, and we may write

$$L_\pm |l, m\rangle = c|l, m \pm 1\rangle, \qquad c \in \mathbb{C}.$$

Supposing that $|l, m\rangle$ have been normalized, the normalization constants c can be calculated from the equation

$$|\mathbf{L}|^2 = L_3^2 \mp L_3 + L_\pm L_\mp$$

(Problem 4). The result is that

$$L_\pm |l, m\rangle = \sqrt{l(l+1) - m(m \pm 1)}\,|l, m \pm 1\rangle.$$

In order not to violate the condition that $m^2 \leq l(l+1)$, repeated applications of $L_\pm$ must eventually yield 0, which can happen only if $l \in \mathbb{Z}^+$. It follows that $L_+|l, l\rangle = L_-|l, -l\rangle = 0$. A classical description of the action of L_- (respectively L_+) is that the direction of the angular momentum vector is changed while its length is held constant, and L_3 varies from a maximum value l to a minimum $-l$ (respectively from the minimum to the maximum). The eigenfunctions $|l, m\rangle$ constitute a $2l + 1$-dimensional representation of the algebra generated by $\mathbf{L}$. The representation is irreducible, since every vector is cyclic (2.3.6; 1). The operator L_+ can be used to construct $|l, l\rangle$, and all the other eigenvectors of a given representation can be gotten by applying L_- to it.

The Eigenfunctions in the x-Representation (3.2.14)

To construct $|l, l\rangle$ algebraically by applying operators to $|0, 0\rangle$, which corresponds to a radially symmetric $\psi(r)$, we rely on the equations

$$[L_3, x_1 \pm ix_2] = \pm(x_1 \pm ix_2),$$
$$[L_\pm, x_1 \pm ix_2] = 0,$$
$$[|\mathbf{L}|^2 - L_3^2 - L_3, x_1 + ix_2] = [L_-, x_1 + ix_2]L_+$$

(Problem 4), which imply that $(x_1 + ix_2)$ sends $|l, l\rangle$ to $|l+1, l+1\rangle$, up to normalization. Hence,

$$|l, m\rangle = L_-^{l-m}(x_1 + ix_2)^l |0, 0\rangle.$$

In the Schrödinger representation (3.2.3), which gives the probability measure $d^3x|\psi(\mathbf{x})|^2$ on $\mathrm{Sp}(\mathbf{x})$, the vector $|0, 0\rangle$ depends only on the radius r, and $|l, m\rangle$ will have the form $Y_l^m(\theta, \varphi)f(r)$.

Simple Special Cases (3.2.15)

1. $l = m = 0$. This state is rotationally invariant, and the probability distribution $|\psi(r)|^2$ it corresponds to is spherically symmetric.
2. $l = \pm m = 1$. $|\psi(\mathbf{x})|^2 \sim |x \pm iy|^2 \sim \sin^2\theta$, and the 1-2-plane takes on the characteristics of an orbital plane.
3. $l = 1, m = 0$. $|\psi(\mathbf{x})|^2 \sim \cos^2\theta$, corresponds to a superposition of orbits in the 1-3 and 2-3-planes.
4. $l = \pm m$. $|\psi(\mathbf{x})|^2 \sim \sin^{2l}\theta$, and the particle is strongly concentrated in the 1-2-plane for large l.

Remarks (3.2.16)

1. It seems paradoxical that L_3 has a discrete spectrum while its constituents x_1p_2 and x_2p_1 each have continuous spectrum. However, since they do not commute, they can not possess precise values at the same time, and the sum of separate measurements of the summands is not acceptable as a measurement of an eigenvalue of the sum L_3. By the axiom of linearity, it is nonetheless possible to determine the average value of L_3 by making separate measurements of x_1p_2 and x_2p_1 on several identical copies of the system.
2. The commutation relations (3.2.7) require a state that is nondispersive for L_3 and $\mathbf{p}$ to satisfy $\langle|\mathbf{p}|\rangle = 0$.
3. Note that $\langle l, m|L_{1,2}|l, m\rangle = 0, (\Delta L_{1,2})^2 = (l(l+1) - m^2)/2$. It is because of the quantum fluctuations of $L_{1,2}$ that $l(l+1)$ always exceeds m^2 unless $l = m = 0$. There are nonzero quantum fluctuations even when $m = \pm l \neq 0$, though their value in that case is the least possible according to (2.2.33; 4) because $[L_1, L_2] = iL_3$.
4. As in (3.1.13), it is possible to characterize the states of minimal indeterminacy of L_1 and L_2 as the eigenvectors of $L_1 - i(\Delta L_1/\Delta L_2)L_2$, because of Remark (2.2.33; 3).

Spin (3.2.17)

Many particles, including electrons and protons, have an intrinsic angular momentum $\mathbf{S}$, known as the **spin**, in addition to their orbital angular momentum $\mathbf{L}$. The spin operators satisfy the commutation rules

$$[S_j, S_k] = i\varepsilon_{jkl}S_l$$

and commute with $\mathbf{x}$ and $\mathbf{p}$. The algebra of observables for particles with spin is the product of the Weyl algebra and the spin algebra: According to (2.3.8; 3), the Hilbert space of any representation is the tensor product of the Hilbert space for the dynamical variables $\mathbf{x}$ and $\mathbf{p}$ and the Hilbert space for the spin variables. More interestingly, the unitary operators $\exp(i\mathbf{S} \cdot \mathbf{e}\delta)$ for electrons and protons (or any particles of half-odd integer spin) are simply ray representations of SO(3), i.e., according to (3.2.4), representations of the universal covering group,

Gloss (3.2.18)

SO(3), that is, the real 3×3 matrices M such that $MM^t = \mathbf{1}$, Det $M = 1$, is connected as a topological space, but it is not simply connected. In other words, there are paths in SO(3) that can not be contracted to a point without breaking. To see why it is not simply connected, map the group space into a ball in $\mathbb{R}^3$ by associating a vector $\mathbf{e}\delta$ with any rotation, $\mathbf{e}$ specifying the axis of rotation and δ the angle. The angle may be restricted to the values $0 \leq \delta \leq \pi$, but then diametrically opposed points must be identified. For example, to rotate from 0 to 2π radians about the axis in the direction of $\mathbf{e}$, first go from 0 to $\pi\mathbf{e}$, which is equivalent to $-\pi\mathbf{e}$, and then return from there to the origin. There is no way to shrink this path down to the point 0, though a path that passed through the ball twice could be shrunk down. (See Figure 7.)
If the group space is doubled up like a two-sheeted Riemann surface, then it becomes simply connected and homeomorphic to the group SU(2). This new group comes into consideration as follows: For the spin matrices $\boldsymbol{\sigma}$ of

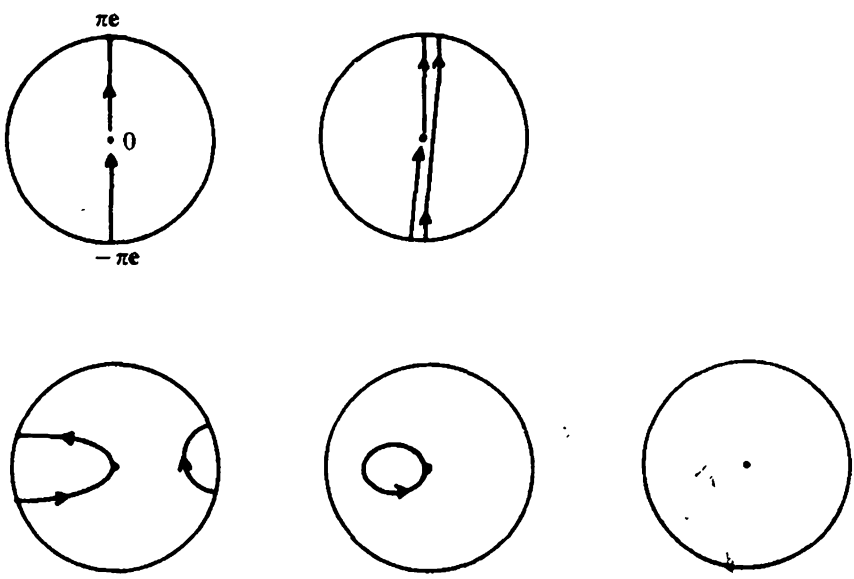


Figure 7 Homotopy of paths in SO(3).

(2.2.37), $-|\mathbf{v}|^2 = \text{Det } \mathbf{v}\cdot\boldsymbol{\sigma}$ for any $\mathbf{v}\in\mathbb{R}^3$, and since any 2×2 matrix with trace 0 can be written as $\mathbf{v}\cdot\boldsymbol{\sigma}$,

$$U^{-1}v_k\sigma_k U = M_{kl}v_l\sigma_k, \qquad U\in SU(2), \qquad M\in SO(3).$$

The homomorphism thereby set up from SU(2) to SO(3) is surjective but not injective, and indeed Schur's lemma shows that the identity in SO(3) corresponds to both $U = \pm\mathbf{1}$. If M is the rotation $\mathbf{e}\delta$, then it corresponds to $U = \exp(i\delta(\boldsymbol{\sigma}\cdot\mathbf{e})/2)$ (Problem 5), and letting δ increase from 0 to 2π brings one from $\mathbf{1}$ to $U = -\mathbf{1}$. Problem 5 also shows that SU(2) is simply connected, and is thus precisely the desired two-sheeted universal covering group, so SO(3) is isomorphic to $SU(2)/\{1, -1\}$.

The Spectrum of S (3.2.19)

The global properties are reflected in the spectrum. For SU(2) we only know that

$$\exp(4\pi i(\mathbf{S}\cdot\mathbf{e})) = \mathbf{1}$$

(4π rather than 2π), so the spectrum of any component may consist of both whole and half-odd integer values. This statement is consistent with our earlier construction of the representations, in which only $2l+1$ was required to be integral.

Representation of S (3.2.20)

Since $|\mathbf{S}|^2$ commutes with $\mathbf{p}$ and $\mathbf{x}$, as do all the components of $\mathbf{S}$, it is a multiple of $\mathbf{1}$ in any irreducible representation. The experimental value found for electrons and protons is $\frac{1}{2}(\frac{1}{2}+1) = \frac{3}{4}$. The appropriate construction of a representation yields the matrices of (2.2.37):

$$\mathbf{S} = \tfrac{1}{2}\boldsymbol{\sigma}$$

(Problem 6). Thus for n electrons, the overall Hilbert space is the antisymmetric tensor product of the Hilbert spaces for the individual electrons, each of which is a copy of $L^2(\mathbb{R}^3, d^3x)\otimes\mathbb{C}^2$.

Problems (3.2.21)

1. Construct an explicit representation of the parity operator (3.2.10). (Hint: write p in the x-representation, decompose $L^2(\mathbb{R}^{3n}, d^{3n}x)$ as $\bigotimes_{k=1}^{n} L^2(\mathbb{R}^3, d^3x)$, introduce polar coordinates on $\mathbb{R}^3$, and see how P acts on the total set $\{f(r)Y_l^m(\theta,\varphi)\}$.)
2. Show that the ψ_k of (3.2.5) are total in $L^2(\mathbb{R}^3, d^3x)$.
3. Show that $\mathbf{x}$ and $\mathbf{p}$ are essentially self-adjoint on D (3.2.6; 3).

4. Verify the facts stated in (3.2.13) and (3.2.14).

5. Show that

   (i) SU(2) is simply connected; and
   (ii) every n-dimensional, continuous, unitary ray representation can be turned into an ordinary representation by an appropriate choice of phase. It is nontrivial, since there are irreducible ray representations of dimension greater than 1 for Abelian groups: see (3.1.6; 6).
   (iii) Find an irreducible ray representation of the (Abelian) Klein group of four. using spin matrices.

6. Show that the construction carried out in (3.2.13) produces $\mathbf{S} = \boldsymbol{\sigma}/2$ on a two-dimensional Hilbert space.

Solutions (3.2.22)

1. $$\mathbf{x} \to -\mathbf{x}: r \to r, \theta \to \pi - \theta, \varphi \to \pi + \varphi,$$

   so

   $$f(r)Y_l^m(\theta, \varphi) \to f(r)Y_l^m(\pi - \theta, \pi + \varphi) = (-1)^l f(r)Y_l^m(\theta, \varphi) = \exp(i\pi l)f(r)Y_l^m(\theta, \varphi);$$

   which implies

   $$P = \exp(i\pi(\sqrt{L^2 + \tfrac{1}{4}} - \tfrac{1}{2})).$$

2. It suffices to consider the one-dimensional case. $\exp(-x^2/2 + itx)$ is the strong limit (s-lim) of $\exp(-x^2/2)\sum_{k=1}^{n}(itx)^k/k!$. Hence it follows from $\int \varphi(x)\exp(-x^2/2)P(x)dx = 0$ that $\int \varphi(x)\exp(-x^2/2 + itx)dx = 0$ for all t, and therefore $\varphi(x)\exp(-x^2/2) = 0$ a.e., so $\varphi = 0$.

3. All vectors of D are entire vectors for x_i and p_i.

4. This merely requires some differentiation.

5. (i) Any matrix $u \in SU(2)$ is of the form

   $$\begin{pmatrix} z_1 & z_2 \\ -z_2^* & z_1^* \end{pmatrix}, \qquad z_i \in \mathbb{C}, |z_1|^2 + |z_2|^2 = 1.$$

   The latter condition can be written as $\sum_{k=1}^{4}|x_k|^2 = 1$ with $z_1 = x_1 + ix_2$, $z_2 = x_3 + ix_4$, $x_k \in \mathbb{R}$, which shows that SU(2) is homeomorphic (and diffeomorphic) to the 3-sphere S^3. All n-spheres other than S^1, however, are simply connected, as can be seen with the following argument: Let

   $$C: t \to x_k(t)\,(0 \le t \le 1; k = 1, 2, 3, 4; x_k(0) = x_k(1))$$

   be a continuous, closed curve in S^3. By the Weierstrass approximation theorem there exist polynomials $P_k(t)$ such that $|x_k(t) - P_k(t)| < \varepsilon$ for all k, t, $P_k(0) = P_k(1) = x_k(0)$, and the curve $C_1: t \to P_k(t)/\sqrt{\sum p_k^2(t)}$ is homotopic to the given curve C for ε small enough. By a theorem of Sard the set of all points of the curve C_1, as a differentiable mapping, has measure 0. Hence it is not possible for it to cover the whole 3-sphere. Therefore there exists a point $p \in S^3$ not on the curve.

Since $S^3\backslash\{p\}$ is homeomorphic to $\mathbb{R}^3$, which is simply connected, C_1 can be continuously contracted to a point.

(ii) Let $u \to U(u)$ be a unitary, n-dimensional ray representation of SU(2), so $U(u)U(v) = \delta(u, v)U(uv)$ with $|\delta| = 1$. The associativity property implies that $\delta(u, v)\delta(uv, w) = \delta(u, vw)\delta(v, w)$, and it is obvious that $\delta(u, \mathbf{1}) = \delta(\mathbf{1}, u) = \mathbf{1}$. Since SU(2) is simply connected, $\sqrt[n]{\text{Det } U(u)}$ is a well-defined number once $\sqrt[n]{\text{Det } U(\mathbf{1})}$ has been fixed. By scaling $U(u) \to U'(u) = U(u)/\sqrt[n]{\text{Det } U(u)}$ one obtains another ray representation with $U'(u)U'(v) = \delta'(u, v)U'(uv)$. However, since Det $U'(u) = 1$, this means that $\delta'^n(u, v) = 1$ for all u and v, so $\delta'(u, v) = 1$ due to the simple connectedness of SU(2).

(iii) Klein's group of four contains four elements, e, a, b, and c, having the multiplication table

	e	a	b	c
e	e	a	b	c
a	a	e	c	b
b	b	c	e	a
c	c	b	a	e

A ray representation can be obtained by setting $e \to \mathbf{1}$, $a \to \sigma_x$, $b \to \sigma_y$, and $c \to \sigma_z$ (cf. (2.2.37)).

6. The two vectors $|\uparrow\rangle$ and $|\downarrow\rangle$ such that $S_+|\uparrow\rangle = S_-|\downarrow\rangle = 0$ span the whole Hilbert space, and the matrix elements can be calculated as in (3.2.13).

3.3 Time-Evolution

As in classical mechanics the quantum-mechanical Hamiltonian generates the time-evolution, which is similar to its classical analogue, except that the influence of the noncommutativity must now be taken into account.

In the last two sections we have seen how to carry over the generation of the groups of translations and rotations from classical mechanics to quantum mechanics. We now attempt the same feat for the time-evolution with a Hamiltonian H, and postulate a

Group of Automorphisms of the Time-Evolution (3.3.1)

The algebra of observables evolves in time according to

$$a(t) = \exp(iHt)a \exp(-iHt) = \sum_{n=0}^{\infty} \frac{(it)^n}{n!} ad_H^n(a),$$

$$ad_H^0(a) \equiv a, \qquad ad_H^n(a) \equiv [H, ad_H^{n-1}(a)], \qquad a \in \mathcal{A}.$$

Remarks (3.3.2)

1. Not every automorphism of a C^* algebra has this kind of representation. However, for our purposes, $\mathscr{A} = \mathscr{B}(\mathscr{H})$, for which every continuous, one-parameter group of automorphisms of the Jordan algebra (2.2.34) (i.e., it must be linear and preserve the symmetric product $\circ$) can be represented unitarily.
2. At this stage H is the classical Hamiltonian with p and q replaced by the operators of the Weyl system. However, because they do not commute, H is not uniquely defined, and in general even the question of a domain of essential self-adjointness is open. The systems we shall consider will not be so problematic, and self-adjointness will be taken care of by the Kato-Rellich theorem (2.5.15).
3. If a and H are bounded, then the series given in (3.3.1) converges because $\|ad_H^n(a)\| \leq 2^n\|H\|^n\|a\|$ for all t, and $t \to a(t)$ is continuous in norm. If H is unbounded, then the time-automorphism is still strongly continuous when $\exp(iHt)$ is, because

$$\|(\exp(iHt)a\exp(-iHt) - a)\psi\| = \|(a\exp(iHt) - \exp(-iHt)a)\psi\|$$
$$\leq \|a(\exp(-iHt) - 1)\psi\| + \|(\exp(-iHt) - 1)a\psi\|.$$

However, $da(t)/dt$ is not necessarily a bounded operator, and thus may not belong to $\mathscr{A}$. It is initially defined as the quadratic form $i[H, a]$ with $D(H)$ for its form domain. If a is itself unbounded, then the question of domain becomes more serious; under certain circumstances the Hermitian form $i[H, a]$ is not closeable, and can certainly not be the quadratic form of a self-adjoint operator.

Let us next investigate in some detail the time-evolution that will later serve as a standard of comparison.

Free Motion in Three Dimensions (3.3.3)

The Hamiltonian for a free particle is

$$H = \frac{|\mathbf{p}|^2}{2m},$$

so in the spectral representation of the momentum H and its resolvent are

$$(H\psi)(\mathbf{p}) = \frac{|\mathbf{p}|^2}{2m}\psi(\mathbf{p}), \qquad D_p(H) = \{\psi \in L^2(\mathbb{R}^3, d^3p) : |\mathbf{p}|^2\psi \in L^2\},$$

$$(R(z)\psi)(\mathbf{p}) = \frac{1}{(|\mathbf{p}|^2/2m) - z}\psi(\mathbf{p}), \qquad (U(t)\psi)(\mathbf{p}) = \exp\left(-\frac{i|\mathbf{p}|^2}{2m}t\right)\psi(\mathbf{p}).$$

It is often desirable to have expressions for these quantities in the spectral representation of x, in which p is written as $-i\,\partial/\partial x$ and the two representations are related by the Fourier–Plancherel formula: The Fourier transformation maps $L^2(\mathbb{R}^3, d^3p) \cap L^1(\mathbb{R}^3, d^3p)$ isometrically onto $L^2(\mathbb{R}^3, d^3x) \cap L^\infty(\mathbb{R}^3, d^3x)$. Since both sets are dense in L^2, the Fourier transformation can be extended to a unitary transformation $L^2 \to L^2$. A calculation of the appropriate Fourier integral shows that

$$(H\psi)(\mathbf{x}) = -\frac{\Delta}{2m}\psi(\mathbf{x}),$$

$$(R(z)\psi)(\mathbf{x}) = \frac{m}{2\pi}\int d^3x' \frac{\exp(ik|\mathbf{x}-\mathbf{x}'|)}{|\mathbf{x}-\mathbf{x}'|}\psi(\mathbf{x}'), \qquad k = \sqrt{2mz},$$

$$(U(t)\psi)(\mathbf{x}) = \left(\frac{m}{2\pi i t}\right)^{3/2}\int d^3x' \exp\left(\frac{im|\mathbf{x}-\mathbf{x}'|^2}{2t}\right)\psi(\mathbf{x}')$$

(Problem 1).

Remarks (3.3.4)

1. The Hamiltonian H is self-adjoint on the set of Fourier transforms $\tilde{\psi}$ of the vectors ψ of $D_p(H)$, and essentially self-adjoint on the Fourier transforms of the vectors of any set D that is dense in $D_p(H)$ in the graph norm. Examples of such states are the vectors of $\mathscr{S}$, the coherent states, and the domain of (3.2.5).
2. The vectors $\psi(\mathbf{x}) \in D_x(H)$ have some continuity properties because the integral kernel of the resolvent in x-space is so nice. Furthermore, variants of Sobolev's inequality show that functions whose derivatives have finite L^2-norms are bounded: Using the kernel for the resolvent we see that if $z = -\alpha^2$, $\alpha \in \mathbb{R}^+$, then

$$\begin{aligned}|\psi(\mathbf{x})| &= |(R(|\mathbf{p}|^2 + \alpha^2)\psi(\mathbf{x})| \\ &= \int d^3x' \frac{\exp(-\alpha|\mathbf{x}-\mathbf{x}'|)}{4\pi|\mathbf{x}-\mathbf{x}'|}[2m(H\psi)(\mathbf{x}') + \alpha^2\psi(\mathbf{x}')] \\ &\leq (2m\|H\psi\| + \alpha^2\|\psi\|)(8\pi\alpha)^{-1/2},\end{aligned}$$

by using the Cauchy–Schwarz inequality and the fact that $\|\exp(-\alpha r)/4\pi r\|^2 = 1/8\pi\alpha$. One can also argue without using the kernel of the resolvent as follows: By the Cauchy–Schwarz inequality,

$$\left(\int |\tilde{\psi}(\mathbf{p})|\,d^3p\right)^2 \leq \int \frac{d^3p}{(|\mathbf{p}|^2+\alpha^2)^2}\int (|\mathbf{p}|^2+\alpha^2)^2|\tilde{\psi}(\mathbf{p})|^2\,d^3p$$

$$= \frac{\pi^2}{\alpha}\|(2mH + \alpha^2)\psi\|^2 \quad \textit{for all} \quad \alpha \in \mathbb{R},$$

which implies

$$|\psi(\mathbf{x})| \leq (2\pi)^{-3/2} \int d^3p |\tilde{\psi}(\mathbf{p})| \leq \frac{\|(2mH + \alpha^2)\psi\|}{\sqrt{8\pi\alpha}}$$
$$\leq \frac{(\alpha^2\|\psi\| + 2m\|H\psi\|)}{\sqrt{8\pi\alpha}}.$$

Thus the functions $\psi(\mathbf{x})$ are bounded. Moreover, since $|\exp(i\mathbf{p}\cdot\mathbf{x}) - \exp(i\mathbf{p}\cdot\mathbf{x}')| \leq \min\{2, |\mathbf{p}||\mathbf{x} - \mathbf{x}'|\} \leq 2^{1-\gamma}|\mathbf{p}|^{\gamma}|\mathbf{x} - \mathbf{x}'|^{\gamma}$ for all $\gamma \in (0, 1)$,

$$|\psi(\mathbf{x}) - \psi(\mathbf{x}')| \leq \int \frac{d^3p|\mathbf{p}|^{\gamma}2^{1-\gamma}}{(|\mathbf{p}|^2 + \alpha^2)} (|\mathbf{p}|^2 + \alpha^2)\tilde{\psi}(\mathbf{p})|x - x'|^{\gamma} \cdot$$
$$\leq C(\gamma)|\mathbf{x} - \mathbf{x}'|^{\gamma}(\alpha^{(\gamma - 1/2)}2m\|H\psi\| + \alpha^{(\gamma + 3/2)}\|\psi\|)$$
$$\text{for all} \quad \gamma \in (0, \tfrac{1}{2}).$$

So $\psi \in D_x(H)$ is in fact Hölder continuous with any exponent $< \frac{1}{2}$. Stronger properties such as C^1 can not be hoped for (in three dimensions), since if $\psi = r^{\gamma}$, $\gamma > \frac{1}{2}$, then $\psi'' \in L^2$ at small r but $\psi'(0) = \infty$. But at any rate, $D(|\mathbf{p}|^2) \subset L^{\infty}(\mathbb{R}^3)$.

3. The operator $U(t)$ also has a continuous integral kernel, and its effect is frequently to smooth functions. It describes how wave-packets damp out; the fact that they damp out is expressed by the weak convergence of $U(t)$ to 0 as $t \to \pm\infty$. For example, on the dense set of L^1 functions, $|(U(t)\psi)(\mathbf{x})| \leq (2\pi t/m)^{-3/3}\|\psi\|_1$. However, since $U(t)$ is invertible, the time-reversed motion is always possible.
4. The easiest way to see that H generates the classical time-automorphism $x \to x + pt$ for $m = 1$ is to use the Weyl operators:

$$\exp(ixs)\exp\left(-\frac{ip^2t}{2}\right)\exp(-ixs) = \exp\left(-\frac{i(p-s)^2t}{2}\right)$$
$$= \exp\left(-\frac{ip^2t}{2}\right)\exp\left(it\left(ps - \frac{s^2}{2}\right)\right) \Rightarrow \exp\left(\frac{ip^2t}{2}\right)\exp(ixs)\exp\left(-\frac{ip^2t}{2}\right)$$
$$= \exp\left(it\left(ps - \frac{s^2}{2}\right)\right)\exp(ixs) = \exp(is(x + pt)).$$

This one-dimensional formula generalizes easily to vectors.

Most of the problems solved in introductory classical mechanics are also pretty easy in quantum theory:

Examples (3.3.5)

1. Free fall. $H = p^2/2 + gx$, $L^2((-\infty, \infty), dx) \supset D \equiv$ the linear hull of $\{x^n \exp(-x^2)\}$. In the spectral representation of p, in which $x = i\,d/dp$, H can be defined as a self-adjoint operator on $D(H) \equiv \{\psi(p) \in L^2((-\infty, \infty),$

dp): ψ is absolutely continuous and $(p^2/2 + ig\, d/dp)\psi \in L^2\}$. On D, $i[H, x] = p$ and $i[H, p] = -g$, so $\bar{x}(t) \equiv x + pt - gt^2/2$ and $\bar{p}(t) \equiv p - gt$ satisfy the same differential equations as $x(t)$ and $p(t)$. Since they agree at $t = 0$ and the vectors of D are entire for them, it follows that $\bar{x}(t) = x(t)$ and $\bar{p}(t) = p(t)$. The quantum fluctuations of these observables satisfy

$$(\Delta x(t))^2 = \Delta x^2 + t^2(\Delta p)^2 + t(\langle xp + px\rangle - 2\langle x\rangle\langle p\rangle),$$
$$(\Delta p(t))^2 = \Delta p^2.$$

The damping out of the wave-packet does not depend on g; the uncertainty in p is constant while that of x grows linearly with Δpt. The spectrum of H is purely continuous, since on $D(H)$ $H\psi = E\psi$ reads

$$H\psi = E\psi : ig\frac{d}{dp}\psi(p) = \left(E - \frac{p^2}{2}\right)\psi(p),$$

which

$$\Rightarrow \psi(p) = c\exp\left(-\frac{i(Ep - p^3/6)}{g}\right) \notin L^2((-\infty, \infty), dp).$$

2. The harmonic oscillator. $H = (p^2 + \omega^2 x^2)/2$; $D \subset L^2((-\infty, \infty), dx)$ as in Example 1 is invariant under H, and by the same argument the classical solution

$$x(t) = x\cos\omega t + \frac{p}{\omega}\sin\omega t,$$
$$p(t) = p\cos\omega t - \omega x\sin\omega t$$

again reproduces the correct quantum-mechanical time-evolution. The mean-square deviations are easily shown to satisfy

$$(\Delta x(t))^2 = (\Delta x)^2\cos^2\omega t + (\Delta p)^2\frac{1}{\omega^2}\sin^2\omega t + \frac{1}{\omega}\cos\omega t\sin\omega t$$
$$\times(\langle xp + px\rangle - 2\langle x\rangle\langle p\rangle).$$

Wave-packets oscillate rather than decaying away. The last contribution cancels out for coherent states (3.1.13); moreover, if $\Delta x^2 = \Delta p^2/\omega^2$, then $(\Delta x(t))^2$ and $(\Delta p(t))^2$ are constant. $H = \omega(a^*a + 1/2)$, where

$$a = (\omega x + ip)(2\omega)^{-1/2}$$

(cf. (3.1.12; 2)), has a pure point spectrum, since $[a, a^*] = \mathbf{1}$ and $[H, a] = -a\omega$ (all acting on D), so $H\psi = E\psi \Rightarrow Ha\psi = (E - \omega)a\psi$. Since $H \geq \omega/2$, there is a vector ψ_0 such that $a\psi_0 = 0$, $H\psi_0 = (\omega/2)\psi_0$, and $H\psi_n = \omega(n + \frac{1}{2})\psi_n$, where $\psi_n = (a^*)^n(n!)^{-1/2}\psi_0$. In the spectral representation of x, $a(2\omega)^{1/2} = (d/dx) + \omega x$, $\psi_0 = \exp(-x^2\omega/2)$ (cf. (3.1.6; 2) and (3.1.12; 2)), and the ψ_n span D completely. Because D is dense in $\mathscr{H}$, H is self-adjoint on D and $\sigma_{ac}(H) = \sigma_s(H) = \varnothing$. Yet $\sigma(H)$ is not determined

by the motion in configuration space alone; $\bar{H} = p_1p_2 + x_1x_2$ produces the same motion of the x_i as $H = (p_1^2 + p_2^2 + x_1^2 + x_2^2)/2$, but $\sigma(\bar{H}) = \mathbb{Z}$ and $\sigma(H) = \mathbb{Z}^+$.

3. A particle in a homogeneous magnetic field. The nonrelativistic version of the Hamiltonian (I: 5.1.9) with the magnetic field in the z-direction is

$$H = \frac{|\mathbf{p} - e\mathbf{A}|^2}{2m} = \frac{m|\dot{\mathbf{x}}|^2}{2}, \qquad \dot{\mathbf{x}} = \frac{1}{m}\left(p_1 + \frac{eB}{2}x_2, p_2 - \frac{eB}{2}x_1, p_3\right)$$

$$= i[H, \mathbf{x}], \left(\mathbf{A} = \frac{B}{2}(-x_2, x_1, 0)\right).$$

Now the variables $(\dot{x}_1, \dot{x}_2)$ and $(\bar{x}_1, \bar{x}_2) = (x_1/2 + p_2/eB, x_2/2 - p_1/eB)$ are canonically conjugate pairs like (x_1, p_1) and (x_2, p_2), since on $D \times D$ as before, $[\dot{x}_1, \dot{x}_2] = ieB$, $[\bar{x}_1, \bar{x}_2] = 1/ieB$, and $[\dot{x}_l, \bar{x}_k] = 0$ for all k and l. Writing $a = (\dot{x}_1 + i\dot{x}_2)\sqrt{m/2\omega}$, $\omega = eB/m$, we find that

$$H = \frac{p_3^2}{2m} + (a^*a + \tfrac{1}{2})\omega, \qquad [a, a^*] = 1.$$

The Hilbert space is a tensor product $\mathscr{H}_{\bar{x}} \otimes \mathscr{H}_{\dot{x}} \otimes \mathscr{H}_{x_3}$ corresponding to the new pairs of conjugate observables, and H is the sum of the H of Example 1 with $g = 0$, acting on the last factor, and the H of Example 2 acting on the second factor. The time-evolution is accordingly

$$x_1(t) = \bar{x}_1 - \frac{1}{\omega}(\dot{x}_2 \cos \omega t - \dot{x}_1 \sin \omega t),$$

$$x_2(t) = \bar{x}_2 + \frac{1}{\omega}(\dot{x}_1 \cos \omega t + \dot{x}_2 \sin \omega t),$$

$$x_3(t) = x_3 + \frac{p_3}{m}t.$$

Thus the constants $\bar{\mathbf{x}}$ function as the center of the orbit, and H, of course, is independent of them. The operator $\dot{x}_1^2 + \dot{x}_2^2$ therefore has an infinitely degenerate point spectrum, as it involves only one pair of conjugate variables. The operator H as a whole has continuous spectrum from $\omega/2$ to ∞, since it includes the kinetic energy in the 3-direction. As with the harmonic oscillator, the zero-point energy $\omega/2$ arises from the indeterminacy relation (3.1.11), according to which

$$H \sim \frac{1}{2}[(\Delta p^2) + \omega^2(\Delta x^2)] \sim \frac{1}{2}\left[\frac{1}{4(\Delta x^2)} + \omega^2(\Delta x^2)\right]$$

has its minimum $\omega/2$ when $\Delta x = (2\omega)^{-1/2}$. As in the classical case (see (I: §5.1)) it is important to distinguish between the canonical angular momentum $\hat{\mathbf{L}} = [\mathbf{x} \times \mathbf{p}]$ and the physical $\mathbf{L} = [\mathbf{x} \times m\dot{\mathbf{x}}]$. The former depends on the gauge, and is constant in the gauge chosen here. The

physical angular momentum is independent of the gauge, but depends on time. In a magnetic field the ground state has $\langle 0|L_z|0\rangle = -1$ (Problem 4), and for its orbit, $\Delta x \sim (\Delta p)^{-1} \sim \omega^{-1/2}$. As in the classical case H is invariant under translation combined with certain gauge transformations.

4. Radial motion in S states. Let $H = -\frac{1}{2}(d^2/dr^2) + V(r)$, where V and $V' \in L^\infty$, and $D(H) = \{\psi \in L^2([0, \infty), dr): \psi \in C^1, \psi'$ is absolutely continuous, $\psi'' \in L^2$, and $\psi(0) = 0\}$, making H self-adjoint according to (2.5.14) and (2.5.15). The operator $r: \psi(r) \to r\psi(r)$ is self-adjoint on $D(r) = \{\psi \in L^2: r\psi \in L^2\}$. Its rate of change $\dot{r} = i[H, r]$ is at first defined as a quadratic form with the domain $D(H) \cap D(r)$, and is a restriction of the quadratic form associated with the Hermitian operator $p_r = -i\, d/dr$. $D(p_r) = \{\psi \in L^2: \psi$ is absolutely continuous, $\psi' \in L^2$, and $\psi(0) = 0\}$. This is the operator studied in (2.5.3; 5). Thus Remark (2.5.13; 1) shows that the time-derivative of a self-adjoint operator need not have any self-adjoint extensions. An integration by parts reveals that the time-derivative of the form p_r is

$$\frac{d}{dt}\, p_r(\psi, \psi) = \int_0^\infty dr \left\{ \left(-\frac{1}{2}\psi''^* + V\psi^* \right)\psi' - \psi^* \frac{\partial}{\partial r}\left(-\frac{1}{2}\psi'' + V\psi \right) \right\}$$

$$= -\int_0^\infty dr.\, \psi^*(r)\psi(r)\frac{dV}{dr} + \frac{1}{2}|\psi'(0)|^2. \qquad \text{(a)}$$

This contains a noncloseable form in addition to the classical force, so $\dot{p}_r$ is not even an operator. Incidentally, (a) implies a relationship for the eigenvectors ψ of H that will be important later,

$$\left\langle \psi \left| \frac{dV}{dr}\, \psi \right. \right\rangle = \frac{1}{2}|\psi'(0)|^2. \qquad \text{(b)}$$

In applications we shall require

The Unitary Time-Evolution of a Time-Dependent Hamiltonian (3.3.6)

The solution of

$$\frac{d}{dt}\, U(t, t_0) = -iH(t)U(t, t_0), \qquad U(t_0, t_0) = \mathbf{1}$$

is

$$U(t, t_0) = 1 + \sum_{n=1}^{\infty} (-i)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n\, H(t_1)H(t_2)\cdots H(t_n)$$

$$\equiv T\left[\exp\left(-i \int_{t_0}^{t} dt'\, H(t') \right) \right]$$

(see (2.4.10; 3)).

Remarks (3.3.7)

1. The operators U are not a one-parameter group, but it is still true that
$$U(t_2, t_1)U(t_1, t_0) = U(t_2, t_0)$$
(Problem 7).
2. If $H(t)$ is a step function, $H(t) = H_j$ for $t_{j-1} \leq t \leq t_j$, then
$$U(t_n, t_0) = \exp(-iH_n(t_n - t_{n-1})) \cdots \exp(-iH_1(t_1 - t_0)).$$
The sum (3.3.6) converges strongly in this case if there is a domain of entire vectors for all H_j, which is invariant under $\exp(-itH_j)$. Hence, passing to the continuous case, a sufficient condition for the series (3.3.6) to converge strongly would be the existence of a domain consisting of entire vectors for all $H(s)$, invariant under $\exp(-itH(s))$, and on which $H(s)$ is continuous enough so that the integrals applied in (3.3.6) to vectors of the domain can be strongly approximated by sums.

Examples (3.3.8)

1. An oscillator with a spatially constant but time-varying force $f \in C^0(\mathbb{R})$. $H(t) = (p^2 + \omega^2 x^2)/2 + xf(t)$. Since the equations of motion are linear,
$$U(t) = T\left[\exp\left(-i\int_0^t dt'\, H(t')\right)\right]$$
produces the classical solution
$$U^{-1}(t)xU(t) = x\cos\omega t + \frac{p}{\omega}\sin\omega t + \xi(t),$$
$$U^{-1}(t)pU(t) = p\cos\omega t - \omega x\sin\omega t + \pi(t),$$
$$\xi(t) = -\frac{1}{\omega}\int_0^t dt'\sin\omega(t - t')f(t'), \qquad \pi(t) = \dot{\xi}(t).$$
Therefore the time-ordered product factorizes as
$$U(t) = \exp(-ip\xi(t))\exp(ix\pi(t))\exp\left(-\frac{it(p^2 + \omega^2 x^2)}{2}\right) \times \text{a phase factor.}$$
Once again, the sum in (3.3.6) converges for all t on entire vectors for x, p, and $p^2 + \omega^2 x^2$, such as the coherent states.
2. An oscillator with a changing frequency. $H(t) = (p^2 + \omega(t)^2 x^2)/2$, and the solution of the linear equation of motion $\dot{x} = p$, $\dot{p} = -\omega^2(t)x$ is the linear relationship
$$x(t) = \Omega_{11}(t)x + \Omega_{12}(t)p,$$
$$p(t) = \Omega_{21}(t)x + \Omega_{22}(t)p,$$

where in our notation the symplectic matrix $\Omega \in \mathrm{Sp}_2$ equals

$$T\left(\exp\left(\int_0^t dt'\begin{pmatrix} 0 & 1 \\ -\omega^2(t') & 0 \end{pmatrix}\right)\right).$$

The unitary transformation $U(t) = T[\exp(-i\int_0^t dt' H(t'))]$ that describes this time-evolution can be decomposed into factors as before: $\Omega \in \mathrm{Sp}_2 \Leftrightarrow$ Det $\Omega = 1$, so Ω has three free parameters and can be written as the product of the symplectic matrices

$$\begin{pmatrix} \cos vs & \frac{1}{v}\sin vs \\ -v\sin vs & \cos vs \end{pmatrix}\begin{pmatrix} e^{\beta} & 0 \\ 0 & e^{-\beta} \end{pmatrix}.$$

Since by Problem 8,

$$\exp\left(\frac{i\beta(px + xp)}{2}\right)(x, p)\exp\left(-\frac{i\beta(px + xp)}{2}\right) = (\exp(\beta)x, \exp(-\beta)p),$$

up to a phase factor $\exp(i\alpha)$,

$$U(t) = \exp(i\alpha)\exp\left(-\frac{is(p^2 + v^2x^2)}{2}\right)\exp\left(\frac{i\beta(xp + px)}{2}\right).$$

It is not possible to write down the classical $\Omega(t)$ for an arbitrary $\omega(t)$, so the functions $v(t)$, $s(t)$, and $\beta(t)$ are also unknown. For some $\omega(t)$ a miracle happens and $\Omega(t)$ is an elementary function; for instance for $\bar{\omega}, \tau \in \mathbb{R}$,

$$\omega(t) = (t + \tau)\bar{\omega}\sqrt{1 - \frac{3}{4[\bar{\omega}(t + \tau)^2]^2}}, \qquad \begin{Bmatrix} c \\ s \end{Bmatrix} \equiv \begin{Bmatrix} \cos \\ \sin \end{Bmatrix}\bar{\omega}\frac{(t + \tau)^2}{2},$$

$\Omega(t) =$

$$\sqrt{\frac{\tau}{t + \tau}}\begin{bmatrix} c + \frac{s}{\bar{\omega}\tau^2} & \frac{s}{\bar{\omega}\tau} \\ \left(\frac{t + \tau}{\tau^2} - \frac{1}{t + \tau}\right)c - \left((t + \tau)\bar{\omega} + \frac{1}{\bar{\omega}\tau^2(t + \tau)}\right)s & \frac{t + \tau}{\tau}c - \frac{s}{\bar{\omega}\tau(t + \tau)} \end{bmatrix}.$$

Remark (3.3.9)

The linear transformations of x and p leave the set K of states

$$\sim \exp\left(\frac{i(x - \gamma)^2}{2\alpha}\right), \alpha, \gamma \in \mathbb{C}, \operatorname{Im}\alpha < 0,$$

invariant: A transformation

$$x \to \Omega_{11}x + \Omega_{12}p + \xi,$$
$$p \to \Omega_{21}x + \Omega_{22}p + \pi,$$

changes $(x - \alpha p - \gamma)|\rangle = 0$ into $(x - \alpha' p - \gamma')|\rangle = 0$ with

$$\alpha' = \frac{\Omega_{12} + \alpha\Omega_{22}}{\Omega_{11} + \alpha\Omega_{21}}, \qquad \text{and} \qquad \gamma' = \xi + \frac{\gamma + \pi(\Omega_{12} + \alpha\Omega_{22})}{\Omega_{11} + \alpha\Omega_{21}},$$

and hence $U|\rangle$ can be written as $\sim\exp(i(x - \gamma')^2/2\alpha')$. Although $\operatorname{Im}\alpha$ remains negative, $\operatorname{Re}\alpha$ does not remain equal to 0. Since the latter fact characterizes coherent states (3.1.13), linear transformations can affect the degree of indeterminacy (cf. (3.3.5; 1)), and Gaussian wave-packets may spread out.

If H is perturbed time-dependently to $H_1(t) = H + H'(t)$, then the eigenvalues of H_1 vary in time, since

$$H_1(t) \neq U^{-1}(t)H_1(0)U(t), \qquad U(t) = T\left[\exp\left(-i\int_0^t dt'\, H_1(t')\right)\right].$$

As time passes, the family of projections $P_1(t)$ onto the eigenvectors of H_1 is more nearly transformed by $U(t)$ into itself the more slowly H' varies in comparison with the differences between energy levels. In other words, the transition probabilities approach zero in the limit of slow variation of H, even if the eigenvalues themselves change significantly.

Example (3.3.10)

Recall Example (3.3.8; 1) and suppose that

$$H(s) = \frac{1}{2}\left(p^2 + \omega^2\left(x + \frac{f(s)}{\omega^2}\right)^2\right) - \frac{f^2(s)}{2\omega^2}, \qquad 0 \leq s \leq 1, \qquad f \in C^1.$$

The question is now whether the time-evolution according to $H(t/\tau)$, $0 \leq t \leq \tau$, transforms the projection onto the ground state of $H(0)$ into that of $H(1)$ as $\tau \to \infty$. The two ground-state eigenvalues are different, as the ground states satisfy

$$H(s)|E_0(s)\rangle = E_0(s)|E_0(s)\rangle, \qquad E_0(s) = \frac{\omega}{2} - \frac{f(s)^2}{2\omega^2},$$

$$a(t)\left|E_0\left(\frac{t}{\tau}\right)\right\rangle \equiv (ip(t) + \omega x(t))\left|E_0\left(\frac{t}{\tau}\right)\right\rangle = -\frac{f(t/\tau)}{\omega}\left|E_0\left(\frac{t}{\tau}\right)\right\rangle,$$

$$a(t) = U^{-1}(t)aU(t).$$

As we saw earlier, the time-evolution of a is then

$$a(t) = a\exp(-i\omega t) - i\int_0^t dt' \exp(-i\omega(t - t'))f\left(\frac{t'}{\tau}\right),$$

or, after integration by parts,

$$a(\tau) = a\exp(-i\omega\tau) - \frac{f(1)}{\omega} + \frac{\exp(-i\omega\tau)}{\omega} f(0)$$

$$+ \frac{\exp(-i\omega\tau)}{\omega} \int_0^1 ds\, f'(s)\exp(i\omega\tau s).$$

If the Fourier transform of f', which occurs in the last term, is denoted $\tilde{f}'(\omega\tau)$, then

$$a(\tau) + \frac{f(1)}{\omega} = \exp(-i\omega\tau)\left(a + \frac{f(0)}{\omega} + \frac{\tilde{f}'(\omega\tau)}{\omega}\right),$$

and, with (3.1.4),

$$|\langle E(0)|E(1)\rangle| = \exp\left(-\left|\frac{\tilde{f}'(\omega\tau)}{2\omega}\right|^2\right).$$

If $f \in C^n$, then $\tilde{f}'(\omega\tau) = 0(\tau^{-n})$ as $\tau \to \infty$; the smoother the perturbation, the smaller the transition probability (cf. (3.3.7; 2)).

This behavior can be shown to occur more generally. Let $H(s)$, $0 \leq s \leq 1$, be a family of self-adjoint operators with a common domain D. An isolated eigenvalue $E(s)$ will be called **regular** iff $P(s)$, the projection onto its eigenvector, is finite-dimensional and continuously differentiable in s, as is $(H(s) - E(s))^{-1}(1 - P(s))$. Under these circumstances, there is an

Adiabatic Theorem (3.3.11)

The probability of transition from a regular eigenvalue with the transformation

$$U_\tau \equiv T\left[\exp\left(i\int_0^t dt' H\left(\frac{t'}{\tau}\right)\right)\right]$$

goes as $O(\tau^{-1})$ *in the limit* $\tau \to \infty$.

Remarks (3.3.12)

1. By assumption $E(s)$ is separated from all other eigenvalues by a nonzero distance for all s, so there is no question of crossing of eigenvalues. It is possible to show that the theorem remains valid when only a finite number of crossings can take place.
2. The whole purpose of the domain assumptions is to ensure that U_τ is defined; they could be weakened in many ways.
3. Roughly speaking, the theorem states that in the limit,

$$H\left(\frac{t}{\tau}\right) \to \sum_i E_i\left(\frac{t}{\tau}\right) U^{-1}(t) P_i U(t).$$

Proof

Let

$$P' = \frac{d}{ds}P(s)\colon P^2 = P \Rightarrow P' = PP' + P'P \Rightarrow PP'P = 0, \Rightarrow P' = [[P', P], P].$$

Now write $P(s) = W(s)W^*(s)$, $P(0) = W^*(s)W(s) = W(0)$, where $W(s)$ is an isometry of the space of eigenvectors belonging to $E(0)$ onto that belonging to $E(s)$. Then $W(s) = P(s)W(s) = W(s)P(0)$, so $W' = P'W + PW'$ and $P' = W'W^* + WW^{*\prime} = [P', P]WW^* - WW^*[P', P] \Leftrightarrow W' = [P', P]W$, which, because $PP'W = PP'PW = 0$ from the result above, implies that $P(s)W'(s) = 0$. The isometry $W(s)$ describes how the eigenvectors of $H(s)$ twist around as functions of s, and this must be compared with the time-evolution according to

$$V_\tau(s) = T\left[\exp\left(-i\tau\int_0^s ds'(H(s') - E(s'))\right)\right], \tag{a}$$

where a convenient phase factor has been included. From $V_\tau^{*\prime} = i\tau V_\tau^*(H-E)$, $(H - E)P = 0$, and the foregoing argument it follows that

$$(V_\tau^*W)' = i\tau V_\tau^*(H - E)PW + V_\tau^*W' = (i\tau)^{-1}V_\tau^{*\prime}(H - E)^{-1}(\mathbf{1} - P)W' \tag{b}$$

(writing H for $H(s)$, etc.). If Equation (b) is integrated by parts, then

$$V_\tau^*(1)W(1) - P(0)$$
$$= (i\tau)^{-1}\left\{V_\tau^*(H - E)^{-1}(\mathbf{1} - P)W'\Big|_0^1 - \int_0^1 ds\, V_\tau^*\frac{d}{ds}((H - E)^{-1}(\mathbf{1} - P)W')\right\}. \tag{c}$$

Since it has been assumed that the eigenvectors remain at least some positive distance apart, the operators $(H - E)^{-1}(\mathbf{1} - P)$ and $(d/ds)((H - E)^{-1}(\mathbf{1} - P))$ are uniformly bounded in s. The operator $\{\ldots\}$ is then also bounded, and (c) implies the adiabatic theorem

$$\|W(1) - V_\tau(1)P(0)\| = O(\tau^{-1}). \qquad \square$$

The Classical Limit (3.3.13)

We saw in Examples (3.3.5; 1) through (3.3.5; 3) that the quantum-theoretical time-automorphism for linear equations of motion is the same as the classical one. The connection between classical and quantum dynamics is not so easy in general, since it is possible that $\langle\dot{p}\rangle = -\langle V'(x)\rangle \neq -V'(\langle x\rangle)$. Yet there is hope that as $\hbar \to 0$ the fluctuations can be neglected, leaving the classical time-evolution. In (3.1.15) we began with

$$W^*(\hbar^{-1/2}z)(x, p)W(\hbar^{-1/2}z) = (x, p) + \hbar^{-1/2}(\xi, \pi), \qquad z = \xi + i\pi,$$

in order to make the heuristic correspondence principle more precise. We ought to be able to show that quantum time-evolution converts this to

$$W^*(\hbar^{-1/2}z)(x(t), p(t))W(\hbar^{-1/2}z) \xrightarrow{\hbar \to 0} U_f^{-1}(t)(x, p)U_f(t) + \hbar^{-1/2}(\xi(t), \pi(t)), \qquad z = \xi(0) + i\pi(0),$$

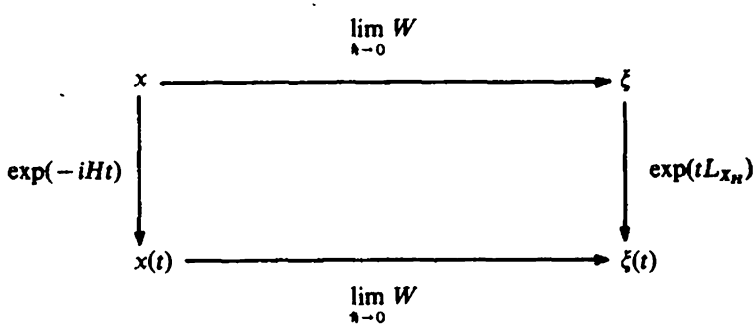
where $(\xi(t), \pi(t))$ are the solutions of the classical equations of motion with initial data $(\xi(0), \pi(0))$, and U_f gives the time-evolution of the equations of motion as linearized about the classical path (cf. (3.3.8; 2)):

$$U_f = T\left[\exp\left(-i\int_0^t dt'\left(\frac{p^2}{2m} + \frac{x^2}{2}V''(\xi(t'))\right)\right)\right]. \tag{3.3.14}$$

In the classical limit (3.1.15) this indeed reproduces the classical trajectory $(\xi(t), \pi(t))$:

$$\lim_{\hbar \to 0} W^*(\hbar^{-1/2}z)(x_\hbar(t), p_\hbar(t))W(\hbar^{-1/2}z) = (\xi(t), \pi(t)).$$

In other words, the diagram



commutes. The mathematically precise statement of this fact uses the Weyl operators:

Theorem (3.3.15)

Let $V \in C^3(\mathbb{R})$ and suppose that $D(V)$ and $D(|x^3V'''|)$ contain K, the set of states $|\alpha|\sqrt{\pi/-\operatorname{Im}\alpha}\,\exp(i(x-\gamma)^2/2\alpha)$, $\alpha, \gamma \in \mathbb{C}$, and $\operatorname{Im}\alpha < 0$. Then for all t for which the classical trajectory $(\xi(t), \pi(t))$ continues to exist,

$$\lim_{\hbar \to 0} W^*(\hbar^{-1/2}z)\exp\left(i\frac{t}{\hbar}H_\hbar\right)\exp(i[r(x - \hbar^{-1/2}\xi(t)) + s(p - \hbar^{-1/2}\pi(t))])$$
$$\times \exp\left(-i\frac{t}{\hbar}H_\hbar\right)W(\hbar^{-1/2}z) = U_f^{-1}(t)\exp(i(rx + sp))U_f(t)$$

in the strong operator topology. The U_f in this formula is defined as in (3.3.14), *$z = \xi(0) + i\pi(0)$, and $H_\hbar = H(x_\hbar, p_\hbar)$ is any self-adjoint extension of the Hermitian operator $(\hbar/2)p^2 + V(\hbar^{1/2}x)$ on K.*

Remarks (3.3.1( )

1. Since $H_\hbar$ is a real, Hermitian operator (see (3.3.19; 5)), its deficiency indices are equal, and thus it has self-adjoint extensions. Any of these extensions serves to define $\exp(itH_\hbar/\hbar)$; in the limit they are all equivalent.
2. If $H_\hbar/\hbar$ is expanded around the classical trajectory in powers of $x_\hbar - \xi(t)$,

$$\begin{aligned} p_\hbar - \pi(t):\frac{p^2}{2} + \hbar^{-1}V(\hbar^{1/2}x) &= \hbar^{-1}\left[\frac{\pi(t)^2}{2} + V(\xi(t))\right] \\ &\quad + \hbar^{-1/2}[\pi(t)(p - \hbar^{-1/2}\pi(t) \\ &\quad + V'(\xi(t))(x - \hbar^{-1/2}\xi(t))] + \cdots \\ &\equiv \hbar^{-1}H_0 + \hbar^{-1/2}H_1 + H_2 + O(\hbar^{1/2}), \end{aligned}$$

then, in addition to $H_0(t)$, which is a multiple of **1**, there arises a linear term $H_1(t) = \hbar^{-1/2}(\pi(t)p + V'(\xi(t))x)$. This is precisely the generator of a displacement by $\hbar^{-1/2}(\xi(t) - \xi(0))$ and, in the momenta, $\hbar^{-1/2}(\pi(t) - \pi(0))$. The left side of (3.3.15) can therefore be written

$$U_\hbar(t)^* \exp(i(rx + sp))U_\hbar(t),$$

where

$$\begin{aligned} U_\hbar(t) = W^*(\hbar^{-1/2}z)\left(T\left[\exp\left(-i\int_0^t dt'(H_1(t') + H_0(t'))\right)\right]\right)^* \\ \cdot \exp\left(-\frac{itH_\hbar}{\hbar}\right)W(\hbar^{-1/2}z). \end{aligned}$$

The theorem thus states that in the limit $\hbar \to 0$, the time-evolution according to $H_\hbar/\hbar$ differs from that according to H_1 by a factor

$$U_f(t) = T\exp\left(-i\int_0^t dt'\, H_2(t')\right),$$

where W has been used to translate the starting point back to the origin.

Proof

In order to show that $\lim_{\hbar\to 0} U_\hbar(t) = U_f(t)$ on K, consider the operator

$$\begin{aligned} U_\hbar(t_1, t_0) \equiv W(\hbar^{-1/2}z)^*\left(T\left[\exp\left(-i\int_0^{t_1} dt' H_1(t')\right)\right]\right)^* \\ \cdot \exp\left(-\frac{i(t_1 - t_0)H_\hbar}{\hbar}\right)T\left[\exp\left(-i\int_0^{t_0} dt' H_1(t')\right)\right] \\ \cdot W(\hbar^{-1/2}z)\exp\left(i\int_{t_0}^{t_1} dt'\, H_0(t')\right) \end{aligned}$$

as in (3.3.6), and compare it with

$$U(t_1, t_0) \equiv T\left[\exp\left(-i\int_{t_0}^{t_1} dt'\left(\frac{p^2}{2} + \frac{V''(\xi(t'))x^2}{2}\right)\right)\right].$$

The set K is invariant under all the unitary factors that arise except possibly for $\exp(-itH_\hbar/\hbar)$; however, since $D(H_\hbar) \supset D(p^2) \cap D(V) \supset K$, the derivative by t_0 in the identity

$$U(t_1, 0) - U_\hbar(t_1, 0) = \int_0^{t_1} dt_0 \frac{d}{dt_0} U_\hbar(t_1, t_0)U(t_0, 0)$$

is justified on K. We find that

$$\begin{aligned}\frac{d}{dt_0} U_\hbar(t_1, t_0)U(t_0, 0) = iU_\hbar(t_1, t_0)\Big\{&\hbar^{-1}V(\xi(t_0) + \hbar^{1/2}x) \\ &- \hbar^{-1}V(\xi(t_0)) - \hbar^{-1/2}V'(\xi(t_0)) \\ &- \frac{V''(\xi(t))x^2}{2}\Big\}U(t_0, 0).\end{aligned}$$

Now, with Taylor's formula, $\|\{\cdots\}\psi\|, \psi \in K$, is bounded by $\hbar^{1/2}\|x^3V'''\psi\|$, and since the $U_\hbar$ are unitary this goes to 0 as $\hbar^{1/2} \to 0$. □

Remarks (3.3.17)

1. The examples looked at earlier show that when $V'' > 0$ the mean-square deviations oscillate about the classical trajectory, when $V'' < 0$ they are exponential functions of time, and when $V'' = 0$ they are linear in time. This corresponds exactly to the behavior of densities of finite spread according to classical stability theory.
2. Since $\hbar$ makes its original appearance only in $(\hbar^2/2m)\Delta$, the limit $\hbar \to 0$ can be reformulated as the limit $m \to \infty$.
3. We have shown only that $U_\hbar$ converges. The conjugation $U \to U^*$ is not strongly continuous but only weakly so, which implies only the weak convergence of $U_\hbar^*$. However, since the limit is unitary and the weak and strong topologies are equivalent on the unitary operators, $U_\hbar^*$ also converges strongly. Finally, although the operator product is not strongly continuous, it is strongly sequentially continuous, so the proof of (3.3.15) goes through.

Classical trajectories generated by a Hamiltonian $H(x, p) = H(x, -p)$ satisfy $x(-t; x(0), p(0)) = x(t; x(0), -p(0))$. Of course, $x \to x, p \to -p$ is not a canonical transformation, and it can not be generated by a unitary trans-

formation in quantum theory either; such a transformation would contradict $[x, p] = i$. The Weyl relations (3.1.2; 1) are nevertheless invariant under the

Antiautomorphism Θ of Reversal of the Motion (3.3.18)

$$\Theta(\alpha A + \beta B) = \alpha\Theta(A) + \beta\Theta(B), \qquad \alpha, \beta \in \overset{\iota}{\mathbb{C}} \quad \text{and} \quad A, B \in W,$$
$$\Theta(AB) = \Theta(B)\Theta(A), \qquad \Theta(W(z)) = W(-z^*).$$

Remarks (3.3.19)

1. Θ preserves the structure of the Jordan algebra, i.e., $\Theta(A \circ B) = \Theta(A) \circ \Theta(B)$, and causes the transformation $\Theta(x) = x$, $\Theta(p) = -p$. If $\Theta(H) = H$ and $\Theta(A) = A$, then $\Theta(A(t)) = \Theta(\exp(iHt)A \exp(-iHt)) = \exp(-iHt)A \times \exp(iHt) = A(-t)$.
2. In the representation (3.1.4) for the W's, Θ is equivalent with complex conjugation to an operation Θ' such that

$$\Theta'(\alpha A + \beta B) = \alpha^*\Theta'(A) + \beta^*\Theta'(B),$$
$$\Theta'(AB) = \Theta'(A)\Theta'(B), \qquad \Theta'(W(z)) = W(z^*).$$

   The operator Θ' also leaves the Weyl relations invariant, and it is easy to check that $\langle z_1|\Theta(W(z))|z_2\rangle = \langle z_2|\Theta'(W(z))|z_1\rangle^*$, where $|z_i\rangle \equiv W(z_i)|u\rangle$. Hence the matrix elements of Hermitian operators and consequently of observables are the same with Θ' as with Θ. A bijection $K: \mathscr{H} \to \mathscr{H}$ is usually defined by

$$K \sum_i \alpha_i |z_i\rangle \equiv \Theta'\left(\sum_i \alpha_i W(z_i)\right)|u\rangle = \sum_i \alpha_i^* |z_i^*\rangle$$

   and is known as **time-reversal**. Note that

$$\langle z_2|(K|z_1\rangle) = \langle u|W(-z_2)W(z_1^*)|u\rangle = \langle u|W(-z_2^*)W(z_1)|u\rangle^*$$
$$= \langle (K|z_2\rangle)|z_1\rangle^*.$$

   Since $\langle z_2|\Theta'(W(z))|z_1\rangle = \langle z_2|KW(z)K|z_1\rangle$, the operator Θ' is equivalent to this antilinear transformation of vectors.
3. Since $\Theta(\mathbf{L}) = -\mathbf{L}$, it would be reasonable to require that $\Theta(\sigma) = -\sigma$. We see incidentally that time-reversible operators $H = \Theta(H)$ must have at least doubly degenerate eigenvalues in the presence of spin. If w is the state associated with a certain eigenvalue of H, then the time-reversed state w_r defined by $w_r(a) = w(\Theta(a))$ is different from w, since for pure states $w(\sigma) = -w_r(\sigma) \neq 0$, although $w(H) = w_r(H)$.
4. It was possible to produce a spatial reflection with an element $\mathscr{P}$ of $\mathscr{U}$ that commutes with H if $H(x, p) = H(-x, -p)$, and thus $\mathscr{P}$ furnishes a constant of the motion (see (3.2.10) and (3.2.11)). However, reversal of the motion is not connected with a constant operator.

5. Hamiltonians that can be time-reversed in the sense of Remark 2 are real differential operators, which always have equal deficiency indices (recall (2.5.13; 4)). Hence, by Theorem (2.5.11), there are self-adjoint extensions, which can be used to define a time-evolution. This is particularly interesting, since classically the existence of collision trajectories can destroy the one-parameter group of the time-evolution (cf. I: §4.5).

Problems (3.3.20)

1. Verify (3.3.3).
2. How do the coherent states (3.1.13) evolve in time with the motions of (3.3.3) and (3.3.5; 2)?
3. (i) Calculate the resolvent $(H - z)^{-1}$ for the H of (3.3.5; 1) as a Fourier integral, and (ii) show that $\sigma_s(H)$ is empty and $\sigma_{ac} = \mathbb{R}$.

   (Hints: For (i) make the ansatz that

$$(H - z)^{-1}\psi(p) = \int_{-\infty}^{\infty} \frac{dp'}{2\pi} \int_{-\infty}^{\infty} \frac{d\lambda}{\lambda - z} K(\lambda, p, p')\psi(p')$$

   and determine K so that

$$\left(ig\frac{d}{dp} + \frac{p^2}{2} - z\right) \int_{-\infty}^{\infty} \frac{d\lambda}{\lambda - z} K(\lambda, p, p') = 2\pi\delta(p - p').$$

   For (ii) use the formula

$$P(a, b) = s\text{-}\lim_{\varepsilon \to 0} \int_a^b \frac{dz}{2\pi i} [(H - z - i\varepsilon)^{-1} - (H - z + i\varepsilon)^{-1}],$$

   where $P(a, b) = \int_a^b dP_H(\alpha)$, and $P_H(\alpha)$ is the spectral projection for H.)
4. Show that in (3.3.5; 3),

   (i) the canonical angular momentum $\hat{L}_3 = [\mathbf{x} \times \mathbf{p}]_3$ is constant, but that the physical $L_3 = [\mathbf{x} \times m\dot{\mathbf{x}}]_3$ is not; and

   (ii) $\langle 0|L_3|0\rangle = -1$ if $a|0\rangle = 0$.
5. Show that the addition of any vector potential, even one depending on the position, always causes an increase in the ground-state energy of a Hamiltonian given just an ordinary potential. This accounts for diamagnetism in hydrogen and helium atoms. (Actually, the statement can be generalized if the exclusion principle is taken into account.)
6. Show that even if ψ is an entire vector for a and b, it need not be an entire vector for $a + b$.
7. Prove the formula of (3.3.7; 1).
8. Prove that in (3.3.8; 2), $U(t) = \exp(i\alpha)\exp(-is(p^2 + \nu^2x^2)/2)\exp(i\beta(xp + px))$.
9. Interpret the adiabatic theorem for the soluble example (3.3.8; 2).

Solutions (3.3.21)

1. $(H\psi)(\mathbf{x}) = -\frac{\Delta}{2m}\psi(\mathbf{x})$: this part is trivial.

$$R(z)\psi : (R(z)\psi)(\mathbf{p}) = 2m\frac{\psi(\mathbf{p})}{|\mathbf{p}|^2 - k^2} \qquad k^2 = 2mz.$$

$$(R(z)\psi)(\mathbf{x}) = \frac{2m}{8\pi^3}\int \frac{\exp(i\mathbf{p}\cdot\mathbf{x})}{|\mathbf{p}|^2 - k^2}\exp(-i\mathbf{p}\cdot\mathbf{x}')\psi(\mathbf{x}')d\mathbf{x}'\,d\mathbf{p}$$
$$= \frac{m}{2\pi}\int \frac{\exp(ik|\mathbf{x} - \mathbf{x}'|)}{|\mathbf{x} - \mathbf{x}'|}\psi(\mathbf{x}')d\mathbf{x}'.$$

$$(U(t)\psi) : (U(t)\psi)(\mathbf{p}) = \exp\left(-\frac{it|\mathbf{p}|^2}{2m}\right)\psi(\mathbf{p}) \Rightarrow (U(t)\psi)(\mathbf{x})$$
$$= \left(\frac{m}{2\pi it}\right)^{3/2}\int d^3x' \exp\left(\frac{im|\mathbf{x} - \mathbf{x}'|^2}{2t}\right)\psi(\mathbf{x}').$$

2. For the free time-evolution, in (3.1.13), $\langle xp + px\rangle = 2\langle x\rangle\langle p\rangle$. Thus $\Delta(x(t))^2 = \Delta x^2 + t^2\Delta p^2 \neq 1/4\Delta(p(t))^2$, and

$$\psi_t(x) = (\Delta x^2 + t^2\Delta p^2)^{-1/4}\exp\left(-\frac{(x - \langle x\rangle - \langle p\rangle t)^2}{4(\Delta x^2 + t^2\Delta p^2)}\left(1 - \frac{it}{2\Delta x^2}\right) + i\langle p\rangle x\right).$$

For the oscillator with $\omega = 1$, x is constant, so the wave-packets do not spread themselves out to nothingness, and

$$\psi_t(x) = \exp\left[-\frac{(x - \langle x\rangle\cos\omega t - \langle p\rangle\sin\omega t + 2i\Delta x^2(\langle p\rangle\cos\omega t - \langle x\rangle\sin\omega t))^2}{4\Delta x^2}\right].$$

3. (i) $(H - z)^{-1}\psi(p) = \int_{-\infty}^{\infty}(dp'/2\pi)\int_{-\infty}^{\infty}d\lambda\ \exp[-i(\lambda(p - p')/g$
$- (p^3 - p'^3)/6g)]\psi(p')/(\lambda - z).$

(ii) If $\psi \in L^1$, then

$$|\langle\psi|P(a,b)\psi\rangle| = \left|\lim_{\varepsilon\to 0}\int_a^b\frac{dz}{2\pi i}\int_{-\infty}^{\infty}\frac{d\lambda\,dp\,dp'}{2\pi}\right.$$
$$\cdot\exp\left[-i\left(\frac{\lambda(p - p')}{g} - \frac{(p^3 - p'^3)}{6g}\right)\right]\psi^*(p)\psi(p')$$
$$\left.\cdot\left(\frac{1}{\lambda - z - i\varepsilon} - \frac{1}{\lambda - z + i\varepsilon}\right)\right|$$
$$\leq \lim_{\varepsilon\to 0}\int_a^b\frac{dz}{\pi}\int_{-\infty}^{\infty}\frac{d\lambda\,dp\,dp'}{2\pi}|\psi(p)\psi(p')|\frac{\varepsilon}{(\lambda - z)^2 + \varepsilon^2}$$
$$\leq \frac{(b - a)}{2\pi}\left(\int_{-\infty}^{\infty}|\psi(p)|dp\right)^2$$
$$\Rightarrow \psi \in \mathscr{H}_{ac} \Rightarrow \mathscr{H}_{ac} = \mathscr{H},$$

since the vectors $\psi \in L^1$ are dense and $\mathscr{H}_{ac}$ is closed.

4. (i) $\hat{L}_3 = (m\omega/2)(\bar{x}_1^2 + \bar{x}_2^2) - (m/2\omega)(\dot{x}_1^2 + \dot{x}_2^2) \Rightarrow [L_3, H] = 0, L_3 = -(m(\dot{x}_1^2 + \dot{x}_2^2)/\omega) + m(\bar{x}_1\dot{x}_2 - \bar{x}_2\dot{x}_1)$ is not constant.
   (ii) $a|0\rangle = 0 \Rightarrow \hat{L}_3|0\rangle = 0, 1, 2, \ldots$. For the orbit with the smallest radius, i.e., the least value of $\bar{x}_1^2 + \bar{x}_2^2$, it is also true that $(\bar{x}_1 - i\bar{x}_2)|0\rangle = 0$, which implies that $\hat{L}_3|0\rangle = 0$.

$$\langle 0|(\bar{x}_1\dot{x}_2 - \bar{x}_2\dot{x}_1)|0\rangle = 0 \Rightarrow \langle 0|L_3|0\rangle = -\frac{2}{\omega}\langle 0|H|0\rangle = -1.$$

5. Let $H_e = (p + eA(x))^2/2m + V(x)$ and $\psi(x) = R(x)\exp(iS(x))$, $R \geq 0$, S real. $\langle\psi|H_e|\psi\rangle = \int d^3x(|\nabla R + i(\nabla S + eA)R|^2/2m + R^2(x)V(x))$

$$\geq \int d^3x(\nabla R^2/2m + R^2V) \geq \langle R|H_0|R\rangle \geq \text{the ground-state energy with } e = 0.$$

6. Let $\mathcal{H} = L^2((-\infty, \infty), dx) \ni \psi(x) = 1$ when $0 \leq x \leq 1$, and otherwise 0, and let $a\psi(x) = \exp(x^2)\psi(x)$, $b\psi(x) = \psi(x + 1) + \psi(x - 1)$. b is bounded, so every vector is entire for it, and ψ is certainly entire for a since $\|a^n\psi\| \leq \exp(n)$. However,

$$\|(a + b)^n\psi\|^2 \geq \|ab^n\psi\|^2 \geq \int_n^{n+1} \exp(2x^2)dx \geq \exp(2n^2),$$

and $\sum_n \exp(2n^2)t^n/n!$ diverges for all $t > 0$.

7. Let $V(t) = U(t, t_1)U(t_1, t_0) - U(t, t_0)$. Then $dV/dt = -iHV$, which implies that $V(t) = 0$, since $V(t_1) = 0$.

8. $\frac{1}{2}(px + xp)$ is the generator of the group $U_\beta: \psi(x) \to \exp(\beta/2)\psi(\exp(\beta)x)$. This follows from the identity $i(xp + px)\psi(x) = 2\partial\exp(\beta/2)\psi(\exp(\beta)x)/\partial\beta|_{\beta=0}$, which holds for entire analytic functions ψ. It implies that $U_\beta xU_{-\beta}\psi(x) = U_\beta(x\exp(-\beta/2)\psi(\exp(-\beta)x)) = \exp(\beta)x\psi(x)$, $U_\beta pU_{-\beta}\psi(x) = U_\beta(-i\exp(-3\beta/2) \times \psi'(\exp(-\beta)x)) = \exp(-\beta)p\psi(x)$.

9. If $t \gg \tau$, then $H(t)|0\rangle \sim (\omega(t)/2)|0\rangle$, and the classical invariant E/ω becomes constant.

3.4 The Limit $t \to \pm\infty$

If particles escape to infinity, their time-evolution approaches that of free particles. In quantum theory this limit is achieved with great topological finesse.

The eigenvectors of H, which span the subspace $\mathcal{H}_p$ of (2.3.16), are related to classical trajectories that remain in compact regions indefinitely. The expectation value of an observable in this case is an almost periodic function $\sum_{j,k}\exp[it(E_j - E_k)]c_{jk}$, for which the time-average exists, but the time-limit does not. The operator $\exp(iHt)$ converges weakly on $\mathcal{H}_{ac}$, since in the spectral representation $\langle f|\exp(iHt)g\rangle = \int dh\exp(iht)f^*(h)g(h)$ approaches zero by the Riemann–Lebesgue lemma. There is, of course, no chance for the unitary operators $\exp(iHt)$ to converge strongly to 0. In order to understand

how some operator can converge strongly as $t \to \pm\infty$, it will be necessary to go more deeply into the ideas introduced with Theorem (2.5.15).

Definition (3.4.1)

H' is said to be **bounded** (respectively, **compact**) **relative** to H_0 iff $D(H') \supset D(H_0)$ and the mapping $H'\colon D_\Gamma(H_0) \to \mathscr{H}$ is continuous (compact). The space $D_\Gamma(H_0)$ is $D(H_0)$ topologized with the graph norm $\| \quad \|_{H_0}$ (2.4.17; 3).

Remarks (3.4.2)

1. Recall that continuous (respectively compact) linear mappings are those that send bounded sets to bounded (relatively compact) sets.
2. Relative boundedness is equivalent to the existence of a constant M such that $\|H'\psi\| \leq M(\|H_0\psi\| + \|\psi\|)$ for all $\psi \in D(H_0)$. Relative compactness in fact implies relative ε boundedness, which means that for all $\varepsilon > 0$ there exists an M such that $\|H'\psi\| \leq \varepsilon\|H_0\psi\| + M\|\psi\|$ for all $\psi \in D(H_0)$. As the Kato–Rellich theorem (2.5.15) showed, this implies that $H(\alpha) = H_0 + \alpha H'$ is self-adjoint on $D(H_0)$. Moreover, the H_0 and $H(\alpha)$ norms are then equivalent, so H' is also relatively compact with respect to all $H(\alpha)$.
3. If c is nonzero and outside the spectrum of H_0, then for all $\chi \in \mathscr{H}$,

$$\begin{aligned}\min\left\{1, \frac{1}{|c|}\right\}\|\chi\| &\leq \min\{1, |c|\}\left(\left\|\frac{H_0}{H_0 - c}\chi\right\|\frac{1}{|c|} + \left\|\frac{1}{H_0 - c}\chi\right\|\right) \\ &\leq \left\|\frac{1}{H_0 - c}\chi\right\|_{H_0} = \left\|\frac{H_0}{H_0 - c}\chi\right\| + \left\|\frac{1}{H_0 - c}\chi\right\| \\ &\leq [1 + (1 + |c|)\|(H_0 - c)^{-1}\|]\|\chi\|,\end{aligned}$$

which implies that the mapping $\mathscr{H} \to D_\Gamma(H_0)\colon \chi \to (H_0 - c)^{-1}\chi$ is continuous in both directions, and thus an isomorphism of these Hilbert spaces. Hence boundedness (respectively, compactness) of the mapping $H'(H_0 - c)^{-1}$:

$$\mathscr{H} \xrightarrow[\text{homeomorphic}]{(H_0 - c)^{-1}} D_\Gamma(H_0) \xrightarrow[\text{continuous (resp., compact)}]{H'} \mathscr{H}$$

is equivalent to the relative boundedness (compactness) of H'. It must similarly be possible to extend the adjoint $(H_0 - c^*)^{-1}H'$\from $D(H')$ to a bounded operator on $\mathscr{H}$.

Examples (3.4.3)

1. If two operators f and g commute, and thus have a common spectral representation on $\mathscr{H} = \oplus_i \mathscr{H}_i$, then g is bounded relative to f if there exists an M such that $|g_i(\alpha)| < M|f_i(\alpha)|$ for all i and α, where g_i and f_i are the multiplication operators on $\mathscr{H}_i$.

2. Let H_0 be the Hamiltonian of free motion (3.3.3) and H' be a multiplication operator $V(x) \in L^2(\mathbb{R}^3, d^3x)$. If the calculation is done in x space, then the Hilbert-Schmidt norm of $V(H_0 - c)^{-1}$ is

$$\|V(H_0 - c)^{-1}\|_2^2 = \mathrm{Tr}(H_0 - c)^{-1}V^2(H_0 - c)^{-1}$$
$$= \int d^3\mathbf{x}\, V^2(\mathbf{x}) \int \frac{d^3p}{(|\mathbf{p}|^2 - c)^2} < \infty \quad \text{for all } -c \in \mathbb{R}^+.$$

The operator $V(H - c)^{-1}$ is therefore in C_2 (see (2.3.21)) and consequently compact. In fact any potential V that falls off faster than $r^{-\varepsilon}$, $\varepsilon > 0$, at infinity and is not too singular at finite x is compact relative to H_0 (Problem 2). Roughly speaking, compact operators fall off in all directions in phase space, in both p and q.

Theorem (3.4.4)

Let V be compact relative to H and bounded, and let P_{ac} be the projection onto the absolutely continuous spectrum of H. Then $V_t P_{ac}$ approaches zero strongly as $t \to \pm\infty$, where $V_t = \exp(iHt)V\exp(-iHt)$.

Proof

Let $c \notin \mathrm{Sp}(H)$, so that for any φ we can write $P_{ac}\varphi = (H - c)^{-1}P_{ac}\psi$. Then

$$\|V_t P_{ac}\varphi\| = \|V(H - c)^{-1}\exp(-iHt)P_{ac}\psi\|.$$

It was shown earlier that $\exp(-iHt)P_{ac} \rightharpoonup 0$, and since $V(H - c)^{-1}$ is a compact operator it sends a weakly convergent sequence into a strongly convergent one. □

Corollaries (3.4.5)

1. Functions that fall off as $r^{-\varepsilon}$ when $r \to \infty$ converge strongly to zero under free time-evolution.
2. Because of the resolvent equation

$$(H_0 + V - z)^{-1} = (H_0 - z)^{-1}(1 - V(H_0 + V - z)^{-1}), \qquad z \notin \mathbb{R},$$

any F that is compact relative to H_0 is also compact relative to $H_0 + V$ provided that V is relatively bounded by $H_0 + V$, which is always the case if V falls off as $r^{-\varepsilon}$ and is thus compact relative to H_0. The time-evolution with such potentials thus makes $F(t)P_{ac} \to 0$, where F is the characteristic function of any finite region in configuration space. This can be interpreted as meaning that the probability that a particle remains in the set given by F vanishes at large times: $\langle\psi_t|F\psi_t\rangle = \|F(t)\psi\|^2 \to 0$ for all $\psi \in P_{ac}\mathcal{H}$, $t \to \pm\infty$. In other words, the particle runs off to infinity. This distinguishes the absolutely continuous spectrum from the singular continuous

spectrum; with the latter a particle keeps returning to near the origin again and again.

Now that the connection with classical physics has been looked into, let us proceed to find the quantum-mechanical analogies of the concepts of (I: §3.4).

Definition (3.4.6)

The algebra $\mathscr{A}$ of the **asymptotic constants** is the set of operators a for which the strong limits

$$a_\pm \equiv \lim_{t \to \pm\infty} \exp(iHt)a \exp(-iHt)$$

exist. The limits themselves form the algebras $\mathscr{A}_\pm$, and we define $\tau_\pm$ as the (surjective) homomorphisms $\mathscr{A} \to \mathscr{A}_\pm : \tau_\pm(a) = a_\pm$.

Remarks (3.4.7)

1. Since the product is not even sequentially continuous in the weak operator topology, the limit must be supposed to exist at least in the strong sense, in order that $\mathscr{A}$ and $\mathscr{A}_\pm$ be algebras and that $\tau_\pm$ be a homomorphism between them. Norm convergence is too much to ask for, as it would contradict the group structure of the time-evolution. If a_t were a Cauchy sequence in the norm $\| \ \|$, then for all ε there would exist a T such that

$$\|a_{t_1} - a_{t_2}\| = \|a - \exp(i(t_2 - t_1)H)a \exp(-i(t_2 - t_1)H)\| \leq \varepsilon$$

for all $t_1, t_2 > T$,

and this is possible only if a_t is a constant.
2. It is immediately clear that $\mathscr{A} \supset \{H\}'$, and since

$$a_\pm = s\text{-}\lim_{t \to \pm\infty} \exp(i(t + \tau)H)a \exp(-i(t + \tau)H) = \exp(i\tau H)a_\pm \exp(-i\tau H)$$

for all $\tau \in \mathbb{R}$,

$\mathscr{A}_\pm \subset \{H\}'$. Since furthermore $\tau_{\pm|\{H\}'} = \mathbf{1}$, it follows that $\mathscr{A}_\pm = \{H\}' \subset \mathscr{A}$, and $\tau_\pm$ are endomorphisms.
3. As explained above, nothing converges on $\mathscr{H}_p$; if P_p is the projection onto this subspace, then $P_p a P_p$ belongs to $\mathscr{A}$ only if it is in $P_p\{H\}'P_p$.
4. If particles escape to infinity, then their momenta p ought to become nearly constant when they are far from any interaction. Consequently, a good candidate for an operator of $\mathscr{A}$ that is not in $\{H\}'$ would be $(\mathbf{1} - P_p)p(\mathbf{1} - P_p)$, or, better, some bounded function of p rather than p itself.

If the time-evolution becomes asymptotically equal to that of H_0, then it is a reasonable expectation that

$$\Omega_{\pm} = \lim_{t \to \pm\infty} \Omega(t) \equiv \lim_{t \to \pm\infty} \exp(iHt)\exp(-iH_0 t)$$

exists. This raises the question of

Topologies in Which the Limit $\lim_{t \to \pm\infty} \Omega(t)$ Might Exist (3.4.8)

1. **Norm convergence**.As remarked in (3.4.7; 1), there is no possibility of this kind of convergence, since

$$\|\Omega(t_1) - \Omega(t_2)\| = \|\exp(iH(t_1 - t_2)) - \exp(iH_0(t_1 - t_2))\| < \varepsilon \quad \text{for all } t_1, t_2 > T$$

   implies that $H = H_0$. Physically, this means that without reference to a particular state, the times $\pm\infty$ are no better than any other times.
2. **Strong convergence**. This allows the possibility that the limit $\Omega_{\pm}$ of the unitary operators $\Omega(t)$ may not be unitary, since the equation $\Omega(t)\Omega^*(t) = \mathbf{1}$ is not necessarily preserved in the limit: As the mapping $a \to a^*$ is only weakly continuous, strong convergence of the Ω implies only weak convergence for the Ω^*. A product sequence $a_n b_n$ converges weakly to ab if $a_n \to a$ and $b_n \to b$. However, no statement can be made about the existence or value of the limit of $b_n a_n$. The following example on l^2 is illustrative of the different kinds of convergence:

$$\Omega_n = \begin{bmatrix} & & & & & \overbrace{}^{n} & 1 \\ 1 & & & & & & \\ & 1 & & & & & \\ & & 1 & & & & \\ & & & 1 & & & \\ & & & & 1 & & \\ & & & & & 1 & \\ & & & & & & 1 \end{bmatrix} \to \Omega = \begin{bmatrix} 1 & & & & & & \\ & 1 & & & & & \\ & & 1 & & & & \\ & & & 1 & & & \\ & & & & 1 & & \\ & & & & & 1 & \\ & & & & & & 1 \end{bmatrix}$$

$$\Omega_n^* = \begin{bmatrix} & 1 & & & & & \\ & & 1 & & & & \\ & & & 1 & & & \\ & & & & 1 & & \\ & & & & & 1 & \\ 1 & & & & & & \\ & & & & & & 1 \end{bmatrix} \to \Omega^* = \begin{bmatrix} 1 & & & & & & \\ & 1 & & & & & \\ & & 1 & & & & \\ & & & 1 & & & \\ & & & & 1 & & \\ & & & & & 1 & \\ & & & & & & 1 \end{bmatrix}$$

The operator Ω_n^* converges only weakly, since $v_n \equiv \Omega_n^*(1, 0, 0, \ldots) = (0, 0, \ldots, \overbrace{1}^{n}, 0, 0, \ldots) \to 0$, while $\|v_n\| = 1$ for all n, so $v_n \not\to 0$. In this case we have $\mathbf{1} = \Omega_n^*\Omega_n \Rightarrow \Omega^*\Omega = \mathbf{1}$, but $\mathbf{1} = \Omega_n\Omega_n^* \not\to \Omega\Omega^* \neq \mathbf{1}$. The situation is the same for $\Omega_\pm$, since they are strong limits of unitary operators. Although $\Omega_\pm^*\Omega_\pm = \mathbf{1}$, since

$$\langle x|\Omega_\pm^*\Omega_\pm x\rangle = \|\Omega_\pm x\|^2 = \lim_{t\to\pm\infty} \|\Omega(t)x\|^2 = \|x\|^2 \text{ for all } x \in \mathscr{H},$$

this only tells us that $\Omega_\pm\Omega_\pm^* = \Omega_\pm\Omega_\pm^*\Omega_\pm\Omega_\pm^*$, i.e., that $\Omega_\pm\Omega_\pm^*$ is a projection. It projects onto a subspace $\mathscr{H}_\pm \subset \mathscr{H}$ on which $\mathscr{H}$ gets mapped unitarily by Ω, and which $\Omega_\pm^*$ maps back onto $\mathscr{H}$ (see Figure 8). These operators are related by $\Omega_{\pm|\mathscr{H}_\pm}^* = \Omega_{\pm|\mathscr{H}_\pm}^{-1}$. In analogy with (3.4.7; 2), $\Omega_\pm^* \exp(i\tau H)\Omega_\pm = \exp(i\tau H_0)$ for all $\tau \in \mathbb{R}$, so H acting on $\mathscr{H}_\pm$ is unitarily equivalent to H_0 on $\mathscr{H}$. Therefore the spectrum of H_0 is the same as a part of the spectrum of H. If H_0 has only an absolutely continuous spectrum (H_0: $f(h) \to hf(h)$ on any summand of the spectral representation), and the eigenvectors of H are called $|E_i\rangle$, then

$$\langle f|\exp(itH_0)\exp(-itH)|E_i\rangle = \int d\mu(h)\exp(it(h - E_i))\langle f(h)|E_i\rangle \to 0$$

as $t \to \pm\infty$

by the Riemann–Lebesgue lemma. The bound states are thus in the kernel of $\Omega_\pm^*$. The strong convergence can be restated as: to every state $\varphi \in \mathscr{H}$ that evolves according to H_0, there exists a "scattering state" $\psi_\pm = \Omega_\pm\varphi$ such that the two states approach each other asymptotically:

$$\lim_{t\to\pm\infty} \|\exp(iHt)\exp(-iH_0t)\varphi - \psi_\pm\|$$

$$= \lim_{t\to\pm\infty} \|\exp(-iH_0t)\varphi - \exp(-iHt)\psi_\pm\| = 0.$$

3. **Weak convergence**. The norm $\|a\| = \sup_{\|x\|=\|y\|=1}|\langle x|ay\rangle|$, as the supremum of weakly continuous functions, is weakly lower semicontinuous, so in any event we know that $\|\Omega_\pm\| \leq 1$. Since the unitary operators are weakly dense in the unit ball, this is apparently the most that can

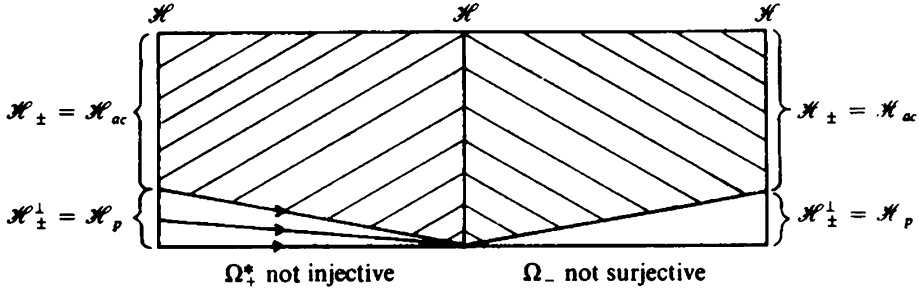


Figure 8 The domains and ranges of Ω^* and Ω.

be said. Weak convergence is not a very powerful property. The limit could simply be zero, as happens for $\exp(itH_0)$. If $\Omega(t)$ converges weakly but not strongly, then $\Omega_\pm$ can not be unitary.

4. **Convergence of Ω^*.** If $\Omega(t) \to \Omega_\pm$, then we know that $\Omega^*(t)$ converges weakly to $\Omega_\pm^*$, and that $\Omega_\pm^*$ maps $\mathscr{H}_\pm$ unitarily onto $\mathscr{H}$ and sends everything else to 0. Since the weak topology and the strong topology are the same for the unitary operators (2.1.28; 5), $\Omega^*(t)$ converges strongly to $\Omega_\pm^*$ on $\mathscr{H}_\pm$, and converges weakly to 0 on its orthogonal complement. Strong convergence on $\mathscr{H}_\pm$ means that to each scattering state $\exp(-itH)\psi$, $\psi \in \mathscr{H}_\pm$, there exists a free state $\exp(-itH_0)\varphi$ that becomes asymptotically equal to it.

Now that we understand something of the insidiousness of Hilbert space, we can state our goals more precisely.

Definition (3.4.9)

(i) If $\exp(itH)\exp(-itH_0)$ converges strongly as $t \to \pm\infty$, we say that the **Møller wave operators** $\Omega_\pm = \lim_{t\to\pm\infty} \exp(itH)\exp(-itH_0)$ **exist.**

(ii) If $\mathscr{H}_\pm \equiv \Omega_\pm \mathscr{H} = \mathscr{H}_p^\perp$, then $\Omega_\pm$ are said to be **asymptotically complete.**

Remarks (3.4.10)

1. The meaning of asymptotic completeness is that other than the bound states $\mathscr{H}_p$, every state approaches a free state as $t \to \pm\infty$. A simple classical example where this fails to be true has been provided by S. Sokolov: an otherwise free particle with an effective mass $\mathscr{M}(x) = \coth^2 x$, $H = p^2/\mathscr{M}(x)$, and $H_0 = p^2$. All incoming trajectories have a dead end at the origin, and the set of scattering trajectories is empty (cf. [4]). Pearson [4] has constructed a potential for which the analogous thing happens in quantum mechanics.
2. Invariance under reversal of the motion (3.3.18) does not suffice to guarantee that $\mathscr{H}_+ = \mathscr{H}_-$. We shall soon encounter many-channel systems for which $\mathscr{H}_+ \neq \mathscr{H}_-$.
3. Since

$$\frac{d}{dt}\Omega(t) = \exp(iHt)i(H - H_0)\exp(-iH_0t) = i\Omega(t)H_1(t),$$

$$H_1(t) \equiv \exp(iH_0t)(H - H_0)\exp(-iH_0t),$$

Ω_+ can also be written formally as

$$\Omega_+ = T\exp\int_0^\infty \mathrm{dt}\, iH_1(t),$$

which, however, does not answer the question of the existence of the infinite integral.

Sufficient Conditions for the Existence and Completeness of $\Omega_\pm$ (3.4.11)

Let $H = H_0 + V$, $\sqrt{V} \equiv V/|V|^{1/2}$, $D(H) = D(H_0)$, and let χ_I be the characteristic function of an interval $I \subset \sigma(H_0)$. If

$$\sup_{\omega \in I}(\|\sqrt{V}\,\delta(H-\omega)\sqrt{V}\| + \|\sqrt{V}\,\delta(H_0-\omega)\sqrt{V}\|) < \infty,$$

then

$$\chi_I(H)\exp(iHt)\exp(-iH_0t)\chi_I(H_0) \quad \text{and} \quad \chi_I(H_0)\exp(iH_0t)\exp(-iHt)\chi_I(H)$$

converge strongly as $t \to \pm\infty$.

Remarks (3.4.12)

1. In the case of a single channel, the spectrum normally has the properties

$$\sigma_{ac}(H_0) = \mathbb{R}^+ = \sigma_{ac}(H),\ \sigma_p(H_0) = \sigma_s(H_0) = \sigma_s(H) = \varnothing,\ \sigma_p(H) \subset \mathbb{R}^-.$$

It is convenient for technical reasons to use the projections χ_I to exclude the particles that move too slowly or too rapidly, by letting $I = (\varepsilon, 1/\varepsilon)$. If the supremum over $\omega \in I$ is finite for all $\varepsilon > 0$, then it follows that $\chi_I(H)\exp(itH)\exp(-itH_0)$ converges on a dense set in Hilbert space, and consequently on the whole space. Since $f(H)\Omega = \Omega f(H_0)$, we expect that

$$\chi_{I'}(H)\exp(iHt)\exp(-iH_0t)\chi_I(H_0) \to 0 \text{ for all } I' \cap I = \varnothing$$

and this is indeed verified in Problem 3. This equation shows that $\chi_I(H)\exp(itH)\exp(-itH_0)\chi_I(H_0)$ has the same limit as

$$\exp(itH)\exp(-itH_0)\chi_I(H_0),$$

so (3.4.10) in fact implies what is required in Definition (3.4.9), viz., that $\exp(itH)\exp(-itH_0)$ converges on a dense set.

2. The operator $\sqrt{V}\,\delta(H-\omega)\sqrt{V}$ is to be interpreted as

$$\lim_{\varepsilon \to 0} \frac{1}{2\pi i}\sqrt{V}\left(\frac{1}{H-\omega-i\varepsilon} - \frac{1}{H-\omega+i\varepsilon}\right)\sqrt{V},$$

and this limit may exist even though $(H-z)^{-1}$ does not exist on the real axis. We shall soon discover that even compactness may survive the limit as $\varepsilon \downarrow 0$.

Proof

Let us make the abbreviations $\psi_I \equiv \chi_I(H_0)\psi$, $\varphi_I \equiv \chi_I(H)\varphi$. Then

$$\begin{aligned}
&\|\chi_I(H)(\exp(iHt_1)\exp(-iH_0t_1) - \exp(iHt_2)\exp(-iH_0t_2))\chi_I(H_0)\psi\| \\
&\quad = \left\|\chi_I(H)\int_{t_1}^{t_2} dt\, \exp(iHt)V\exp(-iH_0t)\psi_I\right\| \\
&\quad = \sup_{\|\varphi\|=1}\left|\int_{t_1}^{t_2} dt\langle\varphi|\chi_I(H)\exp(iHt)V\exp(-iH_0t)\psi_I\rangle\right| \\
&\quad \le \sup_{\|\varphi\|=1}\int_{t_1}^{t_2} dt\|\sqrt{V}\exp(-iHt)\varphi_I\|\cdot\|\sqrt{V}\exp(-iH_0t)\psi_I\| \\
&\quad \le \sup_{\|\varphi\|=1}\left[\int_{t_1}^{t_2} dt\|\sqrt{V}\exp(-iHt)\varphi_I\|^2\cdot\int_{t_1}^{t_2} dt\|\sqrt{V}\exp(-iH_0t)\psi_I\|^2\right]^{1/2}.
\end{aligned}$$

To show convergence, it thus suffices to show that as $t \to \pm\infty$, V_t converges in mean-square to zero (cf. (3.4.4)), whether it evolves in time according to H_0 or to H. To perform the time-integration, we use the generalization of Parseval's formula,

$$\int_{-\infty}^{\infty} dt\|f(t)\|^2 = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\|\tilde{f}(\omega)\|^2,$$

for vectors in Hilbert space:

$$\int_{-\infty}^{\infty} dt\|\sqrt{V}\exp(-iHt)\varphi_I\|^2 = 2\pi\int_{-\infty}^{\infty} d\omega\|\sqrt{V}\,\delta(H-\omega)\varphi_I\|^2.$$

Now note that for any positive operators a and b, $\|\sqrt{b}a\varphi\|^2 \le \|\sqrt{b}\sqrt{a}\|^2 \times \|\sqrt{a}\varphi\|^2 = \|\sqrt{b}a\sqrt{b}\|\cdot\langle\varphi|a\varphi\rangle$, so:

$$\begin{aligned}
&2\pi\int_{-\infty}^{\infty} d\omega\|\sqrt{V}\,\delta(H-\omega)\varphi_I\|^2 \\
&\quad \le 2\pi\int_{-\infty}^{\infty} d\omega\|\sqrt{V}\,\delta(H-\omega)\chi_I(H)\sqrt{V}\|\cdot\langle\varphi_I|\delta(H-\omega)\varphi_I\rangle \\
&\quad \le 2\pi\sup_{\omega\in I}\|\sqrt{V}\,\delta(H-\omega)\sqrt{V}\|\int_{\infty}^{\infty} d\omega\langle\varphi_I|\delta(H-\omega)\varphi_I\rangle \\
&\quad = 2\pi\sup_{\omega\in I}\|\sqrt{V}\,\delta(H-\omega)\sqrt{V}\|\,\|\varphi_I\|^2.
\end{aligned}$$

These relationships are still valid with H replaced by H_0, and show that the integral $\int_{t_1}^{\infty}$ gets arbitrarily small as $t_1 \to \infty$, since the integral $\int_{-\infty}^{\infty}$ exists. This implies the strong convergence of $\Omega(t)$ as $t \to \pm\infty$. □

Examples (3.4.13)

1. A separable potential. Let $H_0 = |\mathbf{p}|^2$, $(V\varphi)(\mathbf{x}) = \lambda\rho(\mathbf{x}) \int d^3x' \rho^*(\mathbf{x}')\varphi(\mathbf{x}')$, in which $\int d^3x |\rho(\mathbf{x})|^2 = 1$, $\int d^3x\, d^3x' \rho(\mathbf{x})\rho^*(\mathbf{x}')/|\mathbf{x} - \mathbf{x}'| = M < \infty$, $\inf_{|\mathbf{p}|^2 \in I} |\tilde{\rho}(\mathbf{p})| > 0$. Since $P = V/\lambda$ is a one-dimensional projection,

$$(H - z)^{-1} = (H_0 - z)^{-1} - \lambda(H_0 - z)^{-1} P (H_0 - z)^{-1} D^{-1}(z),$$
$$D(z) = 1 + \lambda \operatorname{Tr} P(H_0 - z)^{-1} P$$

and

$$P(H - z)^{-1} P = P(H_0 - z)^{-1} P D^{-1}(z).$$

By assumption,

$$P(H_0 - z)^{-1} P = \int d^3p |\tilde{\rho}(\mathbf{p})|^2 (|\mathbf{p}|^2 - z)^{-1}$$
$$= \int d^3x\, d^3x'\, \rho(\mathbf{x})\rho^*(\mathbf{x}') \frac{\exp(i\sqrt{z}|\mathbf{x} - \mathbf{x}'|)}{|\mathbf{x} - \mathbf{x}'|}$$

remains bounded by M for all $\sqrt{z}$. In addition, for all $y > 0$,

$$\lambda^{-1} \operatorname{Im} D(x + iy) = \int d^3p |\tilde{\rho}(\mathbf{p})|^2 \frac{y}{(|\mathbf{p}|^2 - x)^2 + y^2}$$
$$\geq \inf_{|\mathbf{p}|^2 \in I} |\tilde{\rho}(\mathbf{p})|^2 \int_{|\mathbf{p}|^2 \in I} d^3p \frac{y}{(|\mathbf{p}|^2 - x)^2 + y^2}$$

is bounded below, uniformly in $x \in I$. Then

$$\sup_{x \in I} |D^{-1}(x + iy)| \leq \sup_{x \in I} \frac{D(z)}{|\operatorname{Im} D(z)|^2}$$

is also finite in the limit $y \to 0$, and

$$\lim_{y \to 0} \sup_{x \in I} \|\sqrt{V}(H - z)^{-1}\sqrt{V}\| < \infty.$$

2. Potentials $r^{-1-\varepsilon}, 0 < \varepsilon < 1$. In momentum space,

$$\widetilde{r^{-\gamma}} = \int d^3x \exp(i\mathbf{k} \cdot \mathbf{x}) r^{-\gamma} = |\mathbf{k}|^{-3+\gamma} 4\pi\Gamma(2 - \gamma)\sin(2 - \gamma)\pi.$$

Consequently,

$$\operatorname{Tr}(\sqrt{V}\, \delta(H_0 - \omega)\sqrt{V})^n = \int \prod_{i=1}^{n} d^3p_i\, \delta(|\mathbf{p}_i|^2 - \omega)|\mathbf{p}_i - \mathbf{p}_{i+1}|^{-2+\varepsilon}$$
$$= \omega^{-n(1+\varepsilon)/2} \int \prod_{i=1}^{n} d\Omega_i |\mathbf{n}_i - \mathbf{n}_{i+1}|^{-2+\varepsilon},$$

where by convention $\mathbf{p}_{n+1} = \mathbf{p}_1$, and $d\Omega_i$ stands for the solid angle element in the direction of the unit vector $\mathbf{n}_i \equiv \mathbf{p}_i/|\mathbf{p}_i|$. Now,

$$|\mathbf{n}_i - \mathbf{n}_{i+1}|^2 = 2(1 - \cos\theta_i), \qquad \theta_i = \measuredangle(\mathbf{n}_i, \mathbf{n}_{i+1}),$$

and

$$\int \prod_{i=1}^{n} d\Omega_i |\mathbf{n}_i - \mathbf{n}_{i+1}|^{-2+\varepsilon}$$

is smaller than $c(\varepsilon) < \infty$ for $n > 2/\varepsilon$ (Problem 5). Since $\| \quad \| \leq \| \quad \|_n$,

$$\sup_{\omega \in I} \|\sqrt{V}\, \delta(H_0 - \omega)\sqrt{V}\| \leq \sup_{\omega \in I} \omega^{-(1/2)-(\varepsilon/2)} c(\varepsilon) < \infty,$$

where we have taken I as a compact interval $\subset \mathbb{R}^+$. The Hölder continuity of $\sqrt{V}\,\delta(H_0 - \omega)\sqrt{V}$ in the norm $\| \quad \|_n$ implies that the operator $\sqrt{V}(H_0 - x - iy)\sqrt{V}$ remains compact in the limit $y \to 0$ (see Problem 5). If from

$$\sqrt{V}(H - z)^{-1}\sqrt{V} = \sqrt{V}(H_0 - z)^{-1}\sqrt{V} - \sqrt{V}(H - z)^{-1}V(H_0 - z)^{-1}\sqrt{V}$$

we reason that

$$\sqrt{V}(H - z)^{-1}\sqrt{V} = \sqrt{V}(H_0 - z)^{-1}\sqrt{V}(1 + |V|^{1/2}(H_0 - z)^{-1}\sqrt{V})^{-1},$$

then we see that the operators $\sqrt{V}(H - z)^{-1}\sqrt{V}$ and $\sqrt{V}(H_0 - z)^{-1}\sqrt{V}$ differ only by the factor $(1 + |V|^{1/2}(H_0 - z)^{-1}\sqrt{V})^{-1}$. Since

$$|V|^{1/2}(H_0 - z)^{-1}\sqrt{V}$$

is compact and thus has a pure point spectrum with complex eigenvalues $\kappa_i(z)$ the only possible accumulation point of which is zero,

$$\|(1 + |V|^{1/2}(H_0 - z)^{-1}\sqrt{V})^{-1}\| \leq \sup_i |(1 - \kappa_i(z))^{-1}|.$$

The functions $z \to \kappa_i(z)$ are continuous, $z \to |V|^{1/2}(H_0 - z)^{-1}\sqrt{V}$ is norm-analytic in $\mathbb{C}\backslash\mathbb{R}$, and it can be continued to $I \subset \mathbb{R}$. If the eigenfunctions decrease sufficiently fast at infinity, the values z_{ij} for which κ_i equals 1 are eigenvalues of H, because $|V|^{1/2}(H_0 - z)^{-1}|V|^{1/2}\psi = 0$ implies that $(H_0 + V - z)|V|^{-1/2}\psi = 0$. Hence, if $|V|^{-1/2}\psi \in L^2$, then z is an eigenvalue of H. A separate argument is necessary to exclude the values $\kappa_i = 1$ for $z \in \mathbb{R}^+$. Thus if I is any compact set in $(0, \infty)\backslash\{z_{ij}\}$, (3.4.11) is satisfied.

Remarks (3.4.14)

1. The analysis has been restricted to $\varepsilon < 1$ so that the singularity at $r = 0$ could not destroy the relative compactness of V. Since existence of Ω depends on the falling off of the potential as $r \to \infty$, it is clear that it exists

for all V falling off faster than $1/r$, so long as the finite singularities are not strong enough to wreck the self-adjointness [4].

2. If $\varepsilon = 0$, then $V_t^{1/2} \sim (pt)^{-1/2}$, which is not square-integrable in t, even if $p = 0$ is excluded. This is to be expected, because $\Omega_\pm$ also fails to exist classically for the $1/r$ potential (I: 4.2.18; 2).
3. If $\varepsilon = 1$, then the bound of $\|\sqrt{V}\ \delta(H_0 - \omega)\sqrt{V}\|$ is independent of ω, so the supremum over ω in all of $\mathbb{R}$ would be finite. This may seem surprising, since even in classical scattering theory the point $p = 0$ has to be removed, since particles with $p = 0$ never escape. In quantum mechanics, the diffusion of the wave-packets is enough to make $\langle r_t^{-2}\rangle$ square-integrable: With free time-evolution, $\Delta x_t^2 \sim \Delta x_0^2 + t^2/(\Delta x_0)^2$ (cf. (3.3.5; 1), and

$$\int_{-\infty}^{\infty} dt \langle r_t^{-\gamma}\rangle \sim \int_{-\infty}^{\infty} dt \left(\Delta x_0^2 + \frac{t^2}{\Delta x_0^2}\right)^{-\gamma/2} \sim \Delta x_0^{2-\gamma}.$$

If $\gamma = 2$, this is independent of Δx_0, so the bound ought to be independent of φ without the necessity of projecting out a neighborhood of $p = 0$.
4. If there are bound states imbedded in the continuum, then $\exp(itH_0) \times \exp(-itH)$ cannot converge strongly on them, and it is necessary to project them out with a χ_I. With a potential $r^{-\gamma}$, $0 < \gamma < 2$, then by the virial theorem to be proved in §4.1 they do not occur. This theorem states that an eigenvalue of the energy equals $(\gamma - 2)/\gamma$ times the expectation value of the kinetic energy in the corresponding eigenstate. Since the latter quantity is positive, all eigenvalues are negative. If a potential oscillates, then Bragg reflection of waves can produce a bound state, even if in classical mechanics it would be energetically possible for a particle to escape. For example, the function

$$\psi(r) = \frac{\sin r}{a + r - \frac{1}{2}\sin 2r} \in L^2((0, \infty), dr), \qquad a > 0,$$

satisfies the equation

$$\left(-\frac{d^2}{dr^2} + V(r) - 1\right)\psi(r) = 0,$$

$$V(r) = \frac{8 \sin r}{(a + r - \frac{1}{2}\sin 2r)^2}(\sin r - (a + r)\cos r),$$

and it is thus an eigenfunction with eigenvalue $E = 1$ of a potential V, $|V(r)| < \varepsilon \min(1, 1/r)$, where ε can be taken arbitrarily small as a tends to $+\infty$. It can be shown that potentials that approach zero faster than $1/r$ as $r \to \infty$ have no positive eigenvalues ([3], §XIII).

Many-Particle Scattering (3.4.15)

Different groupings are possible in a many-particle system as the particles go off to infinity, some remaining bound together while others get ever farther away from them. Formally, the Schrödinger equation for N particles

acts on a $3N$-dimensional configuration space, and different ways of apportioning the particles into clusters correspond to different regions in $\mathbb{R}^{3N}$. A given distribution of $1, 2, \ldots, N$ into disjoint subsets, such as (1, 2), (3), (4, 5, 6), ..., will be shorthand for the statement that particles 1 and 2 remain bound together, 3 approaches infinity by itself, 4 through 6 are bound, etc. Such a distribution is referred to as a **channel**. Pair potentials $V_{ij}(\mathbf{x}_i - \mathbf{x}_j)$ do not fall off in the directions where $\mathbf{x}_i$ and $\mathbf{x}_j$ are nearly equal, so the asymptotic time-evolution is not described by a unique Hamiltonian, but instead depends on the channel, i.e., on the direction in which the state goes to infinity. If we index the channels with a subscript α, then the interaction I_α between separate clusters goes to zero as $t \to \pm\infty$, and the time-evolution approaches that of $H_\alpha \equiv H - I_\alpha$.

Example (3.4.16)

Consider three particles, and suppose either that the center of mass has been separated out or simply that one of the particles is infinitely heavy, as an approximation to a nucleus K and two electrons e_1 and e_2. Then the appropriate configuration space specifies the relative motion of the two coordinates $\mathbf{x}_1$ and $\mathbf{x}_2$ of the electrons, and there are four channels:
$(K)(e_1)(e_2)$. In this channel all the particles separate, and

$$H = \frac{|\mathbf{p}_1|^2}{2m_1} + \frac{|\mathbf{p}_2|^2}{2m_2} + V_1(\mathbf{x}_1) + V_2(\mathbf{x}_2) + V_{12}(\mathbf{x}_1 - \mathbf{x}_2)$$

breaks up into H_0 and $I_0 = V_1 + V_2 + V_{12}$.
$(K, e_1)(e_2)$. Particle 1 remains bound to the nucleus, while particle 2 escapes:

$$H_1 = \frac{|\mathbf{p}_1|^2}{2m_1} + \frac{|\mathbf{p}_2|^2}{2m_2} + V_1(\mathbf{x}_1), \qquad I_1 = V_2 + V_{12}.$$

$(K, e_2)(e_1)$. The same, with particles 1 and 2 switched.
$(K)(e_1, e_2)$. In this channel particles 1 and 2 remain bound together, which is of course impossible for electrons, but would be realistic in the scattering of a positron from a hydrogen atom. In this case,

$$H_{12} = \frac{|\mathbf{p}_1|^2}{2m_1} + \frac{|\mathbf{p}_2|^2}{2m_2} + V_{12}(\mathbf{x}_1 - \mathbf{x}_2), \qquad I_{12} = V_1 + V_2.$$

Once again, the existence of the Møller operators means that for each φ_α in which the clusters corresponding to a channel α are bound, and which evolves in time by $\exp(-itH_\alpha)$, there is a state ψ_α evolving by $\exp(-itH)$ and asymptotically approaching φ_α:

$$\|\exp(-iHt)\psi_\alpha - \exp(-iH_\alpha t)\varphi_\alpha\| \to 0.$$

Completeness of the Møller operators means that $\mathscr{H}_{ac}(H)$ is spanned by such ψ_α's.

The Møller Wave Operators for Many-Particle Scattering (3.4.17)

If P_α is the projection onto the part of $\mathscr{H}_{ac}(H_\alpha)$ corresponding to the channel α, then the Møller operators

$$\Omega_{\alpha\pm} = \lim_{t\to\pm\infty} \exp(iHt)\exp(-iH_\alpha t)P_\alpha$$

are said to exist whenever the strong limit exists. In that event, the operators $Q_{\alpha\pm} \equiv \Omega_{\alpha\pm}\Omega_{\alpha\pm}^*$ are projections, and asymptotic completeness means that

$$\sum_\alpha Q_{\alpha\pm}\mathscr{H} = \mathscr{H}_{ac}(H).$$

Remarks (3.4.18)

1. The operators P_α can be written as tensor products of the projections onto the bound states within the clusters of the channel and of identity operators in the relative coordinates. For instance, in (3.4.16) the projection P_α for $(K, e_1)(e_2)$ equals $P_p \otimes \mathbf{1}$, where P_p is the projection onto $\mathscr{H}_p(p_1^2/2m + V_1)$. The projections for different α will not generally be orthogonal, since they are related to different, and noncommuting, H_α. Although
$$\exp(itH)\exp(-itH_\alpha)$$
converges on all of $\mathscr{H}$, this limit is not terribly interesting.
2. The equation $\Omega^*\Omega = \mathbf{1}$ of (3.4.8; 2) has the generalization $\Omega_{\alpha\pm}^*\Omega_{\beta\pm} = \delta_{\alpha\beta}P_\alpha$ (Problem 4). As a result, the Q_α are orthogonal for different α:
$$Q_{\alpha\pm}Q_{\beta\pm} = \Omega_{\alpha\pm}\Omega_{\alpha\pm}^*\Omega_{\beta\pm}\Omega_{\beta\pm}^* = \delta_{\alpha\beta}Q_{\alpha\pm}.$$
This is to be expected, since all the Q_α involve the same H and commute with it:
$$\begin{aligned}\exp(iHt)Q_{\alpha\pm}\exp(-iHt) &= \exp(iHt)\Omega_{\alpha\pm}\Omega_{\alpha\pm}^*\exp(-iHt)\\ &= \Omega_{\alpha\pm}\exp(iH_\alpha t)\exp(-iH_\alpha t)\Omega_{\alpha\pm}^* = Q_{\alpha\pm}.\end{aligned}$$
The physical significance of this is that the wave functions $\exp(itH)\psi_\alpha$, $\psi_\alpha = \Omega_{\alpha\pm}\varphi_\alpha$, turn into widely separated clusters after long times, so vectors corresponding to different channels are orthogonal. Since they all evolve according to $\exp(itH)$, this asymptotic orthogonality implies that they are orthogonal at all times.
3. The projections P_α and Q_α are rather unwieldy. $\sum_\alpha P_\alpha \neq P_{ac}$, and it is practically impossible to write Q_α explicitly. That is why it is more convenient to work with operators J_α, which approach P_α under the time-evolution of H_α, in place of the P_α themselves. Then $\Omega_{\alpha\pm}$ can be written as the limit of $\exp(iHt)J_\alpha\exp(-iH_\alpha t)$, since $\exp(iH_\alpha t)J_\alpha\exp(-iH_\alpha t) \to P_\alpha$ implies that $\exp(iHt)J_\alpha\exp(-iH_\alpha t) \to \Omega_{\alpha\pm}$. In Example (3.4.16), electron-hydrogen scattering, a good choice is
$$J_1 = \frac{|\mathbf{x}_1|^4 + |\mathbf{x}_2|^4}{1 + |\mathbf{x}_1|^4 + |\mathbf{x}_2|^4 + |\mathbf{x}_1|^8}, \qquad J_2 = \frac{|\mathbf{x}_1|^4 + |\mathbf{x}_2|^4}{1 + |\mathbf{x}_1|^4 + |\mathbf{x}_2|^4 + |\mathbf{x}_2|^8},$$

$J_{12} = 0, J_0 = 1 - J_1 - J_2$. If $\mathbf{x}_1$ remains in a finite region and $\mathbf{x}_2 \to \infty$, then J_1 goes to 1 and J_2 goes to 0, and vice versa. J_0 becomes 1 only if both particles go to infinity. It will be shown in §4.4 that this heuristic argument can actually show strong convergence.

Criterion (3.4.11) for the existence and completeness of the Møller wave operators does not work for many-body systems, because the pair potentials V_{ij} are not compact relative to H. It is possible to write them as tensor products of a function of $\mathbf{x}_i - \mathbf{x}_j$ and the unit operator in the other coordinates, but a tensor product is compact only if both of its factors are compact. This is where the functions J_α introduced above can be of use, for they decrease exactly in the directions in which I_α is constant, making $J_\alpha I_\alpha$ relatively compact and the methods of (3.4.11) applicable. This can be stated as a simple

Criterion for the Existence and Completeness of $\Omega_{\alpha\pm}$ (3.4.19)

Let J_α be positive operators for which $s\text{-lim } \exp(iH_\alpha t)J_\alpha \exp(-iH_\alpha t) = P_\alpha$ *and* $\sum_\alpha J_\alpha = 1$. *If the strong limits of* $\exp(iHt)J_\alpha \exp(-iH_\alpha t)$ *and*

$$\exp(iH_\alpha t)J_\alpha \exp(-iHt)P_{ac}(H)$$

exist as $t \to \pm\infty$, then $\Omega_{\alpha\pm}$ exist and are complete.

Proof

Since, by assumption, $\|(\exp(-iH_\alpha t)P_\alpha - J_\alpha \exp(-iH_\alpha t))\psi\| \to 0$ for all $\psi \in \mathscr{H}$, $\exp(iHt)\exp(-iH_\alpha t)P_\alpha$ converges strongly just as $\exp(iHt)J_\alpha \exp(-iH_\alpha t)$ does and hence the latter operator converges to $\Omega_{\alpha\pm}$. Then, since

$$(1 - P_\alpha)\Omega_{\alpha\pm}^* = 0,$$

$$\begin{aligned} &s\text{-lim } \exp(iHt)J_\alpha \exp(-iHt)P_{ac}(H) \\ &\quad = s\text{-lim } \exp(iHt)\exp(-iH_\alpha t)(P_\alpha + (1 - P_\alpha)) \\ &\qquad \times \exp(iH_\alpha t)J_\alpha \exp(-iHt)P_{ac}(H) = Q_\alpha. \end{aligned}$$

Consequently,

$$\sum_\alpha Q_\alpha = s\text{-lim } \exp(iHt) \sum_\alpha J_\alpha \exp(-iHt)P_{ac}(H) = P_{ac}(H). \qquad \square$$

Example (3.4.20)

In the three-body system (3.4.16) let $V_{12} = 0$ and suppose that V_1 and V_2 are potentials such that the one-particle Møller operators ω_1 and ω_2 exist and are complete. The J_α have the following form in the different channels: 0-channel. Under the time-evolution according to

$$H_0 = \frac{|\mathbf{p}_1|^2}{2m_1} + \frac{|\mathbf{p}_2|^2}{2m_2},$$

J_1 and J_2 converge strongly to zero: If $\mathbf{x}_i \to \mathbf{x}_i + \mathbf{p}_i t$, then

$$J_i \to \frac{|\mathbf{p}_1|^4 + |\mathbf{p}_2|^4}{|\mathbf{p}_1|^4 + |\mathbf{p}_2|^4 + t^2|\mathbf{p}_i|^8}, \qquad i = 1, 2,$$

and this in turn approaches zero on the dense set of functions the support of which does not contain $\mathbf{p}_i = \mathbf{0}$. Therefore

$$s\text{-lim } \exp(iHt)J_0 \exp(-iH_0 t) = s\text{-lim } \exp(iHt)\exp(-iH_0 t) \times \exp(iH_0 t)J_0 \exp(-iH_0 t) = \omega_1 \otimes \omega_2$$

exists, and

$$s\text{-lim } \exp(iH_0 t)J_0 \exp(-iHt)P_{ac}(H) = s\text{-lim } \exp(iH_0 t)J_0 \times \exp(-iH_0 t)\exp(iH_0 t)\exp(-iHt)P_{ac}(H) = \omega_1^* \otimes \omega_2^*.$$

1-channel. If particle 1 is bound, then

$$J_1 = \frac{|\mathbf{x}_1|^4 + |\mathbf{x}_2|^4}{1 + |\mathbf{x}_1|^4 + |\mathbf{x}_2|^4 + |\mathbf{x}_1|^8}$$

approaches 1 under the time-evolution by

$$H_1 = \frac{|\mathbf{p}_1|^2}{2m_1} + \frac{|\mathbf{p}_2|^2}{2m_2} + V_1(\mathbf{x}_1),$$

since $\mathbf{x}_2 \to \mathbf{x}_2 + t\mathbf{p}_2$ and $\mathbf{x}_1$ remains finite. If it is not bound, then by assumption the time-evolution becomes free, and $J_1 \exp(-iH_1 t)\psi$ approaches $J_1 \exp(-iH_0 t)\omega_1^* \otimes \mathbf{1}\psi$, which goes to 0. Thus

$$s\text{-lim } \exp(iH_1 t)J_1 \exp(-iH_1 t) = P_1$$

and

$$s\text{-lim } \exp(iHt)J_1 \exp(-iH_1 t) = \omega_2 \otimes \mathbf{1} \cdot P_1$$

The 2-channel works just like the 1-channel, and the 1-2-channel is empty. We see that in this trivial case, Criterion (3.4.19) reproduces the earlier results. We shall discuss more interesting examples later.

The operators $\Omega_{\alpha\pm}$ map the motion in channel α, i.e.,

$$a \to \exp(iH_\alpha t)a \exp(-iH_\alpha t),$$

to the actual motion as described by $\exp(iHt)$. Specifically, they produce the homomorphisms $\tau_\pm$ introduced in (3.4.6), and they send $\{H_\alpha\}'$ into $\mathscr{A}_\pm$. All $a \in \{H_\alpha\}'$ projected into channel α are in $\mathscr{A}$,

$$\begin{aligned}\tau_\pm(Q_\alpha a Q_\alpha) &\equiv \lim_{t \to \pm\infty} \exp(iHt)Q_\alpha a Q_\alpha \exp(-iHt) \\ &= \lim_{t \to \pm\infty} \exp(iHt)Q_\alpha \exp(-iH_\alpha t)(P_\alpha + \mathbf{1} - P_\alpha)a \exp(iH_\alpha t)Q_\alpha \\ &\quad \cdot \times \exp(-iHt) = \Omega_{\alpha\pm} a \Omega_{\alpha\pm}^*. \end{aligned} \tag{3.4.21}$$

The set of constants of motion $\{H_\alpha\}'$ will contain the relative momenta of the individual clusters. They commute, and the vectors of their common spectral representation, denoted $|\alpha, k\rangle$, will be somewhat loosely referred to as eigenvectors of the momenta. The vectors $|\alpha, k\rangle$ are in the image of the projections P_α of (3.4.17). The wave operators $\Omega_{\alpha\pm}$ transform $|\alpha, k\rangle$ into the eigenvectors of the asymptotic momenta $|\alpha, k, \pm\rangle \equiv \Omega_{\alpha\pm}|\alpha, k\rangle$ in such a way that, as in Remark (3.4.18; 2),

$$\langle\alpha, k, \pm|\tau_\pm(Q_\alpha a Q_\alpha)|\alpha, k, \pm\rangle = \langle\alpha, k|P_\alpha a P_\alpha|\alpha, k\rangle. \tag{3.4.22}$$

The states $|\alpha, k, \pm\rangle$ thus mean that the outgoing or, respectively, incoming particles have momenta k, and the transition probability from one such configuration to another can be measured macroscopically. As in classical mechanics (I: 3.4.9), this is the purpose of

Definition (3.4.23)

$$S_{\alpha\beta} = \Omega^*_{\alpha+}\Omega_{\beta-}$$

is known as the ***S* matrix in the interaction picture**, and

$$S = \sum_\alpha \Omega_{\alpha-}\Omega^*_{\alpha+}$$

is the ***S* matrix in the Heisenberg picture**.

Remarks (3.4.24)

1. The definition has been given in the form appropriate for a many-body system. One-particle scattering can be considered as a special case with only one channel
2. The action of the $\Omega_{\alpha\pm}$ is depicted schematically in Figure 9:
   Since $\Omega_{\alpha+}\Omega^*_{\alpha-}|\beta, k, -\rangle = \delta_{\alpha\beta}|\alpha, k, +\rangle$, the transition probabilities can be expressed in terms of S as follows:

   $$\langle\alpha, k', +|\beta, k, -\rangle = \langle\alpha, k'|S_{\alpha\beta}|\beta, k\rangle = \langle\alpha, k', +|S|\beta, k, +\rangle.$$

   The operator S is thus a unitary transformation on $\mathscr{H}_{ac}(H)$, whereas $S_{\alpha\beta}$ maps nonorthogonal subspaces on $\mathscr{H}$ isometrically onto one another. Even so, $S_{\alpha\beta}$ is the more useful operator, since it is easier to make calculations with the states $|\alpha, k\rangle$ than with $|\alpha, k, \pm\rangle$.
3. Even if both $\sum_\alpha Q_{\alpha-}$ and $\sum_\alpha Q_{\alpha+}$ equal P_{ac}, it is still possible that $Q_{\alpha-}$ and $Q_{\tau+}$ project onto different subspaces. For example, if a collision in (3.4.16) results in ionization, then one goes from Q_1 to Q_0. This illustrates the earlier remark that the mere existence of $s\text{-}\lim_{t\to\pm\infty}\exp(itH)\exp(-itH_0)$ does not guarantee that $\mathscr{H}_+$ and $\mathscr{H}_-$ are equal. It does not contradict invariance under reversal of the motion, as the operator K of (3.3.19; 2) just maps $\mathscr{H}_-$ onto $\mathscr{H}_+$.

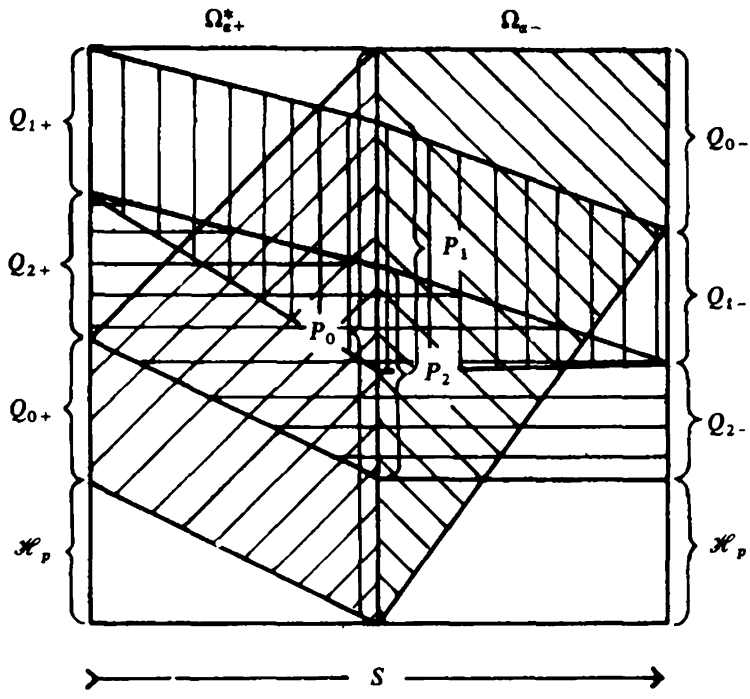


Figure 9 The domains and ranges of $\Omega^*_{\alpha+}$ and $\Omega_{\alpha-}$ in a system with several channels.

4. From $\exp(iHt)\Omega_{\alpha\pm} = \Omega_{\alpha\pm}\exp(iH_\alpha t)$ it follows that $\exp(iHt)S\exp(-iHt) = S$ and $\exp(iH_\alpha t)S_{\alpha\beta}\exp(-iH_\beta t) = S_{\alpha\beta}$. The operator S does not in general commute with all constants of the motion, but only with

$$\bigcap_\alpha \{H_\alpha\}' \cap \{H\}'$$

(cf. (I: 3.4.11; 1)).

5. If $K \in \{H_\alpha\}'$ and $K = P_\alpha K$, then by (3.4.21) $Q_\alpha K Q_\alpha \in \mathscr{A}$, and

$$K_\pm \equiv \tau_\pm(Q_\alpha K_\pm Q_\alpha) = \Omega_{\alpha\pm} K \Omega^*_{\alpha\pm}.$$

Hence S transforms K_- into K_+:

$$K_+ = \Omega_{\alpha+}\Omega^*_{\alpha-} K_- \Omega_{\alpha-}\Omega^*_{\alpha+} = S^* K_- S.$$

For such observables, S gives the total change in time from $t = -\infty$ to $t = +\infty$.

6. If there is only one channel, then

$$S_{\alpha\beta} = s\text{-}\lim_{t\to\infty} \exp(iH_\alpha t)\exp(-2iHt)\exp(iH_\beta t)$$

can be written as

$$S_{00} = T\exp\left\{-i\int_{-\infty}^{\infty} dt\, H'(t)\right\}$$

(recall (3.4.10; 3)). The strong limit exists because $\exp(iH_0t)\exp(-iHt)Q$ converges strongly and $(1-Q)\exp(-iHt)\exp(iH_0t)$ tends strongly to zero.

Scattering operators have been introduced by a comparison of the time-evolution with free motion of the clusters, as suggested by our experience with classical dynamics. It normally turns out, however, that S can be explicitly calculated only with methods that eliminate the time-variable. Sections 3.5 and 3.6 will be devoted to stationary methods.

Problems (3.4.25)

1. Show that if H' is compact relative to H_0, then for every $\varepsilon > 0$ there exists a δ such that $\|H'\psi\| \leq \varepsilon\|H_0\psi\| + \delta\|\psi\|$ for all $\psi \in D(H_0)$. (Hint: $a = H'(H_0 + i)^{-1}$ is compact. Let $P_n = \chi_{[-n,n]}(H_0)$, and show (i) that $\|a(1-P_n)\| \to 0$ and (ii) that $H'P_n$ is bounded for all n.)
2. Show that $V = r^{-\varepsilon}$, $0 < \varepsilon < 2$, is compact relative to $H_0 = p^2$. (Show that $\mathrm{Tr}(V^{1/2}(H_0 + c^2)^{-1}V^{1/2})^n < \infty$ for $n \in \mathbb{Z}^+$, $n > 3/\varepsilon$.)
3. Let V be compact relative to H_0. Show that if $P(I)$ (respectively, $P_0(I)$) is the spectral projection for H (respectively, H_0) onto the interval I, then
$$(1 - P(I))\exp(itH)\exp(-itH_0)P_0(I) \to 0 \qquad \text{as} \qquad t \to \pm\infty.$$
4. Verify that $\Omega_{\alpha\pm}^*\Omega_{\beta\pm} = \delta_{\alpha\beta}P_\alpha$ for the system of three particles (3.4.16).
5. Let $A(\omega) \equiv \sqrt{V}\,\delta(H_0 - \omega)\sqrt{V}$, $V \sim r^{-1-\varepsilon}$ (cf. (3.4.13; 2)). Show that (a) $\|A(\omega)\|_n < c\omega^{-n(1+\varepsilon/2)}$, and (b) there exist $\rho > 0$, $\delta > 0$, and $c < \infty$ such that $\|A(\omega) - A(\omega')\|_n < c|\omega - \omega'|^\rho$ for all $|\omega - \omega'| < \delta$ and all $n > 2/\varepsilon$. From these two facts conclude that $\lim_{y\to 0}\sqrt{V}(H_0 - x - iy)^{-1}\sqrt{V} \in \mathscr{C}_n$.

Solutions (3.4.26)

1. (i) Let $a_n = a^*(1-P_n)a$. $\|a(1-P_n)\|^2 = \sup_{\|\psi\|\leq 1}\langle\psi|a_n\psi\rangle$. The mappings $\psi \to \langle\psi|a_n\psi\rangle$ are weakly continuous, because $\psi_i \to 0 \Rightarrow a\psi_i \to 0$, and
$$\psi \to \langle\psi|(1-P_n)\psi\rangle$$
is strongly continuous. It follows that the sets $\{\psi: \langle\psi|a_n\psi\rangle \geq C\}$ are weakly closed. If $\|a(1-P_n)\|^2$ were greater than $C > 0$ for all n, then the intersection of the decreasing sequence of weakly compact sets $\{\psi: \langle\psi|a_n\psi\rangle \geq C,\ \|\psi\| \leq 1\}$ would not be empty, so there would exist a ψ such that $\|\psi\| \leq 1$ and $\langle\psi|a_n\psi\rangle \geq C$ for all n. This is impossible, since $1 - P_n \to 0$.

   (ii) $H'P_n = a\int_{-n}^{n}(\alpha + i)dP_\alpha$ is the product of two bounded operators. Therefore, if $\psi \in D(H_0)$ and n is sufficiently large, then
$$\|H'\psi\| = \|a(H_0 + i)\psi\|$$
$$\leq \|a(1-P_n)(H_0 + i)\psi\| + \|H'P_n\psi\| \leq \varepsilon\|(H_0 + i)\psi\| + \|H'P_n\|\,\|\psi\|.$$

2. With (2.3.20; 5) and (3.3.3),

$$\begin{aligned}
&\mathrm{Tr}(V^{1/2}(H_0 + c^2)^{-1}V^{1/2})^n \\
&= \int d^3x_1 \dots d^3x_n V(x_1) \frac{\exp(-c|x_1 - x_2|)}{4\pi|x_1 - x_2|} \\
&\quad \times V(x_2) \frac{\exp(-c|x_2 - x_3|)}{4\pi|x_2 - x_3|} \dots V(x_n) \frac{\exp(-c|x_n - x_1|)}{4\pi|x_n - x_1|} \\
&= \int d^3y_1 \dots d^3y_n V(y_1) \frac{\exp(-c|y_2|)}{4\pi|y_2|} V(y_1 + y_2) \frac{\exp(-c|y_3|)}{4\pi|y_3|} \dots \\
&\quad \times V(y_1 + y_2 + \dots + y_n) \frac{\exp(-c|y_2 + y_3 + \dots + y_n|)}{4\pi|y_2 + y_3 + \dots + y_n|}.
\end{aligned}$$

The factor $\exp(-c|y_i|)$ takes care of the convergence of the integral by $dy_2 \dots dy_n$ at infinity, and the integral by dy_1 converges for

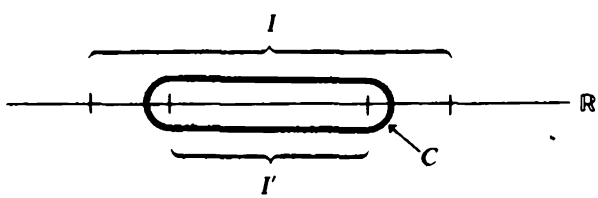
$$|y_1|^{-\varepsilon}|y_1 + y_2|^{-\varepsilon} \dots |y_1 + y_2 + \dots + y_n|^{-\varepsilon},$$

provided that $n\varepsilon > 3$. The singularities at finite points are harmless, as long as $\varepsilon < 2$.

3. Since the operators are bounded in norm by 1 for all t, it suffices to show strong convergence on the dense set of $\varphi \in P_0(I')\mathscr{H}$, where I' is contained in the interior of I. On that set,

$$\begin{aligned}
&(\mathbf{1} - P(I))\exp(iHt)\exp(-iH_0t)P_0(I)\varphi \\
&= \frac{1}{2\pi i}\int_C dz(\mathbf{1} - P(I))\exp(iHt)\left(\frac{1}{H_0 - z} - \frac{1}{H - z}\right)\exp(-iH_0t)P_0(I)\varphi \\
&= \frac{1}{2\pi i}\int_C dz(\mathbf{1} - P(I))\frac{1}{H - z}\exp(iHt)V\exp(-iH_0t)P_0(I)\frac{1}{H_0 - z}P_0(I')\varphi,
\end{aligned}$$

where C is a closed path of integration encircling I' but not cutting $\mathbb{R}\backslash I$ (see figure):



This makes the operators $(\mathbf{1} - P(I))(H - z)^{-1}$ and $(H_0 - z)^{-1}P_0(I')$ uniformly bounded on the path of integration. Theorem (3.4.4) then implies that the expression above converges strongly to zero. (Recall that $V_n \to 0$ and $\|a_n\| = 1$ for all $n \Rightarrow a_nV_n \to 0$.)

4. If $\alpha = \beta$, then this follows from the strong convergence of the operators (see (3.4.8; 2)), so it suffices to verify that

$$w\text{-lim } P_\alpha \exp(iH_\alpha t)\exp(-iH_\beta t)P_\beta = 0$$

when $\alpha \neq \beta$. There are essentially just two cases:
$\alpha = 0, \beta = 1, 2, 3$:

$$\exp(iH_0 t)\exp(-i(H_0 + V_\beta)t)P_\beta \to 0,$$

because

$$\exp(i|\mathbf{p}_1|^2 t)\exp(-i(|\mathbf{p}_1|^2 + V_1(x_1))t)P_p(1) \to 0,$$

etc., since $P_p(1)$ contains only the eigenfunctions ψ_j, $H_1\psi_j = E_j\psi_j$, and

$$\exp(it(|\mathbf{p}_1|^2 - E_j))\psi_j \to 0.$$

$\alpha = 1, \beta = 2$:

$$P_p(1)\exp(i(|\mathbf{p}_1|^2 + V_1)t)\exp(-i|\mathbf{p}_1|^2 t) \otimes \exp(i(|\mathbf{p}_2|^2 t)\exp(-i(|\mathbf{p}_2|^2 + V_2)t)P_p(2) \to 0$$

for the same reason as above. Similarly for $\alpha = 1, \beta = 3$ and $\alpha = 2, \beta = 3$.

5. In (3.4.13; 2), the integral over $(S^2)^n$ is locally like an integral over $\mathbb{R}^{2n}$. Since the integrand depends only on the differences between the n_i, and a $2(n-1)$-fold integral over a homogeneous function of degree $n(-2+\varepsilon)$ is finite whenever $2(n-1) - n(2-\varepsilon) > 0$, it follows that $\|A(\omega)\|_n < \infty$ for $n > 2/\varepsilon$. As a consequence, $\|A(\omega) - A(\omega')\|_n$ is not only finite, but actually goes to zero Hölder-continuously as $\omega' \to \omega$. This guarantees the existence of the principal-value integral in

$$\lim_{y \to 0} \sqrt{V}(H_0 - x - iy)^{-1}\sqrt{V} = i\pi A(x) + P\int dz \frac{A(z) - A(x)}{z - x}$$

in the trace norm.

3.5 Perturbation Theory

Abrupt changes are the rule in infinite-dimensional spaces, but in physics a central question is under what circumstances eigenvalues are affected only slightly by perturbations.

Since most of the problems of physics can not be solved analytically, it is the custom to approximate the solutions by carrying out Taylor expansions about suitably chosen, soluble limiting cases. The perturbed Hamiltonian is typically of the form $H(\alpha) = H_0 + \alpha H'$, which brings up the question of what quantities are analytic in α, and for what range of values. Of especial interest are the resolvent $R(\alpha, z) \equiv (H(\alpha) - z)^{-1}$, the isolated eigenvalues $E_k(\alpha)$ of $H(\alpha)$, and the projections onto them, which can be written

$$P_k(\alpha) \equiv \frac{1}{2\pi i}\int_{C_k(\alpha)} dz\, R(\alpha, z), \tag{3.5.1}$$

where $C_k(\alpha)$ is a closed path encircling $E_k(\alpha)$ and no other points of $\mathrm{Sp}(H(\alpha))$. Although $H(\alpha)$ is not diagonable for all complex values of α, for all α we know (Problem 1).

The Properties of the Projections (3.5.2)

(i) $P_k(\alpha) = P_k^*(\alpha^*)$,
(ii) $P_l(\alpha)P_k(\alpha) = \delta_{lk}P_k(\alpha)$,
(iii) $[P_l(\alpha), R(\alpha, z)] = 0$.
(iv) *Except at the points α_s where the eigenvalues $E_k(\alpha)$ cross, the projections $P_k(\alpha)$ can be continued analytically in α such that* $\dim P_k(\alpha)\mathscr{H} = \operatorname{Tr} P_k(\alpha)$ *is constant throughout the region of analyticity.*

In most quantum mechanics books, operators are blithely manipulated as if they were finite-dimensional matrices. In the same spirit, let us warm up by discussing some finite-dimensional

Examples (3.5.3)

1. $H(\alpha) = \begin{pmatrix} \alpha & 0 \\ 0 & 0 \end{pmatrix}$, $E_{1,2}(\alpha) = \alpha, 0$. $\quad R(\alpha, z) = \begin{pmatrix} 1/(\alpha - z) & 0 \\ 0 & -1/z \end{pmatrix}$,

$$P_1(\alpha) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \qquad P_2(\alpha) = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$

2. $H(\alpha) = \begin{pmatrix} \alpha & 1 \\ 0 & 0 \end{pmatrix}$, $E_{1,2}(\alpha) = \alpha, 0$. $\quad R(\alpha, z) = \begin{pmatrix} 1/(\alpha - z) & 1/z(\alpha - z) \\ 0 & -1/z \end{pmatrix}$,

$$P_1(\alpha) = \begin{pmatrix} 1 & 1/\alpha \\ 0 & 0 \end{pmatrix}, \qquad P_2(\alpha) = \begin{pmatrix} 0 & -1/\alpha \\ 0 & 1 \end{pmatrix}.$$

3. $H(\alpha) = \begin{pmatrix} \alpha(\alpha + 1) & \alpha \\ 0 & \alpha \end{pmatrix}$, $\quad E_{1,2}(\alpha) = \alpha(\alpha + 1), \alpha$.

$$R(\alpha, z) = \begin{pmatrix} 1/(\alpha(\alpha + 1) - z) & -\alpha/(\alpha - z)(\alpha(\alpha + 1) - z) \\ 0 & 1/(\alpha - z) \end{pmatrix},$$

$$P_1(\alpha) = \begin{pmatrix} 1 & 1/\alpha \\ 0 & 0 \end{pmatrix}, \qquad P_2(\alpha) = \begin{pmatrix} 0 & -1/\alpha \\ 0 & 1 \end{pmatrix}.$$

4. $H(\alpha) = \begin{pmatrix} 1 & \alpha \\ \alpha & 0 \end{pmatrix}$, $\quad E_{1,2}(\alpha) = \tfrac{1}{2}(1 \pm \sqrt{1 + 4\alpha^2})$,

$$R(\alpha, z) = \frac{1}{z(z-1) - \alpha^2} \begin{pmatrix} -z & -\alpha \\ -\alpha & 1 - z \end{pmatrix},$$

$$P_{1,2}(\alpha) = \pm\tfrac{1}{2}(1 + 4\alpha^2)^{-1/2} \begin{pmatrix} 1 \pm \sqrt{1 + 4\alpha^2} & 2\alpha \\ 2\alpha & -1 \pm \sqrt{1 + 4\alpha^2} \end{pmatrix}.$$

These examples exhibit the

Singularity Structure of R, E_k, and P_k in the Finite-Dimensional Case (3.5.4)

Let $H(\alpha)$ be a polynomial in α, and define $E_k(\alpha)$ as the poles (in z) of $R(\alpha, z)$.

(i) *The function $(\alpha, z) \to R(\alpha, z)$ is analytic except on $\bigcup_k \{z = E_k(\alpha)\}$.*

(ii) *The eigenvalues and projections $E_k(\alpha)$, $P_k(\alpha)$ are regular except at the crossing points α_s, at which the numbering of the eigenvalues changes. (In Examples 1, 2, and 3, $\alpha_s = 0$, and in Example 4, $\alpha_s = \pm i/2$.) At the points α_s the eigenvalues E_k and projections P_k may have algebraic singularities (Examples 2, 3, 4), but do not necessarily have them (1, 2, and 3).*

(iii) *In any event, $E_k(\alpha)$ is continuous in α. If $E_k(\alpha)$ has a branch point at α_s, then $\|P_k(\alpha)\| \to \infty$ as $\alpha \to \alpha_s$ (but not conversely; see Example 2).*

(iv) *If $\|P_k(\alpha)\|$ remains finite at α_s, then $H(\alpha_s)$ is diagonable (but not conversely; see Example 3).*

Proof

(i) The singularities of $(H(\alpha) - z)^{-1}$ can only originate with zeroes in the denominator $[\mathrm{Det}(H(\alpha) - z)]^{-1} = \prod_k (E_k(\alpha) - z)^{-1}$.

(ii) $\mathrm{Det}(H(\alpha) - z) = (-z)^m + (-z)^{m-1}\mathscr{P}_1(\alpha) + \cdots$, where $\mathscr{P}_i$ are polynomials in α. Hence the $E_k(\alpha)$ are branches of the same algebraic functions, and as such have the desired properties. As a complex integral of the analytic function $R(\alpha, z)$, $P_k(\alpha)$ is analytic unless the contour C gets caught between two singularities, which can happen only at the points α_s. Since the integral (3.5 1) can be written in terms of the E_k and polynomials in α, the singularities at α_s are at worst algebraic.

(iii) The continuity of E_k follows from theorems on algebraic functions, and as a consequence, series expansions for the eigenvalues contain only positive powers of $(\alpha - \alpha_s)^{1/m}$. Suppose that this were also true for the P_k, so that $\|P_k\|$ would remain bounded. By continuing the $E_k(\alpha)$ along a circle above α_s, the E_k having a branch point there are permuted so that E_i becomes E_j for some $j \neq i$. By (3.5.1) the same thing happens with the P_k, so the first terms of $P_k(\alpha) = P_k(\alpha_s) + (\alpha - \alpha_s)^{1/m}P_k^{(1)} + \cdots$ would clearly have to satisfy $P_i(\alpha_s) = P_j(\alpha_s)$. Since $P_i^2(\alpha_s) = P_i(\alpha_s)$, $P_i(\alpha_s)P_j(\alpha_s) = P_j(\alpha_s)P_i(\alpha_s) = 0$, and $P_j^2(\alpha_s) = P_j(\alpha_s)$, this implies that $P_i(\alpha_s) = P_j(\alpha_s) = 0$.

(iv) $H(\alpha)$ is diagonable iff $H(\alpha) = \sum_k E_k(\alpha)P_k(\alpha)$. If E_k and P_k are continuous, then this equation can be continued analytically to α_s. □

Corollaries (3.5.5)

1. As long as $H(\alpha)$ remains nondegenerate, everything is analytic, and H is diagonable.
2. If $H(\alpha)$ is Hermitian whenever α is real, and thus unitarily diagonable, then $\|P_k(\alpha)\| = 1$ on the real axis. Then it follows from (iii) that there can be no

α_s on the real axis at which E_k has an algebraic singularity. This theorem, due to Rellich, is not trivial, as it may at first look, since it does not extend to the case of two parameters: The eigenvalues $\alpha_1 + \alpha_2 \pm \sqrt{2}\sqrt{\alpha_1^2 + \alpha_2^2}$ of the matrix

$$\alpha_1 \begin{pmatrix} 2 & 1 \\ 1 & 0 \end{pmatrix} + \alpha_2 \begin{pmatrix} 0 & 1 \\ 1 & 2 \end{pmatrix}$$

have a branch point at $\alpha_1 = \alpha_2 = 0$.

3. All zeros of $\mathrm{Det}(H(\alpha) - z)$ are eigenvalues, for which reason analytic continuation of one of the $E_k(\alpha)$ always leads to another eigenvalue. This property is lacking on infinite-dimensional spaces. For instance, the eigenvalues of the hydrogen atom go as the square of the charge of the electron, and are thus entire functions in α. Yet they disappear when the charge becomes positive; their analytic continuation is not an eigenvalue.
4. Although $H(\alpha)$ is an entire function, it may happen that a power series for $E_k(\alpha)$ in α has only a finite radius of convergence. However, because of Corollary 2 the radius of convergence is necessarily greater than zero.

Let us now take up the question of how far these results carry over to the infinite-dimensional case. The set of eigenvectors will no longer span the whole Hilbert space, but instead there is the three-fold classification of spectra (2.3.16). It turns out, rather discouragingly, that the classification of spectra can be completely changed by arbitrarily small perturbations.

Theorem (3.5.6)

The operators with pure point spectra are norm-dense in the set of Hermitian elements of $\mathscr{B}(\mathscr{H})$.

Proof

Given any $a = a^* \in \mathscr{B}(\mathscr{H})$ written in the spectral representation (2.3.11), $\mathscr{H} = \bigoplus_i \mathscr{H}_i$, $a_{|\mathscr{H}_i}: \psi(\alpha) \to \alpha\psi(\alpha)$, $\alpha \in \mathrm{Sp}(a)$. Define a_n such that $a_{n|\mathscr{H}_i}$: $\psi(\alpha) \to s_n(\alpha)\psi(\alpha)$, where $s_n(x) = m/n$ for $m/n \le x < (m+1)/n$, $n \in \mathbb{Z}^+$, $m \in \mathbb{Z}$. Then $\|a - a_n\| \le 1/n$, and $\mathrm{Sp}(a_n)$ is the set of values of s_n, i.e., $\{m/n: m \in \mathbb{Z}\}$, which is purely discrete. □

Remarks (3.5.7)

1. More particularly, the theorem states that any operator with pure continuous spectrum can be converted into an operator with pure point spectrum by the addition of an arbitrarily small perturbation. Conversely, there are operators with continuous spectra and arbitrarily small

norm, like $a_n\psi(\alpha) = (1/n)\sin\alpha\psi(\alpha)$, for which $\|a_n\| = 1/n$. These can convert the pure point spectrum of, for instance, the zero operator into a pure continuous spectrum.
2. Theorem (3.5.6) can be strengthened to state that the addition of an operator δ with trace norm (2.3.21) $\|\delta\|_p < \varepsilon$, $p > 1$, can render the spectrum discrete. The theorem does not hold for $p = 1$; if $H_0 = |\mathbf{p}|^2$ and $\|H_0 - H\|_1 < \infty$, then the Møller operators exist, and H_0 and HP_{ac} are unitarily equivalent.
3. The proof also works for unbounded self-adjoint operators.
4. Note that the eigenvalues of s_n have infinite multiplicity and hence belong to the essential spectrum. Nevertheless, the spectrum consists of isolated points, and the next theorem will show that a relatively compact perturbation can not change a continuous spectrum into isolated points.

The essential spectrum σ_{ess} (2.3.18; 4) is less sensitive than the continuous spectrum.

Stability of the Essential Spectrum (3.5.8)

If H' is compact relative to H_0, then $\sigma_{ess}(H_0 + H') = \sigma_{ess}(H_0)$.

Proof

The criterion of (2.3.18; 5) for the essential spectrum can be reformulated as follows: $\lambda \in \sigma_{ess}(H_0) \Leftrightarrow \exists\, \psi_n$: $\|\psi_n\| = 1$, $\psi_n \rightharpoonup 0$, $(H_0 - \lambda)\psi_n \to 0$. By Definition (3.4.1), $H'(H_0 - z)^{-1}$ is compact for all $z \notin \mathrm{Sp}(H_0)$, so

$$(H_0 + H' - \lambda)\psi_n = (H_0 - \lambda)\psi_n + H'(H_0 - z)^{-1}(H_0 - z)\psi_n \to 0,$$

since

$$(H_0 - z)\psi_n = (H_0 - \lambda)\psi_n + (\lambda - z)\psi_n \rightharpoonup 0,$$

and compact operators make weakly convergent sequences strongly convergent. We can then conclude that $\lambda \in \sigma_{ess}(H_0 + H')$, and switching H_0 and $H_0 + H'$ (cf. (3.4.5; 2)) yields the other direction of the theorem. □

Remarks (3.5.9)

1. The addition of a relatively compact potential produces only finitely many bound states under $E_0 < 0$. A classical description would be that the volume of the phase space under E_0 is finite for such systems (cf. (3.5.38; 1)).
2. Compactness is essential. The addition of the bounded operator $\alpha \cdot \mathbf{1}$, $\alpha \in \mathbb{R}$, shifts the whole spectrum of any operator by α.
3. When applying this theorem, it should be remembered that if a is compact and b is bounded, then ab is compact, but $a \otimes b$ may not be.

4. If a Hilbert–Schmidt operator is added as in (3.5.7; 2) to an operator, changing a continuous spectrum to a purely discrete spectrum, then the new eigenvalues must be dense in the continuum of the original operator, since σ_{ess} is unchanged by the addition of a compact operator.

As is reasonable, the shift in the spectrum by α when one adds $\alpha \cdot \mathbf{1}$ is as great as possible with a perturbation by an operator of norm $\leq \alpha$:

Theorem (3.5.10)

If the distance from λ to the spectrum of H_0 satisfies $d(\mathrm{Sp}(H_0), \lambda) > \|H'\|$, then $\lambda \notin \mathrm{Sp}(H_0 + H')$.

Proof

The series

$$\frac{1}{H_0 + H' - \lambda} = \frac{1}{H_0 - \lambda} \sum_{n=0}^{\infty} [H'(\lambda - H_0)^{-1}]^n$$

is convergent in norm, because $\|(H_0 - \lambda)^{-1}\|^{-1} = d(\mathrm{Sp}(H_0), \lambda)$. □

However, if H' is unbounded, then the addition of $\alpha H'$ can change any kind of spectrum in any way, no matter how small α is.

Examples (3.5.11)

1. $H_0 = 0, H' \equiv \psi(x) \to x\psi(x)$ on $L^2((-\infty, \infty), dx)$. $\mathrm{Sp}(H_0 + \alpha H') = \mathbb{R}$ for $\alpha \neq 0$, and $\{0\}$ for $\alpha = 0$.
2. $H_0 = -d^2/dx^2$, $H' = \alpha x^2$: $\sigma_{ac}(H_0) = \mathbb{R}^+$, $\sigma_p(H_0) = \sigma_s(H_0)$ is empty. $\mathrm{Sp}(H_0 + \alpha H') = \sqrt{\alpha} \bigcup_{n=0}^{\infty} \{2n + 1\}$, $\sigma_{ac} = \sigma_s$ is empty if $\alpha > 0$, and $\sigma_{ac}(H_0 + \alpha H') = \mathbb{R}$, $\sigma_p = \sigma_s$ is empty for $\alpha < 0$.

Most physically realistic perturbations are unbounded, so it may seem hopeless to conclude anything about $\mathrm{Sp}(H_0 + \alpha H')$ from $\mathrm{Sp}(H_0)$. Fortunately, the relevant condition is not that H' be small, but only that it be *small in comparison with H_0*.

Theorem (3.5.12)

Let H' be bounded relative to H_0 (3.4.1) and $H(\alpha) = H_0 + \alpha H'$. Then the resolvent $R(\alpha, z) \equiv (H(\alpha) - z)^{-1}$ is analytic in the variables (α, z) throughout some region containing $\{0\} \times \{\mathbb{C} \backslash \mathrm{Sp}(H_0)\}$.

Proof

If $z \notin \mathrm{Sp}(H_0)$, then $H'(H_0 - z)^{-1}$ is bounded, so the series

$$\sum_{n=0}^{\infty} \alpha^n (H'(H_0 - z)^{-1})^n$$

for the resolvent converges for all α small enough. □

Remarks (3.5.13)

1. The more precise form of the region of analyticity depends on the particulars of the operators. If, say,

$$\mathrm{Sp}(H_0) = \mathbb{R}^+, \quad \|H'\psi\| \leq a\|\psi\| + b\|H_0\psi\|,$$

then

$$\|H'(H_0 - z)^{-1}\| \leq a\|(H_0 - z)^{-1}\| + b\|H_0(H_0 - z)^{-1}\|$$

$$\leq \frac{a}{|\mathrm{Im}\, z|} + \frac{b|z|}{|\mathrm{Im}\, z|} \qquad \text{for} \qquad \mathrm{Re}\, z \geq 0,$$

and $\|H'(H_0 - z)^{-1}\| \leq a/|z| + b$ for $\mathrm{Re}\, z \leq 0$, and so the series converges for

$$|\mathrm{Im}\, z| \geq \frac{a|\alpha|}{1 - b^2|\alpha|^2} + \frac{b|\alpha|}{\sqrt{1 - b^2|\alpha|^2}} \sqrt{|\mathrm{Re}\, z|^2 + \frac{a^2|\alpha|^2}{1 - b^2|\alpha|^2}}, \quad \mathrm{Re}\, z \geq 0,$$

$$|z| \geq \frac{a|\alpha|}{1 - b|\alpha|}, \qquad \mathrm{Re}\, z \leq 0.$$

2. The constants a and b of Remark 1 are not determined by H'. The constant b can be chosen smaller at the cost of increasing a. Hence it is difficult to formulate general statements, as in (3.5.10), about how much the spectrum is shifted.

The analyticity of the resolvent means that the results (3.5.4) about the eigenvalues remain valid away from the essential spectrum (see Figure 10).

Theorem (3.5.14)

Let H' be bounded relative to H_0 Then the isolated eigenvalues of finite multiplicity of $H(\alpha) = H_0 + \alpha H'$, as well as the projections onto their eigenvectors, are analytic in α in a neighborhood of the real axis.

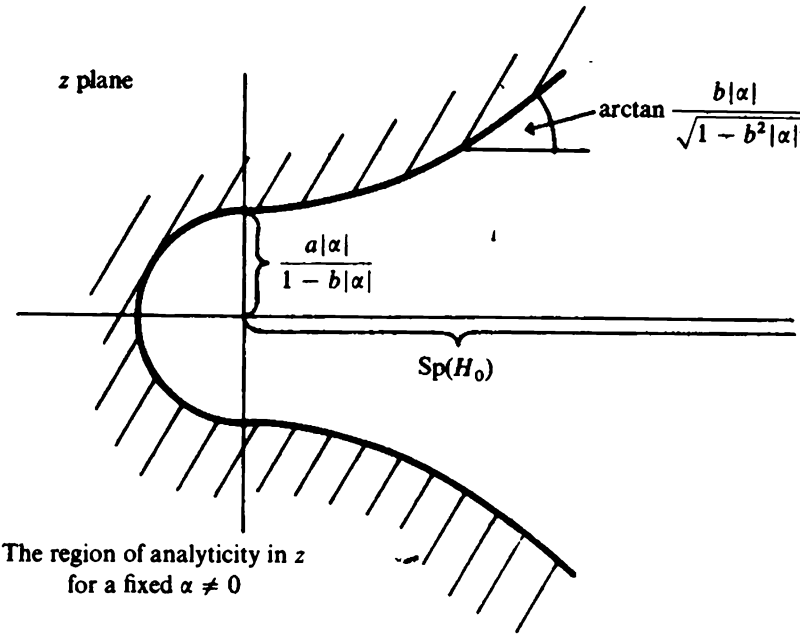


Figure 10 The region of analyticity of the resolvent.

Proof

For any isolated eigenvalue $E(0)$ of H_0, there exists a distance $d \in \mathbb{R}^+$ such that the circle $K = \{z \in \mathbb{C}: |z - E(0)| = d\}$ does not intersect the spectrum of H_0. If $\alpha_0^{-1} = \sup_{z \in K} \|H'(H_0 - z)^{-1}\|$, then $K \times (-\alpha_0, \alpha_0)$ is within the region of analyticity of the resolvent R, and $P_k(\alpha) = (1/2\pi i) \int_K dz\, R(z, \alpha)$ is analytic for $|\alpha| < \alpha_0$. Since $\dim P_k(0)\mathscr{H} < \infty$, it follows that

$$P_k(\alpha)H_k(\alpha) \equiv P_k(\alpha)H(\alpha)P_k(\alpha)$$

is an analytic family of operators of finite rank. In order to transform it into a family of finite matrices, write

$$P_k(\alpha) = W_k(\alpha)P_k(0)W_k^*(\alpha),$$

as in the proof of (3.3.11). As is easy to verify (Problem 4),

$$W_k(\alpha) = P_k(\alpha)[1 + P_k(0)(P_k(\alpha) - P_k(0))P_k(0)]^{-1/2}P_k(0)$$

is a partial isometry and furnishes the desired transformation. If α is sufficiently small, then $\|P_k(\alpha) - P_k(0)\| < 1$, so the factor $[\ldots]^{-1/2}$ can be expanded in a convergent series, making W analytic in α. Therefore

$$P_k(\alpha)H(\alpha)P_k(\alpha) = W_k(\alpha)P_k(0)W_k^*(\alpha)H(\alpha)W_k(\alpha)P_k(0)W_k^*(\alpha)$$

is unitarily equivalent to $H_k(\alpha) \equiv W_k^*(\alpha)H(\alpha)W_k(\alpha)$, which is an operator of finite rank acting on a space $P_k(0)\mathscr{H}$, which is independent of α. In other words, it is a finite-matrix-valued analytic function in α. The propositions (3.5.4) about polynomials $H(\alpha)$ are essentially unchanged for analytic functions $H(\alpha)$—algebraic functions merely become algebroid, that is, locally algebraic, functions. □

The next subject is the derivation of explicit formulas for the change that a perturbation H' causes in an eigenvalue. Let us assume that an interval of $\mathbb{R}$ contains no essential spectrum, but only eigenvalues, and that the $E_k(\alpha)$ and their projections $P_k(\alpha)$ change continuously with α. This is always the case when H' is bounded relative to H_0, but may also happen otherwise. Next, rewrite $H(\alpha)$ as $H_0 + \alpha PH'P + \alpha(H' - PH'P)$, where $P = P_k(0)$ for the k of interest. If $E_k(0) + \alpha PH'P$ has been diagonalized, then the effect of $PH'P$ can be included in E_k, so without loss of generality we may assume that $PH'P = 0$. Since the eigenvector $|\alpha\rangle$: $(H(\alpha) - E(\alpha))|\alpha\rangle = 0$, $\langle\alpha|\alpha\rangle = 1$, varies continuously with α, let $|\alpha\rangle = c|0\rangle + |\perp\rangle$, $\langle 0|\perp\rangle = 0$, $|c|^2 = 1 - \langle\perp|\perp\rangle$, which $\neq 0$ for sufficiently small α. If this is substituted into the eigenvalue equation and the component parallel and perpendicular to $|0\rangle$ are separated, then

$$\begin{aligned} c(E(\alpha) - E(0))|0\rangle &= \alpha PH'|\perp\rangle, \qquad P = |0\rangle\langle 0|, \\ (H_0 - E(\alpha) + \alpha P_\perp H')|\perp\rangle &= -c\alpha H'|0\rangle, \qquad P_\perp = 1 - P. \end{aligned} \tag{3.5.15}$$

This produces

The Brillouin–Wigner Formulas (3.5.16)

$$\begin{aligned} E(\alpha) &= E(0) - \alpha^2\langle 0|H'(H_0 - E(\alpha) + \alpha P_\perp H'P_\perp)^{-1}H'|0\rangle, \\ |\perp\rangle &= -c\alpha(H_0 - E(\alpha) + \alpha P_\perp H'P_\perp)^{-1}H'|0\rangle, \\ c^{-2} &= 1 + \alpha^2\langle 0|H'(H_0 - E(\alpha) + \alpha P_\perp H'P_\perp)^{-2}H'|0\rangle. \end{aligned}$$

Remarks (3.5.17)

1. To ensure that the formal expressions make sense, we must assume that $|0\rangle \in D(H')$ and that $(H_0 - E(\alpha) - \alpha P_\perp H'P_\perp)^{-1}$ exists. If H' and consequently $P_\perp H'P_\perp$ is bounded relative to H_0 and $E(\alpha)$ is isolated, then the series

$$(H_0 - E(\alpha))^{-1}\sum_{n=0}^{\infty}[\alpha P_\perp H'P_\perp(H_0 - E(\alpha))^{-1}]^n$$

converges on $P_\perp\mathscr{H}$ for α small enough, so (3.5.16) are well defined.

2. The eigenvalue $E(\alpha)$ is determined implicitly by (3.5.16). An explicit expression results from a comparison of the power series for both sides of the equation in α. The first few terms are fairly simple:

Lowest-Order Perturbation Theory (3.5.18)

Up to $O(\alpha^2)$,

$$E(\alpha) = E(0) - \alpha^2 \langle 0|H'P_\perp (H_0 - E(0))^{-1} P_\perp H'|0\rangle,$$
$$|\perp\rangle = \alpha (H_0 - E(0))^{-1} H'|0\rangle,$$
$$c = 1 - \frac{\alpha^2}{2} \langle 0|H'(H_0 - E(0))^{-2} H'|0\rangle.$$

Remarks (3.5.19)

1. An objective assessment of (3.5.18), which has been a daily tool for whole generations of physicists, is that it is unsatisfactory in several respects. Its shortcomings are that
   (i) if H' is unbounded, it is not obvious that $E(\alpha)$ should be analytic in α, and indeed it is not analytic in most of the standard examples of perturbation theory—the anharmonic oscillator, Stark effect, Zeeman effect, and hyperfine structure;
   (ii) even if the radius of convergence ρ is greater than zero, the n-th order terms gets so complicated for large n that it is not easy to find out what ρ is;
   (iii) even the condition that $\alpha \ll \rho$ does not guarantee that (3.5.18) will be in close argeement to the true value. For example, the radius of convergence of $\sin(100\alpha)$ is infinite, but linear and parabolic approximations are not useful beyond a short range. If we wish to use (3.5.18), we ought to first show that the function $E(\alpha)$ does not have such wild oscillations.

2. The terms linear in α do not appear in (3.5.16), because $\alpha PH'P$ was defined away at the beginning. As a consequence, the **Feynman–Hellmann** formula

$$\left.\frac{\partial E}{\partial \alpha}\right|_{\alpha=0} = \langle 0|H'|0\rangle$$

holds for nondegenerate eigenvalues. If the eigenvalues are degenerate, one must first choose the right basis in the degeneracy space and be aware that the numbering of the analytic functions $E_k(\alpha)$ will not continue to order them by their magnitudes. For example, the eigenvalues $\pm\alpha$ of

$$H(\alpha) = \alpha H' = \begin{pmatrix} 0 & \alpha \\ \alpha & 0 \end{pmatrix}$$

are not the same as $\alpha\langle 0|H'|0\rangle$ with the vector

$$|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix},$$

and the lowest eigenvalue $E_1(\alpha) = -|\alpha|$ is not differentiable at the point $\alpha = 0$.

3. Formulas (3.5.16) do not assume analyticity. Even without analyticity, (3.5.18) gives the correct asymptotic expansion under our assumptions:

$$\begin{aligned} E(\alpha) - E(0) - \alpha^2\langle 0|H'P_\perp(H_0 - E(0))^{-1}P_\perp H'|0\rangle \\ = \alpha^2\langle 0|H'P_\perp(H_0 - E(0))^{-1}(E(\alpha) - E(0) + \alpha P_\perp H'P_\perp) \\ \times (H_0 - E(\alpha) + \alpha P_\perp H'P_\perp)^{-1}H'|0\rangle = O(\alpha^3), \end{aligned}$$

and similarly at higher orders. However, in the absence of analyticity perturbation theory may lead to nonsense. It may happen that the series diverges for all $\alpha \in \mathbb{R}\backslash\{0\}$ although the discrete eigenvalues persist for all $\alpha \in \mathbb{R}$, or that the series converges, but to the wrong answer.

Examples (3.5.20)

1. $H(\alpha) = p^2 + x^2 + \alpha^2 x^6$. Since the potential of this anharmonic oscillator goes rapidly to infinity for all $\alpha \in \mathbb{R}$ as $|x| \to \infty$, the spectrum remains discrete (see (3.5.38; 1)). Yet $R(\alpha, z)$ is not analytic:

$$-\frac{\partial R}{\partial \alpha^2}\bigg|_{\alpha=0} = (p^2 + x^2 - z)^{-1}x^6(p^2 + x^2 - z)^{-1},$$

is unbounded, since $\|x^3(p^2 + x^2 - z)^{-1}\varphi\|$ can get arbitrarily large.

2. $H(\alpha) = p^2 + x^2 - 1 - 3\alpha x^2 + 2\alpha x^4 + \alpha^2 x^6 = a^*a$, where $a = ip + x + \alpha x^3$. It is clear that $H(\alpha) \geq 0$ for all $\alpha \in \mathbb{R}$, the eigenvalues remain isolated for all $\alpha \in \mathbb{R}$, and $\sigma_{ess}(H(\alpha)) = \varnothing$. However, the eigenfunction $\exp(-x^2/2 - \alpha x^4/4)$ with the eigenvalue 0 belongs to

$$L^2((-\infty, \infty), dx)$$

only for $\alpha \geq 0$. Since perturbation theory produces an asymptotic series for the ground state $E(\alpha)$, which equals 0 for all $\alpha \geq 0$, all the perturbation coefficients must vanish. The series then also converges trivially for all $\alpha \leq 0$, although 0 is no longer an eigenvalue.

More precise information about the positions of the eigenvalues can be obtained with variational methods. They rely on the

Min-Max Principle (3.5.21)

Let H be self-adjoint and bounded from below, and let the eigenvalues be $E_1 \leq E_2 \leq E_3 \leq \cdots \leq E_\infty$ (counting multiplicity), where by definition all E_k lying above the bottom of the essential spectrum E_∞ are set equal to E_∞,

even if E_∞ is not an eigenvalue. Let D_n be an n-dimensional subspace of $D(H)$, let $D_n^\perp$ be its orthogonal complement in $D(H)$, and let Tr_{D_n} be the trace in D_n. Then

$$\sum_{k=i}^{i+j-1} E_k = \inf_{D_{i+j-1}} \sup_{D_j \subset D_{i+j-1}} \mathrm{Tr}_{D_j} H = \sup_{D_{i-1}} \inf_{D_j \subset D_{i-1}^\perp} \mathrm{Tr}_{D_j} H, \qquad i \text{ and } j = 1, 2, \ldots .$$

Proof

See Problem 5. □

Remarks (3.5.22)

1. In particular, $\sum_{n=1}^{j} \langle \psi_n | H \psi_n \rangle$ for any orthonormal system $\{\psi_n\} \subset D(H)$ is always greater than the sum of the first j eigenvalues, counting the bottom of σ_{ess} as an infinitely degenerate eigenvalue. By the use of well chosen trial functions ψ_n provided with several parameters to adjust, excellent upper bounds on $\sum_{n=1}^{j} E_n$ can be obtained.
2. To get an upper bound for E_n itself, take an orthonormal set $\{\psi_1, \ldots, \psi_n\} \subset D(H)$. The greatest eigenvalue of any $n \times n$ matrix $\langle \psi_i | H \psi_k \rangle$ is $\geq E_n$.

The astute reader will have realized from (3.5.18) that the second-order correction ($\sim \alpha^2$) for the ground state is always negative. More generally, (3.5.21) permits the proof of some

Concavity Properties of $E_n(\alpha)$ (3.5.23)

Let $H = H_0 + \alpha H'$, with $D(H') \supset D(H_0)$. Then $\sum_{n=1}^{j} E_n(\alpha)$, $j = 1, 2, \ldots$, are concave functions of α.

Gloss (3.5.24)

Concave functions $f: I \to \mathbb{R}$ are by definition those for which

$$f\left(\sum_{i=1}^{n} \alpha_i x_i\right) \geq \sum_{i=1}^{n} \alpha_i f(x_i), \qquad \alpha_i \geq 0, \ \sum_{i=1}^{n} \alpha_i = 1; \ x_i \in I.$$

The function $-f$ is said to be **convex**. Concave functions f have the following properties:

(i) f is continuous on the interior of I, has right and left derivatives at every point, and has first and second derivatives almost everywhere;
(ii) f'' is a negative distribution ($f'' \, dx$ is a negative measure);
(iii) for $x > 0$, $f(x)$ is concave iff $xf(1/x)$ is concave;
(iv) if $f > 0$ and $1/f$ is concave, then f is convex;
(v) If the functions $f_i(x)$ are concave and $\alpha_i \geq 0$, then $\sum_i \alpha_i f_i(x)$ is concave;

(vi) If $f_i(x)$ is concave, then $\inf_i f_i(x)$ is concave.
(vii) If the functions f_i are concave and $f_1' \geq 0$, then $f_1 \circ f_2$ is concave.

Proof

The expression $\sum_{n=1}^{J} \langle \psi_n | H(\alpha) \psi_n \rangle$ is linear in α, so by Property (vi) its infimum over the ψ_n is concave. □

Remark (3.5.25)

It is necessary that $D(H(\alpha)) = D(H_0)$, so that the infimum is taken over a set independent of α. For instance,

$$E_2(\alpha) = \inf_{\langle \psi | \psi_1(\alpha) \rangle = 0} \langle \psi | H(\alpha) \psi \rangle$$

is not necessarily concave.

Although the min-max principle guarantees that $E_1(\alpha)$ lies below any possible expectation value of $H(\alpha)$, it does not say how close to E_1 the expectation value comes. People who make variational calculations normally convince themselves that they come close by their faith in their pet trial functions. There are, however, a few criteria with which to gauge the accuracy.

Weinhold's Criterion of the Mean-Square Deviation (3.5.26)

There is a spectral value of H in the interval $[\langle H \rangle - \Delta H, \langle H \rangle + \Delta H]$.

Proof

According to (3.5.21), there is a spectral value of $(H - \langle H \rangle)^2$ below $\langle (H - \langle H \rangle)^2 \rangle = (\Delta H)^2$, and hence H has a spectral value nearer to $\langle H \rangle$ than the distance ΔH. □

Remark (3.5.27)

Criterion (3.5.26) can only be used after verifying that the eigenvalue in the interval is indeed the one wanted. For instance, it produces a lower bound for E_1 only if it is known that E_2 is greater than $\langle H \rangle + \Delta H$.

Duffin's Criterion of the Local Energy (3.5.28)

Suppose that $H = |\mathbf{p}|^2 + V(\mathbf{x})$, $D(V) \supset D(|\mathbf{p}|^2)$ *has isolated eigenvalues* E_k. *The eigenvector* $\psi_1(\mathbf{x})$: $H\psi_1 = E_1\psi_1$ *can be assumed to be nonnegative. If* $\psi(\mathbf{x}) > 0$ *and* $E(\mathbf{x}) \equiv H\psi(\mathbf{x})/\psi(\mathbf{x})$, *then* E_1 *lies in the interval* $[\inf_{\mathbf{x}} E(\mathbf{x}), \sup_{\mathbf{x}} E(\mathbf{x})]$.

Proof

Write $\psi_1(\mathbf{x}) = R(\mathbf{x})\exp(iS(\mathbf{x}))$, with R positive and S real (cf. (3.3.21; 5)); then

$$\langle\psi_1|H\psi_1\rangle = \int dx(|\nabla R(\mathbf{x})|^2 + R^2(|\nabla S(\mathbf{x})|^2 + V(\mathbf{x})))$$

$$\geq \int dx(|\nabla R(\mathbf{x})|^2 + R^2 V(\mathbf{x})).$$

For ψ_1 to have the lowest eigenvalue, S must be constant, and can be redefined as 0. This makes $\langle\psi_1|\psi\rangle > 0$, and

$$E_1\langle\psi_1|\psi\rangle = \langle H\psi_1|\psi\rangle = \int dx\, \psi_1(\mathbf{x})\psi(\mathbf{x})E(\mathbf{x}) \begin{matrix}\leq \sup \\ \geq \inf\end{matrix} E(\mathbf{x}) \cdot \langle\psi_1|\psi\rangle. \quad \square$$

Remark (3.5.29)

This criterion does not involve integrals as in the calculation of expectation values, which is an advantage; but at least one of its error bounds is worse than the corresponding bound of (3.5.26) calculated with ψ:

$$(\Delta H)^2 = \int dx(E(\mathbf{x}) - \langle H\rangle)^2\psi(\mathbf{x})^2$$

$$\leq \max\left\{(\langle H\rangle - \inf_{\mathbf{x}} E(\mathbf{x}))^2, (\langle H\rangle - \sup_{\mathbf{x}} E(\mathbf{x}))^2\right\}.$$

If H is of the form $|\mathbf{p}|^2 + V(x)$, then, obviously, $E_1 \geq -\|V\|_\infty$. But even if $V \to -\infty$ somewhere, H may be bounded below. The uncertainty principle leads one to believe that this should always be the case when V approaches $-\infty$ more slowly than $-1/r^2$, which means that V is locally in $L^p, p > \frac{3}{2}$. This is in fact the case, as shown by the

General Lower Bound (3.5.30)

In three dimensions,

$$|\mathbf{p}|^2 + V(\mathbf{x}) \geq -c_p\|V\|_p^{2p/(2p-3)}, \qquad p > \tfrac{3}{2},$$

$$c_p = \Gamma\left(\frac{2p-3}{p-1}\right)^{(2p-2)/(2p-3)}\left(\frac{p-1}{p}\right)^2(4\pi)^{-2/(2p-3)},$$

where the operator $|\mathbf{p}|^2 + V$ is defined by the Friedrichs extension (2.5.19).

Proof

The ground state ψ satisfies the equation

$$\psi(\mathbf{x}) = \int d^3x' G(\mathbf{x} - \mathbf{x}')V(\mathbf{x}')\psi(\mathbf{x}'), \qquad G(\mathbf{x}) = \frac{\exp(-\sqrt{|E|}|\mathbf{x}|)}{4\pi|\mathbf{x}|}$$

because G is the Green function for $|\mathbf{p}|^2 - E$. Young's and Hölder's inequalities imply that if $p \geq 1$, then

$$\|\psi\|_2 \leq \|G\|_q \|V\|_p \|\psi\|_2, \qquad \frac{1}{p} + \frac{1}{q} = 1.$$

We thus calculate that

$$\|G\|_q = \frac{1}{4\pi}\left[\int d^3x \frac{\exp(-q\sqrt{|E|}|\mathbf{x}|)}{|\mathbf{x}|^q}\right]^{1/q}$$

$$= |E|^{(q-3)/2q} \cdot q^{(q-3)/q} \cdot \Gamma^{1/q}(3-q)(4\pi)^{-1/p}.$$

Since this is finite up to the point $p = \frac{3}{2} \Leftrightarrow q = 3$, it can be substituted into the earlier inequality to get an upper bound on $|E_0|$ for the Friedrichs extension with $p > \frac{3}{2}$, $q < 3$. The argument does not work for arbitrary definitions of the sum of the operators $|\mathbf{p}|^2$ and V; the deficiency indices may be nonzero, and the lowest eigenvalue can be arbitrarily negative. □

If H' is positive, then lower bounds for E_k can be obtained from an eigenvalue problem restricted to some subspace (cf. (3.5.21) for contrast):

The Projection Method (3.5.31)

Suppose that $H' \geq 0$ and $P = P^* = P^2$, so that $P(H')^{-1}P$ is bounded and invertible on $P\mathscr{H}$. Then the ordered sequence of numbers $E_i^{(0)}$ such that $H_0|i\rangle = E_i^{(0)}|i\rangle$ with $P|i\rangle = 0$ and E_L for which the operator $P\{(H_0 - E_L)^{-1} + (H')^{-1}\}P$ has eigenvalue zero consists of lower bounds for the ordered sequence of eigenvalues of $H_0 + H'$.

Proof

For any projection Q, $Q \leq 1$, so $(H')^{1/2}Q(H')^{1/2} \leq H'$. If we take $Q = (H')^{-1/2}P(P(H')^{-1}P)^{-1}P(H')^{-1/2}$, then Q is a projection, since $Q = Q^* = Q^2$, and there results $H' \geq P(P(H')^{-1}P)^{-1}P$. Therefore, by the min-max principle, the ordered sequence of eigenvalues of

$$H_L \equiv H_0 + P(P(H')^{-1}P)^{-1}P$$

consists of lower bounds for the eigenvalues of $H = H_0 + H'$, since $H \geq H_L$, and so all expectation values satisfy $\langle\psi|H\psi\rangle \geq \langle\psi|H_L\psi\rangle$. If $|L\rangle$ is an eigenvector of H_L and $P|L\rangle = 0$, then $|L\rangle$ must be one of the $|i\rangle$, and thus E_i is an eigenvalue of H_L. If $P|L\rangle \neq 0$, then we may write

$$P|L\rangle = -P(H')^{-1}P|\rangle,$$

which converts the eigenvalue equation into $(H_0 - E_L)|L\rangle = P|\rangle$, or

$$P|L\rangle = P(H_0 - E_L)^{-1}P|\rangle = -P(H')^{-1}P|\rangle. \qquad \square$$

Special Cases (3.5.32)

1. Let $P = |\chi\rangle\langle\chi|$ be one-dimensional, so the comparison operator is $P \cdot \langle\chi|(H_0 - E_L)^{-1} + (H')^{-1}|\chi\rangle$. Since $E_i^{(0)}$ are trivial lower bounds, we need $\langle i|\chi\rangle \neq 0$, $i = 1, 2, \ldots, n$, in order to raise our estimates of the first n eigenvalues. If we let

$$|\chi\rangle = \sum_{i=1}^{n} c_i|i\rangle, \qquad \sum |c_i|^2 = 1,$$

then the problem becomes to solve the equation

$$\sum_i \frac{|c_i|^2}{E_i^{(0)} - E_L} + \sum_{i,k} c_i^* \langle i|(H')^{-1}|k\rangle c_k = 0.$$

Since $(H')^{-1} > 0$, there is always a solution for E_L between any $E_i^{(0)}$ and $E_{i+1}^{(0)}$. No one-dimensional projection can raise an eigenvalue above the next higher one. More specifically, $E_1^{(0)} + \langle 1|(H')^{-1}|1\rangle^{-1} \leq E_1 \leq E_1^{(0)} + \langle 1|H'|1\rangle$, whenever the left side is $\leq E_2^{(0)}$.

2. If we let $|\chi\rangle = c(H_0 - E_L)|\psi\rangle$, $\|\psi\| = 1$, then we need to find the least solution of

$$\begin{aligned}\langle\psi|H_0 - E_L + (H_0 - E_L)(H')^{-1}(H_0 - E_L)|\psi\rangle \\ = \langle\psi|H - E_L - (H - E_L)(H')^{-1}(H - E_L)|\psi\rangle = 0,\end{aligned}$$

i.e.,

$$E_L = \langle\psi|H|\psi\rangle - \langle\psi|(H - E_L)(H')^{-1}(H - E_L)|\psi\rangle.$$

If $E_L \leq E_2^{(0)}$, then it will be a bound for E_1, and

$$\langle\psi|H|\psi\rangle - \langle\psi|(H - E_L)(H')^{-1}(H - E_L)|\psi\rangle \leq E_1 \leq \langle\psi|H|\psi\rangle,$$

provided that the left side is $\leq E_2^{(0)}$. In this case we are not confined to the use of eigenvectors of H_0, and may equip ψ with some parameters to vary and optimize the bounds. In addition, H can be written in various ways as a sum of H_0 and H'. If we let $H' = (E_2 - E_L) \cdot 1$ (why not, once we know that $E_L < E_2$?), then

$$\langle\psi|(H - E_L)(E_2 - E_L) - (H - E_L)^2|\psi\rangle = 0,$$

which yields **Temple's inequality,**

$$E_1 \geq E_L = \langle H \rangle - \frac{(\Delta H)^2}{E_2 - \langle H \rangle}.$$

If $\Delta H < E_2 - \langle H \rangle$, this improves (3.5.26).

Once the E_k have been localized, the question can be raised of how well the trial function ψ approximates an actual eigenvector $|\ \rangle$. There is little chance for a general pointwise bound, but the accuracy in the L^2 norm, i.e., in the mean-square sense, can be gauged in terms of inner products, for which there are useful estimates.

Bounds for the Overlap Integral (3.5.33)

Let a constant be subtracted from H to adjust the lowest eigenvalue E_1 to 0, and let $|\ \rangle$ be its eigenvector. Then

$$1 - \frac{\langle H \rangle}{E_2} \leq |\langle \psi | \rangle|^2 \leq 1 - \frac{\langle H \rangle^2}{\langle H^2 \rangle}$$

where $\langle\ \rangle$ is the expectation value in the state ψ. (These bounds are due respectively to Eckart and to Farnoux and Wang.)

Proof

Right side: $H\psi$ is orthogonal to $|\ \rangle$, so

$$|\langle |\psi\rangle|^2 \leq 1 - \frac{|\langle \psi | H\psi \rangle|^2}{\|H\psi\|^2}.$$

Left side: Let $P = 1 - |\ \rangle\langle\ |$. Then

$$\langle \psi | P(H - E_2)P\psi \rangle = \langle \psi | H\psi \rangle - E_2(1 - |\langle\ |\psi\rangle|^2) \geq 0. \qquad \square$$

Remarks (3.5.34)

1. It is not difficult to improve these bounds [5]. They show that the relevant facts for the accuracy of ψ in the L^2 sense are smallness of $\langle H \rangle - E_1$ and ΔH and a large isolation distance from E_2.
2. The upper bound holds only for the eigenvector of the ground state E_1, though similar lower bounds hold for excited states.

The motivation for the concepts that have been developed is the study of Hamiltonians of the form $H = |\mathbf{p}|^2 + V$, and we have assumed that there is only a discrete spectrum under the continuum on $\mathbb{R}^+$. The final topic of this

section will be bounds on the number of bound states below a given energy; this in turn excludes σ_{ess} from below such an energy. The discussion begins with a lemma, which seems trivial for attractive potentials, but is surprising for potentials that are partially repulsive.

Monotony of $N(H)$ in the Coupling Constant (3.5.35)

Let $H = |\mathbf{p}|^2 + \lambda V$ be such that $\sigma_{ess}(H)$ is contained in $\mathbb{R}^+$, and let $N(H) \equiv \operatorname{Tr} \Theta(-H)$ be the number of eigenvalues less than zero, counting multiplicity. Then $N(|\mathbf{p}|^2 + \lambda V)$ is a monotonically increasing function of λ for $\lambda > 0$.

Proof

$H_1 \leq H_2 \Rightarrow N(H_1) \geq N(H_2)$ and $N(\lambda H) = N(H)$ for all $\lambda > 0$, so

$$N(|\mathbf{p}|^2 + \lambda_1 V) \geq N\left(\frac{\lambda_1}{\lambda_2}(|\mathbf{p}|^2 + \lambda_2 V)\right) = N(|\mathbf{p}|^2 + \lambda_2 V) \text{ for all } \lambda_1 \geq \lambda_2.$$

□

The number of eigenvalues below $-c^2$, i.e., $N(H + c^2)$, can be estimated above by traces for potentials that are in some trace class relative to $|\mathbf{p}|^2$, that is, by certain integrals.

The Birman–Schwinger Bound (3.5.36)

Let

$$|V|_- = \begin{cases} -V(\mathbf{x}), & \text{where } V(\mathbf{x}) < 0 \\ 0, & \text{otherwise.} \end{cases}$$

Then for all $p \geq 1$,

$$N(|\mathbf{p}|^2 + V + c^2) \leq \|(|\mathbf{p}|^2 + c^2)^{-1/2}|V|_-(|\mathbf{p}|^2 + c^2)^{-1/2}\|_p^p.$$

Proof

$N(|\mathbf{p}|^2 + V + c^2) \leq N(|\mathbf{p}|^2 - |V|_- + c^2)$, and all the eigenvalues of $|\mathbf{p}|^2 - \lambda|V|_- + c^2$ are continuous, decreasing functions of λ. Hence $N(|\mathbf{p}|^2 - |V|_- + c^2)$ equals the number of values of λ for which $|\mathbf{p}|^2 - \lambda|V|_-$ has the eigenvalue $-c^2$ (see Figure 11). Since $|\mathbf{p}|^2 + c^2$ is invertible, it follows from $(|\mathbf{p}|^2 - \lambda|V|_-)\psi = -c^2\psi$ that

$$(|\mathbf{p}|^2 + c^2)^{-1/2}|V|_-(|\mathbf{p}|^2 + c^2)^{-1/2}\varphi = \frac{1}{\lambda}\varphi, \qquad \varphi = (|\mathbf{p}|^2 + c^2)^{1/2}\psi.$$

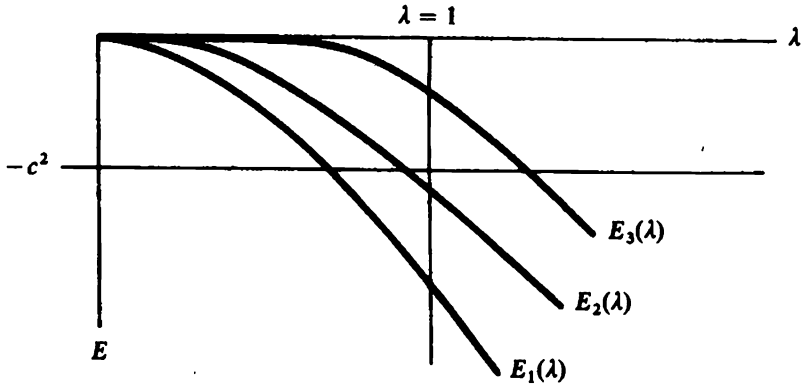


Figure 11 The eigenvalues as functions of the coupling constant.

Thus $N(|\mathbf{p}|^2 - |V|_- + c^2) =$ [the number of eigenvalues $(1/\lambda_i) \geq 1$ of the operator $(|\mathbf{p}|^2 + c^2)^{-1/2}|V|_-(|\mathbf{p}|^2 + c^2)^{-1/2}$]

$$\leq \sum_i \left(\frac{1}{\lambda_i}\right)^p$$

$$= \mathrm{Tr}[(|\mathbf{p}|^2 + c^2)^{-1/2}|V|_-(|\mathbf{p}|^2 + c^2)^{-1/2}]^p. \qquad \square$$

Applications (3.5.37)

1. Bound S-states. If V is radially symmetric, then one can ask about states of definite angular momentum l, where one thinks of the appropriate projection P_l onto an angular-momentum subspace as included in V. The operator $P_0(|\mathbf{p}|^2 + c^2)^{-1}P_0$ has an integral kernel

$$R(r, r') \equiv \frac{1}{crr'}[\sinh rc \exp(-r'c)\Theta(r' - r) + \sinh r'c \exp(-rc)\Theta(r - r')],$$

and, moreover, the bound involving p,

$$\|(|\mathbf{p}|^2 + c^2)^{-1/2}|V|_-(|\mathbf{p}|^2 + c^2)^{-1/2}\|_1 = \mathrm{Tr}|V|_-(|\mathbf{p}|^2 + c^2)^{-1}$$

$$= \int_0^\infty dr|V(r)|_- r^2 R(r, r) = \int_0^\infty dr|V(r)|_- \frac{1 - \exp(-2rc)}{2c},$$

may exist. For $c = 0$, this reduces to **Bargmann's bound**:

$$\text{(The number of bound } S\text{-states of } V(r)) \leq \int_0^\infty dr\, r|V(r)|_-.$$

2. In our discussion of free motion (3.3.3) in three dimensions, we saw that the integral kernel of $(|\mathbf{p}|^2 + c^2)^{-1}$ was $\exp(-c|\mathbf{x} - \mathbf{x}'|)/4\pi|\mathbf{x} - \mathbf{x}'|$, which is infinite where $\mathbf{x} = \mathbf{x}'$. It is thus necessary to choose a larger exponent p; with $p = 2$, we get the bound of **Ghirardi and Rimini**:

$$N(|\mathbf{p}|^2 + V + c^2) \leq \left(\frac{1}{4\pi}\right)^2 \int d^3x\, d^3x' \frac{|V(\mathbf{x})|_- |V(\mathbf{x}')|_-}{|\mathbf{x} - \mathbf{x}'|^2} \cdot \exp(-2c|\mathbf{x} - \mathbf{x}'|).$$

Remarks (3.5.38)

1. The classical analogue of $N(|\mathbf{p}|^2 + V)$ is the volume of phase space of negative energy,

$$\int \frac{d^3x\, d^3p}{(2\pi)^3} \Theta(-|\mathbf{p}|^2 - V(\mathbf{x})) = \frac{1}{6\pi^2} \int d^3x |V|_-^{3/2}.$$

   As $\lambda \to \infty$, $N(|\mathbf{p}|^2 + \lambda V)$ in fact approaches this integral, as will be shown in volume IV. For finite λ the integral is a bound on $N(|\mathbf{p}|^2 + \lambda V)$, with some weakened constant [25].
2. If the potential is radially symmetric, then it is possible to obtain a family of bounds for N_l, the number of bound states of angular momentum l,

$$N_l \leq \frac{(p-1)^{p-1}\Gamma(2p)}{(2l+1)^{2p-1}p^p\Gamma(p)^2} \int_0^\infty dr\, r^{2p-1} |V(r)|_-^p, \qquad p \geq 1.$$

   These bounds are optimal in the sense that for all $p \geq 1$, there is a potential $V_{l,p}$ for which equality holds. By varying p, one can use this formula to evaluate the number of bound states for most potentials to within a few percent.
3. The moments of the eigenvalues can be read off from N by [6]

$$\sum_i |E_i|^\gamma = \operatorname{Tr}|H|^\gamma \Theta(-H) = \int_{-\infty}^0 dE |E|^\gamma \operatorname{Tr} \delta(E - H)$$

$$= \int_{-\infty}^0 dE |E|^\gamma \frac{\partial}{\partial E} N(H - E) = \gamma \int_{-\infty}^0 dE |E|^{\gamma-1} N(H - E).$$

Example (3.5.39)

The Yukawa potential, $V(r) = -\lambda \exp(-r)/r$, $\lambda > 0$. By (3.5.37; 1), the number of bound S-states is at most $\int_0^\infty dr |V(r)| r = \lambda$. If we use the trial function $\psi(\mathbf{x}) = u(r)/r$, $u(r) = (\lambda^3/8\pi)^{1/2} r \exp(-\lambda r/2)$ in (3.5.28), then $H\psi/\psi$

$= -\lambda^2/4 + \lambda(1 - \exp(-r))/r$, so we get the bounds $-\lambda^2/4 \leq E_1 \leq -\lambda^2/4 + \lambda$. The expectation values of $H = |\mathbf{p}|^2 + V$ and H^2 in the state ψ are

$$\langle\psi|H\psi\rangle = \frac{\lambda^2}{4}\frac{2\lambda + 1 - \lambda^2}{(1+\lambda)^2} = -\frac{\lambda^2}{4} + \lambda - \frac{3}{2} + O(1/\lambda)$$

and

$$\langle\psi|H^2\psi\rangle = \frac{\lambda^4}{16}\left[5 - \frac{16\lambda + 12\lambda^2}{(1+\lambda)^2} + \frac{8\lambda}{2+\lambda}\right],$$

$$\Delta H = \frac{1}{2}\left(\frac{\lambda}{1+\lambda}\right)^2\sqrt{\frac{2+3\lambda}{2+\lambda}}.$$

The min-max principle yields the upper bound $\langle\psi|H\psi\rangle$ for E_1, and (3.5.26) gives the lower bound $\langle\psi|H\psi\rangle - \Delta H$, once it is known that $E_2 > \langle\psi|H\psi\rangle + \Delta H$. Because $V > -\lambda/r$, $E_n > -\lambda^2/4n^2$ (see §4.1); consequently, for $\langle\psi|H\psi\rangle \leq -\lambda^2/16$, we have definitely caught the eigenvalue E_1 between two bounds. For λ sufficiently large, the lower bound can be improved with Temple's inequality (3.5.32; 2), since $(\Delta H)^2(E_2 - \langle H\rangle)^{-1} = O(\lambda^{-2})$. The projection method can make use of the exactly soluble case $H_0 = |\mathbf{p}|^2 - \lambda/r$ and $H' = \lambda(1 - \exp(-r))/r$, yielding

$$\langle H'^{-1}\rangle = \frac{\lambda^2}{2}\int_0^\infty dr\, r^3\frac{e^{-\lambda r}}{1-e^{-r}} = 3\sum_{n=0}^{\infty}\frac{\lambda^2}{(\lambda+n)^4} < \lambda^{-2}(3+\lambda),$$

so $-\lambda^2/4 + \lambda^2/(3+\lambda) \leq E_1$. The general bound (3.5.30)

$$E \geq -\left(\int_0^\infty dr\, r^2|V|^p\right)^{2/(2p-3)}\frac{\Gamma(3-q)^{2q/(3-q)}}{p^2}(p-1)^2$$

works only if $p < 3$, and thus never gives the actual asymptotic behavior $\sim\lambda^2$ as $\lambda \to \infty$; for instance, with $p = q = 2$, we get $-\lambda^4/16 \leq E_1$. (See Figure 12.)

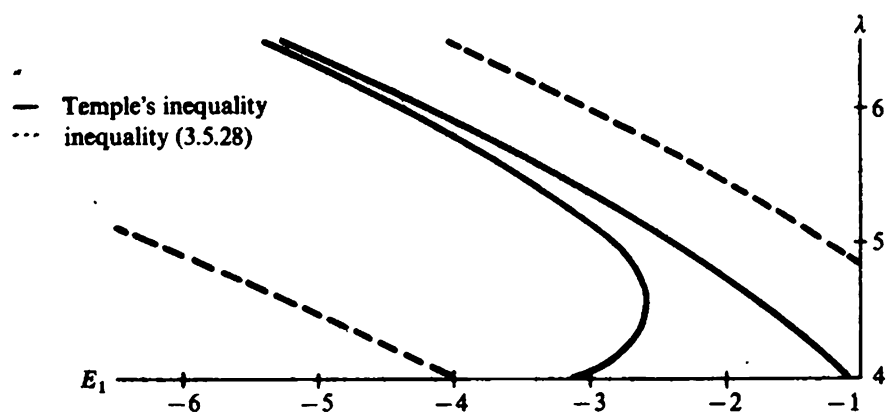


Figure 12 Bounds for the ground state with a Yukawa potential.

Problems (3.5.40)

1. Show that $R(\alpha, z)$ has simple poles at E_k, and $P_k(\alpha) = P_k^*(\alpha^*)$, $P_i(\alpha)P_k(\alpha) = \delta_{ik}P_k(\alpha)$.

2. Show that a is compact iff $\psi_n \to 0 \Rightarrow a\psi_n \to 0$. (Hint: for the "only if" direction, recall that the strong and weak topologies are equivalent on strongly compact sets in Hilbert space.)

3. Show that if H' is compact relative to H_0, then for all $\varepsilon > 0$ there exists a δ such that $\|H'\psi\| \leq \varepsilon\|H_0\psi\| + \delta\|\psi\|$ for all $\psi \in D(H_0)$. (The operator $a = H'(H_0 + i)^{-1}$ is compact. Let $P_n = \chi_{[-n,n]}(H_0)$, and show (i) that $\|a(1 - P_n)\| \to 0$, and (ii) that $H'P_n$ is bounded for all n.)

4. Show that for $|\alpha| < \delta$, $W(\alpha) = P(\alpha)[1 + P(0)(P(\alpha) - P(0))P(0)]^{-1/2}P(0)$, where W is as in the proof of (3.5.14).

5. Prove the min-max principle (3.5.21). (Use the unitary invariance of the trace and note that $\mathrm{Tr}_{D_1 \cup D_2} = \mathrm{Tr}_{D_1} + \mathrm{Tr}_{D_2}$ for D_1 orthogonal to D_2.)

6. Give an example of a 3×3 matrix for which the value $E_2 = \sup_{\|\psi\|=1} E_2(\psi)$, $E_2(\psi) = \inf_{\langle\varphi|\psi\rangle = 0,\ \|\varphi\| = 1} \langle\varphi|H\varphi\rangle$ is attained for some ψ other than ψ_1, the ground state.

Solutions (3.5.41)

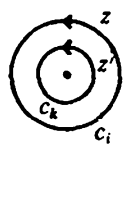
1. Let P_k be the projection onto the eigenvector for E_k. The Laurent series of $(H_0 - z)^{-1}$ is $(E_k - z)^{-1}P_k + (1 - P_k) \times$ analytic factors.

$$2\pi i P_k(\alpha) = \oint_{c_k} dz\, R(\alpha, z) = -\oint_{-c_k} dz\, R(\alpha, z) = -\oint_{c_k} dz^*\, R(\alpha, z^*)$$

$$= -\left[\oint_{c_k} dz\, R(\alpha^*, z)\right]^*.$$

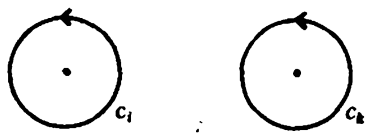
$$P_i(\alpha)P_k(\alpha) = (2\pi i)^{-2}\oint_{c_i}\oint_{c_k} \frac{dz\,dz'}{z - z'}\,[R(\alpha, z) - R(\alpha, z')].$$

$i = k$:



$$(2\pi i)^{-2}\iint \cdots = (2\pi i)^{-1}\oint_{c_i} dz\, R(\alpha, z).$$

$i \neq k$:



$$(2\pi i)^{-2}\iint \cdots = 0.$$

2. Lemma: Let $K \subset \mathscr{H}$ be strongly compact. If $M \subset K$ is weakly closed, then it is also strongly closed. Conversely, if M is strongly closed, then it is also strongly compact, hence weakly compact, hence weakly closed. (See also Problem (2.1.29; 7).)

"only if": $\psi_n \to 0 \Rightarrow a\psi_n \to 0 \Rightarrow a\psi_n \to 0$ because of the lemma and because $\{\psi_n\}$ is bounded.

"if": $(\psi_n \to 0 \Rightarrow a\psi_n \to 0) \Leftrightarrow (\psi_n \to \psi \Leftrightarrow a\psi_n \to a\psi)$.
Now suppose X is a bounded set. To show that aX is strongly relatively compact, it suffices for every sequence $a\psi_n$, $\psi_n \in X$, to contain a strongly convergent subsequence. The sequence ψ_n contains a weakly convergent subsequence $\psi_{n_k} \to \psi \Rightarrow a\psi_{n_k} \to a\psi$.

3. (i) Let $a_n = a^*(1 - P_n)a$. $\|a(1 - P_n)\|^2 = \sup_{\|\psi\| \le 1} \langle\psi|a_n\psi\rangle$. If $\|\cdots\|^2$ were greater than some fixed positive C for all n, then the intersection of the decreasing sequence $\{\psi: \langle\psi|a_n\psi\rangle \ge C, \|\psi\| \le 1\}$ of weakly compact sets would be nonempty, so there would exist a ψ such that $\|\psi\| \le 1$ and $\langle\psi|a_n\psi\rangle \ge C$ for all n. This is impossible, since $1 - P_n \to 0$.

(ii) $H'P_n = a\int_{-n}^{n}(\alpha + i)dP_\alpha$ is the product of two bounded operators. Consequently, if $\psi \in D(H_0)$, then for n sufficiently large, $\psi \in D(H_0)$,

$$\begin{aligned}\|H'\psi\| &= \|a(H_0 + i)\psi\| \le \|a(1 - P_n)(H_0 + i)\psi\| + \|H'P_n\psi\| \\ &\le \varepsilon\|(H_0 + i)\psi\| + \|H'P_n\|\|\psi\|.\end{aligned}$$

4. $\|P(\alpha) - P(0)\| < 1$, $[\ ] > 0$, $[\ ]P_0 = P_0[\ ]$. $WW^* = P[\ ]^{-1/2}P_0[\ ]^{-1/2}P = PP_0[\ ]^{-1}P = P$. $W^*W = P_0[\ ]^{-1/2}P[\ ]^{-1/2}P_0 = [\ ]^{-1/2}P_0[\ ]P_0[\ ]^{-1/2}P_0 = P_0$.

5. We consider only the infinite-dimensional case, so H has arbitrarily many eigenvalues greater than or equal to E_{i+j-1}. Let $H\psi_i = E_i\psi_i$, let $B_{i,j}$ be the subspace spanned by $\{\psi_i, \psi_{i+1}, \ldots, \psi_{i+j-1}\}$,

$$D_j^- = D_j \cap B_{1,i-1}, \qquad D_j^0 = D_j \cap B_{i,j}, \qquad D_j^+ = D_j \cap B_{i+j,\infty},$$

and let d^α be the dimension of D_j^α. In the trace

$$\mathrm{Tr}_{D_j}H = \mathrm{Tr}_{D_j^-}H + \mathrm{Tr}_{D_j^0}H + \mathrm{Tr}_{D_j^+}H$$

the first contribution lies between $E_1 + E_2 + \cdots + E_{d^-}$ and $E_{i-d^- -1} + E_{i-d^-} + \cdots + E_{i-1}$, the second between $E_i + E_{i+1} + \cdots + E_{i+d^0-1}$ and $E_{i+j-d^0-1} + E_{i+j-d^0} + \cdots + E_{i+j-1}$, and the third is $\ge E_{i+j-1}d^+$. Hence

$$\sup_{D_j \subset D_{i+j-1}} \mathrm{Tr}_{D_j}H \ge E_i + E_{i+1} + \cdots + E_{i+j-1}$$

(equality holds for $D_{i+j-1} = B_{1,i+j-1}$); and

$$\inf_{D_j \subset D_{i-1}^\perp} \mathrm{Tr}_{D_j}H \le E_i + E_{i+1} + \cdots + E_{i+j-1}$$

(equality for $D_{i-1} = B_{1,i-1}$).

6. $$H = \begin{bmatrix}1 & 0 & 0\\ 0 & 2 & 0\\ 0 & 0 & 3\end{bmatrix}, \qquad \psi = \left(\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}}\right) \ne \psi_1 = (1, 0, 0).$$

The general form of the φ's orthogonal to ψ is $\varphi = (\alpha, e^{i\varphi}\sqrt{1 - 2|\alpha|^2}, -\alpha)$, with $|\alpha| \le \frac{1}{2}$, and $\langle\varphi|H\varphi\rangle = 2(1 - 2\alpha^2) + (3 + 1)\alpha^2 = 2$ for all α.

3.6 Stationary Scattering Theory

An explicit formula for the scattering operator S is obtainable with an Abelian limit, and analytical methods can be applied to it.

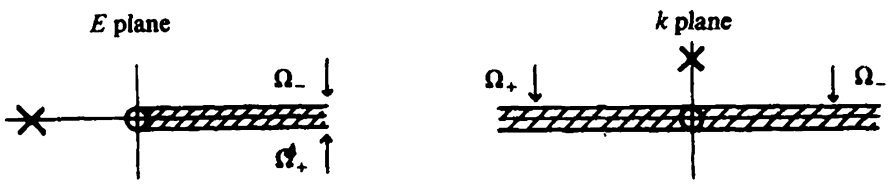
Historically, collision problems could be studied only with the methods of wave mechanics, and not with those of matrix mechanics. It has thus come to be believed that scattering theory should be thought of as concerning the scattering of waves, and not of particles with observables **x** and **p**. More recently, the connections between the two points of view have become better understood, and as a result we shall be able to tie in directly with §3.4. Since we have by now learned which mathematical pitfalls are dangerous and which can be harmlessly circumvented, we shall indulge in formal manipulations without always pausing to investigate the finer points of rigor.

The Møller operators were introduced as time-limits of $\Omega(t) = \exp(iHt) \times \exp(-iH_0 t)$. If they exist, then a fortiori (Problem 1) the limit as $\varepsilon \downarrow 0$ of $\varepsilon \int_0^\infty dt \exp(-\varepsilon t)\Omega(t)$ exists (cf. (I: 3.4.18)), which is an operator that no longer contains time explicitly. Since the integrand is an exponential function of t, the t-integration looks trivial at first sight, but because H and H_0 do not commute, it is not so simple. The difficulty can be eased with the partition of unity $\mathbf{1} = \int_0^\infty dE\, \delta(H_0 - E)$ given by the spectral representation of H_0, which we shall think of as $|\mathbf{p}|^2$. Then only the commuting variable E appears in the integral of the final exponential function, $\exp(-iH_0 t) = \int_0^\infty dE \times \exp(-iEt)\delta(H_0 - E)$, and there is no further obstacle to the integration:

$$\begin{aligned}\Omega_\pm &= s\text{-}\lim_{\varepsilon \downarrow 0} \varepsilon \int_0^\infty dt \int_0^\infty dE \exp(\pm it(H - E \pm i\varepsilon))\delta(H_0 - E) \\ &= s\text{-}\lim_{\varepsilon \downarrow 0} \int_0^\infty \pm\, dE\, i\varepsilon(H - E \pm i\varepsilon)^{-1}\, \delta(H_0 - E) \\ &= \mathbf{1} - s\text{-}\lim_{\varepsilon \downarrow 0} \int_0^\infty dE(H - E \pm i\varepsilon)^{-1} V\, \delta(H_0 - E). \end{aligned} \tag{3.6.1}$$

Remarks (3.6.2)

1. This means that $\Omega_\pm$ can be written in terms of the boundary values of the analytic function $z \to (H - z)^{-1}V$ on the branch cut $\mathbf{R}^+$. The V's that we shall deal with are mapped by this function into compact operators. It will in addition be convenient to use the variable $k \equiv \sqrt{E}$ instead of E to simplify the integrals; the limits in $\Omega_\pm$ simply correspond to $\operatorname{Im} k \downarrow 0$.



Under the right circumstances, the integrands can be continued analytically across the real axis:

$$\|V^{1/2}(H_0 - k^2)^{-1}V^{1/2}\|_2^2 = \int \frac{d^3x\, d^3x'}{(4\pi|\mathbf{x} - \mathbf{x}'|)^2} \times V(\mathbf{x})V(\mathbf{x}')\exp(i(k - k^*)|\mathbf{x} - \mathbf{x}'|)$$

is finite even if $\operatorname{Im} k < 0$, provided that $V(\mathbf{x})$ falls off sufficiently rapidly. If we write

$$\Omega_\pm = \operatorname*{s-lim}_{\varepsilon \downarrow 0} \int_0^\infty 2k\, dk\, \Omega(i\varepsilon \mp k)\delta(H_0 - k^2),$$

then

$$\Omega(k) \equiv 1 - (H - k^2)^{-1}V = (1 + (H_0 - k^2)^{-1}V)^{-1}$$
$$= V^{-1/2}(1 + |V|^{1/2}(H_0 - k^2)^{-1}V^{1/2})^{-1}|V|^{1/2}$$

has only poles, at the points where the compact operator in the denominator has the eigenvalue -1. The branch-point in the variable E at $E = 0$ disappears in the uniformizing variable k.

2. It is customary in wave mechanics to work outside the space L^2 and use plane waves $\varphi = \exp(i\mathbf{k} \cdot \mathbf{x})$ as eigenvectors of H_0. When multiplied by $\Omega_\pm$ they are turned into eigenvectors of H: $\psi_\pm = \Omega_\pm(\mathbf{k})\varphi$, which satisfy the **Lippmann–Schwinger equation**

$$\psi_\pm = \varphi - (H_0 - k^2 \pm i\varepsilon)^{-1}V\psi_\pm, \qquad k = |\mathbf{k}|,$$

because $\Omega(k) = (1 + (H_0 - k^2)^{-1}V)^{-1}$. In the x-representation, this reads

$$\psi_\pm(\mathbf{x}) = \exp(i\mathbf{k} \cdot \mathbf{x}) - \int \frac{d^3x' \exp(\mp ik|\mathbf{x} - \mathbf{x}'|)}{4\pi|\mathbf{x} - \mathbf{x}'|} V(\mathbf{x}')\psi_\pm(\mathbf{x}').$$

The new eigenvectors contain incoming, or respectively outgoing, spherical waves in addition to the plane waves.

Example (3.6.3)

With the separable V of (3.4.13; 1), $\Omega(k) = 1 - \lambda(H_0 - k^2)^{-1}PD^{-1}(k)$, or, written as an integral operator with a momentum-space kernel,

$$(\mathbf{p}'|\Omega_\pm - 1|\mathbf{p}) = -\int_0^\infty 2k\, dk\, \delta(|\mathbf{p}|^2 - k^2) \frac{\lambda\rho^*(\mathbf{p}')\rho(\mathbf{p})}{(|\mathbf{p}'|^2 - k^2 \mp i\varepsilon)} D^{-1}(\mp k),$$

where now

$$D(k) = 1 + \lambda \int \frac{d^3p|\rho(\mathbf{p})|^2}{|\mathbf{p}|^2 - k^2}, \qquad \operatorname{Im} k > 0.$$

If, say $\rho^2 = M^2/(|\mathbf{p}|^2 + M^2)$, $M > 0$, then $D(k) = 1 + (\lambda/4\pi)M^2/(M - ik)$. This function can be continued into the lower k-plane, equivalent to the second sheet in E, though it no longer equals the integral there, but instead develops a pole at $k = -iM$.

In the same way, the time-limit (3.4.24; 6) in S can be recast as an ε limit, the only difference being that the partition of unity is needed on both ends of the expression:

$$S = s\text{-}\lim_{\varepsilon \downarrow 0} \varepsilon \int_0^\infty dE\, dE'\, \delta(H_0 - E)\exp\left(-it\left(H - \frac{E + E'}{2} - i\varepsilon\right)\right)\delta(H_0 - E')dt$$

$$= s\text{-}\lim_{\varepsilon \downarrow 0} \int_0^\infty dE\, dE'\, \delta(H_0 - E)\, \frac{-i\varepsilon}{H - (E + E')/2 - i\varepsilon}\, \delta(H_0 - E'). \qquad (3.6.4)$$

With the second iteration of the resolvent formula (suppose $D(H)$ is $D(H_0)$),

$$(H - z)^{-1} = (H_0 - z)^{-1} - (H_0 - z)^{-1}[V - V(H - z)^{-1}V](H_0 - z)^{-1}$$

and the limit

$$\lim_{\varepsilon \downarrow 0} \frac{-i\varepsilon}{((E - E')/2 - i\varepsilon)((E' - E)/2 - i\varepsilon)} = 2\pi i\, \delta(E - E'),$$

there results

$$S = s\text{-}\lim_{\varepsilon \downarrow 0} \int_0^\infty dE\{1 - 2\pi i\, \delta(H_0 - E)[V - V(H - E - i\varepsilon)^{-1}V]\}\delta(H_0 - E). \qquad (3.6.5)$$

(As usual, S is in the interaction representation.) In order to discuss (3.6.5), we need another operator-valued analytic function of the uniformizing variable k (see (3.6.2; 1)):

$$\begin{aligned} t(k) \equiv V\Omega_-(k) &= V - V(H - k^2)^{-1}V \\ &= V^{1/2}[1 + |V|^{1/2}(H_0 - k^2)^{-1}V^{1/2}]^{-1}|V|^{1/2} \\ &= [V^{-1} + (H_0 - k^2)^{-1}]^{-1} = t^*(-k^*). \end{aligned} \qquad (3.6.6)$$

The domains of definition, especially that of V^{-1}, will have to be checked later. As $\operatorname{Im} k \downarrow 0$,

$$\begin{aligned} t^{-1}(k) - t^{-1}(-k) &= \lim_{\varepsilon \downarrow 0}[(H_0 - k^2 - i\varepsilon)^{-1} - (H_0 - k^2 + i\varepsilon)^{-1}] \\ &= 2\pi i\, \delta(H_0 - k^2) \end{aligned}$$

in the sense of convergence of quadratic forms, and we get

$$1 - 2\pi i\,\delta(H_0 - k^2)t(k) = (t^{-1}(k) - 2\pi i\,\delta(H_0 - k^2))t(k) = t^{-1}(-k)t(k):$$

The Spectral Representation of the S Matrix (3.6.7)

$$S = \int_0^\infty 2k\,dk\; S(k)\delta(H_0 - k^2),$$

$$S(k) = t^{-1}(-k)t(k) = s\text{-}\lim_{\varepsilon \downarrow 0}[1 + (H_0 - k^2 + i\varepsilon)^{-1}V] \cdot [1 + (H_0 - k^2 - i\varepsilon)^{-1}V]^{-1}.$$

From this there follow the

Unitarity Properties of the S Matrix (3.6.8)

(i) $S(k)S(-k) = 1$ on the domain of analyticity.
(ii) $\delta(H_0 - k^2)S(k)^* = S(-k)\delta(H_0 - k^2)$ for k real.

Example (3.6.9)

Recall (3.6.3), with $V = \lambda P$. We find that $t(k) = \lambda PD^{-1}$ and $S(k) = 1 - 2\pi i\,\delta(H_0 - k^2)\lambda PD^{-1}$. Since $\delta(H_0 - k^2)P\,\delta(H_0 - k^2) = \delta(H_0 - k^2)|\rho(k)|^2 \times (k/4\pi)P_0$, where P_l is the projection onto the states of angular momentum $|\mathbf{L}|^2 = l(l+1)$, and $D(k) - D(-k) = 2\pi i(k/4\pi)|\rho(k)|^2$, we find that

$$S = \int_0^\infty 2k\,dk\;\delta(H_0 - k^2)\left(P_0\frac{D(-k)}{D(k)} + 1 - P_0\right).$$

Remarks (3.6.10)

1. Since $[S, H_0] = 0$ it follows that even though $S(k)$ maps functions off the energy shell $H_0 = k^2$, $S(k)\delta(H_0 - k^2)$ does not. The unitary relation $\delta(H_0 - k'^2)S(k')^*S(k)\delta(H_0 - k^2) = \delta(H_0 - k^2)\delta(k'^2 - k^2)$ then holds on the energy shell, and hence $S(k)\,\delta(H_0 - k^2)$ can be written† as $\exp(2i\,\delta(k))\delta(H_0 - k^2)$, where $\delta(k) = \delta(k)^* = -\delta(-k)$. Making use of the spectral representation of $H_0 = |\mathbf{p}|^2$, we can write $\mathscr{H} = L^2(\mathbb{R}^+, 2k\,dk) \otimes L^2(S^2, d\Omega)$, and the operator $\delta(k)$ maps the angular part $L^2(S^2, d\Omega)$ onto itself. The operator $\delta \equiv \delta(\sqrt{H_0})$ then acts on all of $\mathscr{H}$, and $[\delta, H_0] = 0$. If V is spherically symmetric, $[\delta, \mathbf{L}] = 0$, so $\delta(k) = \sum_l \delta_l(k)P_l$, for

† It is unfortunately traditional to use the same letter for the phase-shift $\delta(k)$ and for Dirac's delta function. The reader should be alert for any possible confusion.

$\delta_l(k) \in \mathbb{R}$. Then in the diagonal representation of $|\mathbf{L}|^2$, S becomes a multiplication operator in H_0:

$$S = \int_0^\infty dk^2\, \delta(H_0 - k^2)\exp(2i\delta(k)) = \sum_l \int_0^\infty dk^2\, \delta(H_0 - k^2)P_l \exp(2i\delta_l(k)).$$

2. The unitarity of S implies the **Low equation** for t (as before, defined with $\operatorname{Im} k \downarrow 0$):

$$\begin{aligned} t(-k) - t(k) &= 2\pi i V\Omega\, \delta(H_0 - k^2)\Omega^* V \\ &= 2\pi i t(k)\delta(H_0 - k^2)t(-k), \qquad k \in \mathbb{R}. \end{aligned}$$

3. If the Lippmann-Schwinger equation (3.6.2; 2) is written as $\psi_- = \varphi - (H_0 - k^2)^{-1}t(k)\varphi$, and if we use $\varphi = \exp(i\mathbf{k}\cdot\mathbf{x})$, $\mathbf{k} = k\mathbf{n}$, noting that for $|\mathbf{x}| \gg |\mathbf{x}'|$,

$$\frac{\exp(ik|\mathbf{x} - \mathbf{x}'|)}{|\mathbf{x} - \mathbf{x}'|} \sim \frac{\exp(ikr)}{r}\exp(-ik\mathbf{n}'\cdot\mathbf{x}'), \qquad \mathbf{n}' = \frac{\mathbf{x}}{r},$$

then as $|\mathbf{x}| \to \infty$, in the x-representation,

$$\psi_-(\mathbf{x}) = \exp(i\mathbf{k}\cdot\mathbf{x}) + \frac{\exp(ikr)}{r} f(k; \mathbf{n}', \mathbf{n}),$$

$$f(k; \mathbf{n}', \mathbf{n}) \equiv \frac{-1}{4\pi}\int d^3x'\, d^3x''\, \exp(-ik\mathbf{n}'\cdot\mathbf{x}')\langle x'|t(k)|x''\rangle\exp(ik\mathbf{n}\cdot\mathbf{x}'').$$

The angular dependence f of the outgoing spherical wave is thus determined by t in momentum space on the energy shell. Only this part of t shows up in $\exp(2\pi i\delta(k))\ \delta(H_0 - k^2) = (1 - 2\pi i\ \delta(H_0 - k^2)t(k))\delta(H_0 - k^2)$. In particular, if $[t(k), \mathbf{L}] = 0$, then by comparing coefficients (Problem 6),

$$\begin{aligned} f(k; \mathbf{n}', \mathbf{n}) &= \sum_l \langle \mathbf{n}'|P_l|\mathbf{n}\rangle \frac{\exp(2i\delta_l(k)) - 1}{2ik} \\ &= \sum_l \frac{2l+1}{k} P_l(\cos\theta)\exp(i\delta_l(k))\sin\delta_l(k), \qquad \theta = \measuredangle(\mathbf{n}', \mathbf{n}). \end{aligned}$$

If the plane wave is expanded in spherical harmonics $\exp(i\mathbf{k}\cdot\mathbf{x}) = (\exp(ikr) - \exp(-ikr))/2ikr + \cdots$, then ψ_- becomes asymptotically $(\exp(i(kr + \delta(k)) - \exp(-i(kr + \delta(k)))/2ikr + \cdots$, which shows the significance of δ as the **phase-shift** of a spherical wave.

4. If there are several channels (see (3.4.24; 6)), then the generalization of (3.6.5) is

$$S_{\alpha\beta} = \int_0^\infty dE\left[\delta_{\alpha\beta} - 2\pi i\, \delta(H_\alpha - E)\left(V_\alpha - V_\alpha \frac{1}{H - E - i\varepsilon} V_\beta\right)\right]\delta(H_\beta - E).$$

We shall assume in what follows that V decreases fast enough at infinity that the norm in (3.6.2; 1) remains finite for all k with $\operatorname{Im} k > \kappa_0 < 0$. Then for such k,

$$S(k) = V^{-1/2}D(-k)D^{-1}(k)V^{1/2}, \qquad D(k) = 1 + V^{1/2}(H_0 - k^2)^{-1}|V|^{1/2}$$

is a meromorphic function taking values in $\mathscr{B}(\mathscr{H})$. Our next topic is

The Configuration of the Poles of $S(k)$ (3.6.11)

The scattering operator S has a pole at any value of k at which either $D(k)$ has eigenvalue zero or $D(-k)$ has a pole. Both poles and zeroes occur for $-k^*$ whenever they occur for k. $D(k)$ has no poles in the upper half-plane, but only zeroes, and those are restricted to the imaginary axis.

As depicted in Figure 13, the terminology for these values of k is:

zeroes with $\operatorname{Im} k > 0$	**bound states**
zeroes with $\operatorname{Im} k < 0$ and $\operatorname{Re} k = 0$	**virtual states**
zeroes with $\operatorname{Re} k \neq 0$	**resonances**

Proof

$D(-k^*) = KD(k)K$ is the time-reversed version of $D(k)$ (cf. (3.3.19; 2)), so the two operators have the same poles and zeroes. If $0 = D(k)\psi = \psi + V^{1/2}(H_0 - E)^{-1}V^{1/2}\psi$, then $(H_0 + V - E)\varphi = 0$, where $\varphi \equiv (H_0 - E)^{-1} \times V^{1/2}\psi$. If V decreases sufficiently fast, then φ is square-integrable whenever

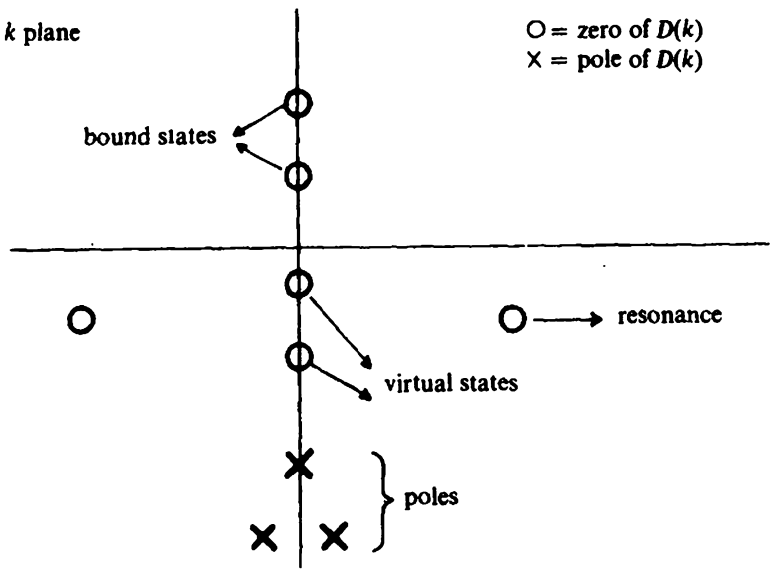


Figure 13 The configuration of the poles and zeroes of $D(k)$.

ψ is, and for such potentials the equation for φ can be solved in L^2 only if $E < 0$, i.e., for k purely imaginary. Complex zeroes and poles can appear after analytic continuation to the second sheet of E, which is the lower half-plane in k. □

Examples (3.6.12)

1. In Example (3.6.9) with $\rho = M^2/(|\mathbf{p}|^2 + M^2)$ as in (3.6.3),

$$S(k) = P_0 \frac{(M - ik)(M(1 + (\lambda/4\pi)M) + ik)}{(M + ik)(M(1 + (\lambda/4\pi)M) - ik)}.$$

   The zero of $D(k)$ at $k = -iM(1 + (\lambda/4\pi)M)$ is a virtual state if $\lambda/4\pi > -1/M$, and a bound state if $\lambda/4\pi < -1/M$. The pole of $D(k)$ at $k = -iM$ produces a pole of S at $k = iM$ (on the first sheet of E at $E = -M^2$).
2. The separable potential $V = \lambda \mathbf{p} \cdot P\mathbf{p}$ interacts only with $l = 1$ states, and the analogous calculation with $P = |\rho\rangle\langle\rho|$, $\rho(p) = M^2/(p^2 + M^2)$ results in

$$D(k) = 1 + \lambda \int d^3p \frac{|\mathbf{p}|^2 M^4}{(|\mathbf{p}|^2 - k^2)(|\mathbf{p}|^2 + M^2)^4} = 1 + \frac{\lambda}{8\pi} \frac{M^2(M - 2ik)}{(M - ik)^2}.$$

   The zeroes at

$$k = -iM\left[1 + \frac{\lambda}{8\pi} M^3 \pm \left(\frac{\lambda}{8\pi} M^3\left(1 + \frac{\lambda}{8\pi} M^3\right)\right)^{1/2}\right]$$

   are virtual states if $\lambda > 0$, resonances if $-8\pi/M^3 < \lambda < 0$, and if $\lambda < -8\pi/M^3$ there is one bound and one virtual state.

Remarks (3.6.13)

1. The poles of $D(k)$ were originally called spurious poles, since it was assumed that all poles of $S(k)$ on the first sheet of E should correspond to bound states. The poles of $D(k)$ have no physical significance, and serve only to show at what point analytic continuation makes the $\| \quad \|_2$ norm in (3.6.2; 1) diverge.
2. $S(k)$ is determined by the phase of $D(k)$, and D approaches 1 at infinity in the upper half-plane. If we normalize the $\delta(k)$, defined in (3.6.10; 1) only modulo π, by setting $\delta(0) = 0$, then a well-known theorem of analytic function theory implies that $-\delta(\infty) = \pi$ times the number of bound states. The more general version of this fact is

Levinson's Theorem (3.6.14)

Let V be compact relative to H_0, and suppose $\mathrm{Tr}|(H_0 - z)^{-1} - (H - z)^{-1}| \leq M(z)$, *where* $M(z) \leq O(|z|^{-1-\varepsilon})$ *as* $|z| \to \infty$ *and* $O(|\mathrm{Im}\, z|^{-1+\varepsilon})$ *as* $\mathrm{Im}\, z \to 0$, $\mathrm{Re}\, z > 0$, $\varepsilon > 0$. *Then 2π times the number of bound states equals*

$i \lim_{k\to\infty} \ln \mathrm{Det}(S(k) - S(0)) = i \lim_{k\to\infty} \mathrm{Tr} \ln(S(k) - S(0))$ if $0 \notin \sigma_p(H)$, so that $S(0)$ is well-defined.

Gloss (3.6.15)

$\ln(1 + A) \equiv -\sum_{n=1}^{\infty}((-1)^n/n)A^n$ is defined for all A with $\|A\| < 1$, and $\mathrm{Det}(1 + A) \equiv \exp(\mathrm{Tr} \ln(1 + A))$ is defined for all A with $\|A\|_1 < \infty$. In general $\ln(AB) \neq \ln A + \ln B$, but $\mathrm{Det}(1 + A)(1 + B) = \mathrm{Det}(1 + B)(1 + A)$ for all $A + B + AB \in \mathscr{C}_1$, and $= \mathrm{Det}(1 + A)\mathrm{Det}(1 + B)$ for all $A, B \in \mathscr{C}_1$ [16]. If $A(z)$: $\mathbb{C} \to \mathscr{C}_1$ is analytic, then it follows that in the domain of analyticity

$$\mathrm{Tr} \frac{d}{dz} \ln(1 + A(z)) = \mathrm{Tr}(1 + A(z))^{-1} A'(z).$$

Proof of (3.6.14)

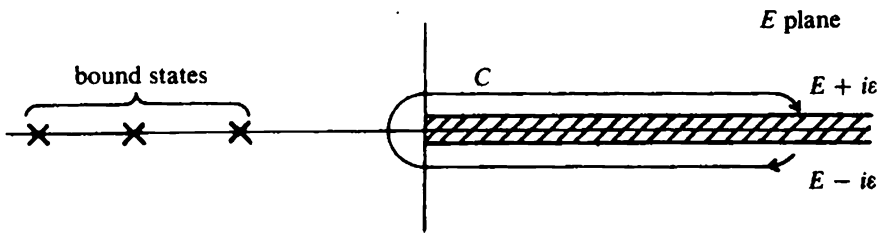
Let $Q_{\pm}(E) = 1 + (H_0 - E \pm i\varepsilon)^{-1} V$, $S(E) = Q_+(E)Q_-^{-1}(E)$. Although $(H_0 - z)^{-1} V$ is compact, it is not trace-class. However, differences of two such terms with different z are trace-class, since $(H_0 - z_1)^{-1} V (H_0 - z_2)^{-1} = [(H_0 - z_1)^{-1} - (H - z_1)^{-1}][1 + (V - z_1 + z_2)(H_0 - z_2)^{-1}]$. This justifies the following formal manipulations:

$$\begin{aligned}
\mathrm{Tr} \frac{d}{dE} \ln S(E) &= \mathrm{Tr}\, Q_- Q_+^{-1}[Q'_+ Q_-^{-1} - Q_+ Q_-^{-1} Q'_- Q_-^{-1}] \\
&= \mathrm{Tr}(Q_+^{-1} Q'_+ - Q_-^{-1} Q'_-) \\
&= \mathrm{Tr}\{[1 + (H_0 - E + i\varepsilon)^{-1} V]^{-1} (H_0 - E + i\varepsilon)^{-2} V \\
&\quad - (\varepsilon \leftrightarrow -\varepsilon)\} \\
&= \mathrm{Tr}\left[\frac{1}{H_0 - E + i\varepsilon} - \frac{1}{H - E + i\varepsilon} - (\varepsilon \leftrightarrow -\varepsilon)\right].
\end{aligned}$$

If we do the integration over E, then

$$\mathrm{Tr} \ln S(E) = \mathrm{Tr} \int_C dz((H - z)^{-1} - (H_0 - z)^{-1}),$$

where C, the contour of the complex integration, is as shown below:



By assumption, the circle $K: |z| = E$ can be appended to C, since the extra contribution goes to 0 as $E \to \infty$. In this limit $C \cup K$ encircles all the poles of $(H - z)^{-1}$, but does not contain $Sp(H_0)$. The proposition then follows from the residue theorem. □

Example (3.6.16)

In the case of the separable potential (3.4.13; 1),

$$\mathrm{Tr}((H_0 - z)^{-1} - (H - z)^{-1}) = \lambda \,\mathrm{Tr}(H_0 - z)^{-1} P (H_0 - z)^{-1} D^{-1}(z)$$

$$= D^{-1}(z) \frac{\partial}{\partial z} D(z).$$

In (3.6.3) we found that $D(z) = 1 + (\lambda/4\pi)M^2/(M - i\sqrt{z})$ for $\rho^2(p) = M^2(|\mathbf{p}|^2 + M^2)^{-1}$. Therefore

$$\frac{\partial}{\partial z} D(z) = \frac{i}{2\sqrt{z}} \frac{\lambda}{4\pi} \frac{M^2}{(M - i\sqrt{z})^2},$$

and the assumptions of (3.6.14) are satisfied. In fact,

$$\delta(k) = \arctan \frac{kM^2\lambda/4\pi}{M^2(1 + (\lambda/4\pi)M) + k^2}$$

has the limits $\delta(0) = 0$, $\delta(\infty) = 0$ if $1 + (\lambda/4\pi)M > 0$, and $\delta(\infty) = -\pi$ if $1 + (\lambda/4\pi)M < 0$. If, however, we pass to the limit $M \to \infty$, $\lambda \uparrow 0$, so that $\lambda_r \equiv M(1 + (\lambda/4\pi)M)$ stays finite, then $S(k) = (\lambda_r - ik)/(\lambda_r + ik)$. In this case, $\delta(k) = -\arctan(k/\lambda_r)$ varies between 0 and $\pi/2$ times signum λ_r. For $\lambda_r < 0$ (a virtual state) as well as for $\lambda_r > 0$ (a bound state), (3.6.14) is violated, since then $D(\infty) \neq 1$.

The classical scattering transformation (I: §3.4) for, say, a particle in a central potential in $\mathbb{R}^2$, is a canonical transformation that leaves p_r and L asymptotically invariant as $r \to \infty$, and as a consequence has an asymptotic generator $2\delta(p_r, L)$:

$$(r, \theta; p_r, L) \to \left(r - 2\frac{\partial \delta}{\partial p_r}, \theta - 2\frac{\partial \delta}{\partial L}; p_r, L\right).$$

Thus the generator contains information about the scattering angle $-2\partial\,\delta/\partial L$ and about $-2\partial\,\delta/\partial p_r$, the amount by which a particle evolving according to H outdistances one evolving according to H_0. This distance corresponds to a delay time $2(m/p)(\partial\delta/\partial p_r)$. Similarly, in quantum theory $\exp(-2i\,\delta(p))x \times \exp(2i\,\delta(p)) = x - 2\partial\,\delta/\partial p$, and the amount of delay can be generally defined as follows.

The Møller transformations turn $\mathbf{x}$ into $\mathbf{x}_\pm \equiv \lim_{t \to \pm\infty}(\mathbf{x}(t) - t\mathbf{p}(t))$. Classically this means that trajectories that become tangent to the actual trajectory as $t \to \pm\infty$ are at $\mathbf{x}_\pm$ when $t = 0$. The time-delay is the difference of the time the actual trajectory spends in a ball of radius R centered at the origin and the time spent by these free trajectories, in the limit $R \to \infty$.

Suppose a trajectory enters the ball at $-T_-$, leaves at T_+, and that R is so large that the motion is free outside the ball. Then

$$\mathbf{x}(\pm T_\pm) = \mathbf{x}_\pm \pm T_\pm \mathbf{p}_\pm,$$

and if this equation is multiplied by $\mathbf{p}_\pm$, we find that

$$T_+ + T_- = \frac{|\mathbf{p}_+|\sqrt{R^2 - b_+^2} - \mathbf{x}_+ \cdot \mathbf{p}_+}{|\mathbf{p}_+|^2} + \frac{|\mathbf{p}_-|\sqrt{R^2 - b_-^2} + \mathbf{x}_- \cdot \mathbf{p}_-}{|\mathbf{p}_-|^2},$$

where $b_\pm$ are the smallest distances the free trajectories come to the origin. The times spent by the free trajectories in the ball are $2(\sqrt{R^2 - b_\pm^2}/|\mathbf{p}_+|)$, so with $R \to \infty$, the time-delay

$$\begin{aligned} D \equiv{}& \text{time of actual trajectory} - \text{time of free trajectory} \\ ={}& \frac{\mathbf{x}_- \cdot \mathbf{p}_- - \mathbf{x}_+ \cdot \mathbf{p}_+}{|\mathbf{p}_+|^2}. \end{aligned}$$

It turns out that there is a direct relationship between D and the S matrix and the virial:

Definitions of the Time-Delay (3.6.17)

(i) $D = \Omega_-(1/|\mathbf{p}|)(\mathbf{x}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{x})(1/2|\mathbf{p}|)\Omega_-^*$
$\quad -\Omega_+(1/|\mathbf{p}|)(\mathbf{x}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{x})(1/2|\mathbf{p}|)\Omega_+^*$;

(ii) $D = P_{ac}(1/\sqrt{H})\int_{-\infty}^{\infty} dt(2V_t + \mathbf{x}_t\cdot\nabla V_t)(1/\sqrt{H})P_{ac}$;

(iii) $D = w\text{-}\lim_{R\to\infty} \Omega_- \int_{-\infty}^{\infty} dt\{\exp(iHt)\Theta(R^2 - |\mathbf{x}|^2)\exp(-iHt)$
$\quad -\exp(iH_0t)\Theta(R^2 - |\mathbf{x}|^2)\exp(-iH_0t)\}\Omega_-^*$;

(iv) $D = -i\Omega_- S^{-1}\int_0^\infty dE\,\delta(H_0 - E)(\partial S(E)/\partial E)\Omega_-^*$;

where $H_0 = |\mathbf{p}|^2/2$ and $H = H_0 + V$.

Remarks (3.6.18)

1. Definitions (i) and (ii) are possible whenever scattering theory works, i.e., for V falling off as $r^{-1-\varepsilon}$. In Definition (iv), however, it has so far been shown that $\partial S/\partial E$ is well-defined only for $r^{-4-\varepsilon}$ fall off.
2. It is clear because of its classical meaning that D should be independent of the choice of the point $\mathbf{x}$ on the trajectory. Therefore D should commute with H. This follows formally from (i), since

$$\begin{aligned} \exp(iHt)D\exp(-iHt) ={}& \Omega_+ \frac{1}{|\mathbf{p}|}\{(\mathbf{x}+\mathbf{p}t)\cdot\mathbf{p} + \mathbf{p}\cdot(\mathbf{x}+\mathbf{p}t)\}\frac{1}{2|\mathbf{p}|}\Omega_+^* \\ & - \Omega_- \frac{1}{|\mathbf{p}|}\{(\mathbf{x}-\mathbf{p}t)\cdot\mathbf{p} + \mathbf{p}\cdot(\mathbf{x}-\mathbf{p}t)\}\frac{1}{2|\mathbf{p}|}\Omega_-^* \\ ={}& D. \end{aligned}$$

However, D is different for different trajectories; like S, it does not commute with spatial translations.

3. For repulsive potentials $\sim r^{-\nu}$,

$$D = (2 - \nu)P_{\alpha c} \frac{1}{\sqrt{H}} \int_{-\infty}^{\infty} dt\, V(t) \frac{1}{\sqrt{H}} P_{\alpha c}.$$

If $\nu = 2$, then $D = 0$. If $\nu > 2$, then $D < 0$. This means that the actual trajectory spends less time in the ball than the straight trajectory does, since its path is shorter. If $\nu < 2$, then D is positive, and the dominant effect of V is to brake the particle. Note that from (iv), the phase-shift for such potentials is a monotonic function of E.

4. In the wave picture an incident wave $\exp(-ikr)$ is turned into $\exp(i(kr + 2\delta(k)))$. If we assume a wave-packet narrowly concentrated about k_0 and expand $\delta(k) = \delta(k_0) + (k - k_0)(\partial\delta(k_0)/\partial k_0) + \cdots$, then the coefficient of k becomes $r + 2(\partial\,\delta(k)/\partial k)$ instead of r. Thus the center of the wave-packet is shifted from $r = k_0 t$ to $r = k_0(t - 2(\partial\delta/\partial E))$ after the scattering.

5. If there are resonances at $\pm k_r - ib$, then

$$S(k) = \frac{(-k - k_r + ib)(-k + k_r + ib)}{(k - k_r + ib)(k + k_r + ib)} \times \text{slowly varying factors.}$$

Ignoring the slowly varying parts,

$$-i \frac{\partial}{\partial k^2} \ln S(k) \cong \frac{b}{k} \left[\frac{1}{(k - k_r)^2 + b^2} + \frac{1}{(k + k_r)^2 + b^2} \right].$$

If $b \ll k_r$, then there is a sharp maximum $\sim 1/(bk_r)$ at the resonance energy, at which $\delta(k)$ passes rapidly through 90°. For this reason $1/(bk_r)$ can be thought of as a lifetime, which can become so extremely long that there is hardly any difference between resonances and bound states. This happens for α particles radiating from nuclei.

6. If the potential is radial, then $2\,\delta_l(k)$ is the same as the classical generator of the scattering transformation, and (3.6.17) reduces to the classical formula.

The Equivalence of the Definitions of D

(i) $\Leftrightarrow$ (ii): Introduce the generator $G \equiv (\mathbf{x} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{x})/2$ of dilatations. On the one hand

$$iP_{\alpha c} \frac{1}{\sqrt{H}} \int_{-T}^{T} dt\, \exp(iHt)[G, H]\exp(-iHt) \frac{1}{\sqrt{H}} P_{\alpha c}$$

$$= P_{\alpha c} \frac{1}{\sqrt{H}} (\exp(-iHT)G \exp(iHT)$$

$$- \exp(iHT)G \exp(-iHT)) \frac{1}{\sqrt{H}} P_{\alpha c},$$

and on the other this equals (see (3.3.20; 8))

$$P_{ac}\frac{1}{\sqrt{H}}\int_{-T}^{T}dt\,\exp(iHt)(\mathbf{x}\cdot\nabla V-|\mathbf{p}|^2)\exp(-iHt)\frac{1}{\sqrt{H}}P_{ac}$$

$$=-4TP_{ac}+P_{ac}\frac{1}{\sqrt{H}}\int_{-T}^{T}dt\,\exp(iHt)(2V+\mathbf{x}\cdot\nabla V)$$

$$\cdot\exp(-iHt)\frac{1}{\sqrt{H}}P_{ac}.$$

Now $G=\exp(-iH_0t)G\exp(iH_0t)+T|\mathbf{p}|^2$ and $P_{ac}(1/\sqrt{H})\exp(iHT)|\mathbf{p}|^2\times\exp(-iHT)(1/\sqrt{H})P_{ac}\to 2$ as $T\to\pm\infty$. Thus the equality of the two expressions reduces to the equality of (i) and (ii) in the limit $T\to\infty$.

(i) $\Leftrightarrow$ (iv):

$$\text{(i)}=\frac{1}{2}\Omega_-\left(\frac{1}{\sqrt{H_0}}G\frac{1}{\sqrt{H_0}}-S^{-1}\frac{1}{\sqrt{H_0}}G\frac{1}{\sqrt{H_0}}S\right)\Omega_-^*$$

$$=\frac{1}{2}\Omega_-\frac{1}{\sqrt{H_0}}S^{-1}[S,G]\frac{1}{\sqrt{H_0}}\Omega_-^*,\ \text{since } [S,H_0]=0.$$

But

$$[G,S]=i\frac{\partial}{\partial\alpha}\int_0^\infty dE\,\delta(H_0\alpha^{-2}-E)S(E)|_{\alpha=1}$$

$$=2i\int_0^\infty dE\,\delta(H_0-E)\frac{\partial S(E)}{\partial E},$$

since the angular part of $S(E)$ is unaffected by dilatations, so this means that (i) $\Leftrightarrow$ (iv).

(iii) $\Leftrightarrow$ (iv): This equivalence can be shown with the same methods but is slightly more involved. A proof will be sketched in Problem 2. □

The quantity related to S that is of interest in experimental physics is the cross-section σ. Following the classical theory (I: §3.4), we define the cross-section as the number of particles scattered into a given solid angle per unit area of incident particles. The momentum distribution of the incident particles is described by a wave-function $\varphi(\mathbf{k})$ in $L^2(\mathbb{R}^3, d^3k/(2\pi)^3)$. In reality a particle is never precisely aimed at the scattering target, but is rather a beam with momentum concentrated near $\mathbf{k}_0$, while its width in x-space will be macroscopic. The initial state is best described as a mixture

$$\frac{1}{F}\int_F d^2a\,|\exp(i\mathbf{a}\cdot\mathbf{k})\varphi(\mathbf{k})\rangle\langle\exp(i\mathbf{a}\cdot\mathbf{k})\varphi(\mathbf{k})|,$$

letting φ have compact support containing $\mathbf{k}_0 = (0, 0, \sqrt{E})$ and letting $\mathbf{a} = (a_1, a_2, 0)$ be a translation in the plane of the impact parameter, which is averaged over a surface F, the beam cross-sectional area. We next find the probability of measuring the momentum of the outgoing state in some cone C so far from $\mathbf{k}_0$ that $\varphi_{|C} = 0$, and there is no danger of measuring an unscattered particle. In this computation the 1 in S in (3.6.5) does not contribute, and with $\psi = -2\pi i \int dE\, \delta(H_0 - E)t\, \delta(H_0 - E)\varphi$, $t = -4\pi f$, we obtain

$$\frac{(2\pi)^{-3}}{F} \int_F d^2a \int_C d^3k |\psi(\mathbf{k})|^2 = \frac{(2\pi)^{-9}}{F} \int_F d^2a \int d^3k\, d^3k'\, d^3k''$$
$$\cdot \int_0^\infty dE\, \delta(|\mathbf{k}|^2 - E)\delta(|\mathbf{k}'|^2 - E)8\pi^2 f(\mathbf{k}, \mathbf{k}')8\pi^2 f^*(\mathbf{k}, \mathbf{k}'')\delta(|\mathbf{k}''|^2 - E)$$
$$\cdot \exp(i\mathbf{k}' \cdot \mathbf{a})\varphi(\mathbf{k}')\exp(-i\mathbf{k}'' \cdot \mathbf{a})\varphi^*(\mathbf{k}'').$$

To get σ this has to be divided by the probability that the particle arrives through a unit area, i.e., $1/F$. Afterwards, we may let F become infinite, so $\int d^2a \exp(i(\mathbf{k}' - \mathbf{k}'') \cdot \mathbf{a}) = (2\pi)^2\, \delta^2(\mathbf{k}'_\perp - \mathbf{k}''_\perp)$, where $\perp$ denotes the projection into the 1-2-plane. Because $\delta^2(\mathbf{k}'_\perp - \mathbf{k}''_\perp)\delta(|\mathbf{k}'|^2 - |\mathbf{k}''|^2) = \delta^3(\mathbf{k}' - \mathbf{k}'')/2k'_3$ and $\int_0^\infty k^2\, dk \delta(k^2 - |\mathbf{k}'|^2) = |\mathbf{k}'|/2$, we get

$$\sigma\, d\Omega = d\Omega \int \frac{dk'^3}{(2\pi)^3} |\varphi(\mathbf{k}')|^2 |f(\mathbf{k}, \mathbf{k}')|^2 \frac{|\mathbf{k}'|}{|k'_3|}.$$

If φ is narrowly enough concentrated about $\mathbf{k}_0$ that we may set $|\mathbf{k}'|/|k'_3|$ to 1 and regard $f(\mathbf{k}, \mathbf{k}')$ as a constant, then because of the normalization the detailed form of φ becomes irrelevant, and we obtain a formula for the

Scattering Cross-Section (3.6.19)

$$\sigma(\mathbf{k}, \mathbf{k}_0) = |f(\mathbf{k}, \mathbf{k}_0)|^2, \qquad \sigma_t = \int d\Omega_k\, \sigma(\mathbf{k}, \mathbf{k}_0).$$

Remarks (3.6.20)

1. We have considered the probability of measuring a momentum $\mathbf{k}$ as $t \to \infty$. Since

$$s\text{-}\lim_{t\to\infty} \frac{\mathbf{x}(t)}{|\mathbf{x}(t)|} = s\text{-}\lim_{t\to\infty} \frac{\mathbf{p}(t)}{|\mathbf{p}(t)|}$$

(Problem 3), this equals the probability of measuring $\mathbf{x}$ in the same angular direction.

2. The scattering amplitude f is also the coefficient of the asymptotic spherical wave (3.6.10; 3). The complete wave-function $|\psi_-|^2$, however, is not asymptotically dominated by $|f|^2/r^2$, but instead by $|\varphi|^2$ and an interference factor $\sim 1/r$.

3. We learned in (II: §3.3 and 3.4) that the details of the exact wave-function ψ are quite complicated. For instance, $\sigma_t = \int d^3\Omega\, \sigma$ does not simply describe the shadow cast by an object, but rather refers to the asymptotic region in which the shadow dissolves (the Frauenhofer region of (II: 3.4.42)).

Properties of the Scattering Amplitude (3.6.21)

If k is real, then

(i) $f(k; \mathbf{n}', \mathbf{n}) - f(k; \mathbf{n}, \mathbf{n}')^* = (1/2\pi) \int d\Omega''\ f(k; \mathbf{n}', \mathbf{n}'') f(k; \mathbf{n}, \mathbf{n}'')^* ik$;
(ii) $f(k; \mathbf{n}', \mathbf{n}) = f(k; -\mathbf{n}, -\mathbf{n}')$, *provided that* $KVK = V$;
(iii) $f(k; \mathbf{n}', \mathbf{n}) = f(k; -\mathbf{n}', -\mathbf{n})$, *provided that* $PVP = V$.

Time-reversal K and parity P were defined in (3.3.19; 2) *and* (3.2.10).

Proof

(i) This follows from (3.6.10; 2), since for real k, $t(-k) = t(k)^*$.
(ii) If H and H_0 are invariant under K, then $KSK = S^*$, and so $Kt(k)K = t(k)^*$. From the rules $K^2 = \mathbf{1}$, $\langle a|Kb\rangle = \langle Ka|b\rangle^*$, $K\mathbf{p}K = -\mathbf{p}$ it follows that $\langle \mathbf{n}'|t(k)|\mathbf{n}\rangle = \langle \mathbf{n}'|Kt(k)^*K|\mathbf{n}\rangle = \langle -\mathbf{n}'|t(k)^*|-\mathbf{n}\rangle^* = \langle -\mathbf{n}|t(k)|-\mathbf{n}'\rangle$.
(iii) This proposition follows from $Pt(k)P = t(k)$ and $PpP = -p$. □

Example (3.6.22)

With the separable potential (3.6.9), $f(k; \mathbf{n}', \mathbf{n}) = 4\pi\lambda\rho^*(k\mathbf{n}')\rho(k\mathbf{n})D^{-1}(k)$. This satisfies (i), and invariance under Θ' means that $\rho^*(\mathbf{k}) = \rho(-\mathbf{k})$, which implies (ii). Invariance under P means that $\rho(\mathbf{k}) = \rho(-\mathbf{k})$, which implies (iii).

Remarks (3.6.23)

1. If $\mathbf{n} = \mathbf{n}'$, then (i) becomes the **optical theorem**, $\sigma_t(k) = 4\pi\ \mathrm{Im}\, f(k; \mathbf{n}, \mathbf{n})/k$. The information contained in the forward scattering amplitude includes the total scattering cross-section.

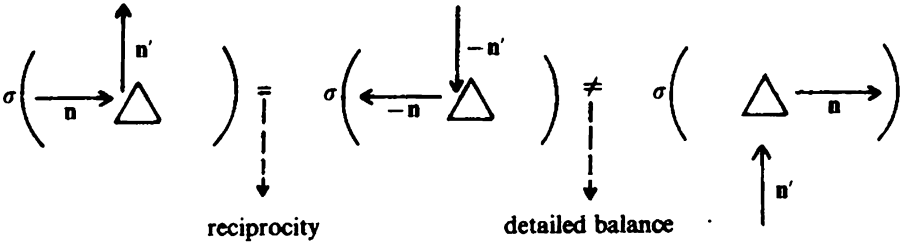


Figure 14 Scattering from a triangle.

2. Proposition (ii) goes by the name of **reciprocity**. It states that if there is invariance under Θ', then the reversed motion is also possible: $\sigma(k; \mathbf{n}', \mathbf{n}) = \sigma(k; -\mathbf{n}, -\mathbf{n}')$.
3. Propositions (iii) and (ii) together imply that $\sigma(k; \mathbf{n}', \mathbf{n}) = \sigma(k; \mathbf{n}, \mathbf{n}')$, which is referred to as **detailed balance**. It is not valid for scattering from targets that are not invariant under reflections (see Figure 14).
4. For radial potentials the expression for f in (3.6.10; 3) makes

$$\sigma_t = \sum_l \sigma_l, \qquad \sigma_l(k) = \frac{4\pi}{k^2}(2l + 1)\sin^2 \delta_l(k).$$

The total cross-section is the sum of the contributions of all possible definite angular momenta, each of which is maximized by the **unitarity bound**

$$\sigma_l \leq \frac{4\pi}{k^2}(2l + 1).$$

This bound is attained at a resonance; for instance, with

$$\exp(2i\delta_l) = \frac{k - k_0 + ib}{k - k_0 - ib}$$

the l contribution would be

$$\sigma_l = \frac{4\pi}{k^2}(2l + 1)\frac{b^2}{(k - k_0)^2 + b^2}.$$

This is four times the geometric area of a circular ring bounded by impact parameters $b_l = l/k$ and b_{l+1}:

$$\frac{4\pi}{k^2}(2l + 1) = 4\pi(b_{l+1}^2 - b_l^2).$$

The b_l are the distances out from the center of the target at which the particle has to be aimed in order to have angular momentum l with linear momentum k.

5. As $k \to 0$ the unitarity bound diverges, and σ_l may become infinite. Yet for most potentials δ_l goes as k^{2l+1} as $k \to 0$, so only $l = 0$ contributes to σ_t. In terms of the **scattering length** $a \equiv -\lim_{k\to 0} \delta_0(k)/k = -f(0; \mathbf{n}, \mathbf{n})$,

$$\lim_{k\to 0} \sigma_t(k) = 4\pi a^2.$$

6. In classical physics potentials that extend to infinity, such as r^{-n}, always produce infinite total cross-section, since no matter how large the impact parameter b is, there is always a nonzero scattering angle $\sim b^{-n}$. This is no longer the case in quantum theory when the potential decreases faster than r^{-2} (Problem 4). The classical argument breaks down because the indeterminacy in the scattering angle should go as b^{-1}, which eventually

dominates the classical scattering angle. This sort of reasoning can not, however, explain why the critical value should be $\eta_c = 2$; especially as it depends greatly on the dimension ($\eta_c = (1 + d)/2$).

7. Although S is a continuous function of V in the strong topology [8], f is not likewise continuous, since it involves matrix elements with plane waves, which are not square-integrable. It can thus happen that the forward scattering amplitude, and thus also σ_t, are finite for an r^{-2} potential cut off arbitrarily far away, but become infinite as the cut-off goes to infinity, even though the potentials are arbitrarily close in norm.

It remains to discuss how f can be calculated explicitly or, if that is impossible, how to assess the accuracy of approximations to it. If two particles interact through a radial potential, the problem is to solve an ordinary differential equation, and $\delta(k)$ can be found by numerical integration. When there are more particles, however, we are confronted with a nontrivial partial differential equation. It is therefore advisable to survey the more general methods that are available. In the absence of better ideas, one frequently falls back on a series expansion in V, called the Born approximation. The hope is that at high energies, for which the kinetic energy overwhelms the potential energy, the result becomes accurate. Whether the hope is fulfilled depends on an

Error Estimate for the Born Approximation (3.6.24)

Let $V \in L^1$, so $v_k \equiv |V|^{1/2} \exp(i\mathbf{k}\cdot\mathbf{x}) \in L^2$. The n-th Born Approximation $f^{(n)}$ to $f(k; \mathbf{n}', \mathbf{n})$,

$$-f^{(n)}(k; \mathbf{n}', \mathbf{n}) = 4\pi\langle v_{k'}|V|^{1/2}|V|^{-1/2}\sum_{m=0}^{n}(|V|^{1/2}|(k^2 - H_0)^{-1}V|^{1/2})^m|v_k\rangle$$

satisfies

$$|f(k; \mathbf{n}', \mathbf{n}) - f^{(n)}(k; \mathbf{n}', \mathbf{n})| \leq \frac{\|K\|^n}{1 - \|K\|}\int d^3x\,|V(\mathbf{x})|,$$

where $K = |V|^{1/2}(H_0 - k^2)^{-1}|V|^{1/2}$. Since

$$\|K\|^4 \leq (\mathrm{Tr}\, KK^*KK^*)$$

$$= \int\prod_{i=1}^{4}\frac{d^3x_i}{(4\pi)^4}V(\mathbf{x}_i)\frac{\exp(ik(|\mathbf{x}_1 - \mathbf{x}_2| - |\mathbf{x}_2 - \mathbf{x}_3| + |\mathbf{x}_3 - \mathbf{x}_4| - |\mathbf{x}_4 - \mathbf{x}_1|))}{|\mathbf{x}_1 - \mathbf{x}_2||\mathbf{x}_2 - \mathbf{x}_3||\mathbf{x}_3 - \mathbf{x}_4||\mathbf{x}_4 - \mathbf{x}_1|}$$

$$\equiv N(k)$$

goes to zero as $k \to \infty$ by the Riemann–Lebesgue lemma, for all $n \geq 1$ and $\varepsilon > 0$ there exists an energy great enough that $|f - f^{(n)}| < \varepsilon$.

Remark (3.6.25)

If $N(0) < 1$ and the sign of V does not change, then the Born approximation converges for all k, since $N(k) \leq N(0)$. This can only occur, however, when there are no bound states (see §3.5). In essence, the power-series expansion has a chance only if V is small or E large.

Example (3.6.26)

By setting $D(k)$ to 1 in (3.6.9), one gets the first Born approximation. If, say, $\rho(k) = M^2/(k^2 + M^2)$ as before, the function D becomes $1 + (\lambda/4\pi)M^2/(M - ik)$, so

$$|D|^2 - 1 = \frac{\lambda}{2\pi} \frac{M^3}{M^2 + k^2} \left(1 + \frac{\lambda M}{8\pi}\right).$$

When $\lambda M \gg 1$, the error is on the order of one percent for $k > M^2\lambda$.

If $H \geq 0$, it is straightforward to use the projection method (3.5.31) to obtain a fairly accurate upper bound for $t - V$ at $E = 0$ with the inequality $H^{-1} \geq P(PHP)^{-1}P$. If H has n bound states, then the correction to the first Born approximation may be positive, or even infinite, when there happens to be a bound state at $E = 0$. If the exact bound states were known exactly, the negative parts of H^{-1} could be projected out. If they are only approximately known, then the following lemma reduces the bound to the inversion of a finite-dimensional matrix:

Lemma (3.6.27)

Suppose that an invertible, Hermitian operator a has n negative eigenvalues, and is positive on the subspace perpendicular to their eigenvectors. For any n-dimensional projection P such that $Pa^{-1}P < 0$, $a \geq P(Pa^{-1}P)^{-1}P$.

Proof

If $\chi \in a^{-1}P\mathscr{H}$, then $\langle\chi|a|\chi\rangle = \langle\chi|P(Pa^{-1}P)^{-1}P|\chi\rangle$ follows trivially. If $\chi \notin a^{-1}P\mathscr{H}$ and Q is the projection onto $P\mathscr{H} \cup \{\chi\}$, then we must have $\text{Det } Qa^{-1}Q/\text{Det } Pa^{-1}P \geq 0$, as otherwise $Qa^{-1}Q$ would have $n + 1$ negative eigenvalues (since $Pa^{-1}P$ has n, $Qa^{-1}Q$ has at least n). This would contradict the hypothesis that a, and thus a^{-1}, have just n negative eigenvalues because of the min-max principle. Since by Problem 8 the ratio of the determinants is up to a positive constant equal to $\langle\chi|a|\chi\rangle - \langle\chi|P(Pa^{-1}P)^{-1}P|\chi\rangle$, the proposition follows. □

Corollary (3.6.28)

Let P be an n-dimensional projection. If $H \geq 0$, and PHP is invertible on $P\mathscr{H}$, then

$$\langle\chi|V - t|\chi\rangle \geq \langle\chi|VP(PHP)^{-1}PV|\chi\rangle.$$

If H has n negative eigenvalues, but is otherwise positive, then this equation is still true provided that $PHP < 0$.

Frequently one has intuitive feelings about what would constitute a good approximation to t. These beliefs can be tested with

Kohn's Variational Principle (3.6.29)

Let V_t be a comparison potential for which it is possible to calculate $t_t \equiv V_t - V_t(H_0 + V_t - E)^{-1}V_t \equiv V_t\Omega_t$. This differs from the exact t as follows:

$$t(k) = t_t(k) + \Omega_t^*(k)(V - V_t)\Omega_t(k) - \Omega_t^*(k)(V - V_t)(H - k^2)^{-1}(V - V_t)\Omega_t(k).$$

Remarks (3.6.30)

1. The operator identity (3.6.29) is easy to verify. Its advantage is that the first correction can be calculated when the problem has been solved with V_t, and only the second involves the resolvent of H. Since the second term is quadratic in $(V - V_t)$, there is hope that a good choice of V_t makes it small.
2. If it is known that H is positive aside from n bound states, then (3.6.27) can be used in the last term for $k = 0$, to produce an upper bound for the scattering length. If $V_t = 0$, $\Omega_t = \mathbf{1}$, then it agrees with (3.6.28), which shows that (3.6.28) can be improved on with a superior choice of V_t. If $V \geq 0$, then $0 \leq H_0 \leq H$, so $1/H \leq 1/H_0$, from which we also obtain a lower bound.

Example (3.6.31)

Let $|\ \rangle = 1$ be the vector (of L^∞, not L^2) of a plane wave with $\mathbf{k} = \mathbf{0}$, and let V be such that all inner products of the form

$$b_n = \left\langle \left| \underbrace{V\frac{1}{H_0}V\frac{1}{H_0}\cdots V}_{n} \right| \right\rangle$$

exist and $H > 0$. Substituting $|\chi\rangle = |\ \rangle, P = H_0^{-1}V|\ \rangle\langle|\ VH_0^{-2}V|\ \rangle^{-1}\langle|\ VH_0^{-1}$ into (3.6.28), we discover that $\langle|\ t(0)|\ \rangle \leq b_1 - b_2^2/(b_2 + b_3)$. If V is approxi-

mated with the separable potential $V_t \equiv V|\rangle\langle|V|\rangle^{-1}\langle|V$, so that $(V - V_t)|\rangle = 0$, then from (3.6.3),

$$\Omega_t(0) = 1 - (b_1 + b_2)^{-1} \frac{1}{H_0} V|\rangle\langle|V,$$

$$\langle|t_t|\rangle = \frac{b_1^2}{b_1 + b_2},$$

$$(V_t - V)\Omega_t(0)|\rangle = \frac{b_1}{b_1 + b_2} V \frac{1}{H_0} V|\rangle - \frac{b_2}{b_1 + b_2} V|\rangle,$$

$$\langle|\Omega_t^*(0)(V - V_t)\Omega_t(0)|\rangle = \frac{b_1^2 b_3 - b_1 b_2^2}{(b_1 + b_2)^2}.$$

In Problem 7 it is shown that the upper bound

$$\begin{aligned}\langle|t|\rangle &\le \langle|t_t|\rangle + \langle|\Omega_t^*(0)(V - V_t)\Omega_t(0)|\rangle \\ &\quad - |\langle|\Omega_t^*(0)(V - V_t)\frac{1}{H_0} V|\rangle|^2 \langle|V \frac{1}{H_0} V + V \frac{1}{H_0} V \frac{1}{H_0} V|\rangle^{-1} \\ &= \frac{b_1^2}{b_1 + b_2} - \frac{(b_2^2 - b_3 b_1)b_1}{(b_1 + b_2)^2} - \frac{(b_1 b_3 - b_2^2)^2}{(b_2 + b_3)(b_1 + b_2)^2}\end{aligned}$$

is valid provided that $H > 0$. If V is also > 0, then there is a complementary lower bound (cf. (3.6.30; 2),

$$\begin{aligned}&\frac{b_1}{b_1 + b_2} - \frac{(b_2^2 - b_3 b_1)b_1 + b_2^3 - 2b_1 b_2 b_3 + b_1^2 b_4}{(b_1 + b_2)^2} \\ &\quad = \langle|t_t|\rangle + \langle|\Omega_t^*(0)(V - V_t)\Omega_t(0)|\rangle \\ &\quad = \langle|\Omega_t^*(0)(V - V_t)H_0^{-1}(V - V_t)\Omega_t(0)|\rangle \le \langle|t_t|\rangle.\end{aligned}$$

These inequalities hold as well for potentials that do not lend themselves easily to analytical or numerical methods. If V is specialized to the radial case, say $V = \alpha$ if $r < 1$ and otherwise 0, then $\langle|t|\rangle$ can be calculated as $1 - \alpha^{-1/2}\tanh(\alpha^{1/2})$ (Problem 5), which allows the calculation of all the b_n and thereby the bounds. At the radius of convergence $\alpha = \pi^2/4$ of the Born approximation the accuracy is still measured in $\%_{00}$, and they are acceptable well beyond that point (see Figure 15).

Problems (3.6.32)

1. Show that $V(t) \to V \Rightarrow V = \text{s-lim}_{\varepsilon \downarrow 0} \varepsilon \int_0^\infty \exp(-\varepsilon t)V(t)dt$.

2. Show that $w\text{-lim}_{R\to\infty} \int_{-\infty}^0 dt\, t_t^0(\Omega_-^* \chi_R \Omega_- - \chi_R) = 0$, if $\|\int_{-\infty}^0 dt(\exp(-iHt)\Omega_- - \exp(-iH_0 t))\varphi\| < \infty$ for all φ, on a dense set ($\chi_R = \Theta(R^2 - |\mathbf{x}|^2)$). Use the result to show that (iii) $\Leftrightarrow$ (iv) in (3.6.17).

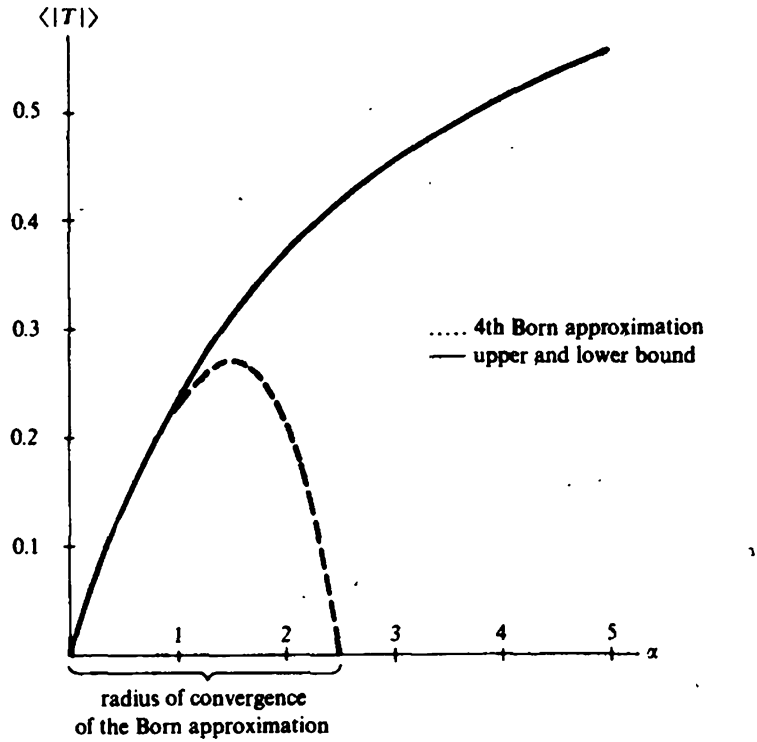


Figure 15 Bounds and approximation for the scattering length of a spherical square-well potential.

3. Let $s\text{-}\lim_{t\to\pm\infty}\mathbf{p}_t = \mathbf{p}_\pm$ (in the sense of (2.5.8; 3)). Show that $s\text{-}\lim_{t\to\pm\infty}\mathbf{x}(t)/|\mathbf{x}(t)| = \pm\mathbf{p}_\pm/|\mathbf{p}_\pm|$, and conclude that $\lim_{t\to\pm\infty}\Delta(\mathbf{x}(t)/|\mathbf{x}(t)|) = \Delta(\mathbf{p}_\pm/|\mathbf{p}_\pm|)$.

4. Suppose that as $r \to \infty$, the potential V goes as $\lambda r^{-2-\varepsilon}$, $\varepsilon > 0$. Show that if $k \neq 0$ and λ is within the radius of convergence of the Born approximation, then $\sigma_t < \infty$. (Since σ_t can be infinite only because of the sum over l, and the Born approximation becomes exact for large l, the statement actually holds for all larger λ as well. If $V = \lambda/r^2$, $\delta_l \sim \sqrt{l^2+\lambda} - l \sim \lambda/l$ and $\sum_l (2l+1)\sin^2\delta_l \sim \sum_l 1/l$ diverges logarithmically.)

5. Calculate the scattering length for the potential $V(r) = \lambda\Theta(1-r)$. (Write $\psi(\mathbf{x}) = (u_l(r)/r)Y_l^m$, $u(0) = 0$.)

6. Calculate the normalization factors of the scattering amplitude in (3.6.10; 3).

7. Derive the upper bound of (3.6.31).

8. Let Q be the projection onto $P\mathscr{H} \oplus \psi$, $\psi \perp P\mathscr{H}$. Show that $\mathrm{Det}\, QbQ = (\langle\psi|b|\psi\rangle - \langle\psi|bP(PbP)^{-1}Pb\psi\rangle)\mathrm{Det}\, PbP$, and use this fact to fill in the gap in the proof of (3.6.27).

9. Calculate the generator $\delta(E, L)$ for the classical scattering transformation (I: 3.4.10; 2) for the potential γ/r^2, and compare with the phase-shift $\delta_l(E)$. What is the delay time D?

Solutions (3.6.33)

1. If $\delta > 0$, there exists a τ such that $\|(V - V(t))\psi\| \leq \delta$ when $t \geq \tau$, so $\varepsilon \int_0^\infty \exp(-\varepsilon t) \times V(t)dt = \varepsilon \int_0^\tau \exp(-\varepsilon t)V(t)dt + \varepsilon \int_\tau^\infty \exp(-\varepsilon t)(V(t) - V)dt + \varepsilon \int_\tau^\infty \exp(-\varepsilon t)V\,dt$, and the first integral $\to 0$ as $\varepsilon \downarrow 0$, the third equals V, and the second is bounded by $\limsup_{\varepsilon \downarrow 0} \varepsilon\|\int \cdots \psi\| \leq \delta$.

2. Let $\psi_t = \exp(-iHt)\Omega_-\varphi$ and $\varphi_t = \exp(-iH_0t)\varphi$. It must first be verified that the expectation value with the state φ is integrable in time: $|\langle\psi_t|\chi_R\psi_t\rangle - \langle\varphi_t|\chi_R\varphi_t\rangle| \leq |\langle(\psi_t - \varphi_t)|\chi_R\varphi_t\rangle| + |\langle\psi_t|\chi_R(\varphi_t - \psi_t)\rangle| \leq 2\|\psi_t - \varphi_t\|$, so by assumption the integral $\int_{-\infty}^0 dt$ is bounded, and indeed uniformly in R. By the dominated convergence lemma, we may then interchange the integration $\int_{-\infty}^0 dt$ and the limit $R \to \infty$, and the latter yields zero, since $\chi_R \to \mathbf{1} = \Omega_-^*\Omega_-$.

   Derivation of the formula for D. The equations $\Omega_+ S = \Omega_-$ and $\tau_t^0 S = S$ can be used to rewrite D_R, with $D = \lim_{R\to\infty} D_R$, as

$$D_R = \int_0^\infty dt\, \tau_t^0[S^{-1}\chi_R S - \chi_R] + \int_{-\infty}^0 dt\, \tau_t^0[\Omega^*\chi_R\Omega_- - \chi_R]$$

$$+ S^{-1}\int_0^\infty dt\, \tau_t^0[\Omega_+^*\chi_R\Omega_+ - \chi_R]S.$$

   As a consequence of the previous result, the last two summands approach 0 weakly as $R \to \infty$. For the first integral we use the Fourier transform $\tilde{S}(t)$ of $S(E)$, the part of S on the energy shell, and write

$$S = \int dt\, \tilde{S}(t)\exp(itH_0), \qquad [\tilde{S}(t), H_0] = 0.$$

   The last integral then becomes

$$S^{-1}\int_0^\infty dt \int_{-\infty}^\infty dt'[\tau_t^0\chi_R \exp(it'H_0)\tilde{S}(t') - \tilde{S}(t')\tau_t^0 \exp(it'H_0)\chi_R]$$

$$= S^{-1}\int_0^\infty dt \int_{-\infty}^\infty dt'[\tau_t^0\chi_R\tilde{S}(t') - \tilde{S}(t')\tau_{t+t'}^0\chi_R]\exp(it'H_0)$$

$$= S^{-1}\int_0^\infty dt \int_{-\infty}^\infty dt'[\tau_t^0\chi_R, \tilde{S}(t')]\exp(it'H_0)$$

$$+ S^{-1}\int_{-\infty}^\infty dt' \int_0^{t'} dt\, \tilde{S}(t')\tau_t^0\chi_R \exp(it'H_0).$$

   In the limit as $R \to \infty$, χ_R approaches 1 strongly, so the first term goes to 0 and the last approaches

$$S^{-1}\int_{-\infty}^\infty dt'\, t'\tilde{S}(t')\exp(it'H_0) = -iS^{-1}\int_0^\infty dE\, \delta(H_0 - E)\frac{\partial S(E)}{\partial E}.$$

3. By assumption,

$$\frac{\mathbf{x}(t)}{t} = \frac{\mathbf{x}(0)}{t} + \frac{1}{t}\int_0^t dt'\, \mathbf{p}(t')$$

converges strongly to $\mathbf{p}_\pm$, since $s\text{-lim}_{t\to\infty} a/t = 0$ for every self-adjoint operator a, and by Problem 1 the second term is $\mathbf{p}_\pm$. Hence the bounded functions $\mathbf{x}(t)/|\mathbf{x}(t)|$ converge strongly, which implies the convergence of the mean-square deviation of bounded functions: $a_n \to a \Rightarrow \langle|a_n^2|\rangle = \|a_n|\rangle\|^2 \to \|a|\rangle\|^2 = \langle|a^2|\rangle$.

4. By (3.6.24) we know that $|f| < c|f^{(0)}|$ in the circle of convergence, so it suffices to show that the total cross-section is finite in the Born approximation. This is

$$\langle\exp(i\mathbf{k}\cdot\mathbf{x})|V\,\delta(H_0 - k^2)V|\exp(i\mathbf{k}\cdot\mathbf{x})\rangle = \int\frac{d^3p}{(2\pi)^3}|\tilde{V}(\mathbf{p}-\mathbf{k})|^2\,\delta(|\mathbf{p}|^2 - k^2).$$

Since $\tilde{V} \sim |\mathbf{p}-\mathbf{k}|^{-1+\varepsilon}$, the angular part of the integral is finite (cf. (3.4.13; 2)).

5. The solution of the Schrödinger equation

$$\left(-\frac{\partial^2}{\partial r^2} + V(r)\right)u(r) = 0: u(r) = \begin{cases} (\sqrt{\lambda}\cosh\sqrt{\lambda})^{-1}\sinh\sqrt{\lambda}r & r \le 1 \\ r + \dfrac{\tanh\sqrt{\lambda}}{\sqrt{\lambda}} - 1 & r \ge 1 \end{cases}$$

has to be compared with $\lim_{k\to 0}(1/k)\sin(kr + \delta(k))$ when $r > 1$. The result is that $a \equiv -\lim_{k\to 0}\delta(k)/k = 1 - \tanh(\sqrt{\lambda})/\sqrt{\lambda}$.

6. We have

$$-2\pi i\int_0^\infty\frac{p'^2\,dp'}{(2\pi)^3}\,\delta(p'^2 - p^2)\langle n'|t|n\rangle = -\frac{2pi}{4\pi}\frac{\langle n'|t|n\rangle}{4\pi}$$
$$= \sum_l\langle n'|P_l|n\rangle(\exp(2i\,\delta_l) - 1).$$

By the addition theorem for the spherical harmonics,

$$\langle n'|P_l|n\rangle = \sum_m Y_l^{-m}(n')Y_l^m(n) = \frac{2l+1}{4\pi}P_l(\cos\theta),$$

so

$$f = \frac{\langle n'|t|n\rangle}{-4\pi} = \sum_l\frac{2l+1}{k}\exp(i\,\delta_l)\sin\delta_l P_l(\cos\theta).$$

7. $H^{-1} \ge P(PHP)^{-1}P$ and $P = H_0^{-1}V|\rangle\langle|VH_0^{-1}(\langle|VH_0^{-2}V|\rangle)^{-1}$ together imply $\langle|\Omega_t^*(0)(V - V_t)H^{-1}(V - V_t)\Omega_t(0)|\rangle \ge |\langle|\Omega_t^*(0)(V - V_t)H_0^{-1}V|\rangle|^2$
$$\times\langle|VH_0^{-1}(H_0 + V)H_0^{-1}V|\rangle^{-1}.$$

8. $(\text{Det } QbQ)^{-1/2} = \pi^{-(n+1)/2}\int\prod_{i=0}^n dx_i\exp(-\sum_{i,j=0}^n x_i x_j b_{ij})$, $n = \text{Dim } P$, $b_{00} = \langle\psi|b|\psi\rangle$. With the integration variables $\bar{x}_k = x_k + x_0 b_{0j}c_{jk}$, $k = 1,\ldots,n$, $c = (PbP)^{-1}$,

$$\sum_{i,j=0}^n x_i x_j b_{ij} = \sum_{k,l=1}^n\bar{x}_k\bar{x}_l b_{kl} + x_0^2(b_{00} - b_{0k}c_{kl}b_{l0}).$$

The relationship between the determinants results from integration over x_0 and the $\bar{x}_k$. If ψ is not orthogonal to $P\mathscr{H}$, the ratio is simply changed by a positive factor, since $\text{Det } M'bM = \text{Det } b(\text{Det } M)^2$. The proposition then follows with $b = a^{-1}$ and $\psi = a\chi$.

9. $\delta(E, L) = L - \sqrt{L^2 + 2\gamma}$, $(2/\pi)\delta_l = l + \frac{1}{2} - \sqrt{(l+\frac{1}{2})^2 + 2\gamma} \Rightarrow D = 0$.

Atomic Systems 4

4.1 The Hydrogen Atom

The hydrogen atom is so simple that a complete mathematical analysis can be made. This analysis was a watershed of atomic physics.

The quantum-mechanical treatment of the problem of two particles interacting through a $1/r$ potential follows the outlines of the classical theory (I: §4.2). It starts with the Hamiltonian

$$H = \frac{|\mathbf{p}_1|^2}{2m_1} + \frac{|\mathbf{p}_2|^2}{2m_2} + \frac{\alpha}{|\mathbf{x}_1 - \mathbf{x}_2|}, \qquad \alpha = e_1 e_2, \tag{4.1.1}$$

which acts a priori on $\mathscr{H} = \mathscr{H}_1 \otimes \mathscr{H}_2$, where $\mathscr{H}_i$ is the Hilbert space of the i-th particle. The system can be decomposed into two independent parts by the

Separation into Center-of-Mass and Relative Coordinates (4.1.2)

The unitary transformation

$$(\mathbf{x}_1, \mathbf{x}_2; \mathbf{p}_1, \mathbf{p}_2) \to (\mathbf{x}_{cm}, \mathbf{x}; \mathbf{p}_{cm}, \mathbf{p}),$$

$$\mathbf{x}_{cm} = \frac{m_1\mathbf{x}_1 + m_2\mathbf{x}_2}{m_1 + m_2}, \qquad \mathbf{x} = \mathbf{x}_1 - \mathbf{x}_2; \qquad \mathbf{p}_{cm} = \mathbf{p}_1 + \mathbf{p}_2;$$

$$\mathbf{p} = \frac{\mathbf{p}_1 m_2 - \mathbf{p}_2 m_1}{m_1 + m_2},$$

changes H into $H = H_{cm} + H_r$, where

$$H_{cm} = \frac{|\mathbf{p}_{cm}|^2}{2M}, \qquad H_r = \frac{|\mathbf{p}|^2}{2m} + \frac{\alpha}{|\mathbf{x}|}, \qquad M = m_1 + m_2, \qquad m = \frac{m_1 m_2}{m_1 + m_2},$$

Remarks (4.1.3)

1. The Hilbert space can also be written as $\mathscr{H} = \mathscr{H}_{cm} \otimes \mathscr{H}_r$, where the operators H_{cm} and H_r act nontrivially only on the factors $\mathscr{H}_{cm}$ and respectively $\mathscr{H}_r$.
2. The question of self-adjointness is answered by (3.3.4; 1) and (3.4.25; 2): Since $1/r$ is compact relative to $|\mathbf{p}|^2$, H_r is self-adjoint on $D(|\mathbf{p}|^2)$, and $\sigma_{ess}(H_r) = \mathbb{R}^+$.
3. The operator H_{cm} generates the free motion of the center of mass. The invariance group is similar to that of the classical situation: The ten generators of the Galilean group, H_{cm}, $\mathbf{p}_{cm}$, $\mathbf{k}_{cm} \equiv \mathbf{p}_{cm} t - \mathbf{x}_{cm} M$, and $\mathbf{L}_{cm} = [\mathbf{x}_{cm} \times \mathbf{p}_{cm}]$, do not form a Lie algebra, since $[p_l, k_j] = i\,\delta_{lj} \cdot M$ is not a linear combination of them. If M is considered as an additional element of the algebra of observables, then there is an 11-dimensional Lie algebra $\mathscr{A}$. The center $\mathscr{A}' \cap \mathscr{A}''$, which consists of the functions of M alone, creates a superselection rule (see (2.3.6; 7)), unless M is represented as a multiple of 1. As in (I: 4.1.10; 3), the Galilean group is the factor group by the center, and $\mathscr{A}$ produces only a ray representation of it. This happens because $\mathbf{p}_{cm}$ and $\mathbf{k}_{cm}$ of course generate the transformations $\mathbf{x}_{cm} \to \mathbf{x}_{cm} + \mathbf{a} + \mathbf{v}t$ and $\mathbf{p}_{cm} \to \mathbf{p}_{cm} + M\mathbf{v}$ on $\mathbb{R}^6$, and, according to (3.1.6; 5), the unitary operators $W(z)$ give only a ray representation of $\mathbb{R}^6$. This means that although

$$\exp(i\mathbf{v} \cdot \mathbf{k}_{cm}) = \exp\left(\frac{-itM|\mathbf{v}|^2}{2}\right)\exp(-i\mathbf{x}_{cm} \cdot \mathbf{v}M)\exp(i\mathbf{p}_{cm} \cdot \mathbf{v}t)$$

causes the transformation $\mathbf{x}_{cm} \to \mathbf{x}_{cm} + \mathbf{v}t$, $\mathbf{p}_{cm} \to \mathbf{p}_{cm} + M\mathbf{v}$, the wavefunction gains an additional phase factor $\exp(-itM|\mathbf{v}|^2/2)$, which is, however, not observable, since only relative phases can be measured.

The Hamiltonian H_{cm} was discussed in detail in (3.3.3), so we turn to H_r. The first fact we know is that $\sigma(H_{cm}) = \sigma_{ess}(H_r) = \mathbb{R}^+$, and the question arises of whether $\sigma_p(H_r) \subset \mathbb{R}^-$ (recall (3.4.14; 4)). This is answered by the

Virial Theorem (4.1.4)

If $(H_r - E)\psi = 0$, $\psi \in \mathscr{H}_r$, *then*

$$E = \frac{1}{2}\left\langle \psi \middle| \frac{\alpha}{r}\psi \right\rangle = -\langle \psi | H_0 \psi \rangle.$$

Proof

The dilatation U such that $U^{-1}(\beta)(\mathbf{x}, \mathbf{p})U(\beta) = (\exp(\beta)\mathbf{x}, \exp(-\beta)\mathbf{p})$, $\beta \in \mathbb{R}$, which was used in (3.3.8; 2), acts on H_r by $U^{-1}(\beta)H_r U(\beta) = \exp(-2\beta)H_0 + \exp(-\beta)\alpha/r$, where $H_0 = |\mathbf{p}|^2/2m$. The equations

$$\left\langle \left(\exp(2\beta)H_0 + \exp(\beta)\frac{\alpha}{r} - E\right)\psi \middle| U(\beta)\psi \right\rangle = 0 = \left\langle \left(H_0 + \frac{\alpha}{r} - E\right)\psi \middle| U(\beta)\psi \right\rangle$$

can be combined so that

$$-\left\langle \left(\frac{1 - \exp(2\beta)}{\beta}H_0 + \frac{1 - \exp(\beta)}{\beta}\frac{\alpha}{r}\right)\psi \middle| U(\beta)\psi \right\rangle = 0 \qquad \text{for all } \beta \in \mathbb{R}\setminus\{0\}.$$

As $\beta \to 0$, the left side converges to $(2H_0 + \alpha/r)\psi$ and the right to ψ. Since the convergence is in the strong sense, this proves (4.1.4). □

Corollary (4.1.5)

Since $H_0 \geq 0$, if $\alpha < 0$, then all the eigenvalues of H_r are negative, and if $\alpha \geq 0$, then it has no eigenvalues.

Remarks (4.1.6)

1. The usual argument, which runs that $0 = \langle\psi|i[H_r, \mathbf{x}\cdot\mathbf{p}]\psi\rangle = \langle\psi|2H_0 + \alpha/r|\psi\rangle$ is not quite conclusive, since $D(\mathbf{x}\cdot\mathbf{p}) \not\supset D(H_r)$, and a priori it applies only to $\psi \in D(H_r) \cap D(\mathbf{x}\cdot\mathbf{p})$.
2. The analytic perturbation theory of §3.5 works without modification for the negative eigenvalues. Thus an alternative argument using (3.5.19; 2) would run: On dimensional grounds $E(\alpha) = m\alpha^2 c$ for some numerical constant c, and hence $\alpha\,\partial E/\partial\alpha = \langle\alpha/r\rangle = 2E$.
3. The action of the dilatation also shows that if $\alpha < 0$, then there must be infinitely many eigenvalues accumulating at the point 0; given any $\psi \in D(H_r)$, there exists $\tau_0 \in \mathbb{R}^+$ such that

$$\langle U(\tau_0)\psi | H_r U(\tau_0)\psi\rangle$$
$$= \exp(-2\tau_0)\left\langle \psi \middle| \frac{|\mathbf{p}|^2}{2m}\psi \right\rangle + \alpha\exp(-\tau_0)\left\langle \psi \middle| \frac{1}{r}\psi \right\rangle < 0.$$

If ψ is compactly supported, then there exists a sequence $\tau_0 < \tau_1 < \tau_2 \ldots$, for which the supports of $U(\tau_i)\psi$ are disjoint, so H_r is a diagonal matrix on the subspace spanned by the vectors $U(\tau_i)\psi$. The claim then follows from the min-max principle (3.5.21).

The next topic will be $\sigma_p(H_r)$, and the last part of this section will be devoted to $\sigma_{ess}(H_r)$. Both discussions will make use of

Constants of the Motion (4.1.7)

The commutant $\{H_r\}'$ *contains the vectors* $\mathbf{L}$ *and* $\mathbf{F} = \frac{1}{2}[\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p}] + m\alpha\mathbf{x}/r$. *They are related by*

(i) $[H, L_m] = 0, [L_m, F_l] = i\varepsilon_{mls}F_s$,
(ii) $[H, F_m] = 0, [F_m, F_l] = -2imH_r\varepsilon_{mls}L_s$,
(iii) $\mathbf{L} \cdot \mathbf{F} = \mathbf{F} \cdot \mathbf{L} = 0$,
(iv) $|\mathbf{F}|^2 = 2mH_r(|\mathbf{L}|^2 + 1) + m^2\alpha^2$.

Proof

(i) This is because H acts as a scalar and $\mathbf{F}$ as a vector under rotations.
(ii) This is somewhat more subtle; the example of Problem (3.1.17; 4) leaves doubts as to how to proceed. The equation $[H, F_m] = 0$ has to hold on domains that are invariant under finite transformations to show that $[\exp(iHt), \exp(iFs)] = 0$ (recall Definition (3.1.7)). Actually, by Problem 1 it suffices to show that $(d/dt)\exp(iHt)F\exp(-iHt) = 0$, which will be done in Problem 2. The calculation of commutators involving $\mathbf{F}$ is often easier when it is written as $\mathbf{F} = (i/2)[\mathbf{p}, |\mathbf{L}|^2] + m\alpha\mathbf{x}/r$.
(iii) It is clear that $\mathbf{L} \cdot \mathbf{x} = \mathbf{L} \cdot \mathbf{p} = 0$, since there are no products of non-commuting observables. With (i) this implies (iii).
(iv) This requires some calculations, done in Problem 3. □

Corollary (4.1.8)

Special combinations of $\mathbf{L}$ and $\mathbf{F}$, namely $A_k = (L_k + F_k/\sqrt{-2mH_r})P/2$ and $B_k = (L_k - F_k/\sqrt{-2mH_r})P/2$, where $P \equiv \Theta(-H_r)$ is the projection onto the functions of the negative spectrum of H_r, satisfy the commutation relations of two independent angular momenta:

$$[A_k, A_j] = i\varepsilon_{kjm}A_m, \qquad [B_k, B_j] = i\varepsilon_{kjm}B_m, \qquad [A_k, B_j] = 0.$$

They are, however, not independent, as

$$|\mathbf{A}|^2 = |\mathbf{B}|^2 = -P\left(\frac{1}{4} + \frac{m\alpha^2}{8H_r}\right). \tag{4.1.9}$$

According to the discussion of §3.2, $|\mathbf{A}|^2$ and $|\mathbf{B}|^2$ can have only the eigenvalues $\beta(\beta + 1)$, $\beta = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$, and by (4.1.9) their eigenvalues are the same. Each eigenvector belongs to a $(2\beta + 1)^2$-fold degenerate **supermultiplet**, the members of which have the same eigenvalue for $|\mathbf{A}|^2$ and $|\mathbf{B}|^2$,

but differ in their eigenvalues for A_z and B_z. They are eigenvectors of H_r, and by (4.1.9) its eigenvalues obey **Balmer's formula,**

$$E_n = -\frac{m\alpha^2}{2n^2}, \qquad n = 2\beta + 1 = 1, 2, 3 \ldots . \tag{4.1.10}$$

Remarks (4.1.11)

1. The operators **A** and **B** each satisfy the Lie algebra of O(3), which is identical to that of SU(2). As there is no reason that only the representations of O(3) should arise, the values of β may be either integral or half-odd integral.
2. Of course, **L** generates the algebra O(3) and has eigenvalues $l(l+1)$, l integral. If the eigenvalues of $|\mathbf{F}|^2$ in (4.1.7(iv)) are expressed in terms of n and l,

$$|\mathbf{F}|^2|\rangle = m^2\alpha^2\left(1 - \frac{l^2 + l + 1}{n^2}\right)|\rangle,$$

then it is apparent that $l \leq n - 1$. Hence for a given n, the values l can assume are $0, 1, \ldots, n-1$.

3. Balmer's formula shows why

$$K \equiv \frac{1}{\sqrt{r}}(H_0 - z)^{-1}\frac{1}{\sqrt{r}}, \qquad z \notin \mathbb{R}^+,$$

belongs to C_p (2.3.21) for p integral only if $p \geq 4$: As we saw in the proof of (3.5.36), if $z \in \mathbb{R}^-$, then the eigenvalues λ_n of K are the values of $1/|\alpha|$ for which $H_0 - |\alpha|/r$ has the eigenvalue z. That being so, (4.1.10) makes $-z\lambda_n^2 = m/(2n^2)$, and the n-th eigenvalue has degeneracy n^2. But then

$$\|K\|_p^p = \sum_{n=1}^{\infty} n^2\lambda_n^p$$

for p integral is finite only for $p \geq 4$.

Construction of the Eigenvectors of H_r (4.1.12)

Since there is no difference in the algebraic situation, we can proceed as with the eigenvectors of the angular momentum (3.2.13). In each supermultiplet there is a state $|\rangle$ of greatest A_3 and B_3, so

$$A_+|\rangle = B_+|\rangle = 0 \Leftrightarrow F_+|\rangle = L_+|\rangle = 0, \quad F_\pm \equiv F_1 \pm iF_2, \text{ etc.} \tag{4.1.13}$$

The other states are then obtained by applications of $A_-^p B_-^q$, $0 \leq p, q \leq n-1$. Since F_+ is constructed with x_+, p_+,† and observables that commute with

† These should be distinguished from the $\mathbf{x}_\pm$, $\mathbf{p}_\pm$, etc. of (3.4.6).

$|\mathbf{L}|^2$, it raises l by 1 (cf. (3.2.14)); thus if $F_+|\rangle = 0$, then $|\rangle$ already has the greatest angular momentum possible in the supermultiplet. If an eigenvector $|n, l, m\rangle$ is specified by its eigenvalues for H_r, $|\mathbf{L}|^2$, and L_3, then the original basis state is $|\rangle \equiv |n, n-1, n-1\rangle$, and $|n, l, m\rangle = L_-^{l-m} F_-^{n-1-l}|\rangle$.

Eigenfunctions in the x-Representation (4.1.14)

If we write

$$F_+ = \frac{i}{2}(p_+|\mathbf{L}|^2 - |\mathbf{L}|^2 p_+) + \frac{m\alpha x_+}{r}$$

and calculate the action of p_+ and x_+ on the eigenvectors (up to a constant—see Problem 4),

$$ip_+|n, l, l\rangle = \left(\frac{d}{dr} - \frac{l}{r}\right)|n, l+1, l+1\rangle,$$

$$\frac{x_+}{r}|n, l, l\rangle = |n, l+1, l+1\rangle,$$

then Equation (4.1.13) becomes

$$F_+|n, n-1, n-1\rangle = \left(-n\left(\frac{d}{dr} - \frac{n-1}{r}\right) + m\alpha\right)|n, n-1, n-1\rangle = 0.$$

The solution is

$$|n, n-1, n-1\rangle = cr^{n-1}\exp(m\alpha r/n)Y_{n-1}^{n-1}(\theta, \varphi),$$

which is in $L^2((0, \infty), r^2\,dr) \otimes L^2(S^2)$ when $\alpha < 0$, and is the original basis vector of the supermultiplet.

Remarks (4.1.15)

1. The vector $|n, n-1, n-1\rangle$ has the maximal angular momentum and is related to a classical circular orbit, whereas $|n, 0, 0\rangle$ corresponds to a classical trajectory through the origin. However, in quantum theory the latter vector is a spherically symmetric wave-function, since it distinguishes no direction.
2. The wave-function $|n, n-1, n-1\rangle$ decreases in r as $\exp(-r/nr_b)$, where $r_b = 1/|m\alpha| = 0.529 \times 10^{-10}$ m., but its maximum is attained at $r = n(n-1)r_b$. This is in accordance with the rough estimate (1.2.3) and the virial theorem, which requires that $\langle 1/r\rangle \sim n^{-2}$.
3. A calculation of the expectation values yields

$$\langle n, n-1, m|r|n, n-1, m\rangle = r_b n(n+\tfrac{1}{2}),$$

$$\langle n, n-1, m|r^2|n, n-1, m\rangle = r_b^2 n^2(n+\tfrac{1}{2})(n+1),$$

which reveals that the relative mean-square deviation $\Delta r/\langle r\rangle = 1/\sqrt{2n+1}$ vanishes in the limit $n \to \infty$. The state $|n, n-1, n-1\rangle$ gets concentrated ever more strongly on a circle in the $x-y$-plane.

4. States of smaller l, and hence greater eccentricity, can be produced by successive applications of F_- to $|n, n-1, n-1\rangle$ as in (4.1.12), and an example is computed in Problem 5.

We conclude the discussion of σ_p here and turn to σ_{ess}. We begin with the basic fact about this part of the spectrum.

The Absence of Singular Spectrum (4.1.16)

$$\sigma_{sing}(H_r) = \varnothing, \text{ so } \sigma_{ac}(H_r) = \sigma_{ess}(H_r) = \mathbb{R}^+.$$

Proof

If the dilatation used in the virial theorem (4.1.4) is continued into the complex plane, then $U(\tau)$, $\tau \in \mathbb{C}$, becomes unbounded, but is still defined on the dense set D of analytic vectors (see (2.4.23; 5)). The action of U on H_r can be continued analytically, and

$$\langle\varphi|(H_r - z)^{-1}\psi\rangle = \left\langle U(\tau^*)\varphi\middle|\left(\exp(2\tau)H_0 + \exp(\tau)\frac{\alpha}{r} - z\right)^{-1}U(\tau)\psi\right\rangle,$$

for

$$\tau \in \mathbb{C},\ \varphi, \psi \in D.$$

Since multiplication by the complex number e^τ does not affect the relative compactness of α/r, we conclude that

$$\sigma_{ess}\left(\exp(2\tau)H_0 + \exp(\tau)\frac{\alpha}{r}\right) = \sigma_{ess}(\exp(2\tau)H_0) = \exp(2\tau)\mathbb{R}^+.$$

The matrix elements of the resolvent in states $\varphi, \psi \in D$ can thus be continued analytically from $\mathbb{R}^+$ into the complex plane as far as $e^{2\tau}\mathbb{R}^+$, the rotated positive axis (see Figure 16):

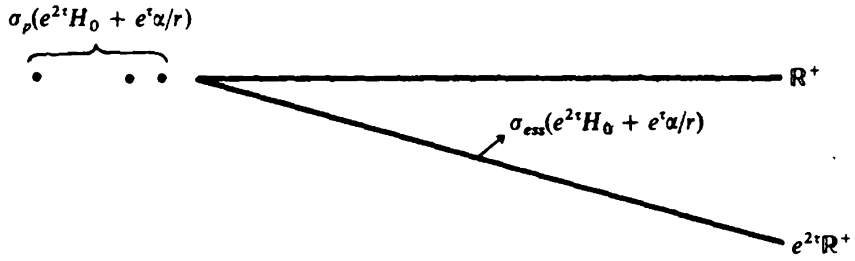


Figure 16 Spectrum of the dilated Hamiltonian.

This implies the absence of σ_{sing}, since

$$\langle\varphi|(\Theta(H_\tau - a) - \Theta(H_\tau - b))\psi\rangle$$
$$= \lim_{\varepsilon\to 0}\int_a^b \frac{dz}{2\pi i}\langle\varphi|((H_\tau - z - i\varepsilon)^{-1} - (H_\tau - z + i\varepsilon)^{-1})\psi\rangle,$$

$a, b > 0$, is the integral of an analytic function and thus approaches 0 as $a \to b$. Since D is dense, σ_{ess} contains no part concentrated on a set of Lebesgue measure 0. □

Remarks (4.1.17)

1. Only the matrix elements with φ and $\psi \in D$ can be continued beyond $\mathbb{R}^+$; the analytic function $\mathbb{C} \to \mathscr{B}(\mathscr{H})$: $z \to (H_\tau - z)^{-1}$ is not continuable past $\mathbb{R}^+$, as the resolvent becomes unbounded there.
2. As regards the eigenvalues of finite multiplicity of $H(\tau) \equiv \exp(2\tau)H_0 + \exp(\tau)\alpha/r$, they are also analytic in τ; the difference $H(\tau) - H(\tau - \delta)$ is bounded relative to $H(\tau)$ for δ small enough, so the perturbation theory of §3.5 is applicable. This implies that the eigenvalues $E(\tau)$ of $H(\tau)$ are independent of τ (as long as they persist), since if τ is real, $H(\tau)$ and H_τ are unitarily equivalent and therefore have identical spectra. But analytic functions that agree on $\mathbb{R}$ are equal everywhere.
3. The eigenfunctions $|\tau\rangle = U(\tau)|0\rangle$ of $H(\tau)$ are likewise analytic in τ, which implies that $(d/d\tau)|\tau\rangle - id|\tau\rangle \in L^2$ if $U(\tau) = \exp(-i\,d\,\tau)$, so $|\tau\rangle \in D(d)$. This justifies the formal proof (4.1.6; 1) of the virial theorem a posteriori.
4. In this simple case the integral kernel of the resolvent $R_z = (H_\tau - z)^{-1}$ is known explicitly. In the x-representation it involves Whittaker functions [9], [10]:

$$R_z(\mathbf{x}_1, \mathbf{x}_2) = \frac{\Gamma(1 - i\nu)}{4\pi|\mathbf{x}_1 - \mathbf{x}_2|}\,[W'_{i\nu;\,1/2}(-i\sqrt{z}(r_1 + r_2 + |\mathbf{x}_1 - \mathbf{x}_2|))$$
$$\times M_{i\nu;\,1/2}(-i\sqrt{z}(r_1 + r_2 - |\mathbf{x}_1 - \mathbf{x}_2|))$$
$$- W_{i\nu;\,1/2}(-i\sqrt{z}(r_1 + r_2 + |\mathbf{x}_1 - \mathbf{x}_2|))$$
$$\times M'_{i\nu;\,1/2}(-i\sqrt{z}(r_1 + r_2 - |\mathbf{x}_1 - \mathbf{x}_2|))],$$
$$\nu = \frac{\alpha}{4\sqrt{z}}, \qquad m = \tfrac{1}{2}.$$

In the p-representation this becomes

$$R_z(\mathbf{p}_1, \mathbf{p}_2) = \frac{\delta^3(\mathbf{p}_1 - \mathbf{p}_2)}{|\mathbf{p}_1|^2 - z}$$
$$- \frac{\alpha}{8\pi^2 z}\int_0^1 d\rho\,\rho^{i\nu}\frac{(1-\rho^2)\rho^2}{\left[|\mathbf{p}_1 - \mathbf{p}_2|^2 - \dfrac{(1-\rho)^2}{\rho}\dfrac{(z - |\mathbf{p}_1|^2)(z - |\mathbf{p}_2|^2)}{4z}\right]^2}$$

[9]. As we see, suitable matrix elements are analytic in z on a two-sheeted Riemann surface, but have an essential singularity at $z = 0$. The proof that was given for (4.1.16) can also be used in more complicated situations, for which there is no explicit expression for R_z.

In §3.4 we learned that σ_{ac} is associated with the states for which the particle escapes to infinity. Experience with the classical problem allows no hope that the time-evolution approaches that of H_0, since $\mathbf{x}(t) - t\mathbf{p}(t)/m \sim \ln t$. The operator $\exp(iH_r t)\exp(-iH_0 t)$ is not much good, either; it converges weakly to 0 as $t \to \infty$. On the other hand, there again exist some useful

Asymptotic Constants of the Motion (4.1.18)

Let P be the projection onto the vectors of $\sigma_{ac}(H_r)$. Then $(P\mathbf{p}P, P(\mathbf{x}/r)P, P(1/r)P) \in \mathscr{A}$ and s-$\lim_{t\to\pm\infty}$ $(P\mathbf{p}P, P(\mathbf{x}/r)P, P(1/r)P) = (\mathbf{p}_\pm, \pm\mathbf{p}_\pm/|\mathbf{p}_\pm|, 0)$ ($\mathbf{p}_\pm$ in the sense of (3.4.6)).

Proof

(i) Convergence of the Momenta. The claim will be proved only for $\alpha > 0$; the proof is more involved if $\alpha < 0$, and the reader is referred to [11]. In the repulsive case the radial component of the momentum p_r increases monotonically and is bounded, so it is suitable as a Liapunov function. As in classical mechanics (I: 5.3.8), when H_r is expressed in terms of p_r, it becomes

$$H_r = \frac{1}{2m}\left(p_r^* p_r + \frac{|\mathbf{L}|^2}{r^2}\right) + \frac{1}{r}.$$

(details in Problem 6, with $\alpha = 1$). If $L^2(\mathbb{R}^3, d^3x)$ is mapped unitarily to $L^2(S^2, d\Omega) \otimes L^2([0, \infty), dr)$ by $\psi \to u/r$, then p_r becomes identical to the operator p_r of (3.3.5; 4). Let $p_r(t)$ as usual mean $\exp(iH_r t)p_r \exp(-iH_r t)$, so that by (3.3.5; 4(a)),

$$\left\langle Y_l^m \frac{u(r)}{r} \middle| \frac{d}{dt} p_r Y_l^m \frac{u(r)}{r} \right\rangle = \int_0^\infty dr\, u^*(r)u(r)\left[\frac{1}{r^2} + \frac{l(l+1)}{r^3}\right] + \frac{1}{2}|u'(0)|^2.$$

Since $\|p_r\psi\| \le \langle\psi|H_r\psi\rangle$, this means that r^{-2} is integrable in time, as is to be expected from $r \sim t$:

$$\int_0^T dt \left\| \frac{1}{r(t)}\psi \right\|^2 \le \langle\psi|p_r(T) - p_r(0)|\psi\rangle \le 2\|\psi\|\langle\psi|H_r\psi\rangle^{1/2}. \quad \text{(a)}$$

Since this bound is independent of T, given any $\psi \in D(H_r)$ and $\varepsilon > 0$, there exists a T such that

$$\int_T^\infty dt \left\| \frac{1}{r(t)}\psi \right\|^2 < \varepsilon. \quad \text{(b)}$$

In order to avoid some technical difficulties caused by the presence of unbounded operators, let us examine $R\mathbf{p}R$, where $R = (H_r + c)^{-1}$, $c \in \mathbb{R}^+$. Now,

$$\frac{d}{dt} Rp_i(t)R = R \frac{x_i(t)}{r(t)^3} R$$

so

$$\begin{aligned}
\left\| \int_T^\infty dt \frac{d}{dt} Rp_i(t)R\psi \right\| &= \sup_{\|\varphi\|=1} \left| \int_T^\infty dt \left\langle R\varphi \left| \frac{x_i(t)}{r(t)^3} R\psi \right. \right\rangle \right| \\
&\leq \sup_{\|\varphi\|=1} \int_T^\infty dt \left| \left\langle R\varphi \left| \frac{1}{r(t)^2} R\psi \right. \right\rangle \right| \\
&\leq \sup_{\|\varphi\|=1} \left[\int_0^\infty dt \left\| \frac{1}{r(t)} R\varphi \right\|^2 \right]^{1/2} \left[\int_T^\infty dt \left\| \frac{1}{r(t)} R\psi \right\|^2 \right]^{1/2} \\
&\leq \text{const} \left[\int_T^\infty dt \left\| \frac{1}{r(t)} R\psi \right\|^2 \right]^{1/2},
\end{aligned}$$

where we have used (a). On account of (b), as $T \to \infty$ this becomes arbitrarily small, which implies the strong convergence of $P\mathbf{p}(t)P$. The operator R maps the Hilbert space into $D(H_r)$, which is a domain of essential self-adjointness for $\mathbf{p}(t)$ and $\mathbf{p}_\pm$. Therefore $\mathbf{p}$ converges strongly to $\mathbf{p}_\pm$ on a domain of essential self-adjointness, and consequently strongly in the sense of (2.5.8; 3) (see Problem 8).

(ii) Convergence of $\mathbf{x}/r$ and $1/r$. The first of these has already been handled in Problem (3.6.32; 3), and the second follows from $\mathbf{x}(t)/t \to \pm \mathbf{p}_\pm/m$. □

Remarks (4.1.19)

1. Proposition (4.1.18) implies that all finite functions of these operators converge to the same functions of the asymptotic constants (cf. (2.5.8; 3)). As usual there are domain questions for unbounded operators. The statement $a_n\psi \to a\psi$ for all $\psi \in D$, a dense set, does not suffice for $a_n \to a$. To see this, suppose a and b are two different self-adjoint extensions of a densely defined operator c, and set $a_n = b$ for all n, $D = D(c)$. Since $a_{|D(c)} = b_{|D(c)}$, convergence is trivial, but finite functions of a and b may genuinely differ. Only if D is a domain of essential self-adjointness for all a_n and for a can one conclude that $a_n \to a$ (Problem 8).
2. In order that the Møller operators still exist, H_0 might be modified somehow depending on the p_i but so as to describe the correct asymptotic motion. The trouble is that any such H_0 depends on time explicitly, so U_t^0 is not simply $\exp(-itH_0(t))$, and the time-evolution is not being compared with a one-parameter groups of automorphisms. One possibility is $U_t^0 = \exp(-i(t|\mathbf{p}|^2/2m + m\alpha(\ln t)/|\mathbf{p}|))$, as $\exp(iH_r t)U_t^0$ in fact

converges to the desired wave operator. Since the modified H_0 still commutes with $\mathbf{p}$, this also shows that the $p_i(t)$ converge. We are, however, less interested in pure existence theorems than in explicit computations, so this line of reasoning will not be pursued further.

Corollaries (4.1.20)

1. Since H is constant, $PHP = |\mathbf{p}_+|^2/(2m) = |\mathbf{p}_-|^2/(2m)$.

2. $PFP = \frac{1}{2}[\mathbf{p}_\pm \times \mathbf{L} - \mathbf{L} \times \mathbf{p}_\pm] \pm \dfrac{m\alpha \mathbf{p}_\pm}{|\mathbf{p}_\pm|} = \dfrac{i}{2}[\mathbf{p}_\pm, |\mathbf{L}|^2] \pm \dfrac{m\alpha \mathbf{p}_\pm}{|\mathbf{p}_\pm|}$.

The lesson of this is that the state of affairs concerning asymptotic constants is just as in the classical theory (I: 4.2.21; 1). In order to find the analogue of (I: 4.2.20) in quantum theory, it is only necessary to take some care with the noncommutativity of the various observables. This being done, one finds the

Connection between $\mathbf{p}_+$ and $\mathbf{p}_-$ (4.1.21)

$$p_k^+ = p_k^- \frac{|\mathbf{L}|^2 + i\eta - \eta^2}{|\mathbf{L}|^2 - i\eta + \eta^2} + [\mathbf{p}_- \times \mathbf{L} - \mathbf{L} \times \mathbf{p}_-]_k \frac{\eta}{|\mathbf{L}|^2 - i\eta + \eta^2}$$

$$= p_k^- \frac{|\mathbf{L}|^2(1 + i\eta) + i\eta - \eta^2}{|\mathbf{L}|^2 - i\eta + \eta^2} - i\eta |\mathbf{L}|^2 p_k^- \frac{1}{|\mathbf{L}|^2 - i\eta + \eta^2},$$

$$\eta(H_r) \equiv \frac{Pm\alpha}{\sqrt{2mH_r}}.$$

Proof

$$\begin{aligned} 2\varepsilon_{ijk} F_j L_k &= \varepsilon_{ijk}[\varepsilon_{jmn}(p_m^\pm L_n - L_m p_n^\pm) \pm 2\eta p_j^\pm] L_k \\ &= -p_i^\pm L^2 + p_k^\pm L_i L_k - L_k p_i^\pm L_k \pm 2\eta(F_i \mp \eta p_i^\pm) \pm 2i\eta p_i^\pm \\ &= -2p_i^\pm L^2 \pm 2\eta F_i - 2\eta^2 p_i^\pm \pm 2i\eta p_i^\pm . \end{aligned}$$

Substitution for $\mathbf{F}$ from (4.1.20; 2) then proves the claim. □

Remarks (4.1.22)

1. The first part of the formula is the analogue of (I: 4.2.20), and follows since $\mathbf{p}_+$ is related to $\mathbf{p}_-$ by reflection through $\mathbf{F}$ (see (I: 4.2.18; 1)).

2. The connection between $\mathbf{p}_+$ and $\mathbf{p}_-$ in the spectral representation of $|\mathbf{L}|^2$, L_3, and $H_r P = |\mathbf{p}_\pm|^2/2m$, can be read off from the second part of the formula:

The Scattering Transformation (4.1.23)

$$S = \frac{\Gamma(\frac{1}{2} + \sqrt{|\mathbf{L}|^2 + \frac{1}{4}} + i\eta(H_r))}{\Gamma(\frac{1}{2} + \sqrt{|\mathbf{L}|^2 + \frac{1}{4}} - i\eta(H_r))}$$

connects the momenta $\mathbf{p}_+$ *and* $\mathbf{p}_-$ *by*

$$\mathbf{p}_+ = S^{-1}\mathbf{p}_- S.$$

Proof

Since S commutes with $\mathbf{L}$, it can be written in the tensor-product representation of (3.6.10; 1), with the eigenvectors $|l, m\rangle \in L^2(S^2, d\Omega)$ of $|\mathbf{L}|^2$ and L_3, as

$$S|l, m\rangle \otimes \varphi(k) = \exp(2i\delta_l(k))|l, m\rangle \otimes \varphi(k).$$

The component p_3^+ commutes with L_3 and H_r and, like x_3 of (3.2.14), changes l by 1. If we take the matrix element $\langle l + 1, m| \cdot |l, m\rangle$ of the second form of (4.1.21), then we find that

$$\frac{\langle l + 1, m|p_3^+|l, m\rangle}{\langle l + 1, m|p_3^-|l, m\rangle} = \frac{l + 1 - i\eta}{l + 1 + i\eta} = \exp(2i(\delta_l - \delta_{l+1})).$$

Proposition (4.1.23) follows from this recursively, if we set $\exp(2i\delta_0(k)) = \Gamma(1 + i\eta(k))/\Gamma(1 - i\eta(k))$ by convention. □

Remarks (4.1:24)

1. As discussed in (I: 4.2.21), S is not determined uniquely by the conditions $S^{-1}\mathbf{p}_- S = \mathbf{p}_+$ and $S^{-1}\mathbf{L}S = \mathbf{L}$; the unitary elements of the commutant of the algebra $\mathscr{A}$ formed from $\mathbf{p}_-$ and $\mathbf{L}$ remain unspecified. Note that $\{\mathscr{A}\}'$ consists of functions of the energy, so this arbitrariness just corresponds to a choice of $\delta_0(k)$. This amounts to an overall phase and has no effect on the scattering cross-section for $\mathbf{k} \neq \mathbf{k}'$. On the other hand, the time-delay is now infinite instead of $\partial\delta(k)/\partial k^2$, because $m\mathbf{x} - \mathbf{p}t \sim \ln t$ as $t \to \infty$.
2. As $\ell \to \infty$ the phase-shift δ_l diverges as $\sum_l (l + 1)^{-1}$. This is why we were not able to normalize δ_∞ to zero, but chose instead to fix δ_0. It thus happens that δ_0 violates the rule for the scattering phase-shift δ and scattering length a valid for short-range potentials, that $V > 0 \Rightarrow \delta < 0 \Rightarrow a > 0$ and $V < 0 \Rightarrow \delta > 0 \Rightarrow a < 0$ (see (3.6.5) and (3.6.23; 5)): If δ_∞ were 0, then δ_l would be negative for positive α and positive for negative α.

3. The scattering transformation S does not commute with all the constants of the motion (cf. (I: 4.21.4)). For instance, $S^{-1}\mathbf{F}S = \mathbf{F} - 2\eta\mathbf{p}_+$.
4. The scattering matrix has been calculated in the Heisenberg representation. In the interaction representation (see (3.4.23) and (3.4.24; 6)) S_{00} is related to it through $\Omega_-^* S\Omega_- = S_{00}$ and $\Omega_-^* H_r\Omega_- = H_0$. In other words S_{00} is obtained from S by the replacement of H_r with H_0, or $|\mathbf{p}_-|^2$ with $|\mathbf{p}|^2$.
5. Although Proposition (3.6.11) about the poles of S was derived only under restrictive assumptions on V, it remains true that S contains the information of Balmer's formula: $\exp(2i\,\delta_l(k))$ has poles at $k = -ime^2/(l + n_r)$, $n_r = 1, 2, \ldots$. They are in the upper half-plane if $\alpha < 0$, in which case the values of $k^2/2m$ are precisely the energies of the bound states.

Now that the phase-shifts δ_l are known, let us recall the definition in (3.6.10; 3) and calculate (Problem 7) the

Scattering Amplitude (4.1.25)

$$f(k; \mathbf{n}', \mathbf{n}) = \sum_{l=0}^{\infty} \frac{2l+1}{2ik} P_l(\cos\theta)\left[\frac{\Gamma(1+l+i\eta)}{\Gamma(1+l-i\eta)} - 1\right]$$

$$= \frac{i\eta}{2k}\left(\frac{4}{|\mathbf{n}-\mathbf{n}'|^2}\right)^{1+i\eta}\frac{\Gamma(1+i\eta)}{\Gamma(1-i\eta)} - \frac{1}{2ik}\,\delta^2(\mathbf{n}-\mathbf{n}').$$

Remarks (4.1.26)

1. The sum over l converges on the dense set of finite linear combinations of Y_l^m, for example, but is singular for $\mathbf{n} = \mathbf{n}'$.
2. The first contribution to the scattering amplitude

$$f(k; \mathbf{n}', \mathbf{n}) \sim (\sin\theta/2)^{-2-2i\eta}$$

is a well-defined distribution for all $\mathbf{n}$ and $\mathbf{n}' \in S^2$, and represents the unitary operator S as an integral operator with a kernel. This fact is lost in the Born approximation; the $i\eta$ disappears from the exponent, and f becomes nonintegrably singular. As a whole, f remains singular even after subtraction of the delta function in the forward direction; it is a distribution rather than an ordinary function.
3. The cross-section is the same as classically (I: 4.2.22),

$$\sigma(k; \mathbf{n}, \mathbf{n}') = |f(k; \mathbf{n}, \mathbf{n}')|^2 = \frac{\alpha^2}{16(k^2/2m)^2}\sin^{-4}\frac{\theta}{2}.$$

Problems (4.1.27)

1. Show that if a is self-adjoint and b is essentially self-adjoint on a domain D invariant under all $\exp(iat)$, $t \in \mathbb{R}$, then a and $\bar{b} \equiv$ the closure of b in the sense of (3.1.7) commute if $\exp(iat)b\exp(-iat)\psi = b\psi$ for all $\psi \in D$ and $t \in \mathbb{R}$.

2. Show that

   (i) $D(F) \supset D(H_r) \cap D_{\text{fin}}(L^2)$, where D_{fin} consists of the finite linear combinations of the Y_l^m;

   (ii) $\mathbf{F}$ is essentially self-adjoint on $D(H_r) \cap D_{\text{fin}}(L^2)$;

   (iii) For all φ and $\psi \in D(H_r) \cap D_{\text{fin}}(L^2)$, $d/dt\langle\varphi|\exp(iH_r t)F\exp(-iH_r t)|\psi\rangle = 0$. Use Problem 1 to verify that $[H, \mathbf{F}] = \mathbf{0}$.

3. Verify (4.1.7(ii)) and (4.1.7(iv)).

4. Compute the action of $p_\pm$ and p_3 on $|l, m\rangle$.

5. Compute $|2, 0, 0\rangle = F_3|2, 1, 0\rangle$ in the x-representation.

6. Express $|\mathbf{p}|^2$ in terms of $p_r = (1/r)(\mathbf{x}\cdot\mathbf{p}) - i/r$, r, and $|\mathbf{L}|^2$.

7. Calculate the sum over l in (4.1.25).

8. Show that if $a_n\psi \to a\psi$ for all $\psi \in D$, a domain of essential self-adjointness for all a_n and a, then $a_n \to a$ in the sense of (2.5.8; 3).

Solutions (4.1.28)

1. $D(\bar{b}) = \{\psi$: there exists a sequence $\psi_n \in D$ such that $\psi_n \to \psi$, and $b_n\psi$ converges$\}$.

$$b\exp(iat)\psi = \exp(iat)b\psi \qquad \text{for all} \quad \psi \in D \Rightarrow$$

$$\bar{b}\exp(iat)\psi = \exp(iat)\bar{b}\psi \qquad \text{for all} \quad \psi \in D(\bar{b}),$$

since $b\exp(iat)\psi_n = \exp(iat)b\psi_n$.

$$b\psi_n \to \bar{b}\psi,\ \exp(iat)b\psi_n \to \exp(iat)\bar{b}\psi,\ \exp(iat)\psi_n \to \exp(iat)\psi,$$

and consequently $b\exp(iat)\psi_n$ converges, which implies that $\exp(iat)\psi \in D(\bar{b})$, and $\bar{b}\exp(iat)\psi = \exp(iat)\bar{b}\psi$. Let $\mathscr{C}$ be the finite linear combinations of $\exp(iat)$. Then $\bar{b}c\psi = c\bar{b}\psi$ for all $c \in \mathscr{C}$ and $\psi \in D(\bar{b})$. Furthermore, let $U = (b - i)(\bar{b} + i)^{-1}$. Every vector $\varphi \in \mathscr{H}$ is equal to $(\bar{b} + i)\psi$ for some $\psi \in D(\bar{b})$; thus $U\varphi = (\bar{b} - i)\psi$. $c\varphi = c(\bar{b} + i)\psi = (\bar{b} + i)c\psi$, $Uc\varphi = (\bar{b} - i)c\psi = c(\bar{b} - i)\psi = cU\varphi$, so $Uc = cU$ for all $c \in \mathscr{C}$. Therefore every bounded function of $\bar{b}$ commutes with $\mathscr{C}$.

2. (i) $\|F_j\psi\| \le c_1\||\mathbf{L}|^2 p_j\psi\| + c_2\|p_j\psi\| + c_3\|\psi\|$ for some $c_i \in \mathbb{R}^+$. Since p_j changes the angular momentum by 1, $\||\mathbf{L}|^2 p_j\psi\| \le c_4\|p_j\psi\| \le c_5\langle\psi|PH_r\psi\rangle^{1/2}$, and so $\|F_j\psi\| < \infty$ for all $\psi \in D(H_r) \cap D_{\text{fin}}(|\mathbf{L}|^2)$.

   (ii) $D(H_r) \cap D_{\text{fin}}(|\mathbf{L}|^2)$ contains the set $\{x_1^{q_1}x_2^{q_2}x_3^{q_3}\exp(-|\mathbf{x}|^2/2),\ q_i = 0, 1, 2, \ldots,$ and finite linear combinations$\}$, on which $\mathbf{F}$ is essentially self-adjoint.

(iii)
$$\langle\varphi(t)|i[H, F_k]\psi(t)\rangle = \langle\varphi(t)|i\alpha\left[\frac{x_k}{r^3}, |\mathbf{L}|^2\right] + \alpha i\left[\frac{|\mathbf{L}|^2}{2r^2}, \frac{x_k}{r}\right]|\psi(t)\rangle = 0,$$

since $[|\mathbf{L}|^2, r] = 0$ and $D(|\mathbf{L}|^2/r^2) \supset D(H_r) \cap D_{\text{fin}}(|\mathbf{L}|^2)$. As a consequence, the matrix elements of $\mathbf{F}(t)$ and $\mathbf{F}(0)$ are the same with the vectors of

$$D(H_r) \cap D_{\text{fin}}(|\mathbf{L}|^2).$$

Therefore the unique self-adjoint extensions are the same, which is the criterion for commutativity by Problem 1.

3. The commutation relations used below follow from $[\mathbf{p}, f(\mathbf{x})] = -i\nabla f(\mathbf{x}), [\mathbf{x}, f(\mathbf{p})] = i\nabla f(\mathbf{p})$, and the identities $[ab, c] = a[b, c] + [a, c]b$ and

$$[ab, cd] = ac[b, d] + a[b, c]d + c[a, d]b + [a, c]db:$$

$$|\mathbf{F}|^2 = \left([\mathbf{p} \times \mathbf{L}] - i\mathbf{p} + \frac{m\alpha\mathbf{x}}{r}\right) \cdot \left([\mathbf{p} \times \mathbf{L}] - i\mathbf{p} + \frac{m\alpha\mathbf{x}}{r}\right)$$

(because $[\mathbf{p} \times \mathbf{L}] = -[\mathbf{L} \times \mathbf{p}] + 2i\mathbf{p}$).

$$\mathbf{p} \cdot [\mathbf{p} \times \mathbf{L}] = [\mathbf{p} \times \mathbf{p}] \cdot \mathbf{L} = 0, [\mathbf{p} \times \mathbf{L}] \cdot \mathbf{p} = (-[\mathbf{L} \times \mathbf{p}] + 2i\mathbf{p}) \cdot \mathbf{p} = 2i|\mathbf{p}|^2.$$

$$[\mathbf{p} \times \mathbf{L}] \cdot \mathbf{x} = (-[\mathbf{L} \times \mathbf{p}] + 2i\mathbf{p}) \cdot \mathbf{x} = |\mathbf{L}|^2 + 2i\mathbf{p} \cdot \mathbf{x},$$

$$\mathbf{x} \cdot [\mathbf{p} \times \mathbf{L}] = [\mathbf{x} \times \mathbf{p}] \cdot \mathbf{L} = |\mathbf{L}|^2.$$

$$|[\mathbf{p} \times \mathbf{L}]|^2 = |\mathbf{p}|^2|\mathbf{L}|^2 - (\mathbf{p} \cdot \mathbf{L})^2 = |\mathbf{p}|^2|\mathbf{L}|^2.$$

From these equations, $|\mathbf{F}|^2 = |\mathbf{p}|^2|\mathbf{L}|^2 + 2|\mathbf{p}|^2 + m\alpha|\mathbf{L}|^2/r + 2im\alpha(\mathbf{p} \cdot \mathbf{x})/r - |\mathbf{p}|^2 - im\alpha(\mathbf{p} \cdot \mathbf{x})/r + m\alpha|\mathbf{L}|^2/r - im\alpha(\mathbf{x}/r \cdot \mathbf{p}) + m^2\alpha^2$. Since $[\mathbf{x}, \mathbf{p} \cdot \mathbf{x}] = i\mathbf{x}$ and $[\mathbf{p} \cdot \mathbf{x}, 1/r] = i/r$, the final result is that $|\mathbf{F}|^2 = |\mathbf{p}|^2|\mathbf{L}|^2 + |\mathbf{p}|^2 + 2m\alpha|\mathbf{L}|^2/r + 2m\alpha/r + m^2\alpha^2 = m^2\alpha^2 + 2mH_r(|\mathbf{L}|^2 + 1)$. The commutation relations for the components of $\mathbf{F}$ follow from the formula $\mathbf{F} = |\mathbf{p}|^2\mathbf{x} - (\mathbf{p} \cdot \mathbf{x})\mathbf{p} + 2m\alpha\mathbf{x}/r$ and the formulas given above, as well as $[\mathbf{x}, |\mathbf{p}|^2] = 2i\mathbf{p}$, $[\mathbf{p} \cdot \mathbf{x}, |\mathbf{p}|^2] = 2i|\mathbf{p}|^2$, $[\mathbf{p}, 1/r] = i\mathbf{x}/r^3$, $[|\mathbf{p}|^2, 1/r] = i\mathbf{x}/r^3 \cdot \mathbf{p} + i\mathbf{p} \cdot \mathbf{x}/r^3$, and $\mathbf{x} \cdot \mathbf{p} - \mathbf{p} \cdot \mathbf{x} = 3i$, which can be verified directly.

4. In the x-representation, $\partial/\partial z = \cos\theta(\partial/\partial r) - (\sin\theta/r)(\partial/\partial\theta)$. Because $\cos\theta\, Y_l^l = cY_{l+1}^l$ and $\sin\theta\, Y_l^l = lcY_{l+1}^l$, and because of the analogous facts for $\partial/\partial x$ and $\partial/\partial y$, we find that $ip_3|n, l, l\rangle = c(\partial/\partial r - l/r)|n, l + 1, l\rangle$ and

$$ip_+|n, l, l\rangle = c'\left(\frac{\partial}{\partial r} - \frac{l}{r}\right)|n, l + 1, l + 1\rangle.$$

(The vector $ip_-|n, l, l\rangle$ is a linear combination of $(\partial/\partial r - l/r)|n, l + 1, l - 1\rangle$ and $(\partial/\partial r + (l + 1)/r)|n, l - 1, l - 1\rangle$.) (See also (3.2.14).)

5. $|2, 0, 0\rangle = (m\alpha)^{3/2}(1 - (m\alpha r/2))\exp(-m\alpha r/2)/\sqrt{8\pi}$.

6. First note that owing to the facts listed in Solution 3, p_r^* is formally equal to p_r, and

$$|\mathbf{L}|^2 = x_k p_l x_l p_s \varepsilon_{ikl}\varepsilon_{stl} = |\mathbf{x}|^2|\mathbf{p}|^2 + i(\mathbf{x} \cdot \mathbf{p}) - (\mathbf{x} \cdot \mathbf{p})(\mathbf{x} \cdot \mathbf{p}),$$

so $|\mathbf{p}|^2 = p_r^2 + |\mathbf{L}|^2/r^2$. If we now map $L^2(\mathbb{R}^3, d^3x)$ unitarily to $L^2(S^2, d\Omega) \otimes L^2(\mathbb{R}^+, dr)$ by $\psi \to u/r$, then p_r becomes the Hermitian operator $-i\, d/dr$ of Example (3.3.5; 4). It fails, however, to be self-adjoint; $p_r^* \supset p_r$, because $D(p_r) = \{\psi \in L^2 : \psi$ is absolutely continuous, $\psi' \in L^2$, and $\psi(0) = 0\} \subset D(p_r^*) = \{\psi \in L^2 : \psi$ is absolutely continuous, and $\psi' \in L^2\}$. A more precise statement is that $|\mathbf{p}|^2 = p_r^* p_r + |\mathbf{L}|^2/r^2$.

7. If $t = \cos\Theta$, then

$$(\sin\Theta/2)^{-2-2i\eta} = \sum_{l=0}^{\infty} 2^{i\eta}(2l+1)P_l(t)\int_{-1}^{1}(1-z)^{-i\eta-1}P_l(z)dz.$$

By recourse to Rodrigues's formula we find that

$$\int_{-1}^{1}\cdots = \frac{1}{2^l l!}\int_{-1}^{1}(1-z)^{-i\eta-1}\frac{d^l}{dz^l}(z^2-1)^l\,dz$$

$$= \frac{1}{2^l l!}(1+i\eta)\cdots(l+i\eta)\times\int_{-1}^{1}(1-z)^{-i\eta-l-1}(1-z)^l(1+z)^l\,dz$$

$$= \frac{1}{2^l l!}\frac{\Gamma(l+1+i\eta)}{\Gamma(1+i\eta)}2^{-i\eta+l}\times\frac{\Gamma(-i\eta)\Gamma(l+1)}{\Gamma(l+1-i\eta)}$$

$$= \frac{-1}{i\eta}\frac{\Gamma(1-i\eta)}{\Gamma(1+i\eta)}\frac{\Gamma(l+1+i\eta)}{\Gamma(l+1-i\eta)}2^{-i\eta}$$

and $(\sin\Theta/2)^{-2-2i\eta} = \sum(1/-i\eta)(2l+1)\exp(i\delta_l)P_l(\cos\Theta)$, provided that δ_0 is chosen as 0.

8. Let $\psi = (a+i)\varphi, \varphi \in D$. $((a_n+i)^{-1} - (a+i)^{-1})\psi = (a_n+i)^{-1}(a-a_n)\varphi \to 0$, since $\|(a_n+i)^{-1}\| \le 1$, and analogously if $i \to -i$. However, $(a \pm i)D$ is dense in $\mathscr{H}$, so $(a_n \pm i)^{-1}\psi \to (a \pm i)^{-1}\psi$ for all $\psi \in \mathscr{H}$.

4.2 The Hydrogen Atom in an External Field

Experiments subjecting atoms to constant electric and magnetic fields were indispensible to the understanding of atomic spectra. The effect of weak fields is seemingly just a moderate shift in the energy levels, but in fact the underlying mathematical problem is drastically changed.

The fields applied in laboratory experiments are usually weak in comparison with atomic fields, and appear to have only slight influence on atomic structure. In the other extreme, with the high magnetic fields B prevailing on neutron stars, the radius $(eB)^{-1/2}$ of the lowest magnetic orbital (cf. (3.3.5; 3)) can be smaller than the Bohr radius, and the atom contracts around the magnetic lines of force. In very strong electric fields autoionization occurs, and we shall see that even an arbitrarily small electric field destroys the point spectrum of an atom. It is amusing that this problem was one of the first successes of the perturbation theory developed in §3.5, despite its not being applicable in the absence of a point spectrum. One of our goals will be to find the sense in which perturbation theory is still asymptotically valid.

We give the Hamiltonian (4.1.1) the perturbations of (3.3.5; 1) or (3.3.5; 3), thereby obtaining the

Hamiltonians for the Stark and Zeeman Effects (4.2.1)

$$H_E = \frac{|\mathbf{p}|^2}{2m} + \frac{\alpha}{|\mathbf{x}|} + eEx_3 \equiv H_0 + \lambda H',$$

$$H_0 = \frac{|\mathbf{p}|^2}{2m} + \frac{\alpha}{|\mathbf{x}|}, \qquad H' = x_3, \qquad \lambda = eE,$$

$$H_B = \frac{1}{2m}\left(\left(p_1 + \frac{eB}{2}x_2\right)^2 + \left(p_2 - \frac{eB}{2}x_1\right)^2 + p_3^2\right) + \frac{\alpha}{|\mathbf{x}|} \equiv H_0 + \lambda H',$$

$$H_0 = \frac{|\mathbf{p}|^2}{2m} + \frac{\alpha}{|\mathbf{x}|} - \frac{eB}{2m}\hat{L}_3, \qquad H' = x_1^2 + x_2^2, \qquad \lambda = \frac{e^2B^2}{8m},$$

$\hat{\mathbf{L}} = [\mathbf{x} \times \mathbf{p}]$ is the canonical angular momentum of (3.3.5; 3).

Since H' is not bounded relative to H_0, the question of the self-adjointness of H_E and H_B must be confronted. Serious difficulties are not to be expected, because quantum mechanics mollifies a $1/r$ singularity, and once something has been done about the singularity at $r = 0$, a classical electron in these potentials would evolve in a reasonable way and would not reach any boundaries in a finite time. Roughly speaking, it could be argued that if there is a $c \in \mathbb{R}^+$ such that $|d/dt(|\mathbf{p}|^2 + |\mathbf{x}|^2)| \leq c(|\mathbf{p}|^2 + |\mathbf{x}|^2)$, then $|\mathbf{p}(t)|^2 + |\mathbf{x}(t)|^2 \leq \exp(ct)(|\mathbf{p}(0)|^2 + |\mathbf{x}(0)|^2)$, so neither the momentum nor the position coordinate could get unboundedly large in a finite time. The condition that $|\dot{N}| \leq cN$ is equivalent to $\pm\dot{N} + cN \geq 0$, and this argument can be made precise with a lemma on

Self-adjointness on the Domain of Operators Bounded Exponentially in Time (4.2.2)

Let H be Hermitian and $N \geq 1$ self-adjoint with $D(N) \subset D(H)$, and suppose there exists a $c \in \mathbb{R}^+$ such that $\langle\psi|(\pm i[H, N] + cN)\psi\rangle > 0$ for all $\psi \in D(N)$. Then H is essentially self-adjoint on $D(N)$.

Proof

Recalling (2.5.10; 1) we shall show that given any $\gamma \in \mathbb{R}^+$, if $\langle\varphi|(H \pm i\gamma)\psi\rangle = 0$ for all $\psi \in D(N)$, then $\varphi = 0$. Specifically, that fact would imply that

$$0 = 2\,\mathrm{Im}\langle\varphi|(H \pm i\gamma)N^{-1}\varphi\rangle = \pm 2\gamma\langle\varphi|N^{-1}\varphi\rangle - \langle N^{-1}\varphi|i[H, N]N^{-1}\varphi\rangle,$$

which is consistent with the assumptions of the lemma and with $\gamma > c/2$ only if $\varphi = 0$. As remarked in (2.5.13; 2), the conclusion then holds for all $\gamma \in \mathbb{R}^+$. □

Application (4.2.3)

Now let $N_{E,B} = H_{E,B} + \omega^2|\mathbf{x}|^2$, $\omega \in \mathbb{R}$ and sufficiently large. They are self-adjoint operators on $D(|\mathbf{p}|^2 + |\mathbf{x}|^2)$, because the other terms in $H_{E,B}$ are bounded relative to these. Then note that

$$\pm i[H_{E,B}, N_{E,B}] = \pm i\left[\frac{|\mathbf{p}|^2}{2m}, |\mathbf{x}|^2\right] = \mp \frac{1}{m}(\mathbf{p}\cdot\mathbf{x} + \mathbf{x}\cdot\mathbf{p}) < cN_{E,B}.$$

This leads to the conclusion that H_E and H_B are essentially self-adjoint on $D(|\mathbf{p}|^2 + |\mathbf{x}|^2)$.

The Hamiltonians of (4.2.1) thus determine the time-evolution uniquely; however, there is such a vast difference between $\lambda = 0$ and $\lambda < 0$ that the perturbation theory developed in §3.5 is deprived of its foundations. Moreover, at large distances α/r is insignificant compared with the external field, which therefore controls the action. Suitable bases for comparison are thus free fall (3.3.5; 1) for H_E and motion in a repulsive harmonic force for H_B with $\lambda < 0$.

Existence of the Møller Operators (4.2.4)

Let $H_E(\alpha)$ and $H_B(\alpha)$ be as in (4.2.1). *Then*

$$\Omega_\pm = \underset{t \to \pm\infty}{s\text{-lim}} \exp(iH_{E,B}(\alpha)t)\exp(-iH_{E,B}(0)t)$$

exist for H_E if $\lambda \neq 0$ and for H_B if $\lambda < 0$.

Remarks (4.2.5)

1. As was discussed in §4.1, the Møller operators do not exist if $\lambda = 0$. The external fields make the time-limit more tractable, because although $1/r$ is not integrable in time when $\mathbf{x} \to \mathbf{x} + \mathbf{p}t$, it is if $\mathbf{x} \to \mathbf{x} + \mathbf{p}t + \mathbf{g}t^2$ or $\mathbf{x} \to \mathbf{x}\cosh(t) + \mathbf{p}\sinh(t)$.
2. It follows from $\Omega^* H(\alpha)\Omega = H(0)$ that $H(\alpha)$ has the same spectrum when restricted to the range of Ω as $H(0)$. This shows that $\sigma_{ac}(H_E) = \mathbb{R}$ if $\lambda \neq 0$ and $\sigma_{ac}(H_B) = \mathbb{R}$ if $\lambda < 0$. The unboundedness below is easy to see using trial functions supported far away from the origin in regions where the potential is very negative. It is clear from this why the analytic perturbation theory of §3.5 is impossible.

3. Completeness of the Møller operators $\Omega_\pm$ would imply that $\sigma_p = \sigma_{sing} = \varnothing$. Though this is the case, the proof is more difficult; the interested reader is referred to [12].

Proof

As in (3.4.11), we begin by taking the time-derivative of $\Omega(t)$, though we shall require only the rough estimate

$$\int_{-\infty}^{\infty} dt \|\exp(iHt)V\exp(-iH_0t)\psi\| = \int_{-\infty}^{\infty} dt \|V\exp(-iH_0t)\psi\|$$

$$\leq \left(\int_{-\infty}^{\infty} \frac{dt}{1+t^2}\right)^{1/2} \left(\int_{-\infty}^{\infty} dt(1+t^2)\|V\exp(-iH_0t)\psi\|^2\right)^{1/2}.$$

Since we are showing that a sequence of bounded operators converges strongly, we may restrict to a total set, $\{\psi = \exp(-|\mathbf{x}-\bar{\mathbf{x}}|^2/2b^2),\ \bar{\mathbf{x}} \in \mathbb{R}^3,\ b \in \mathbb{R}^+\}$. In units where $2m = 1$ and $Ee = 2g$, both $H_E(0)$ and

$$\exp(2itgx_3)\exp(-it^2p_3g)\exp(-it|\mathbf{p}|^2)$$

produce the time-evolution $(x_1, x_2, x_3; p_1, p_2, p_3) \to (x_1 + p_1t, x_2 + p_2t, x_3 + p_3t + gt^2; p_1, p_2, p_3 + 2gt)$; therefore their difference is only a multiple of **1**. By Solution (3.3.21; 2),

$$(\exp(-it|\mathbf{p}|^2)\psi)(x) = \left[\exp\frac{-|\mathbf{x}-\bar{\mathbf{x}}|^2}{2(b^2+t^2b^{-2})}\right](1+t^2b^{-4})^{-3/4},$$

while $\exp(-it^2p_3g)$ displaces x_3 by gt^2, and $\exp(2itgx_3)$ drops out because it commutes with V. Thus it remains to show that

$$\int_0^{\infty} dt(1+t^2)(1+t^2b^{-4})^{-3/2} \int \frac{d^3x}{r^2} \exp\frac{-|\mathbf{x}-\bar{\mathbf{x}}(t)|^2}{(b^2+t^2b^{-2})} < \infty,$$

$$(\bar{x}_1(t), \bar{x}_2(t), \bar{x}_3(t)) = (\bar{x}_1, \bar{x}_2, \bar{x}_3 + gt^2),$$

which follows from a simple change of variables (Problem 1). The proof for H_B is very similar; it is only necessary to take the harmonic motion in (3.3.21; 2) with an imaginary frequency. This makes $\bar{\mathbf{x}}(t) = \mathbf{x}\cosh(vt)$, and the convergence is even easier. □

The foregoing results show immediately that the resolvent

$$(H_0 + \lambda H' - z)^{-1},\ z \in \mathbb{C}\backslash\mathbb{R},$$

is not analytic in λ at $\lambda = 0$, where H has been divided into H_0 and H' as in (4.2.1). Perturbation theory will thus fail to converge as an expansion in the

external field. It is reasonable to wonder, however, whether the perturbation-theoretic formulas still have some meaning or become pure nonsense. Despite the lack of analyticity, we at least have

Strong Continuity in λ (4.2.6)

The function $\lambda \to (H_0 + \lambda H' - z)^{-1}$, for $z \in \mathbb{C}\backslash\mathbb{R}$ and H_0 and H' as in (4.2.1), *is a continuous mapping on $\mathscr{B}(\mathscr{H})$ in the strong topology.*

Proof

The resolvent equation

$$(H_0 - z)^{-1} - (H_0 + \lambda H' - z)^{-1} = \lambda(H_0 + \lambda H' - z)^{-1}H'(H_0 - z)^{-1}$$

obviously holds on $(H_0 - z)D(|\mathbf{p}|^2 + |\mathbf{x}|^2)$, since $D(|\mathbf{p}|^2 + |\mathbf{x}|^2) \subset D(H')$. The operator H_0 is essentially self-adjoint on $D(|\mathbf{p}|^2 + |\mathbf{x}|^2)$, which means that $(H_0 - z)D(|\mathbf{p}|^2 + |\mathbf{x}|^2)$ is dense, because its closure is $(H_0 - z)D(H_0)$, which is all of $\mathscr{H}$ by (2.5.5). Since the resolvent is bounded by $|\operatorname{Im} z|^{-1}$ in norm, uniformly in λ, the strong continuity in λ follows from the strong continuity on a dense set. □

Proposition (4.2.6) implies that as $\lambda \to 0$ any bounded, continuous function of $H_0 + \lambda H'$ converges strongly to the same function of H_0. On the same abstract level we can in fact state the following

Continuity Properties of the Spectrum (4.2.7)

(i) *For all $z \in \operatorname{Sp}(H_0)$ there exists a $z(\lambda) \in \operatorname{Sp}(H_0 + \lambda H')$ such that*

$$\lim_{\lambda \to 0} z(\lambda) = z.$$

(ii) *For all a and $b \in \mathbb{R}$ such that $a < b$ and $a, b \notin \sigma_p(H_0)$, the projections $P_{(a,b)}(H_0 + \lambda H')$ converge strongly to $P_{(a,b)}(H_0)$.*

Remarks (4.2.8)

1. Proposition (i) means that the spectrum of the limiting operator can not suddenly get larger. Example (3.5.11; 1) shows that it is possible for it to contract suddenly from $\mathbb{R}$ to $\{0\}$. If H' were an analytic perturbation, then norm continuity of the resolvent in λ can be used to exclude this possibility.
2. If the interval (a, b) contains only one eigenvalue of H_0, then (ii) implies that $P_{(a,b)}(H_0 + \lambda H')$ converges to the projection onto the eigenspace of the eigenvalue.

3. The requirement that $a \notin \sigma_p(H_0)$ is a necessary one; suppose, as in (3.5.11; 1), that $H_0 = 0$ and $H' = x$, as operators on $L^2((-\infty, \infty), dx)$, and let $\chi_{(0,1)}$ be the characteristic function of (0, 1). Then

$$\chi_{(0,1)}(\lambda x) = P_{(0,1)}(H_0 + \lambda H') \to P_{(0,\infty)}(x),$$

but $\chi_{(0,1)}(0) = 0$.

Proof

(i) We shall show, equivalently, that $(a, b) \cap \mathrm{Sp}(H_0 + \lambda H')$ being empty for all sufficiently small λ implies that $(a, b) \cap \mathrm{Sp}(H_0)$ is empty. By the spectral theorem the latter statement is equivalent to

$$\left\| \left(H_0 - \frac{a+b}{2} + \mathrm{i}\frac{b-a}{2} \right)^{-1} \right\| \leq \frac{\sqrt{2}}{(b-a)}.$$

By assumption,

$$\left\| \left(H_0 + \lambda H' - \frac{a+b}{2} + \mathrm{i}\frac{b-a}{2} \right)^{-1} \right\| \leq \frac{\sqrt{2}}{(b-a)}$$

for sufficiently small λ. Since the operator norm is strongly lower semicontinuous ($\|\cdot\| = \sup_{\|\psi\|=1} \|\cdot\psi\|$), $R_\lambda \to R$, which implies that $\|R\| \leq \liminf \|R_\lambda\|$, from which the proposition follows.

(ii) To generalize from convergence of continuous functions to that of characteristic functions, recall that there exist continuous functions f_n and g_n, $0 \leq f_n \leq \chi_{(a,b)}$ and $g_n \geq \chi_{[a,b]}$, such that $f_n \uparrow \chi_{(a,b)}$ and $g_n \downarrow \chi_{[a,b]}$ pointwise. Hence, by Problem 2, $f_n(H_0) \to \chi_{(a,b)}(H_0)$ and $g_n(H_0) \to \chi_{[a,b]}(H_0)$. Since a and $b \notin \sigma_p(H_0)$, $P_{(a,b)}(H_0) = P_{[a,b]}(H_0)$, so $\chi_{(a,b)}(H_0) = \chi_{[a,b]}(H_0)$. This implies that for all ψ and ε there exist continuous functions $f \leq \chi_{(a,b)} \leq \chi_{[a,b]} \leq g$ such that $\|(f(H_0) - g(H_0))\psi\| \leq \varepsilon$. Consequently,

$$\begin{aligned}
&\|(P_{(a,b)}(H_0 + \lambda H') - P_{(a,b)}(H_0))\psi\| \\
&\quad \leq \|(P_{(a,b)}(H_0 + \lambda H') - f(H_0 + \lambda H'))\psi\| \\
&\qquad + \|(f(H_0 + \lambda H') - f(H_0))\psi\| + \|(P_{(a,b)}(H_0) - f(H_0))\psi\| \\
&\quad \leq \|(g(H_0 + \lambda H') - f(H_0 + \lambda H'))\psi\| \\
&\qquad + \|(f(H_0 + \lambda H') - f(H_0))\psi\| + \|(g(H_0) - f(H_0))\psi\| \\
&\quad \leq \|(g(H_0 + \lambda H') - g(H_0))\psi\| + 2\|(f(H_0 + \lambda H') - f(H_0))\psi\| \\
&\qquad + 2\|(g(H_0) - f(H_0))\psi\|
\end{aligned}$$

is arbitrarily small. □

In the case we have been interested in, H_0 has a point spectrum, but Proposition (4.2.7) does not guarantee that the point spectrum persists when

λ is changed from 0. The point spectrum can not disappear without a trace, however; instead, there is a sort of

Spectral Concentration (4.2.9)

Let E_0 be an isolated eigenvalue of H_0 of finite multiplicity and P_0 be the associated projection. Suppose that $P_0H'P_0$ exists and has eigenvalues E'_j with projections P_j, $\sum_j P_j = P_0$. Then for all $\varepsilon > 0$ and η, $0 < \eta < 2$,

$$s\text{-}\lim_{\lambda \to 0} P_{(E_0 + \lambda E'_j - \varepsilon\lambda^\eta,\, E_0 + \lambda E'_j + \varepsilon\lambda^\eta)}(H_0 + \lambda H') = P_j.$$

Remarks (4.2.10)

1. In the cases we have examined (4.2.1), the exponential fall-off of the eigenvectors of H_0 makes them belong to $D(H')$, so the finiteness of $P_0H'P_0$ is clear.
2. Proposition (4.2.9) states that to order λ^η, $\eta < 2$, the spectrum shrinks down around the eigenvalues predicted by first-order perturbation theory. The proposition is easily generalized to higher order.

Proof

Let ψ_j be one of the vectors spanning the range of P_j, so $H_0\psi_j = E_0\psi_j$ and $H'\psi_j = E'_j\psi_j$. Then the ψ constructed by perturbation theory (3.5.18) is undeniably an eigenvector of $H_0 + \lambda H'$ to $O(\lambda^2)$ (cf. (3.5.19; 3)):

$$\begin{aligned}\|(H_0 + \lambda H' - E_0 - \lambda E'_j)(\psi_j - \lambda(H_0 - E_0)^{-1}(H' - E'_j)\psi_j)\|^2 \\ = \lambda^4 \|(H' - E'_j)(H_0 - E_0)^{-1}(H' - E'_j)\psi_j\|^2.\end{aligned}$$

(Recall that $\lambda E'_j$ was incorporated into H_0 in §3.5.) Now, if μ_j is the probability measure associated with the vector $(\mathbf{1} - \lambda(H_0 - E_0)^{-1}(H' - E'_j))\psi_j \equiv \psi_j(\lambda)$, the operator $H_0 + \lambda H'$, and the interval

$$I_j(\lambda) = (E_0 + \lambda E'_j - \varepsilon\lambda^\eta,\, E_0 + \lambda E'_j + \varepsilon\lambda^\eta),$$

then we get the estimate

$$\lambda^4 \|(H' - E'_j)(H_0 - E_0)^{-1}(H' - E'_j)\psi_j\|^2 = \int_{-\infty}^{\infty} d\mu_j(h)(h - E_0 - \lambda E'_j)^2$$

$$\geq \varepsilon^2\lambda^{2\eta} \int_{h \notin I_j(\lambda)} d\mu_j(h) = \varepsilon^2\lambda^{2\eta} \|(\mathbf{1} - P_{I_j(\lambda)}(H_0 + \lambda H'))\psi_j(\lambda)\|^2.$$

Because $\psi_j(\lambda) \to \psi_j$, $\eta < 2$, it follows that $(\mathbf{1} - P_{I_j(\lambda)}(H_0 + \lambda H'))\psi_j \to 0$. Since the vectors ψ_j span the range of P_j, this implies the norm convergence $P_{I_j(\lambda)}(H_0 + \lambda H')P_j \Rightarrow P_j$. By (4.2.7(ii)), once $I_j(\lambda_0)$ no longer contains anything but the eigenvalue $E_0 + \lambda E'_j$, the projections $P_{I_j(\lambda_0)}(H_0 + \lambda H')$ converge strongly to $P_{I_j(\lambda_0)}(H_0) = P_j$. Therefore, if $\lambda < \lambda_0$, then

$$P_{I_j(\lambda)}(H_0 + \lambda H') = P_{I_j(\lambda)}(H_0 + \lambda H')P_{I_j(\lambda_0)}(H_0 + \lambda H') \to P_j. \qquad \square$$

At first sight, Theorem (4.2.9) appears without physical significance. For instance, in the trivial example of (4.2.8; 3), perturbation theory does not work, since 0 is an infinitely degenerate eigenvalue of H_0; with $E_0 = E_j = 0$, $\eta < 1$, Theorem (4.2.9) is still valid, yet nothing distinguishes the spectral value 0 of the operator λx. The experimentally detectable consequences of (4.2.9) are brought to light by consideration of the

Indeterminacy Relation of Time and Energy (4.2.11)

The probability that an initial state ψ is again measured at a later time t is $|\langle\psi|\exp(-iHt)\psi\rangle|^2$. For this reason, $\tau(\psi) \equiv \frac{1}{2}\int_{-\infty}^{\infty} dt\,|\langle\psi|\exp(-iHt)\psi\rangle|^2$ is referred to as the lifetime of ψ. If the support of ψ in the spectral representation of H is contained in the interval $(E_0 - \varepsilon, E_0 + \varepsilon)$, then $\tau(\psi) \geq 1/8\pi\varepsilon$.

Proof

As in the proof of (3.4.11), it follows from Parseval's equation that $\tau(\psi) = \int (d\omega/4\pi)|\langle\psi|\delta(H - \omega)\psi\rangle|^2$, and then by the Cauchy–Schwarz inequality,

$$1 = \left(\int_{E_0-\varepsilon}^{E_0+\varepsilon} d\omega\langle\psi|\delta(H-\omega)\psi\rangle\right)^2$$

$$\leq \int_{E_0-\varepsilon}^{E_0+\varepsilon} d\omega' \int_{E_0-\varepsilon}^{E_0+\varepsilon} d\omega\langle\psi|\delta(H-\omega)\psi\rangle^2 = 8\pi\varepsilon\tau(\psi). \qquad \square$$

If a perturbed operator is strongly but not norm continuous, then an eigenvalue E_0 may disappear into a continuum that springs into existence. However, even if this happens, for small λ the state ψ_0 has a long lifetime:

The Lifetimes of Eigenstates that have Disappeared into the Continuum (4.2.12)

With the assumptions of (4.2.9), *for all $\varepsilon > 0$ there exists a $\lambda_0 > 0$ such that $\tau(\psi_j) > 2/\varepsilon\lambda^\eta$ for all λ, $0 < \lambda < \lambda_0$.*

Proof

Let $\psi_I = P_{I(\lambda)}\psi_j$. The strong convergence of the operator $H(\lambda)$ implies the existence of a λ_0 such that $\|\psi_I - \psi_j\| = \|(P_{I(\lambda)} - P_j)\psi_j\| < \varepsilon/2$ for all λ, $0 < \lambda < \lambda_0$. Therefore

$$\|\psi_I\|^2 = \int_{E-\varepsilon\lambda^\eta}^{E+\varepsilon\lambda^\eta} d\omega\langle\psi_j|\delta(H-\omega)\psi_j\rangle \geq 1 - \varepsilon,$$

so this proposition follows from (4.2.11). $\square$

Now that the mathematical state of affairs is understood, let us return to the physical problem and examine $H_B = H_0 + \lambda H'$. The situation is only half as bad as it might be, since the point spectrum is preserved for the physical values $\lambda \geq 0$; this follows immediately from the min-max principle, since the term linear in B, which was built into the H_0 of (4.2.1), is simultaneously diagonable with $\hat{L}_3$ (see (3.3.20; 4)), and $e^2B^2(x_1^2 + x_2^2)/8m$ is a positive perturbation. The number of eigenvalues of H_B under a given energy E is therefore at most the same as the number of eigenvalues $E^{(0)}_{n,l,l_3} \equiv -(m\alpha^2/2n^2) - (eB/2m)l_3$ of H_0 under E. This argument leads straightaway to

Bounds for the Eigenvalues of H_B (4.2.13)

The lowest eigenvalue E_{l_3} of H_B, where l_3 is a given eigenvalue of $\hat{L}_3$, satisfies

$$E^{(0)}_{l_3+1,l_3,l_3} \leq E_{l_3} \leq E^{(0)}_{l_3+1,l_3,l_3} + \frac{e^2B^2}{8m}\langle l_3 + 1, l_3, l_3 | x_1^2 + x_2^2 | l_3 + 1, l_3, l_3\rangle,$$

$$H_0|n, l, l_3\rangle = E^{(0)}_{n,l,l_3}|n, l, l_3\rangle.$$

Remarks (4.2.14)

1. These bounds show that the divergence of perturbation theory does not diminish the usefulness of the linear formula for small B. It can in fact be shown that the perturbation series is Borel summable [3].
2. The term α/r is compact relative to the rest of H_B (Problem 6), so the essential spectrum of H_B begins at $eB/2m > 0$, as in (3.3.5; 3).
3. At this stage, (4.2.11) applies only to particles without spin. The presence of spin adds a term $B\mu S_3$ to H_B, where for an electron the spin magnetic moment μ is $2 \cdot [1.0011596] \cdot e/2m$. The new term is simultaneously diagonable with H_0; as long as the relativistic spin-orbit coupling is left out, the difference is a simple additive constant.

To finish the section off, we discuss the Stark effect in greater detail. As we saw that if $E \neq 0$, then $\sigma_{ac}(H_E) = \mathbb{R}$ and $\sigma_p(H_E) = \sigma_s(H_E) = \varnothing$, one might well wonder how so many physicists have made successful careers measuring and calculating the eigenvalues of H_E. The underlying reasons are some nice

Stark-Effect Delicacies for Mathematical Connoisseurs (4.2.15)

(i) When $E \neq 0$, suitable expectation values of the resolvent $(H_E - z)^{-1}$ have a branch cut along $\mathbb{R}^-$, and the poles of the resolvent when $E = 0$ move onto the second sheet when the field E is switched on.

(ii) The imaginary part of the position of the pole associated with the ground state goes as $\exp(-\alpha^3/6eE)$ as $E \to 0$. The small imaginary part shows up

as a long lifetime (4.2.12) and as a sharp resonance in the scattering matrix (4.2.4), and hence as a long time-delay (3.6.17).

(iii) Perturbation theory leads to the correct asymptotic power-series for the positions of the poles, all coefficients being integrals of real functions and hence real. The imaginary part is invisible in perturbation theory, since it goes to zero faster than any power of the applied field.

(iv) Since any reasonable procedure for resumming the perturbation series will lead to something real, it can not give the exact position of the pole. However, if one begins with a complex electric field E, Borel sums the series, and then lets Im E tend to zero, the complex poles can be found exactly.

The proofs of these mathematical facts can be found in [13]. The physics underlying the complex poles is the quantum-mechanical tunneling effect, by which an electron has some probability of reaching a position with large $-x_3$. If the field is not too large, then the time taken for the tunneling is so long that the effect can be neglected in any conceivable experiment.

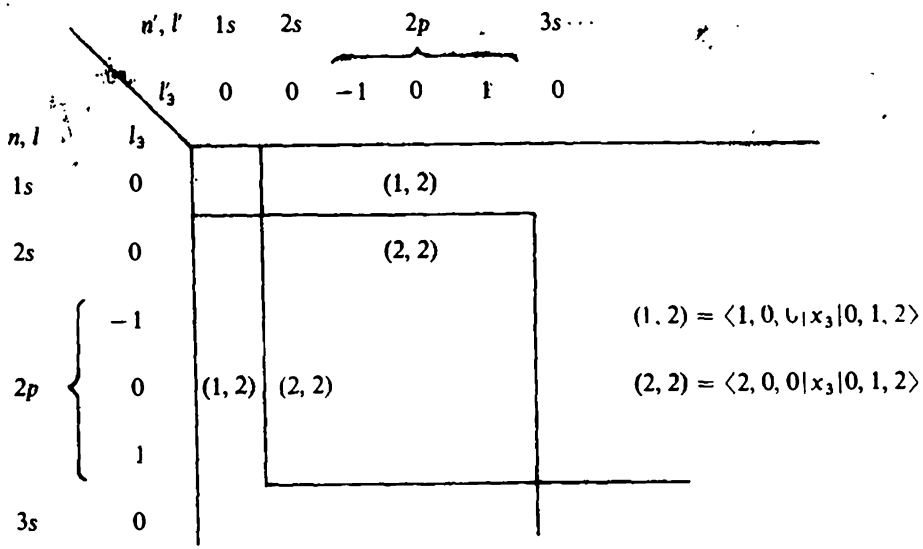
Let us next ascertain the energies at which the spectrum is asymptotically concentrated. We shall not come up with any bounds for the (nonexistent) eigenvalues.

First-Order Perturbation Theory (4.2.16)

The first step is to diagonalize H' in the degeneracy spaces of H_0. From (2.3.14) and the conservation of $\hat{L}_3$ we get

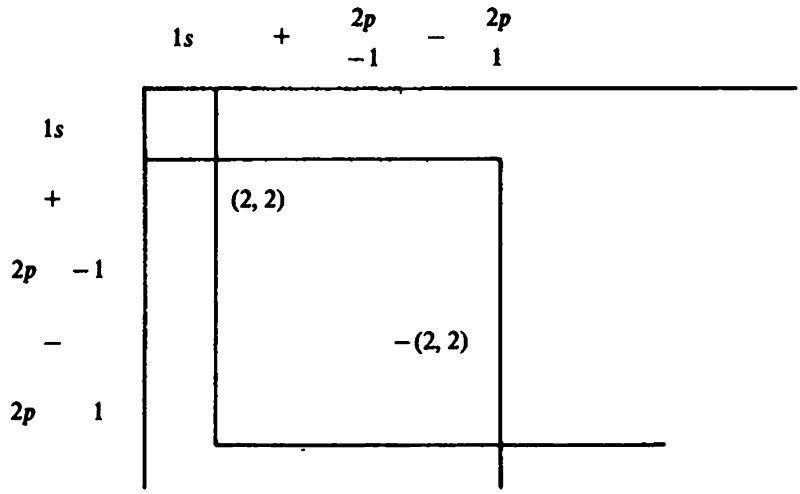
$$\langle n, l, l_3|x_3|n', l', l_3'\rangle = \delta_{l_3,l_3'}\,\delta_{l,l'\pm 1}\langle n, l, l_3|x_3|n', l \mp 1, l_3\rangle,$$

so in the simplest cases H' looks as follows, represented as a matrix:



This is diagonalized with the combinations

$$|\pm\rangle = (1/\sqrt{2})(|2,0,0\rangle \pm |2,1,0\rangle):$$



It is apparent that to first order in E, the values E_{n,l,l_3} are unchanged for $n = 1$ and shifted by $\pm eE\langle 2,0,0|x_3|2,1,0\rangle$ for $n = 2$, $l_3 = 0$ (Problem 5).

Remarks (4.2.17)

1. Unsophisticated feelings are vindicated in that, as with the Zeeman effect, the first-order correction to the energy is just the field strength times the dipole moment.
2. This result seems to contradict a general theorem: *The expectation value of the dipole moment is zero in eigenstates of an operator that commutes with the parity P.* Proof: $H|\rangle = E|\rangle \Rightarrow P|\rangle = \pm|\rangle$, so $\langle|x_3|\rangle = -\langle|Px_3P|\rangle = -\langle|x_3|\rangle$. The explanation is that the conditions of the theorem are incomplete; *it must also be assumed that all the eigenvectors with the same E have the same parity*, which is not true in the Stark effect.
3. Relativistically, the $S_{1/2} - P_{3/2}$ degeneracy is removed in the Dirac equation and, moreover, the Lamb shift separates the $P_{1/2}$ and $S_{1/2}$ levels. Then the theorem of Remark 2 applies, and, strictly speaking, there is no linear Stark effect.
4. Since the more precise formula for the splitting of the energies is

$$\frac{\varepsilon_{2s} + \varepsilon_{2p}}{2} \pm \sqrt{\left(\frac{\varepsilon_{2s} - \varepsilon_{2p}}{2}\right)^2 + (eE\langle z\rangle)^2},$$

where the ε's are the eigenvalues for $E = 0$, and since $\varepsilon_{2s} - \varepsilon_{2p}$ is very small, the splitting soon becomes virtually linear in E.

Problems (4.2.18)

1. Show that $\int_0^\infty dt(1+t^2)(1+t^2b^{-4})^{-3/2}\int(d^3x/r^2)\exp(-|\mathbf{x}-\bar{\mathbf{x}}(t)|^2/(b^2+t^2b^{-2}))<\infty$, $\bar{\mathbf{x}}(t)=(\bar{x}_1,\bar{x}_2,\bar{x}_3+gt^2)$.
2. Show that if $f_n(x)\downarrow f(x)\geq 0$, then $f_n\to f$ strongly as a multiplication operator.
3. Calculate $\langle n,l,l_3|x_1^2+x_2^2|n,l,l_3\rangle$ for $n=1$ and 2.
4. Find an example of projection operators P_n converging strongly to P for which $\dim P_n=\infty$ but $\dim P<\infty$.
5. Calculate $\langle 2,0,0|x_3|2,1,0\rangle$.
6. Let $a_{|M}$ be the restriction of an operator a to the part of the Hilbert space on which $|\hat{L}_3|\leq M$. Show that $H_{B|M}(\alpha)$ is compact relative to $H_{B|M}(\alpha=0)$.

Solutions (4.2.19)

1. First write r^{-2} as $\int_0^\infty ds\exp(-sr^2)$. The resulting Gaussian integrations over x_1, x_2, and x_3 are easy to do by completing the squares in the exponents. To indicate how the calculation then proceeds, consider, for simplicity, $b=1$ – the calculation for $b\neq 1$ is similar. Then

$$\int_0^\infty \frac{dt}{\sqrt{1+t^2}}\int_0^\infty ds\int_{\mathbb{R}^3} d^3x\exp\left(-sr^2-\frac{x_1^2+x_2^2+(x_3+gt^2)^2}{1+t^2}\right)$$

$$=\text{const}\int_0^\infty \frac{dt}{\sqrt{1+t^2}}\int_0^\infty \frac{ds}{(s+(1+t^2)^{-1})^{3/2}}$$

$$\times\exp\left(-\frac{g^2t^4}{1+t^2}\left(1-\frac{1}{1+s(1+t^2)}\right)\right),$$

where the square in the exponent was completed in the last step. The two remaining integrations are easy to estimate if the domain of integration is divided into $0\leq s, t\leq 1$; $1\leq s,t<\infty$; and the rest.

2. By Lebesgue's dominated convergence theorem, $\int d\mu(x)|\psi(x)|^2(f_n(x)-f(x))^2\to 0$.
3. In units where $m\alpha=1$,

$$|1,0,0\rangle=\frac{1}{\sqrt{\pi}}\exp(-r),$$

$$|2,0,0\rangle=\frac{1}{\sqrt{8\pi}}\left(1-\frac{r}{2}\right)\exp(-r/2),$$

$$|2,1,\pm 1\rangle=\frac{1}{8\sqrt{\pi}}r\exp(-r/2)\sin\theta\exp(\pm i\varphi),$$

$$|2,1,0\rangle=\frac{1}{4\sqrt{2\pi}}r\exp(-r/2)\cos\theta,$$

(cf. (4.1.27; 5)), and the corresponding expectation values are 2, 28, 24, and 12.

4. Let P_n be the operator in $\mathcal{B}(l^2)$, represented diagonally with entries

$$(\underbrace{0, 0, \ldots, 0}_{n}, 1, 1, \ldots).$$

Then $\operatorname{Tr} P_n = \infty$, but $P_n \to 0$.

5. $\langle 2, 0, 0|x_3|2, 1, 0\rangle = -\frac{1}{2}$.

6. We shall show that the graph norm of H_B provides a finer topology on the subspace when $\alpha = 0, B > 0$ than when $\alpha = 0, B = 0$. The rest of the argument is like the one for the relative compactness when $B = 0$. First note that if $2m = 1$,

$$\begin{aligned} a\|(|\mathbf{p}|^2 + \lambda(x_1^2 + x_2^2) - w\hat{L}_3)\psi\| + b\|\psi\| \\ \geq a\|(|\mathbf{p}|^2 + \lambda(x_1^2 + x_2^2))\psi\| + (b - M)\|\psi\|, \end{aligned}$$

and by use of the commutation relations,

$$\begin{aligned} \langle\psi|(|\mathbf{p}|^2 + \lambda(x_1^2 + x_2^2))^2\psi\rangle = \langle\psi||\mathbf{p}|^4 + 2\lambda(|\mathbf{p}|(x_1^2 + x_2^2)|\mathbf{p}| - 2) \\ + \lambda^2(x_1^2 + x_2^2)^2|\psi\rangle \geq \langle\psi||\mathbf{p}|^4\psi\rangle - 4\lambda\|\psi\|^2, \end{aligned}$$

so

$$a\|(|\mathbf{p}|^2 + \lambda(x_1^2 + x_2^2) - w\hat{L}_3)\psi\| + b\|\psi\| \geq a\||\mathbf{p}|^2\psi\| + (b - M - 2\lambda)\|\psi\|.$$

Since the norms $a\|H_B\psi\| + b\|\psi\|$ are equivalent for all a and $b > 0$, the proposition follows.

4.3 Helium-like Atoms

Although the Schrödinger equation for helium-like atoms is not exactly soluble, it is possible to make statements about it with arbitrarily good accuracy. For that reason it has been a touchstone of quantum mechanics.

The explanation of the spectrum of the helium atom was one of the early successes of the new quantum theory, since the old quantum theory, which was nothing more than classical mechanics bolstered with ad hoc quantum assumptions, was unable to cast much light on the problem. Even today, the set of problems connected with helium must be reckoned among the brilliant successes of mathematical physics. While Schrödinger's equation can not be solved for helium in terms of familiar functions, it is not only possible to formulate valid general statements about the spectrum of the Hamiltonian, but, indeed, the art of inequalities is so far advanced that rather exact bounds are available for the eigenvalues.

When dealing with two or more electrons, one must bring the exclusion principle into play. However, its importance will be limited in this situation, because of the additional spin degree of freedom. Any orbital can be occupied by two electrons, so long as their spins are antiparallel (a singlet state).

Forces that do not affect the spin cause no transitions between states of parallel (triplet) and antiparallel spin, so the spin part of the problem can be dealt with separately. The orbital wave-functions may be either symmetric or antisymmetric, and associated with either singlet or triplet spin vectors.

In addition to helium, we shall also be interested in the ions H^-, Li^+, Be^{++}, etc., the Hamiltonians of which are the same except that they have different values of the perturbation parameter. Moreover, elementary particle physics has created the possibility of replacing one e^- with a μ^- or other negatively charged particle, i.e., of varying the mass. We began the discussion of hydrogen by introducing center-of-mass and relative coordinates. The mass of the nucleus made its appearance in the latter part of the problem only through the reduced mass, and the problem was otherwise the same as the limit where the nuclear mass was set to infinity. As section 4.6 will be devoted to the study of the nuclear motion, let us immediately pass to this limit. It will remain to be determined how valid the results of this section are for systems like $e^-\mu^+e^-$ or $e^-e^+e^-$.

Once the usual list of necessary remarks has been checked off, things will progress rather rapidly to more detailed and less trivial matters. We start with the

Hamiltonian of an Atom with Two Electrons (4.3.1)

$$H = \frac{1}{2m}(|\mathbf{p}_1|^2 + |\mathbf{p}_2|^2) - Ze^2\left(\frac{1}{|\mathbf{x}_1|} + \frac{1}{|\mathbf{x}_2|}\right) + e^2\frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|}$$

can be put into normal form with a dilatation $\mathbf{p} \to Zme^2\mathbf{p}$, $\mathbf{x} \to (Zme^2)^{-1}\mathbf{x}$ and separation of the factors:

$$H(\alpha) = H(0) + \alpha H' \equiv Z^{-2}e^{-4}m^{-1}H = \tfrac{1}{2}(|\mathbf{p}_1|^2 + |\mathbf{p}_2|^2) - \frac{1}{|\mathbf{x}_1|} - \frac{1}{|\mathbf{x}_2|} + \frac{\alpha}{|\mathbf{x}_1 - \mathbf{x}_2|}, \qquad \alpha = \frac{1}{Z}.$$

Remark (4.3.2)

The perturbation parameter α is not a continuous variable in reality, but it can assume many different values, $1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}$, etc., corresponding to H^-, He, Li^+, Be^{++}, etc.

Since the potential energy is ε-bounded relative to the kinetic energy (see (4.4.5)), we know the

Domain of Self-Adjointness (4.3.3)

$$D(H) = (D(|\mathbf{p}|^2) \otimes \mathbb{C}^2) \wedge (D(|\mathbf{p}|^2) \otimes \mathbb{C}^2) \subset (L^2(\mathbb{R}^3) \otimes \mathbb{C}^2) \wedge (L^2(\mathbb{R}^3) \otimes \mathbb{C}^2).$$

Gloss (4.3.4)

The spin acts on the two-dimensional Hilbert space $\mathbb{C}^2$, so the Hilbert space appropriate for an electron with spin is $L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$. As was mentioned in (3.1.16), a system of two electrons is associated with the antisymmetric tensor product $\wedge$ (recall (I: 2.4.38)) of two such spaces.

We now turn to the task of locating the continuous spectrum of $H(\alpha)$. It turns out to be quite easy, because the perturbation is positive when $\alpha > 0$ and could at most move the spectrum upward.

The Beginning of the Essential Spectrum (4.3.5)

$$\sigma_{ess}(H(\alpha)) = \sigma_{ess}(H(0)) = [-\tfrac{1}{2}, \infty).$$

Proof

As remarked in (2.3.18; 5), for all $E \in [-\frac{1}{2}, \infty)$ we must find an orthogonal sequence ψ_n with norms bounded away from zero such that $(H - E)\psi_n \to 0$. Let φ_1 be the ground-state wave-function $|1, 0, 0\rangle$ of (4.1.14), let $R > 0$, and let $\chi_n(r)$ be a sequence of functions supported in $(2^n R, 2^{n+1}R)$ and such that $(|\mathbf{p}|^2/2 - E - \frac{1}{2})\chi_n \to 0$. (For instance, take $\chi_n(r) \sim \exp(ikr)/r$, $k^2/2 = E + \frac{1}{2}$, cut off outside $(2^n R, 2^{n+1}R)$ and smoothed out at the ends.) Then the sequence $\psi_n \equiv \varphi_1(\mathbf{x}_1)\chi_n(\mathbf{x}_2)$ is as required, since

$$\left\| \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} \psi_n \right\| \sim (2^n R)^{-1}. \qquad \square$$

Remarks (4.3.6)

1. The physical significance of the continuum starting at $-\frac{1}{2}$ is that one electron stays put in the ground state while the other runs off to infinity.
2. Mathematically speaking, we see that the potential energy may fail to be compact relative to the kinetic energy (it moves the essential spectrum) even when it is relatively ε-bounded.

The next topic is the point spectrum. It is clear that H is semibounded, since $H' > 0$, so $\sigma_p(H) \subset [-1, \infty)$. It will also be shown that if $\alpha < 1$, then there are infinitely many eigenvalues. This is to be expected on physical grounds, since an electron at a large distance would not see a fully screened nuclear charge, and it is known that an arbitrary weak $1/r$ potential has infinitely many bound states. To prove it, it is necessary to find another infinite set of orthogonal trial functions, with which H can be written as a diagonal matrix with eigenvalues less than $-\frac{1}{2}$, the bottom of the essential spectrum of

hydrogen. We construct them by putting one electron in the ground state φ_1 of $|\mathbf{p}_1|^2/2 - 1/r_1$ and pulling the other one far away:

$$\langle \varphi_1(\mathbf{x}_1) \otimes \psi(\mathbf{x}_2) | H | \varphi_1(\mathbf{x}_1) \otimes \psi(\mathbf{x}_2) \rangle = -\tfrac{1}{2} + \langle \psi(\mathbf{x}_2) | \frac{|\mathbf{p}_2|^2}{2} - \frac{1}{r_2} | \psi(\mathbf{x}_2) \rangle$$

$$+ \alpha \langle \varphi_1(\mathbf{x}_1) \otimes \psi(\mathbf{x}_2) | \frac{1}{r_{12}} | \varphi_1(\mathbf{x}_1) \otimes \psi(\mathbf{x}_2) \rangle.$$

The repulsion of the first electron shows up for the other one as an effective potential, which we expect to fall off as α/r_2 at large distances. Indeed, in Problem 5 it is calculated as

$$\langle \varphi_1(\mathbf{x}_1) | \frac{\alpha}{r_{12}} | \varphi_1(\mathbf{x}_1) \rangle = \frac{\alpha}{r_2} - \alpha \exp(-2r_2)\left(1 + \frac{1}{r_2}\right). \tag{4.3.7}$$

Consequently,

$$\langle H \rangle = -\frac{1}{2} + \langle \psi(\mathbf{x}_2) | \frac{|\mathbf{p}_2|^2}{2} - \frac{1-\alpha}{r_2} - \alpha\left(1 + \frac{1}{r_2}\right)\exp(-2r_2) | \psi(\mathbf{x}_2) \rangle.$$

Given disjointly supported functions ψ_j, if $k \neq j$, then $\langle \varphi \otimes \psi_j | H | \varphi \otimes \psi_k \rangle = 0$. By dilating and translating, we can arrange that

$$\langle \psi_j | \frac{|\mathbf{p}|^2}{2} - \frac{1}{r} + \alpha\left(1 + \frac{1}{r}\right)\exp(-2r) | \psi_j \rangle < 0,$$

so $\langle \varphi \otimes \psi_j | H | \varphi \otimes \psi_k \rangle = \varepsilon_k \delta_{jk}$, $\varepsilon_k < -\frac{1}{2}$. This proves

The Infinitude of the Point Spectrum (4.3.8)

If $\alpha < 1$, then $H(\alpha)$ of (4.3.1) *has infinitely many eigenvalues below $-\frac{1}{2}$, the bottom of its essential spectrum.*

Remark (4.3.9)

The exclusion principle was not mentioned, because it still makes no difference. If the two spin states are denoted $\uparrow$ and $\downarrow$, then the state $(\uparrow\varphi_1(1) \otimes \downarrow\psi(2) - \downarrow\psi(1) \otimes \uparrow\varphi_1(2))/\sqrt{2}$ leads to the same expectation value.

The virial theorem (4.1.4) made use only of the effect of dilatation on the kinetic and potential energies. The existence of more electrons does not change this, so we likewise have a

Virial Theorem (4.3.10)

If $(H(\alpha) - E)\psi = 0$, then $E = -\langle \psi | T | \psi \rangle = -\frac{1}{2}\langle \psi | 1/r_1 + 1/r_2 - \alpha/r_{12} | \psi \rangle$.

Corollary (4.3.11)

$H(\alpha)$ has no eigenvalues $E \geq 0$.

Remarks (4.3.12)

1. One might guess that there is a point spectrum only for $E < -\frac{1}{2}$. We shall, however, discover eigenvalues embedded in the essential spectrum between $-\frac{1}{2}$ and 0—in fact infinitely many if $\alpha < 1$. They correspond to states whose decay is prevented by conservation laws for various quantum numbers.
2. We shall later rule out the existence of singular spectrum, so σ consists of σ_p between -1 and $-\frac{1}{2}$, both σ_p and σ_{ac} between $-\frac{1}{2}$ and 0, and only σ_{ac} above 0.

This delineates the rough features of the spectrum. Let us next take up some finer details; since the eigenvalues of $H(\alpha)$ are analytic in α, we can start with $H(0)$ and track them as α is switched on.

The Point Spectrum of $H(0)$ (4.3.13)

Let $\varphi_{n,l,m,s}$ be the eigenfunctions $|n, l, m\rangle$ of (4.1.14) *times spin eigenfunctions* ($s = \pm\frac{1}{2}$). *Then*

$$\varphi_{n_1,l_1,m_1,s_1^{(1)}}\varphi_{n_2,l_2,m_2,s_2^{(2)}} - \varphi_{n_2,l_2,m_2,s_2^{(1)}}\varphi_{n_1,l_1,m_1,s_1^{(2)}}$$

is an eigenfunction of $H(0)$ with eigenvalue $-(n_1^{-2} + n_2^{-2})/2$. It is $4n_1^2n_2^2$-fold degenerate if $n_1 \neq n_2$, and $2n_1^2(2n_1^2 - 1)$-fold degenerate if $n_1 = n_2$.

Remarks (4.3.14)

1. All states with $n_1 > 1$ and $n_2 > 1$ have energies $\geq -\frac{1}{4}$, and hence live in the continuum beginning at $-\frac{1}{2}$.
2. The operator $H(0)$ possesses a copious commutant,

$$\{H(0)\}' \supset \{\mathbf{L}_1, \mathbf{F}_1, \sigma_1, \mathbf{L}_2, \mathbf{F}_2, \sigma_2\}.$$

These constants divide the spectrum and keep the discrete states from decaying into the continuum.

3. Parity (3.2.11) was not listed separately among the constants, since it can be expressed with the angular momentum as in (3.2.22; 1). As states evolve according to $H(0)$, the parities of the individual electrons, $P_i \equiv (-1)^{l_i}$, $l_i = \sqrt{L_i^2 + \frac{1}{4}} - \frac{1}{2}$, are separately conserved. The total parity

$P \equiv P_1 P_2 = (-1)^{l_1 + l_2}$ is not necessarily $(-1)^l$, however, since $\mathbf{L} \equiv \mathbf{L}_1 + \mathbf{L}_2$ can have any l such that $|l_1 - l_2| \leq l \leq l_1 + l_2$. There thus exist

States of Natural and Unnatural Parity (4.3.15)

If $P = (-1)^l$, then the state is said to have **natural parity**, and if $P = (-1)^{l+1}$, then it has **unnatural parity**.

Example (4.3.16)

If n_1 or n_2 equals 1, then l equals l_2 or l_1, and the resultant state has natural parity, $(-1)^{l_2} = (-1)^l$ or $(-1)^{l_1} = (-1)^l$. Hence the isolated point spectrum has natural parity. The first state with unnatural parity has $l_1 = l_2 = l = 1$, $P = +$. The wave-function has the form $(\mathbf{x}_1 \wedge \mathbf{x}_2) f(r_1, r_2)$, and if $n_1 = n_2 = 2$, the energy is $-\frac{1}{4}$. In the subspace of unnatural parity, the continuum begins at $E = -\frac{1}{8}$, for $n_1 = 2, n_2 = \infty$.

Constants of the Motion when $\alpha \neq 0$ (4.3.17)

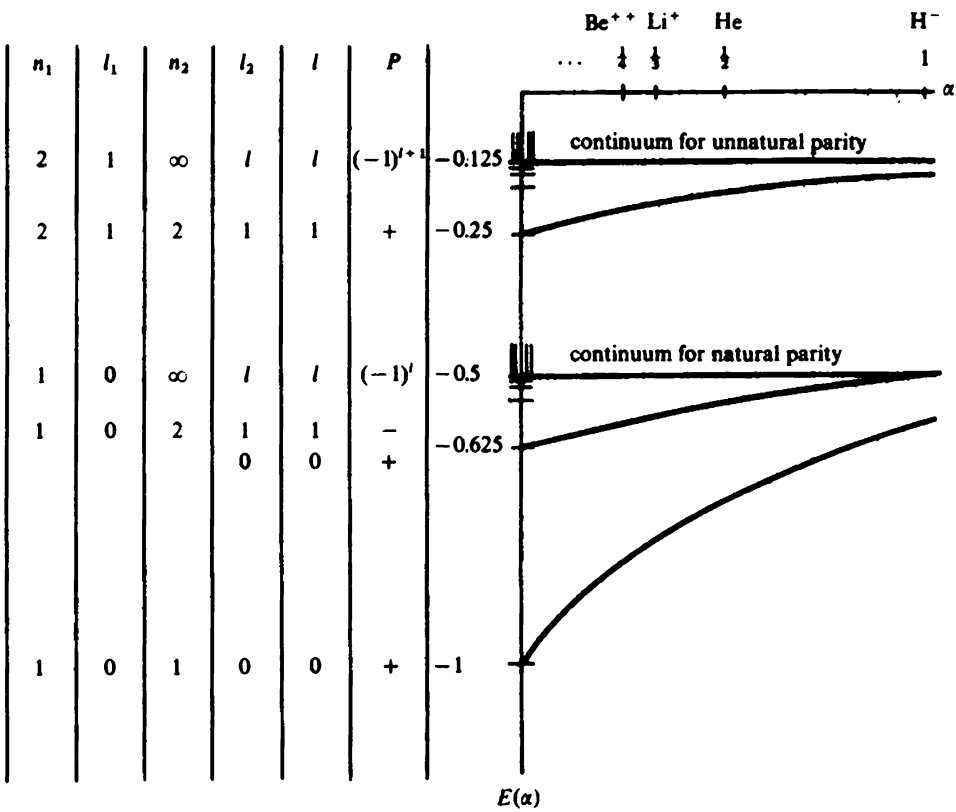
If $\alpha \neq 0$, then in addition to H, the quantities $\mathbf{L}$, P, σ_1, and σ_2 are conserved.

Physical Consequences of Conservation of Parity (4.3.18)

1. Parity must now be listed separately, since it is independent of $\mathbf{L}$. The Hilbert space decomposes into subspaces of natural and unnatural parity, which are not mixed by $H(\alpha)$. Hence discrete states of unnatural parity continue to exist within the continuum of natural parity. Just as in (4.3.5) the beginning of the continuum of unnatural parity at $-\frac{1}{8}$ is not affected when α is switched on. Since the eigenvalue of unnatural parity at $-\frac{1}{4}$ varies continuously with α, it remains isolated from the continuum of this part of the Hilbert space for α sufficiently small.
2. Eigenstates of $H(0)$ with natural parity and energies $E > -\frac{1}{2}$ when $\alpha > 0$ are not prevented from decaying into states with one electron in the ground state and the other running off to infinity. This is observed as the Auger effect.
3. States of unnatural parity are prevented from decaying to states with one electron in the ground state and the other running to infinity, since the final state would have natural parity. Conservation of parity likewise prevents their creation by direct collisions of electrons with atoms. In reality they are not absolutely stable, since they can decay by the interactions neglected in $H(\alpha)$, for example by electromagnetic radiation. The possible transitions are significantly slower than the Auger transitions.

4. Scattering theory reveals that there are many more constants in the absolutely continuous part of the spectrum, namely all the constants of $H(0)$, such as P_1 and P_2, after being transformed with the Møller operators.

We have seen that the perturbation with $\alpha \neq 0$ has broken the immense symmetry group of $H(0)$ and has separated the highly degenerate unperturbed states. Since H' is a positive perturbation, the eigenvalues $E_l(\alpha)$ are increasing functions of α. The way they depend on it is roughly as depicted in the figure below:



To locate the eigenvalues as functions of α more exactly, recall that not only do they increase monotonically, but that, moreover, the sum of the first n of them, $n = 1, 2, 3, \ldots$, is also concave in α by (3.5.23). We can even state a more refined proposition on the

Concavity of the Eigenvalues (4.3.19)

Let $E(\alpha)$ be the sum of the n lowest eigenvalues in a subspace of definite quantum numbers. Then $-(-E(\alpha))^{1/2}$ is concave in α.

Proof

Write $H = \frac{1}{2}(|\mathbf{p}_1|^2 + |\mathbf{p}_2|^2) - \alpha_0(1/r_1 + 1/r_2) + \alpha/r_{12}$. Then a dilatation argument (cf. (4.3.1)) shows that $E(\alpha, \alpha_0)$ is of the form $\alpha_0^2 f(\alpha/\alpha_0)$, which is concave not just in α alone, but in (α, α_0). The condition $f'' \leq 0$ generalizes to $E_{,\alpha\alpha}E_{,\alpha_0\alpha_0} - (E_{,\alpha\alpha_0})^2 \geq 0$, which implies that $2ff'' \geq (f')^2$, so

$$\frac{\partial^2}{\partial\alpha^2}(-\sqrt{-f(\alpha)}) \leq 0. \qquad \square$$

Remarks (4.3.20)

1. Eigenvalues can cross at finitely many points, at which f may not be differentiable. In such cases, it can be approximated arbitrarily well with C^∞ functions, which justifies the proof.
2. If m is not set equal to 1, then the theorem states that E is concave in the three variables $(1/m, \alpha, \alpha_0)$. The dedicated reader may check that this provides no new information.

Corollaries (4.3.21)

1. Linear bounds can be improved by parabolic bounds. For instance, by (3.5.32; 1), if $(H_0 - E_1(0))|0\rangle = 0$, then

$$E_1(0) + \alpha\langle 0|(H')^{-1}|0\rangle^{-1} \leq E_1(\alpha) \leq E_1(0) + \alpha\langle 0|H'|0\rangle,$$

the lower bound holding provided that

$$\alpha \leq \alpha_0 \equiv (E_2(0) - E_1(0))\langle 0|(H')^{-1}|0\rangle.$$

Since $-(-E_1(\alpha))^{1/2}$ is now known to be concave, the linear bounds $g(\alpha) \leq g(0) + \alpha g'(0)$, $g = -\sqrt{-f}$, imply:

$$E_1(0)\left(1 + \frac{\alpha}{\alpha_0}\left(\sqrt{\frac{E_2(0)}{E_1(0)}} - 1\right)\right)^2 \leq E_1(\alpha) \leq E_1(0)\left(1 + \frac{\alpha}{2}\frac{\langle 0|H'|0\rangle}{E_1(0)}\right)^2.$$

2. If $\alpha_1 < \alpha < \alpha_2$, then

$$\frac{-\sqrt{-f(\alpha)} + \sqrt{-f(\alpha_1)}}{\alpha - \alpha_1} \leq \frac{f'(\alpha)}{2\sqrt{-f(\alpha)}} \leq \frac{-\sqrt{-f(\alpha_2)} + \sqrt{-f(\alpha)}}{\alpha_2 - \alpha},$$

so, if $|\alpha\rangle$ is the eigenvector such that $(H_0 + \alpha H' - E_1(\alpha))|\alpha\rangle = 0$, then we obtain bounds on f', and hence on the expectation value of H':

$$\frac{2}{\alpha - \alpha_1}(\sqrt{E_1(\alpha)E_1(\alpha_1)} - |E_1(\alpha)|) \leq f'(\alpha) = \langle\alpha|\frac{1}{r_{12}}|\alpha\rangle$$

$$\leq \frac{2}{\alpha_2 - \alpha}(|E_1(\alpha)| - \sqrt{E_1(\alpha)E_1(\alpha_2)}),$$

Applications (4.3.22)

1. The ground state of parahelium ($(1s)^2$): The vector $|0\rangle$ has the form $(\uparrow\downarrow - \downarrow\uparrow)\varphi_1(r_1)\varphi_1(r_2)/\sqrt{2}$, where $\varphi_1(r) = 2\exp(-r)$, and $E_1(0) = -1$, $E_2(0) = -\frac{5}{8}$. Problem 3 is to calculate that $\langle 0|1/r_{12}|0\rangle = \frac{5}{8}$ and $\langle 0|r_{12}|0\rangle = \frac{35}{16}$. Hence $\alpha_0 = \frac{105}{128}$, and

$$\min\left\{-\frac{5}{8}, -\left(1-\alpha\frac{128}{105}\left(1-\sqrt{\frac{5}{8}}\right)\right)^2 = -(1-\alpha\cdot 0.2553)^2\right\}$$

$$\leq E_1(\alpha) \leq -\left(1-\frac{5\alpha}{16}\right)^2$$

$$= -(1-\alpha\cdot 0.3152)^2.$$

2. The ground state of orthohelium ($(1s)(2s)$):

$$|0\rangle = \uparrow\uparrow(\varphi_1(r_1)\varphi_2(r_2) - \varphi_2(r_1)\varphi_1(r_2))/\sqrt{2},$$

where $\varphi_2(r) = \exp(-r/2)(1-r/2)/\sqrt{2}$, $E_1(0) = -\frac{5}{8}$, $E_2(0) = -\frac{5}{9}$.

$$\langle 0|\frac{1}{r_{12}}|0\rangle = \frac{17}{81} - \frac{16}{729},$$

$$\langle 0|r_{12}|0\rangle = \frac{25}{4} - \frac{11}{324} + \frac{2^{12}}{3^9} - \frac{5^2 2^7}{3^9}, \qquad \alpha_0 = 0.4348$$

(see Figures 17 and 18), and

$$\min\left\{-\frac{5}{9}, -\frac{5}{8}\left(1-\frac{\alpha}{0.4348}\left(1-\sqrt{\frac{8}{9}}\right)\right)^2 = -\frac{5}{8}(1-\alpha\cdot 0.1315)^2\right\}$$

$$\leq E_1(\alpha)$$

$$\leq -\frac{5}{8}(1-\alpha\cdot 0.1503)^2.$$

3. The lowest state with $L = 1$, i.e., $(1s)(2p)$: $|0\rangle = (\uparrow\downarrow \mp \downarrow\uparrow)(\varphi_1(r_1)\varphi_2(\mathbf{x}_2) \pm \varphi_2(\mathbf{x}_1)\varphi_1(r_2))/2$, $\varphi_2(\mathbf{x}) = Y_1^0(\theta)r\exp(-r/2)/\sqrt{4!}$, once again $E_1 = -\frac{5}{8}$, $E_2 = -\frac{5}{9}$, $\langle 0|1/r_{12}|0\rangle = \frac{59}{243} \pm \frac{112}{6561}$,

$$\langle 0|r_{12}|0\rangle = 5.2449 \mp 0.1366, \quad \alpha_0 = (0.35471, 0.37372),$$

$$\min\left\{-\frac{5}{9}, -\frac{5}{8}\left(1-\alpha\cdot\frac{0.16123}{0.15303}\right)^2\right\} \leq E(\alpha) \leq -\frac{5}{8}\left(1-\alpha\cdot\frac{0.2091}{0.1792}\right)^2.$$

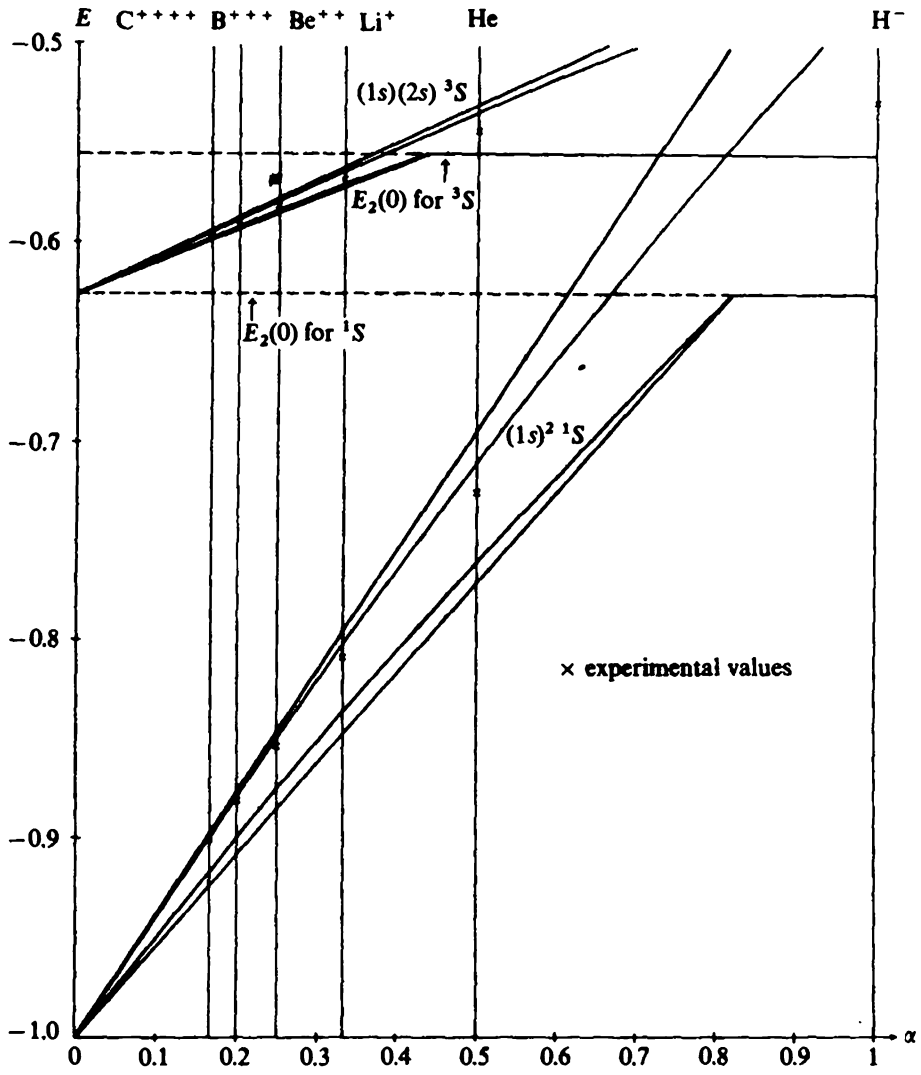


Figure 17 Linear and parabolic bounds for $(1s)^2\ {}^1S$ and $(1s)(2s)\ {}^3S$.

Remarks (4.3.23)

1. The rate of change at $\alpha = 0$ is exactly $\langle 0|H'|0\rangle$, which shows that $(1s)(2s)$ is the more energetically favorable state with $n = 2$. This is plausible, since the s orbitals are more densely concentrated near the nucleus, and are thus shielded less by the other electron. By first-order perturbation theory the $(1s)(2p)$ state with spin 1 is favored (Hund's rule), since the exclusion principle then makes the electrons avoid each other and feel less

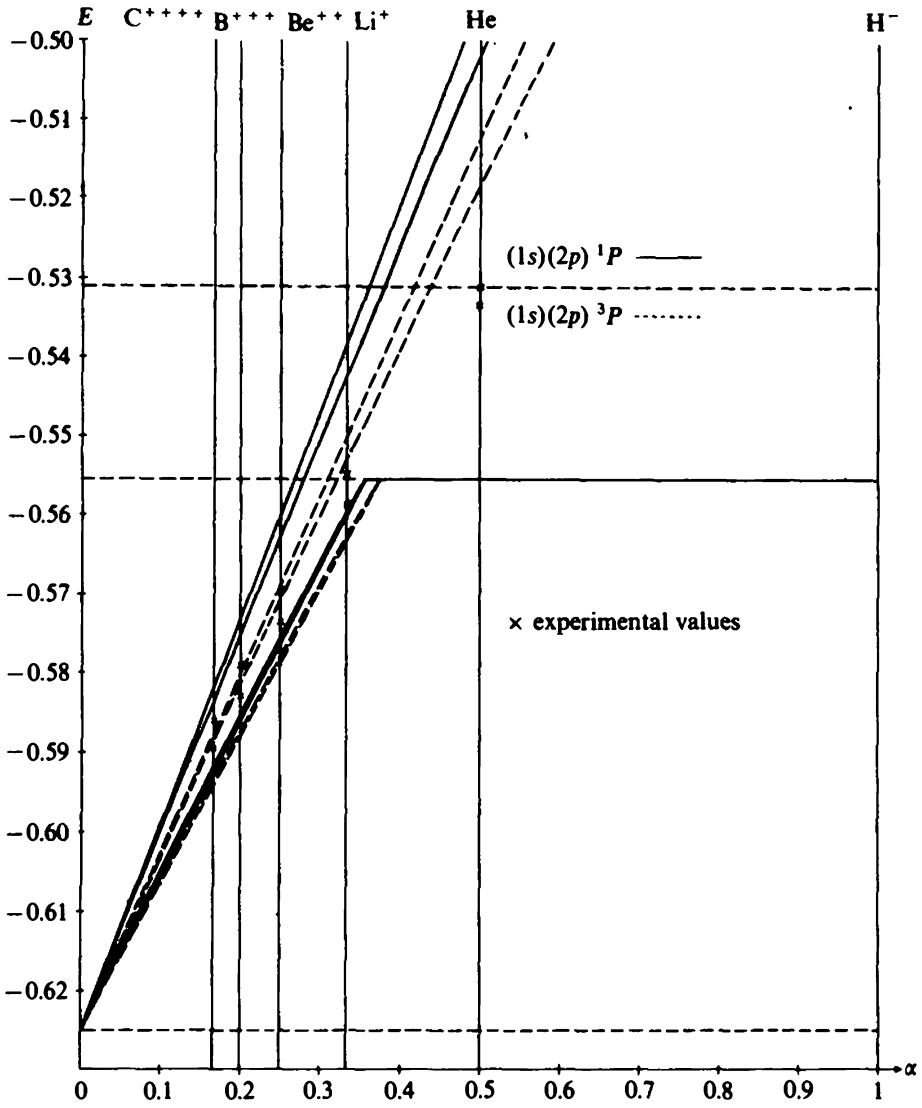


Figure 18 Linear and parabolic bounds for $(1s)(2p)\ ^3P$ and $(1s)(2p)\ ^1P$.

Coulombic repulsion. Our bounds, however, are not yet precise enough to prove this tendency for strictly positive α.

2. It is easy to see with $\langle n, l|r|n, l\rangle = (3n^2 - l(l+1))/2$ that the inequalities $\langle r\rangle\langle 1/r\rangle \geq 1$ and $\langle r_{12}\rangle \leq \langle r_1 + r_2\rangle$ are not at all weak.
3. The main drawback of the results that have been presented is that the lower bounds break down when $E(\alpha) > E_2$. The discussion in (3.5.32; 1) shows that only the use of many-dimensional projections can remedy this.

Ground States with Two-Dimensional Projections (4.3.24)

1. Consider the two lowest parastates with $\alpha = 0$,

$$|(1s)^2\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \otimes \varphi_1(1)\varphi_1(2),$$

$$|(1s)(2s)\rangle = \frac{1}{2}(\uparrow\downarrow - \downarrow\uparrow) \otimes (\varphi_1(1)\varphi_2(2) + \varphi_2(1)\varphi_1(2)),$$

and calculate the matrices

$$\begin{pmatrix} \langle(1s)^2|r_{12}|(1s)^2\rangle & \langle(1s)^2|r_{12}|(1s)(2s)\rangle \\ \langle(1s)(2s)|r_{12}|(1s)^2\rangle & \langle(1s)(2s)|r_{12}|(1s)(2s)\rangle \end{pmatrix}$$

$$= \begin{pmatrix} 2.1875 & -0.6371 \\ -0.6371 & 0.1706 \end{pmatrix} \equiv M_L^{-1},$$

$$\begin{pmatrix} \langle(1s)^2|\frac{1}{r_{12}}|(1s)^2\rangle & \langle(1s)^2|\frac{1}{r_{12}}|(1s)(2s)\rangle \\ \langle(1s)(2s)|\frac{1}{r_{12}}|(1s)^2\rangle & \langle(1s)(2s)|\frac{1}{r_{12}}|(1s)(2s)\rangle \end{pmatrix}$$

$$= \begin{pmatrix} 0.625 & 0.1263 \\ 0.1263 & 0.2318 \end{pmatrix} \equiv M_U.$$

The matrix

$$\begin{pmatrix} E_1(0) & 0 \\ 0 & E_2(0) \end{pmatrix} + \alpha M$$

has eigenvalues

$$E_{1,2} = \frac{\varepsilon_1 + \varepsilon_2}{2} + \alpha\frac{M_{11} + M_{22}}{2} \mp \sqrt{\left(\frac{\varepsilon_1 - \varepsilon_2}{2} + \alpha\frac{M_{11} - M_{22}}{2}\right)^2 + \alpha^2 M_{12}^2}$$

($\varepsilon_1 = E_1(0)$, $\varepsilon_2 = E_2(0)$), which, by use of M_L and M_U, are respectively lower bounds for the first two states, provided that they lie below $E_3(0)$, and upper bounds.

2. Problem 4 gives the analogous calculation for the other states looked at in (4.3.22), with the 2×2 matrices of H' and $(H')^{-1}$ for the states $(1s)(2s)$ and $(1s)(3s)$ and, respectively, $(1s)(2p)$ and $(1s)(3p)$.

Upper Bounds using Two-Parameter Trial Functions (4.3.25)

To comply with the desire of the electron for more freedom of movement, it is reasonable to use the functions $\exp(-\gamma r_1 - \beta r_2) \pm \exp(-\beta r_1 - \gamma r_2)$ and $Y_1(1)r_1 \exp(-\gamma r_1 - \beta r_2) \pm Y_1(2)r_2 \exp(-\beta r_1 - \gamma r_2)$ as trial functions for the ground states with $L = 0, 1$ and $S = 0, 1$, and to minimize the expectation value of H as β and γ vary. The table below lists the optimal parameters as functions of α. It makes it clear that the outer electrons come nearer to escaping when the nuclear charge is smaller.

Variational Calculations

state $^S(L)$	$(1s)(1s)\ ^1S$		$(1s)(2s)\ ^3S$		$(1s)(2p)\ ^3P$		$(1s)(2p)\ ^1P$	
α	β	γ	β	γ	β	γ	β	γ
1.	0.283	1.039	0.000		0.000		0.001	1.001
0.75	0.452	1.070	0.094	0.982	0.129	0.999	0.123	1.001
0.5	0.588	1.085	0.161	0.984	0.272	0.997	0.240	1.002
0.3333	0.695	1.097	0.202	0.979	0.361	0.994	0.322	1.003
0.25	0.754	1.108	0.222	0.975	0.400	0.993	0.366	1.003
0.2	0.769	1.082	0.232	0.970	0.424	0.992	0.392	1.001

Remarks (4.3.26)

1. Figures 19a, b, and c show the greater detail in the pictures that one obtains with the use of two-dimensional projections and the variational ansatz (4.3.25). The plot shows the square root of the energy; it is apparent that the experimental points lie close to the straight lines, and hence that Proposition (4.3.19) is a nearly optimal concavity property.
2. The parabolic upper bounds (4.3.21) can also be obtained with this variational argument, using $\exp(-rZ_{\text{eff}})$ in place of the ground state of H_0 and optimizing Z_{eff}. For the ^1S state this leads to $Z_{\text{eff}} = 1 - 5\alpha/16$, which reflects the partial screening of the nuclear charge.
3. Our bounds are good enough to separate the states ^3S, ^3P, and ^1P, which are degenerate when $\alpha = 0$, and to prove that Hund's rule orders them correctly.
4. With more numerical effort and trial functions having several parameters quite accurate upper bounds are obtainable. Temple's inequality (3.5.32; 2) then provides complementary lower bounds. Pekeris and Kinoshita used this technique to achieve a fantastic accuracy for the ground state. For practical purposes the eigenvalue problem can be considered solved up to $\alpha = \frac{1}{2}$ (helium).

The foregoing results are still rather poor for $\alpha = 1$, the negative hydrogen ion H^-. We know that if $\alpha < 1$, then there are infinitely many bound states

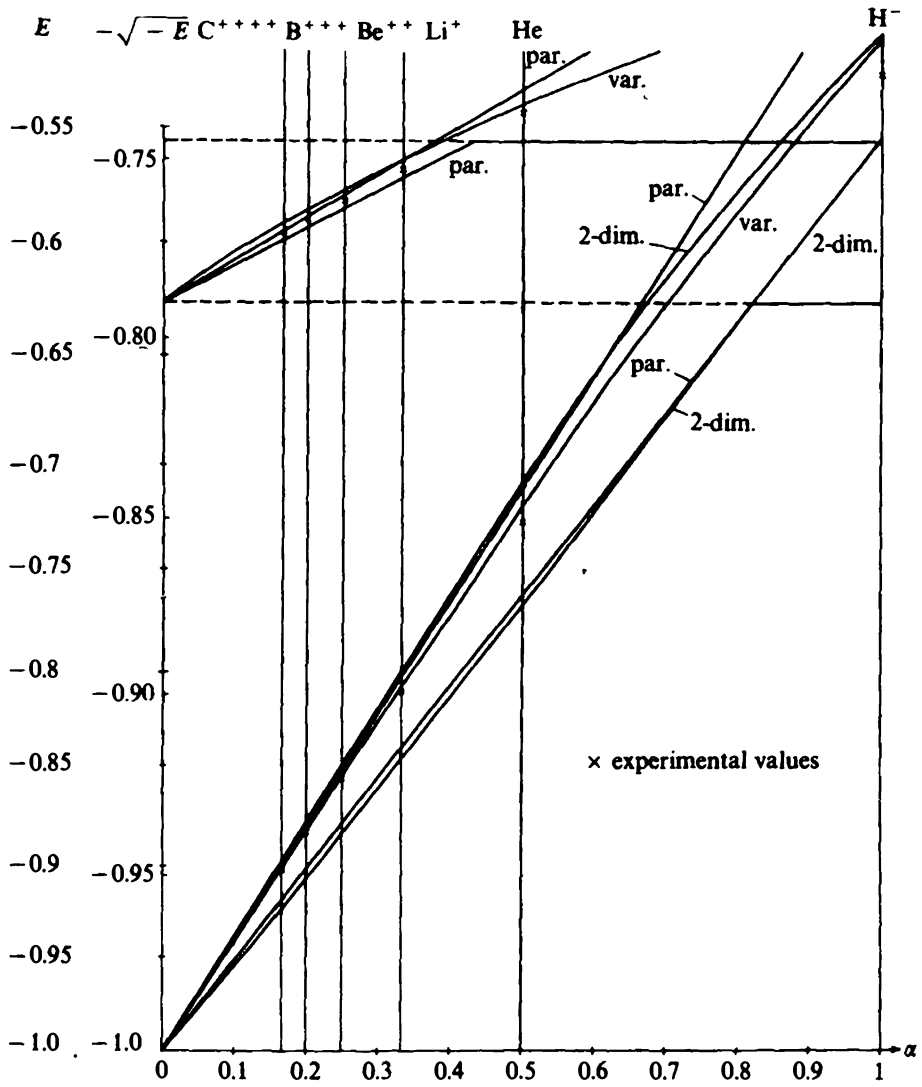


Figure 19a Variational calculation, parabolic bounds, and two-dimensional bounds for $(1s)^2\ {}^1S$ and $(1s)(2s)\ {}^3S$.

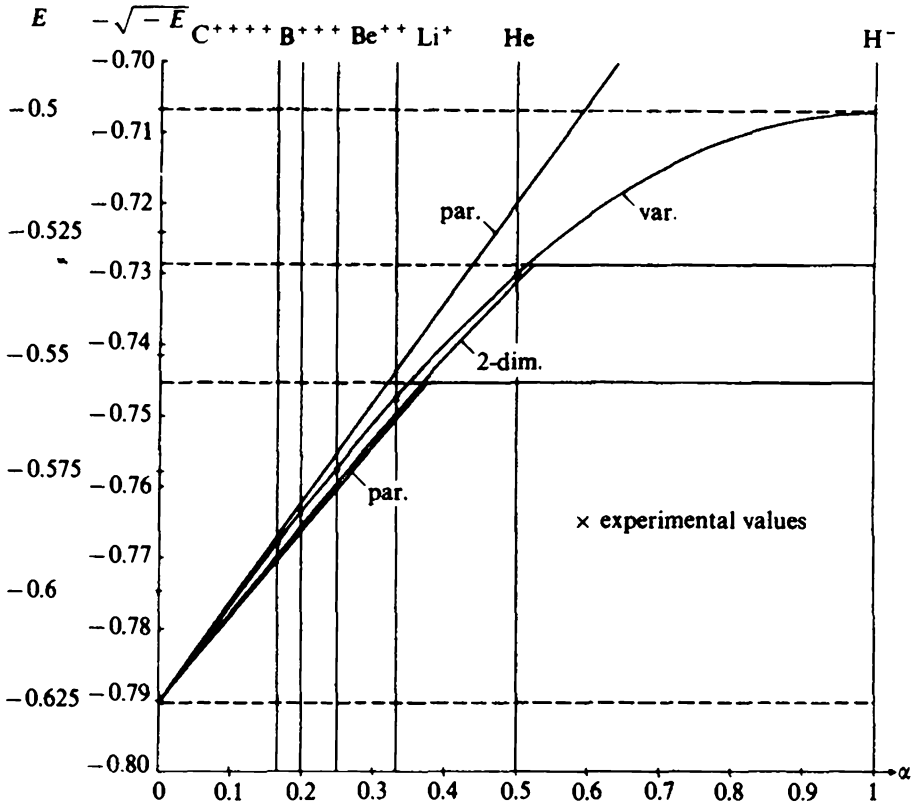


Figure 19b Variational calculation, parabolic bounds, and two-dimensional bounds for $(1s)(2p)\ ^3P$.

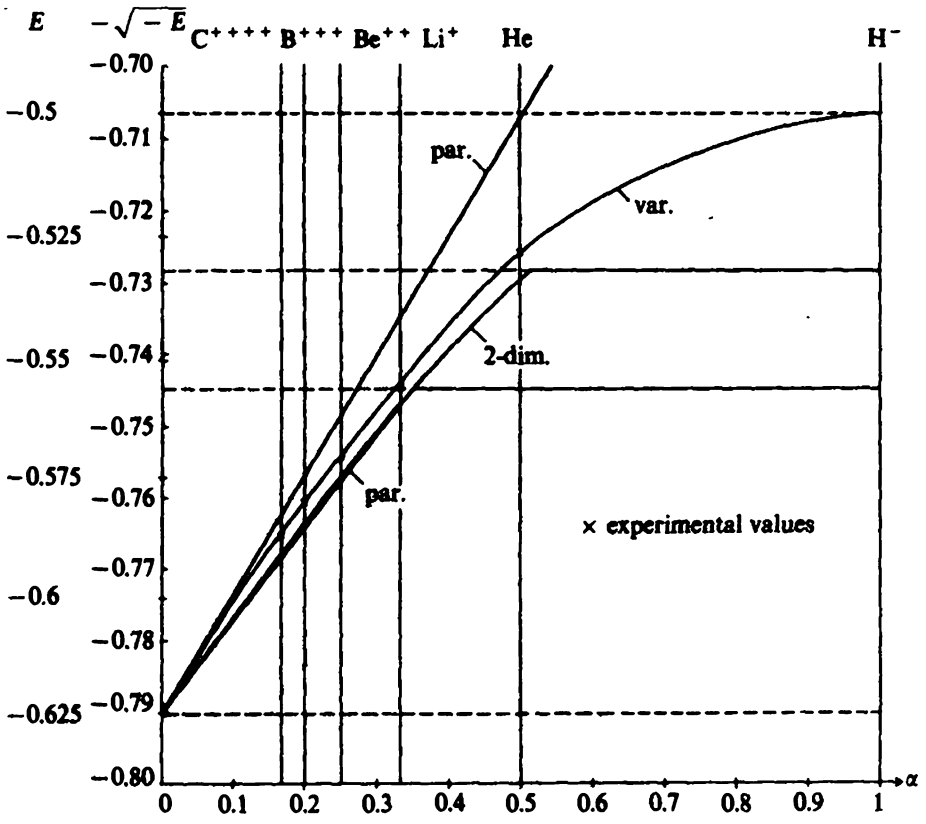


Figure 19c Variational calculation, parabolic bounds, and two-dimensional bounds for $(1s)(2p)\ ^1P$.

(4.3.8), but if $\alpha = 1$ we have as yet definitely found only one state of natural parity with the improved upper bounds. What happens to the infinitely many other states—do they move into the continuum when $\alpha = 1$, or remain isolated? The former alternative has been proved recently by Hill [15].

Bound States for $\alpha = 1$ (4.3.27)

$$H = \frac{|\mathbf{p}_1|^2}{2} + \frac{|\mathbf{p}_2|^2}{2\mu} - \frac{1}{|\mathbf{x}_1|} - \frac{1}{|\mathbf{x}_2|} + \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|}$$

has exactly two nondegenerate eigenvalues if $\mu = 1$. They develop continuously out of the ground states for $\alpha < 1$ in the subspaces of natural and of unnatural parity. If the ratio μ of the masses is sufficiently different from 1, then σ_p disappears entirely.

Remarks (4.3.28)

1. We shall consider only the subspace of natural parity; the argument can be extended to cover unnatural parity as well.
2. The case $\mu \neq 1$ is realistic for the system $p\mu^-e^-$. Since the Bohr radius of a muon is smaller than r_B of the electron by the ratio of the masses, a factor of 207, one would guess that it completely shields the proton, and that the electron is no longer bound. We shall see that the failure to bind happens for much less extreme mass ratios; yet it is difficult to find the exact value of μ at which σ_p disappears.
3. The strategy of the proof is to find an operator $H_L \leq H$ for which it can be shown that there is no (or only one) eigenvalue below the continuum at $-\frac{1}{2}$. More effort is required to show that there are no eigenvalues in the continuum of the same quantum number, and that part of the proof will not be given here. It necessitates verifying that such states are unstable under the addition of H'; see [3] and (4.4.13; 3).

Proof

(i) $\mu > \pi$. Let us do the easy part first and show that there exist no bound states if $\mu > \pi$. The ground state of $H(0)$ has energy $-(1 + \mu)/2$, and the continuum begins at $-\mu/2$. If particle 2—let us call it the muon—is excited, then the energy of the state becomes at least $-\frac{1}{2}(1 + \mu/4)$, which is in the continuum as soon as $\mu > \frac{4}{3}$. If P_0 is the projection onto the ground state $2\mu^{3/2}\exp(-\mu r_2)$ of the muon, and $P = \mathbf{1} \otimes P_0$, then clearly

$$\frac{|\mathbf{p}_2|^2}{2\mu} - \frac{1}{r_2} \geq -\frac{\mu}{2}P - \frac{\mu}{8}(1 - P).$$

As in (3.5.31) we now use the inequality

$$|\mathbf{x}_1 - \mathbf{x}_2|^{-1} \geq P(P|\mathbf{x}_1 - \mathbf{x}_2|P)^{-1}P \equiv V_L(r_1)P,$$

from which it is easy to calculate

$$V_L(r_1) = \left[\left(\frac{\mu^3}{\pi}\right)\int d^3x_2 \exp(-2\mu r_2)|\mathbf{x}_1 - \mathbf{x}_2|\right]^{-1}$$
$$= \mu\left[\mu r_1 + \frac{1}{\mu r_1} - \exp(-2\mu r_1)\left(\frac{1}{2} + \frac{1}{\mu r_1}\right)\right]^{-1} \qquad (4.3.29)$$

(Problem 3). Since

$$\frac{|\mathbf{p}_1|^2}{2} - \frac{1}{|\mathbf{x}_1|} + \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} \geq -\frac{1}{2},$$

we finally get

$$H \geq \left(-\frac{\mu}{2} + \frac{|\mathbf{p}_1|^2}{2} - \frac{1}{r_1} + V_L(r_1)\right)P + \left(-\frac{\mu}{8} - \frac{1}{2}\right)(1 - P). \qquad (4.3.30)$$

To show that $H \geq -\mu/2$ it must be verified that $|\mathbf{p}|^2/2 - 1/r + V_L(r) \geq 0$. First note that

$$-\frac{1}{r} + \left[r + \frac{1}{\mu^2 r} - \exp(-2\mu r)\left(\frac{1}{2\mu} + \frac{1}{\mu^2 r}\right)\right]^{-1}$$
$$= -\frac{1}{r}\left[1 + \frac{r^2\mu^2}{1 - \exp(-2\mu r)\left(1 + \frac{\mu r}{2}\right)}\right]^{-1} \geq -\frac{1}{r(1 + r^2\mu^2)}.$$

The Bargmann bound (3.5.37; 1) shows that there is no bound state if $2\int_0^\infty dr/(1 + r^2\mu^2) = (\pi/\mu) < 1$, that is, if the mass of the muon is greater than π times the mass of the electron.

(ii) $\mu = 1$. In this case the P used above, projecting onto wave-functions of the form $f(\mathbf{x}_1)\exp(-\mu r_2)$ does not do the trick, since $\exp(-r_1)f(\mathbf{x}_2)$ has just as low energy. Hence for two electrons it is preferable to use the Hilbert spaces $\mathscr{H}_2^{\pm}$ of functions of the form

$$f_{\pm}(\mathbf{x}_1, \mathbf{x}_2) = (\exp(-r_1)f(\mathbf{x}_2) \pm f(\mathbf{x}_1)\exp(-r_2))$$
$$\otimes\begin{pmatrix}\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)\\ \uparrow\uparrow\end{pmatrix}, \qquad f \in L^2(\mathbf{R}^3). \qquad (4.3.31)$$

As usual the arrows stand for the spin functions, and we may assume that f is orthogonal to $\exp(-r)$ in $\mathscr{H}_2^-$. The spaces $\mathscr{H}_2^{\pm}$ are invariant under operators of the form

$$\bar{h} = P_0(1) \otimes h(2) + h(1) \otimes P_0(2) \qquad (4.3.32)$$

(the argument of the operator indicates which factor it acts on). The space $L^2(\mathbb{R}^3)$ is mapped into $\mathscr{K}_2^{\pm}$ and $\mathscr{B}(L^2(\mathbb{R}^3))$ is mapped into $\mathscr{B}(\mathscr{K}_2^{\pm})$ by (4.3.31) and (4.3.32) in such a way that

$$\langle f | h\bar{g}\rangle = 2\langle (1 \pm P_0)f | h(1 \pm P_0)g\rangle. \tag{4.3.33}$$

The procedure used in the first part of the proof can now be mimicked; first project onto the union of the image spaces of the projections $\mathscr{P}_1$ and $\mathscr{P}_2$:

$$\mathscr{P}_1 = r_{12}^{1/2} P_0(1) V_L(x_2) r_{12}^{1/2}, \qquad \mathscr{P}_2 = r_{12}^{1/2} P_0(2) V_L(x_1) r_{12}^{1/2},$$

where $r_{12} \equiv |\mathbf{x}_1 - \mathbf{x}_2|$ and V_L is as in (4.3.29) with $\mu = 1$. Following the notation of (2.2.35) the projection onto the union will be called $\mathscr{P}_1 \vee \mathscr{P}_2$. As we learned there,

$$\mathscr{P}_2 \geq \mathscr{P}_2\mathscr{P}_1\mathscr{P}_2 \geq \mathscr{P}_2\mathscr{P}_1\mathscr{P}_2\mathscr{P}_1\mathscr{P}_2 \geq \cdots \geq \mathscr{P}_1 \wedge \mathscr{P}_2,$$

which can be rewritten for $\mathscr{P}_1 \vee \mathscr{P}_2 = \mathbf{1} - (\mathbf{1} - \mathscr{P}_1) \wedge (\mathbf{1} - \mathscr{P}_2)$, though it involves lengthy expressions. Fortunately, for our purposes the following inequalities are sufficient:

$$\mathscr{P}_1 \wedge \mathscr{P}_2 \leq \tfrac{1}{2}(\mathscr{P}_1\mathscr{P}_2\mathscr{P}_1 + \mathscr{P}_2\mathscr{P}_1\mathscr{P}_2) \Leftrightarrow$$
$$\mathscr{P}_1 \vee \mathscr{P}_2 \geq \mathscr{P}_1 + \mathscr{P}_2 - \mathscr{P}_1\mathscr{P}_2 - \mathscr{P}_2\mathscr{P}_1 + \tfrac{1}{2}(\mathscr{P}_1\mathscr{P}_2\mathscr{P}_1 + \mathscr{P}_2\mathscr{P}_1\mathscr{P}_2). \tag{4.3.34}$$

This can be simplified with the observation that although $\mathscr{P}_1$ and $\mathscr{P}_2$ do not commute, they have a common eigenfunction $\in L^2(\mathbb{R}^6)$, i.e., when normalized,

$$\chi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\pi}\sqrt{\frac{16 r_{12}}{35}} \exp(-r_1 - r_2), \qquad \mathscr{P}_i\chi = \chi.$$

This function has eigenvalue -1 for the operator $-\mathscr{P}_1\mathscr{P}_2 - \mathscr{P}_2\mathscr{P}_1 + (\mathscr{P}_1\mathscr{P}_2\mathscr{P}_1 + \mathscr{P}_2\mathscr{P}_1\mathscr{P}_2)/2$. Since it can be shown (Problem 2) that in $\mathscr{K}_2^+$ the other eigenvalues of the operator are positive, (4.3.34) leads to

$$\mathscr{P}_1 \vee \mathscr{P}_2 \geq \mathscr{P}_1 + \mathscr{P}_2 - |\chi\rangle\langle\chi| \tag{4.3.35}$$

(from here on we work only in $\mathscr{K}_2^+$). The projection method (3.5.31) then shows that

$$\frac{1}{r_{12}} \geq r_{12}^{-1/2}\mathscr{P}_1 \vee \mathscr{P}_2 r_{12}^{-1/2} \geq P_0(1)V_L(2) + P_0(2)V_L(1) - \tfrac{16}{35}P_0(1)P_0(2). \tag{4.3.36}$$

The next thing to show is that there are no additional negative eigenvalues of

$$H_0 + r_{12}^{-1}, \qquad H_0 = \tfrac{1}{2} + \tfrac{1}{2}(|\mathbf{p}_1|^2 + |\mathbf{p}_2|^2) - r_1^{-1} - r_2^{-1}.$$

The operator H_0 leaves the spaces $\mathscr{H}_2^{\pm}$ invariant and acts on them as

$$H_0 f_{\pm} = \overline{\left(\frac{1}{2}|\mathbf{p}|^2 - \frac{1}{r}\right) f_{\pm}} = \overline{\left(\frac{1}{2}|\mathbf{p}|^2 - \frac{1}{r} + \begin{matrix} \frac{1}{4} P_0 \\ 0 \end{matrix}\right) f_{\pm}}.$$

On the orthogonal complement of $\mathscr{H}_2^{\pm}$ no electron is in the ground state, so $H_0 > \frac{1}{4}$. If $P^{\pm}$ are the projections onto $\mathscr{H}_2^{\pm}$, then (4.3.36) allows us to write

$$H_0 + r_{12}^{-1} \geq P^{\pm}\overline{\left(\frac{1}{2}|\mathbf{p}|^2 - \frac{1}{r} + V_L(r) + \begin{matrix} P_0\left(\frac{1}{4} - \frac{8}{35}\right) \\ 0 \end{matrix}\right)} + \frac{1}{4}(1 - P^{\pm}).$$

Since $\frac{1}{4} > \frac{8}{35}$, we have to verify that $h \equiv |\mathbf{p}|^2/2 - 1/r + V_L(r)$ has only one bound state, whereas $(1 - P_0)h(1 - P_0)$ has none. The first statement can be proved analytically by noting, as in (i), that $h \geq |\mathbf{p}|^2/2 - 2/r(1 + r)^2$, but making a more detailed calculation. As in the proof of (3.5.36) we find the number of values $\lambda \leq 1$ for which there is a $\psi \in L^2$ satisfying

$$\frac{|\mathbf{p}|^2}{2}\psi = \frac{1}{2}\left(\frac{-1}{r}\frac{\partial^2}{\partial r^2}r + \frac{l(l+1)}{r^2}\right)\psi = \frac{2\lambda}{r(1+r)^2}\psi.$$

With the change of variables $r = z/(1 - z)$, $\psi = r^l w(z)$, this becomes the hypergeometric equation $z(1 - z)w'' + 2(l + 1 - z)w' + 4\lambda w = 0$, the well-known properties of which include the requirement that $\lambda = (n + 2l + 1)(n + 2l + 2)/4$, $n = 0, 1, 2, \ldots$; $\lambda = \frac{1}{2} < 1$ only if $n = l = 0$. Hence there is at most one bound state. The proof for $\mathscr{H}_2^-$ takes a longer discussion, and can be read in [15]. □

Remarks (4.3.37)

1. The proof for H^- can be generalized for finite but large nuclear masses. It is certainly not valid for all nuclear masses, as pe^-p has many bound states.
2. If $Z > 1$ ($\alpha < 1$), then a muon in the ground state should effectively reduce the nuclear charge at larger distances by 1, and the electronic spectrum should be a Balmer spectrum with $Z - 1$ in place of Z, i.e., $\sim(1 - \alpha)^2$. To show this mathematically, write

$$\begin{aligned}\frac{1}{2}\left(|\mathbf{p}_1|^2 + \frac{|\mathbf{p}_2|^2}{\mu}\right) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\alpha}{r_{12}} \\ \geq P\left(-\frac{\mu}{2} + \frac{|\mathbf{p}_1|^2}{2\mu_1} + |\mathbf{p}_1|^2\frac{\mu_1 - 1}{2\mu_1} - \frac{1-\alpha}{r_1}\right. \\ \left. + \alpha\left(V_L(r_1) - \frac{1}{r_1}\right)\right) + \left(-\frac{\mu}{8} - \frac{1}{2}\right)(1 - P)\end{aligned}$$

and choose μ_1 large enough that $|\mathbf{p}|^2/2\mu_1 + \alpha(V_L(r) - 1/r)$ just remains ≥ 0. The value $\alpha\mu_1/\mu = 1/\pi$ of part (i) was improved to $\alpha\mu_1/\mu = \frac{1}{2}$ in part (ii), so

$$H \geq \left(-\frac{\mu}{2} + \frac{|\mathbf{p}_1|^2}{2}\left(1 - \frac{2\alpha}{\mu}\right) + \frac{1-\alpha}{r_1}\right)P + \left(-\frac{\mu}{8} - \frac{1}{2}\right)(1 - P).$$

Hence, for the state of the electron with principle quantum number n,

$$-\frac{1}{2}\left(\mu + \frac{(1-\alpha)^2}{n^2}\left(1 - \frac{2\alpha}{\mu}\right)^{-1}\right) \leq E_n \leq -\frac{1}{2}\left(\mu + \frac{(1-\alpha)^2}{n^2}\right).$$

The upper bound results from the use of trial functions of the form $\chi \equiv \varphi(\mathbf{x}_1)\exp(-\mu r_2)$. Since

$$\int d^3x_2 |\mathbf{x}_2 - \mathbf{x}_1|^{-1} \exp(-2\mu r_2) \Big/ \int d^3x_2 \exp(-2\mu r_2)$$

stays $\leq 1/r_1$,

$$\langle\chi|H\chi\rangle \leq -\frac{\mu}{2} + \langle\varphi|h\varphi\rangle, \qquad h \geq \frac{|\mathbf{p}|^2}{2} - \frac{1-\alpha}{r}.$$

The right side then comes from the min-max principle. If $\mu \sim 200$, the eigenvalues are estimated in this way to within a few percent.

For practical purposes the problem of finding the eigenvalues of H can be considered solved; the next interesting question is what the eigenfunctions are like. Proposition (3.5.33) produces narrow bounds in the L^2 sense for good trial functions, but we wish to answer qualitative questions about the electron-cloud of the two-electron problem, and hope to do so with methods that generalize for complex atoms. These questions concern the limits as $r \to \infty$ and $r \to 0$, and are not only mathematically accessible, but also of interest to chemists and nuclear physicists.

The Asymptotic Behavior of the Electron Density (4.3.38)

For $r > r_0$, a sufficiently large constant, the one-electron density of the ground state, $\rho(\mathbf{x}_1) = \int d^3x_2 |\psi(\mathbf{x}_1, \mathbf{x}_2)|^2$, satisfies **Hoffmann-Ostenhof and Morgan's inequality,**

$$c_- r^{(1-\alpha)/\sqrt{2\varepsilon_1}-1} \exp(-\sqrt{2\varepsilon_1}\, r) \leq \sqrt{\rho(r)} \leq c_+ r^{(1-\alpha)/\sqrt{2\varepsilon_1}-1} \exp(-\sqrt{2\varepsilon_1}\, r),$$

where $\varepsilon_1 = -E_1 - \frac{1}{2}$ and $r_0 < r < \infty$, $0 < c_- < c_+ < \infty$.

Remark (4.3.39)

The basic mathematical reason that the averaged eigenfunctions fall off exponentially is as follows: The operator $\exp(i\mathbf{s}\cdot(\mathbf{x}_1 + \mathbf{x}_2))$ generates the transformation $\mathbf{x}_i \to \mathbf{x}_i$, $\mathbf{p}_i \to \mathbf{p}_i + \mathbf{s}$, $H \to H + \mathbf{s}\cdot(\mathbf{p}_1 + \mathbf{p}_2)/m + |\mathbf{s}|^2/m \equiv H_{\mathbf{s}}$. Since the new term is bounded relative to $|\mathbf{p}_1|^2 + |\mathbf{p}_2|^2$, the family of operators $H_{\mathbf{s}}$ is analytic in the sense of (3.5.12). The eigenvectors $\varphi_{\mathbf{s}}$ are connected by $\exp(i\mathbf{s}\cdot(\mathbf{x}_1 + \mathbf{x}_2))$, so

$$\int d^3x_1\, d^3x_2\, |\exp(i\mathbf{s}\cdot(\mathbf{x}_1 + \mathbf{x}_2))\varphi(\mathbf{x}_1, \mathbf{x}_2)|^2 < \infty$$

for all $\mathbf{s} \in U$, some complex neighborhood of the origin. Theorem (4.3.38) shows in detail how the ionization energy determines the functional behavior at large r.

The proof proceeds via two lemmas which are of some independent interest. We first generalize the fact used in the proof of (3.5.28) that the kinetic energy of $\sqrt{\rho}$ is dominated by the actual kinetic energy.

The Schrödinger Inequality (4.3.40)

$$\left(-\frac{\Delta}{2} - \frac{1}{r} + \alpha V_L(r) + \varepsilon_1\right)\sqrt{\rho} \leq 0,$$

where V_L is as in (4.3.29), *with* $\mu = 1$.

Proof

The Schrödinger equation

$$\left(\frac{1}{2}(|\mathbf{p}_1|^2 + |\mathbf{p}_2|^2) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\alpha}{r_{12}}\right)\psi = E\psi$$

implies that

$$E\rho(r) = -\frac{1}{r}\rho(r) - \frac{1}{2}\int d^3x_2 \psi^*(\mathbf{x}_1, \mathbf{x}_2)\ddot{\Delta}_1\psi(\mathbf{x}_1, \mathbf{x}_2)$$
$$+ \int d^3x_2\, \psi^*(\mathbf{x}_1, \mathbf{x}_2)\left(-\frac{\Delta_2}{2} - \frac{1}{r_2} + \frac{\alpha}{r_{12}}\right)\psi(\mathbf{x}_1, \mathbf{x}_2),$$

where $f\ddot{\Delta}g \equiv (f\Delta g + g\Delta f)/2$. The Cauchy–Schwarz inequality can be used in the equation $\Delta_1\sqrt{\rho} = \nabla_1((\nabla_1\rho)/2\sqrt{\rho})$ to show that, in the sense of distributions,

$$-\sqrt{\rho}\,\Delta_1\sqrt{\rho} \leq -\int \psi^*\ddot{\Delta}_1\psi\, d^3x_2.$$

Since $\Delta_1\rho/2 = |\nabla_1\sqrt{\rho}|^2 + \sqrt{\rho}\,\Delta_1\sqrt{\rho}$, $-\sqrt{\rho}\,\Delta_1\sqrt{\rho} = -\int \psi^*\vec{\Delta}_1\psi\, d^3x_2 - \int |\nabla_1\psi|^2\, d^3x_2 + |\nabla_1\rho|^2/4\rho$. The last two terms are then ≤ 0 by Cauchy-Schwarz applied to $|\nabla_1\rho|^2 = 4|\int \psi^*\nabla_1\psi\, d^3x_2|^2$. Moreover, if $-\frac{1}{2} + \alpha V_L(r_1) \leq -\frac{1}{8}$, then the operator inequality

$$\frac{1}{2}|\mathbf{p}_2|^2 - \frac{1}{r_2} + \frac{\alpha}{r_{12}} \geq \frac{1}{2}|\mathbf{p}_2|^2 - \frac{1}{r_2} + \alpha P_0 V_L(r_1) \geq -\frac{1}{2} + \alpha V_L(r_1),$$

holds for the last term (see (3.5.31)); otherwise a two-dimensional projection is called for. This implies that

$$\left(-E - \frac{1}{r} - \frac{1}{2} + \alpha V_L(r)\right)\rho - \frac{1}{2}\sqrt{\rho}\,\Delta\sqrt{\rho} \leq 0. \qquad \square$$

Monotony of the Ground-State Wave-Function in the Potential and Sources (4.3.41)

Suppose that f, g, V, and W are nonnegative on a domain Ω, that f and g are continuous on $\bar{\Omega}$, and that $V \leq W$, $A \leq B$. If $\Delta f \leq Vf + A$ and $\Delta g \geq Wg + B$ on Ω and $f \geq g$ on $\partial\Omega$, then $f \geq g$ on all of Ω.

Gloss (4.3.42)

It is assumed that f and g are continuous, so Δf and Δg exist at least in the sense of distributions. If Ω is not a bounded region, then it must be assumed that f and g vanish at infinity. Although the source terms A and B do not appear in the usual Schrödinger equation, they will be needed below.

Proof

Let $D \equiv \{x \in \Omega: g > f\}$; on D we have $\Delta(g - f) \geq Wg - Vf + B - A \geq 0$. In one dimension a function of positive curvature, i.e., a convex function, attains its maximum at one of the end points. Likewise, a subharmonic function F on $\mathbb{R}^n$, i.e., a function for which $\Delta F \geq 0$, attains its maximum on the boundary. Since continuity makes $g = f$ on ∂D, g can not exceed f on D, and therefore D is empty. $\square$

Proof of (4.3.38)

(i) The upper bound. We know that $V_L > 1/r - 1/r^3$, and by (4.3.40),

$$\Delta\sqrt{\rho} \geq 2\left(\varepsilon_1 - \frac{1-\alpha}{r} - \frac{\alpha}{r^3}\right)\sqrt{\rho}.$$

If

$$j = \frac{1-\alpha}{\sqrt{2\varepsilon_1}} \quad \text{and} \quad f = \frac{1}{r}\exp(-\sqrt{2\varepsilon_1}\,r)(r^j + \beta r^{j-1}),$$

then

$$\Delta f = \left[2\varepsilon_1 - 2\frac{1-\alpha}{r} + \frac{[j(j-1) + 2\beta\sqrt{2\varepsilon_1}]r^{-2} + (j-1)(j-2)\beta r^{-3}}{1+\beta/r}\right] f.$$

Choosing $\beta < 0$ such that if $r > r_1$, then

$$[j(j-1) + 2\beta\sqrt{2\varepsilon_1}]r^{-2} + (j-1)(j-2)\beta r^{-3} < \left(-\frac{\alpha}{r^3} - \frac{\beta\alpha}{r^4}\right)\cdot 2,$$

we can identify the function $\sqrt{\rho}$ as the g of the subharmonic comparison lemma (4.3.41). In addition, we have to take $r_0 = \max\{-\beta, r_1, r_2\}$, where r_2 is the largest root of $\varepsilon_1 = (1-\alpha)/r_2 + \alpha/r_2^3$. Then the assumptions of (4.3.41) are satisfied on $\Omega = \{r: r > r_0\}$, if we take

$$c_+ \geq \frac{r_0\rho(r_0)\exp(\sqrt{2\varepsilon_1}\, r_0)}{r_0^{\frac{1}{2}}(1 - |\beta|/r_0)}.$$

(ii) The lower bound. Let $\varphi(\mathbf{x})$ be the ground state of $|\mathbf{p}|^2/2 - 1/r$ and ψ be the ground state of H (4.3.1). Since φ and ψ are nonnegative, the Cauchy–Schwarz inequality implies that

$$0 \leq f(\mathbf{x}_1) \equiv \int d^3x_2\, \varphi(\mathbf{x}_2)\psi(\mathbf{x}_1, \mathbf{x}_2) \leq \sqrt{\rho(\mathbf{x}_1)}.$$

Now,

$$\begin{aligned} 0 &= \int d^3x_2\, \varphi(\mathbf{x}_2)(H - E_1)\psi(\mathbf{x}_1, \mathbf{x}_2) \\ &= \left(-\frac{\Delta}{2} - \frac{1}{r_1} + \varepsilon_1\right) f + \alpha \int d^3x_2 \frac{\varphi(\mathbf{x}_2)\psi(\mathbf{x}_1, \mathbf{x}_2)}{|\mathbf{x}_1 - \mathbf{x}_2|}. \end{aligned}$$

If r_1 is large, then we may estimate

$$\begin{aligned} \int d^3x_2 \frac{\varphi(\mathbf{x}_2)\psi(\mathbf{x}_1, \mathbf{x}_2)}{|\mathbf{x}_1 - \mathbf{x}_2|} &= \int_{r_2 \leq \sqrt{r_1}} + \int_{r_2 \geq \sqrt{r_1}} \\ &\leq \frac{f(r_1)}{r_1 - \sqrt{r_1}} + c\exp(-\sqrt{r_1})\sqrt{\rho}, \end{aligned}$$

since $\varphi \sim \exp(-r)$ and ρ remains bounded. Then with the upper bound for $\sqrt{\rho}$ we find that

$$\frac{1}{2}\Delta f \leq \left(\varepsilon_1 - \frac{1}{r} + \frac{\alpha}{r - \sqrt{r}}\right) f + c'\exp(-\sqrt{2\varepsilon_1 - \delta}\, r - \sqrt{r}),$$

and the assumptions of (4.3.41) can be satisfied by taking $g = c'' \exp(-\sqrt{2\varepsilon_1} r) r^{j-1}(1 + \beta r^{-1/2})$; a somewhat longer argument [24] is needed to convince one that c'' and β can be chosen appropriately. Since $\varphi > 0$, $f(x_1) = 0$ only if $\psi(\mathbf{x}_1, \mathbf{x}_2) = 0$ for all $\mathbf{x}_2$. In particular, it is not possible for f to vanish for all $\mathbf{x}_1 \in I = (a, \infty)$, as ψ would then be 0 on $I \times I$ and therefore on the domain of analyticity containing $I \times I$. Thus for all $|\mathbf{x}_1|$ sufficiently large, $f(\mathbf{x}_1) > 0$, and we obtain a lower bound of the same asymptotic form as the upper bound. □□

The next topic is the electron density near the nucleus. The equation $\rho(0) = (1/2\pi)\langle dV/dr\rangle$ follows from (3.3.5; 4(b)) for a particle in a central potential V, and a generalization of this equation would be worthwhile. The probability that an electron remains at the nucleus is subject to a focusing of the electronic waves at the origin, which is not easy to understand from the particle point of view. For a convex potential like $V = r^2$, dV/dr increases with r, so $\rho(0)$ is greater for the more highly excited states. Classically, a lessened $\rho(0)$ is to be expected for $V = r^2$, since the particle flies through the origin with a greater speed. If the potential is concave, like $-1/r$, then the ordering of $\rho(0)$ accords with classical intuition.

Bounds for $\rho(0)$ (4.3.43)

$$\frac{1}{2\pi}|E_1|(E_2 - E_1) + \alpha\rho_{12}(0) \leq \rho(0) \leq \frac{1}{2\pi}\langle\psi_1|r_1^{-2}|\psi_1\rangle,$$

where

$$\rho(0) = \int d^3x_1\, d^3x_2 |\psi_1(\mathbf{x}_1, \mathbf{x}_2)|^2\, \delta^3(\mathbf{x}_1),$$

$$\rho_{12}(0) = \int d^3x_1\, d^3x_2 |\psi_1(\mathbf{x}_1, \mathbf{x}_2)|^2\, \delta^3(\mathbf{x}_1 - \mathbf{x}_2),$$

$$H\psi_1 = E_1\psi_1.$$

Proof

The upper bound (which holds for all eigenvectors). If $u(\mathbf{x}_1, \mathbf{x}_2) = r_1\psi_1(\mathbf{x}_1, \mathbf{x}_2)$, the Schrödinger equation becomes

$$-\frac{\partial^2}{\partial r_1^2} u + Wu = 0,$$

$$W = r_1^{-2}|\mathbf{L}_1|^2 - \Delta_2 - \frac{2}{r_1} + \frac{2\alpha}{r_{12}} - 2E.$$

Since

$$\psi_1(0, \mathbf{x}_2) = \frac{\partial}{\partial r_1} u(\mathbf{x}_1, \mathbf{x}_2)|_{r_1=0},$$

$$\rho(0) = -\frac{1}{2\pi} \int d^3x_1\, d^3x_2 \frac{\partial u}{\partial r_1} \frac{\partial^2 u}{\partial r_1^2} r_1^{-2}.$$

With the integration by parts in (3.3.5; 4),

$$\rho(0) = -\frac{1}{2\pi} \int d^3x_1\, d^3x_2 \frac{\partial u}{\partial r_1} r_1^{-2} Wu$$

$$= (2\pi)^{-1} \left(\langle \psi_1 | r_1^{-2} - \frac{|\mathbf{L}_1|^2}{r_1^3} | \psi_1 \rangle - \alpha \langle \psi_1 | \frac{\mathbf{x}_1 \cdot (\mathbf{x}_1 - \mathbf{x}_2)}{r_1 |\mathbf{x}_1 - \mathbf{x}_2|^3} | \psi_1 \rangle \right).$$

Since $|\psi_1|^2$ is symmetric in $\mathbf{x}_1$ and $\mathbf{x}_2$, the latter term contributes negatively:

$$\langle \psi_1 | \frac{r_1^2 - \mathbf{x}_1 \cdot \mathbf{x}_2}{r_1 r_{12}^3} | \psi_1 \rangle = \frac{1}{2} \langle \psi_1 | r_{12}^{-3} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) (r_1 r_2 - \mathbf{x}_1 \cdot \mathbf{x}_2) | \psi_1 \rangle \geq 0.$$

The lower bound. This part of the proof requires a lemma:

A Bound on the Mean-Square Deviation (4.3.44)

$$(\Delta a)^2 \leq \frac{\langle 1 | [a, [H, a]] | 1 \rangle}{2(E_2 - E_1)},$$

where $H|1\rangle = E_1|1\rangle$, *and it is assumed that the two lowest eigenvalues* E_1 *and* E_2 *are* $\leq \inf \sigma_{\text{ess}}$, *that* $|1\rangle \in D(a)$, *and* Δa *is calculated with* $|1\rangle$.

Proof

$$\begin{aligned} \langle 1 | a(Ha - aH) | 1 \rangle &= -\langle 1 | (Ha - aH) a | 1 \rangle \\ &= \langle 1 | a(\mathbf{1} - |1\rangle\langle 1|)(Ha - aH) | 1 \rangle \\ &\geq (E_2 - E_1)(\langle 1 | a^2 | 1 \rangle - \langle 1 | a | 1 \rangle^2). \end{aligned}$$ □

If we now set $a = \mathbf{p}_1$ in the lemma, then

$$|\Delta \mathbf{p}_1|^2 = \langle |\mathbf{p}_1|^2 \rangle = |E_1| \leq \frac{\langle |\Delta_1 (-1/r_1 + \alpha/r_{12})| \rangle}{2(E_2 - E_1)}$$

$$= \frac{2\pi}{E_2 - E_1} [\rho(0) - \alpha \rho_{12}(0)].$$ □□

Remarks (4.3.45)

1. We calculated only the contribution from $\mathbf{L} = 0$ to $\rho(0)$ in (3.3.5; 4(b)), but since $|\psi_l|^2 \sim r^{2l}$ for reasonable potentials, the term $|\mathbf{L}|^2/r^3$ contributes nothing in the case of a single particle.
2. If $\bar{\rho}$ denotes the spherical average of $\rho(r)$ at the nucleus, then its derivative satisfies the **cusp condition**

$$\left.\frac{d\bar{\rho}}{dr}\right|_{r=0} = -2\rho(0). \tag{4.3.46}$$

This can be seen by multiplying the equation $u'' = Wu$ by ψ and integrating over Ω and $\mathbf{x}_2$:

$$\frac{d\bar{\rho}}{dr} = \frac{r}{4\pi}\int\left(\psi W\psi - \psi\frac{\partial^2}{\partial r_1^2}\psi\right)d\Omega\, dx_2.$$

In the limit $r \to 0$, the only contribution is $-2r_1^{-1}$ from W, yielding (4.3.46). Hence we have the bounds

$$-\frac{1}{\pi}\langle\psi_1|r^{-2}|\psi_1\rangle \leq \left.\frac{d\bar{\rho}}{dr}\right|_{r=0} \leq -\frac{1}{\pi}|E_1|(E_2 - E_1) - 2\alpha\rho_{12}(0).$$

The section closes with a discussion of more general expectation values of r^ν. The first facts of interest are the

Monotonic Properties of $\langle a^\nu\rangle$ (4.3.47)

If a is a positive operator, then the functions $\mathbb{R} \to \bar{\mathbb{R}}: \nu \to \langle a^\nu\rangle^{1/\nu}$ increase monotonically, and the functions $\nu \to -\ln\langle a^\nu\rangle$ are concave.

Proof

This follows immediately from Hölder's inequality when the expectation values are written in a spectral representation. □

Remarks (4.3.48)

1. If the only available estimates for $\langle a^\nu\rangle$ with certain values of ν are not very satisfactory, then (4.3.47) can help out by using better estimates for other values of ν and interpolating.
2. Often the calculation of expectation values of an operator can be reduced to finding accurate bounds for some energy; for instance, if $E(\beta)$ is the eigenvalue of $H + \beta b$, then $\langle b\rangle = \partial E(\beta)/\partial\beta$. Since $E(\beta)$ is concave, bounds on $\partial E/\partial\beta$ can be obtained from bounds on $E(\beta)$. In this way our knowledge of $E(\alpha)$ gives us the expectation value of $1/r_{12}$, and thereby, with the virial theorem, of $\langle|\mathbf{p}_1|^2\rangle = \langle|\mathbf{p}_2|^2\rangle = |E|$ and $\langle 1/r_1\rangle = \langle 1/r_2\rangle$.

The line of reasoning indicated in Remark 2 will not be pursued further, as it soon leads to extensive computations. Instead, we shall only cite some general inequalities for expectation values involving r and $\mathbf{p}$. Since they are simply variants of the indeterminacy relations, and the more detailed form of the interaction does not enter, numerically they leave much to be desired in our special cases.

Lower Bounds for $\langle r^\nu\rangle^{1/\nu}$ (4.3.49)

$\nu = 2$: Since $|\mathbf{p}|^2/2 + r^2\omega^2/2 \geq 3\omega/2$, it follows that if $\omega = \frac{3}{2}\langle|\mathbf{p}|^2\rangle$ then $\langle r^2\rangle \geq 9/4\langle|\mathbf{p}|^2\rangle$ and $\langle r^2\rangle^{1/2} \geq \frac{3}{2}\langle|\mathbf{p}|^2\rangle^{-1/2}$.

$\nu = 1$: $|\mathbf{p}|^2/2 + gr \geq (g/2)^{2/3}\cdot c$, where c is the first zero of the Airy function $Ai(x)$, $c = 2.338\ldots$. Then $\langle r\rangle \geq 1.2446\langle|\mathbf{p}|^2\rangle^{-1/2}$.

$\nu = -1$: $|\mathbf{p}|^2/2 - \alpha/r \geq -\alpha^2/2$: $\langle 1/r\rangle^{-1} \geq \langle|\mathbf{p}|^2\rangle^{-1/2}$.

$\nu = -2$: By (2.5.23; 6), $|\mathbf{p}|^2/2 - 1/8r^2 \geq 0$, so $\langle 1/r^2\rangle^{-1/2} \geq \frac{1}{2}\langle|\mathbf{p}|^2\rangle^{-1/2}$.

Upper Bounds for $\langle r^\nu\rangle^{1/\nu}$ (4.3.50)

If we take $\mathbf{a} = \mathbf{x}_1 r_1^{q-1}$ in (4.3.44), and note that in a rotationally invariant state $\langle\mathbf{a}\rangle = 0$ and $[\mathbf{a}, [H, \mathbf{a}]] = |\nabla\mathbf{a}|^2 = r^{2q-2}(2 + q^2)$, then $\langle r^{2q}\rangle \leq (2 + q^2)\langle r^{2q-2}\rangle(2(E_2 - E_1))^{-1}$. Combining this with earlier results we get some useful inequalities for integral values of ν, $-2 \leq \nu \leq 2$:

$\nu = 2$: With $q = 1$ in the formula just derived,

$$\langle r^2\rangle^{1/2} \leq \sqrt{3/2}(E_2 - E_1)^{-1/2}.$$

$\nu = 1$: With $q = \frac{1}{2}$, $\langle r\rangle \leq \frac{9}{8}\langle 1/r\rangle(E_2 - E_1)^{-1} \leq \frac{9}{8}\langle|\mathbf{p}|^2\rangle^{1/2}/(E_2 - E_1)$. As an imprecise inequality is used twice, the result is very weak.

$\nu = -1$: In the case of interest the virial theorem implies that $\langle 1/r_1\rangle \geq |E_1|$, $\langle 1/r_1\rangle^{-1} \leq |E_1|^{-1}$ (in atomic units).

$\nu = -2$: With $q = 0$ in the formula, $\langle r^{-2}\rangle^{-1/2} \leq (E_2 - E_1)^{-1/2}$.

The thrust of these inequalities is that an average of r can not get too small without increasing the kinetic energy greatly, and it can not get too large without reducing the spacing of the eigenvalues. If E_1 and E_2 are taken as known for helium, then with the virial theorem the following bounds are found for $\langle r^\nu\rangle^{1/\nu}$ in atomic units, some of which can be improved with (4.3.48; 1):

ν	lower bound	upper bound
2	0.88	1.408
1	0.73	2.535
−1	0.587	0.689
−2	0.293	1.150

By Corollary (4.3.21; 2), $\langle 1/r\rangle^{-1} \simeq 0.61$. These inequalities are too general to be more precise; much greater numerical effort would be called for.

Since $\langle r^{-2}\rangle$ is important for calculating $\rho(0)$, we shall improve the result for $\nu = -2$ with the aid of (2.2.33; 3). It follows from $i\langle a^*b - b^*a\rangle \leq \langle a^*a\rangle + \langle b^*b\rangle$ with $a = p_r + ic/r$ and $b, c \in \mathbb{R}$ that

$$\langle r^{-2}\rangle c(1-c) + \langle r^{-1}\rangle 2bc - b^2 - \langle |\mathbf{p}|^2\rangle \leq 0.$$

If this is optimized in b and c, then

$$\langle r^{-2}\rangle^2 - 4\langle |\mathbf{p}|^2\rangle\langle r^{-2}\rangle + 4\langle r^{-1}\rangle^2\langle |\mathbf{p}|^2\rangle \leq 0 \Rightarrow$$

$$\langle r^{-2}\rangle \lessgtr 2\langle |\mathbf{p}|^2\rangle(1 \pm \sqrt{1 - \langle r^{-1}\rangle^2/\langle |\mathbf{p}|^2\rangle}).$$

Then the virial theorem finally produces

Bounds for $\langle r^{-2}\rangle$ given E_1 '4.3.51)

Given two electrons and $\alpha > 0$,

$$\langle r^{-2}\rangle \lessgtr 2|E_1|(1 \pm \sqrt{1 - |E_1|}).$$

Problems (4.3.52)

1. Show that the operator with integral kernel $\varphi(\mathbf{x})V_L(\mathbf{x})|\mathbf{x} - \mathbf{x}'|V_L(\mathbf{x}')\varphi(\mathbf{x}')$ has only one positive eigenvalue, and the rest of its spectrum is negative. (Hint: dominate $|\mathbf{x} - \mathbf{y}|$ as the integral kernel of a quadratic form by a form with kernel $f(\mathbf{x})f(\mathbf{y})$.
2. Show that $r_{12}^{-1/2}(\mathscr{P}_1\mathscr{P}_2 + \mathscr{P}_2\mathscr{P}_1)r_{12}^{-1/2}$ has only one positive eigenvalue on the space of symmetric functions, and conclude that $r_{12}^{-1} \geq r_{12}^{-1/2}(\mathscr{P}_1 + \mathscr{P}_2 - |\chi\rangle\langle\chi|)r_{12}^{-1/2}$.
3. Calculate $\langle 0|1/r_{12}|0\rangle$ and $\langle 0|r_{12}|0\rangle$ in (4.3.21; 1). Note that the normalization of $\varphi_1(r)$ above did not contain the angular factor $1/\sqrt{4\pi}$.
4. Calculate the 2×2 matrices M_L^{-1} and M_L for $(1s2p)$ and $(1s3p)$ (see (4.3.24; 2)).
5. Calculate the screened potential of (4.3.7).
6. Show that for Coulomb systems $\langle V^2\rangle = 3E^2 + \langle T^2\rangle$, where T and V are respectively the kinetic and the potential energy, and expectation values are taken with eigenvectors of H.

Solutions (4.3.53)

1. Let $f(\mathbf{x}, \mathbf{y}) = 8\pi \int d^3q(\exp(i\mathbf{q}\cdot\mathbf{x}) - 1)(\exp(-i\mathbf{q}\cdot\mathbf{y}) - 1)/|\mathbf{q}|^4 - |\mathbf{x}| - |\mathbf{y}| + |\mathbf{x} - \mathbf{y}|$. Then note that $f(\mathbf{x}, \mathbf{y}) = 0$, since $\Delta_x f(\mathbf{x}, \mathbf{y}) = \Delta y f(\mathbf{x}, \mathbf{y}) = f(0, \mathbf{y}) = f(\mathbf{x}, 0) = 0$ and $f(\lambda\mathbf{x}, \lambda\mathbf{y}) = \lambda f(\mathbf{x}, \mathbf{y})$. The integral is evidently the kernel of a positive form. Consequently,

$$\begin{aligned}|\mathbf{x} - \mathbf{y}| &\leq |\mathbf{x}| + |\mathbf{y}| \\ &= \tfrac{1}{2}(1 + |\mathbf{x}|)(1 + |\mathbf{y}|) - \tfrac{1}{2}(1 - |\mathbf{x}|)(1 - |\mathbf{y}|) \\ &\leq \tfrac{1}{2}(1 + |\mathbf{x}|)(1 + |\mathbf{y}|)\end{aligned}$$

as a form inequality. The proposition then follows from the min-max principle applied to the operators obtained by multiplying on both sides by φV_L.

2. The operator $P_0(1)V_L(\mathbf{x}_2)r_{12}P_0(2)V_L(\mathbf{x}_1) + P_0(2)V_L(\mathbf{x}_1)r_{12}P_0(1)V_L(\mathbf{x}_2) = K^{(2)}$ has the expectation values

$$\langle\Phi|K^{(2)}|\Phi\rangle = 2\int d^3x_2\, d^3x_2'\, f(\mathbf{x}_2)K^{(1)}(\mathbf{x}_2, \mathbf{x}_2')f(\mathbf{x}_2'),$$

where

$$f(\mathbf{x}_2) = \int d^3x_1\, \varphi_1(\mathbf{x}_1)\Phi(\mathbf{x}_1, \mathbf{x}_2),$$

and

$$K^{(1)}(\mathbf{x}_2, \mathbf{x}_2') = \varphi_1(\mathbf{x}_2)V_L(\mathbf{x}_2)|\mathbf{x}_2 - \mathbf{x}_2'|V_L(\mathbf{x}_2')\varphi_1(\mathbf{x}_2'),$$

provided that $\Phi(\mathbf{x}_1, \mathbf{x}_2) = \Phi(\mathbf{x}_2, \mathbf{x}_1)$. By problem 1, $K^{(1)}$ and thus $K^{(2)}$ each have only one positive eigenvalue, and the same must be true of $\mathscr{P}_1\mathscr{P}_2 + \mathscr{P}_2\mathscr{P}_1$. Since we know that the positive eigenvalue is 2 and that $|\chi\rangle$ is the associated eigenvector, $\mathscr{P}_1\mathscr{P}_2 + \mathscr{P}_2\mathscr{P}_1 < 2|\chi\rangle\langle\chi|$. The proposition then follows from $\mathscr{P}_1\mathscr{P}_2\mathscr{P}_1 + \mathscr{P}_2\mathscr{P}_1\mathscr{P}_2 \geq 2|\chi\rangle\langle\chi|$.

3. $$\langle 0|\frac{1}{r_{12}}|0\rangle = 16\int_0^\infty dr_1\, r_1^2 \exp(-2r_1)\int_0^\infty dr_2\, r_2^2 \exp(-2r_2)$$
$$\times \int_{-1}^{1}\frac{dz}{2}(r_1^2 + r_2^2 - 2r_1r_2z)^{-1/2}$$
$$= 16\int_0^\infty dr_1\, r_1 \exp(-2r_1)\int_0^\infty dr_2\, r_2 \exp(-2r_2)\cdot\begin{cases} r_2, \text{ when } r_1 > r_2 \\ r_1, \text{ when } r_2 > r_1. \end{cases}$$

For $\langle 0|r_{12}|0\rangle$ the z-integral is $\int_{-1}^{1} dz(r_1^2 + r_2^2 - 2r_1r_2z)^{1/2}/2$ instead of $\int_{-1}^{1} dz(r_1^2 + r_2^2 - r_1r_2z)^{-1/2}/2$.

4. $M_L^{-1} =$

$$\frac{1}{2}\begin{bmatrix} \langle(1s2p) \pm (2p1s)|r_{12}|(1s2p) \pm (2p1s)\rangle & \langle(1s2p) \pm (2p1s)|r_{12}|(1s3p) \pm (3p1s)\rangle \\ \langle(1s3p) \pm (3p1s)|r_{12}|(1s2p) \pm (2p1s)\rangle & \langle(1s3p) \pm (3p1s)|r_{12}|(1s3p) \pm (3p1s)\rangle \end{bmatrix}.$$

Symmetric:

$$M^{-1} = \begin{bmatrix} 5.11 & -1.77 \\ -1.77 & 12.58 \end{bmatrix}, \qquad M = \begin{bmatrix} 0.21 & 0.02 \\ 0.02 & 0.08 \end{bmatrix},$$

$$E_{1,2} = -\frac{5.17}{144} \pm \frac{\alpha}{2}(0.206 + 0.08) \mp \sqrt{\left(-\frac{5}{144} + \frac{\alpha}{2}(0.206 - 0.08)\right)^2 + \alpha^2\, 0.029^2},$$

$$E_{1,2} = -0.590 + \alpha\, 0.145 \mp \sqrt{(-0.035 + \alpha\, 0.061)^2 + \alpha^2\, 0.00084}.$$

Antisymmetric:

$$M^{-1} = \begin{bmatrix} 5.38 & -1.65 \\ -1.65 & 12.64 \end{bmatrix}, \qquad M = \begin{bmatrix} 0.194 & 0.025 \\ 0.025 & 0.082 \end{bmatrix},$$

$$E_{1,2} = -0.590 + \alpha\, 0.138 \mp \sqrt{(-0.035 + \alpha\, 0.056)^2 + \alpha^2\, 0.00064}.$$

5. $\langle\varphi_1(\mathbf{x}_1)|\frac{1}{r_{12}}|\varphi_1(\mathbf{x}_1)\rangle = \frac{4}{r_2}\int_0^{r_2}\exp(-2r_1)r_1^2\,dr_1 + 4\int_{r_2}^{\infty}\exp(-2r_1)r_1\,dr_1.$

6. It follows from $V = H - T$ that $\Delta V = \Delta T$ if the deviation is calculated in an eigenstate of H. The proposition then follows from the virial theorem. \

4.4 Scattering Theory of Simple Atoms

After the point spectrum of two particles in a Coulomb field has been analyzed, we are ready to study the continuous spectrum. Its physical significance can be understood by seeing how scattering theory applies in this case.

The scattering of several particles is a set of complicated diffraction problems in $\mathbb{R}^{3n}$, with potentials falling off in some directions but not in others. Due to the lack of simplicity the subject has long been used as a proving ground for any conceivable assumption or approximation, the validity of which was wholly obscure. Our first job will be to make physical sense of the continuous spectrum. We have seen that the wave-functions of the bound states fall off exponentially, making the particles localized near the nucleus. One would expect that in the other states one or more particles are asymptotically free. The first step in proving this is to show that there is no singular spectrum, which is associated with particles that wander arbitrarily far away but keep returning on occasion. The only known realistic examples of nontrivial singular spectrum are some clever models due to D. B. Pearson in which the potential consists of an array of barriers as for a band model, but for which the allowed bands are Cantor sets, and the energy spectrum is $\mathbb{R}^+$. The potentials either extend to infinity or fall off very slowly, and one would not expect any singular spectrum in scattering from an atom. In fact, it does not exist for Coulomb systems [22].

We next wish to exclude the possibility, mentioned in (3.4.10; 1), of waves entering the region of interaction, never to come out again. The relative compactness of the potentials, which was a key fact in the proof of asymptotic completeness for one-particle scattering, is now lacking. L. Faddeev was the first to figure out how to group compact parts of the resolvent. For energies less than the ionization energy it is straightforward to prove existence and completeness of the Møller operators, yet above the ionization threshold there is still no simple way to verify asymptotic completeness.

A physicist's work has only begun with the proof of existence of the wave-operators; actual calculations of what can be measured are needed. What accuracy can be guaranteed for the numerical results of various computations? The experience of volume II, §3.4, prepares us for the worst, as the interference effects in diffraction problems get so complicated as to make a mockery of mankind's calculating skills. In consequence it is all the more

welcome to learn that the persistent efforts of L. Spruch, R. Blankenbecler, R. Sugar, and many others in recent decades have led to operator inequalities that bound the scattering parameters in many limiting cases with amazing precision.

Let us start by bettering our understanding of σ_{ess} and discovering the fate of the discrete states of H_0 that are embedded in the continuum. Our earlier analysis made ready use of the compactness of the $V(H_0 - z)^{-1}$ occurring in $(H - z)^{-1} = (H_0 - z)^{-1}(1 + V(H_0 - z)^{-1})^{-1}$, but, as already mentioned, this fact breaks down for several particles interacting through pair potentials. We therefore start by finding a representation of the resolvent in which the effect of the interaction on the spectrum can be deduced with arguments about compactness. We shall restrict ourselves to the 3-body problem, though the method clearly generalizes to n particles.

If the potentials are relatively bounded, the resolvent can always be expanded in a norm-convergent series,

$$(H(\alpha) - z)^{-1} = \sum_{n=0}^{\infty} \sum_{\gamma_1=1}^{3} \cdots \sum_{\gamma_n=1}^{3} (-1)^n R_0 v_{\gamma_1} R_0 v_{\gamma_2} \cdots R_0 v_{\gamma_n} R_0,$$

$$R_0 \equiv (T - z)^{-1}, \qquad v_1 = -\frac{1}{r_1}, \qquad v_2 = -\frac{1}{r_2}, \qquad v_3 = \frac{\alpha}{r_{12}},$$

$$T = \frac{1}{2}(|\mathbf{p}_1|^2 + |\mathbf{p}_2|^2), \tag{4.4.1}$$

with the proviso that $d(z, \mathrm{Sp}(T)) = d(z, \mathbb{R}^+) = |\mathrm{Im}\, z|$ when $\mathrm{Re}\, z > 0$ or $|z|$ when $\mathrm{Re}\, z \leq 0$ is large enough, for

$$\left\| \frac{1}{r} R_0 \psi \right\| \leq \varepsilon \|\psi\| + a\|R_0 \psi\| \leq (\varepsilon + a[d(z, \mathbb{R}^+)]^{-1})\|\psi\|.$$

With only one electron all the summands other than the first, R_0, were compact. Since any norm limit of compact operators is compact, we concluded that the essential spectrum remains unchanged. The situation at hand is different, since the operators act on tensor products, and even though each contribution is compact on one factor when $n > 0$, it is not compact on both. In order to understand how the resolvent factorizes, write R_0 as the norm-convergent integral

$$R_0 = \int_C \frac{d\xi/2\pi i}{(\frac{1}{2}|\mathbf{p}_1|^2 - \xi)(\frac{1}{2}|\mathbf{p}_2|^2 - z + \xi)}, \tag{4.4.2}$$

where the contour of complex integration is $C = (\mathbb{R}^+ - i\varepsilon) \cup (-i\varepsilon, i\varepsilon) \cup (\mathbb{R}^+ + i\varepsilon)$, $0 < \varepsilon < |\mathrm{Im}\, z|$. Then

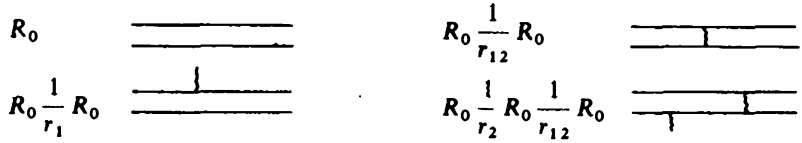
$$R_0 \frac{1}{r_1} R_0 = \int_{C \times C} \frac{d\xi_1\, d\xi_2}{(2\pi i)^2} \frac{1}{(\frac{1}{2}|\mathbf{p}_1|^2 - \xi_1)} \frac{1}{r_1} \frac{1}{(\frac{1}{2}|\mathbf{p}_1|^2 - \xi_2)}$$

$$\otimes \frac{1}{(\frac{1}{2}|\mathbf{p}_2|^2 - z + \xi_1)} \frac{1}{(\frac{1}{2}|\mathbf{p}_2|^2 - z + \xi_2)}, \tag{4.4.3}$$

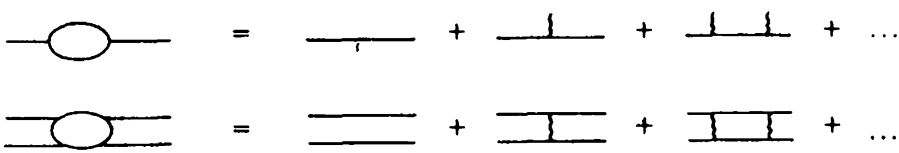
and the integrand is of the form compact $\otimes$ bounded. Yet if there are two different potentials, both factors become compact:

$$R_0 \frac{1}{r_1} R_0 \frac{1}{r_2} R_0 = \int \frac{d\xi_1\, d\xi_2\, d\xi_3}{(2\pi i)^3} \frac{1}{(\frac{1}{2}|\mathbf{p}_1|^2 - \xi_1)} \frac{1}{r_1} \frac{1}{(\frac{1}{2}|\mathbf{p}_1|^2 - \xi_2)} \frac{1}{(\frac{1}{2}|\mathbf{p}_1|^2 - \xi_3)} \otimes \frac{1}{(\frac{1}{2}|\mathbf{p}_2|^2 - z + \xi_1)} \frac{1}{(\frac{1}{2}|\mathbf{p}_2|^2 - z + \xi_2)} \frac{1}{r_2} \frac{1}{(\frac{1}{2}|\mathbf{p}_2|^2 - z + \xi_3)}. \tag{4.4.4}$$

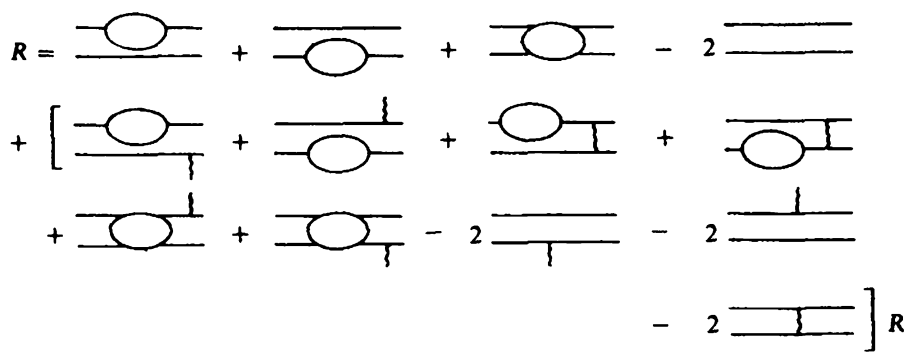
This is also the case if r_1 or r_2 is replaced with r_{12}. Hence, while the contributions to (4.4.1) having all γ_i equal are not compact, all the others are. There is a graphical shorthand for the terms in (4.4.1), whereby electrons are drawn as lines and interactions $1/r_\gamma$ are drawn as wavy lines connecting electronic lines if $\gamma = (12)$ and extending outward from electronic lines if $\gamma = 1$ or 2:



etc. The graphs of the products in (4.4.1) are the graphs of the factors joined together, so the set of graphs contains the whole algebraic structure of the operators. The noncompact operators are the disconnected graphs, which means that the electronic lines are either not connected to one another or not connected to the outside. The connected graphs, that is, the compact operators, are an ideal of the algebra. Thus, with the notation



the graphical representation of the resolvent equation is



The translation of this as formulas is known as the

Weinberg–Van Winter Equation (4.4.5)

$$
\begin{aligned}
R &= D + JR,\\
D &= \left(T - \frac{1}{r_1} - z\right)^{-1} + \left(T - \frac{1}{r_2} - z\right)^{-1} + \left(T + \frac{\alpha}{r_{12}} - z\right)^{-1}\\
&\quad - 2(T - z)^{-1},\\
J &= \left(T - \frac{1}{r_1} - z\right)^{-1}\left(-\frac{1}{r_2} + \frac{\alpha}{r_{12}}\right) + \left(T - \frac{1}{r_2} - z\right)^{-1}\left(-\frac{1}{r_1} + \frac{\alpha}{r_{12}}\right)\\
&\quad - \left(T + \frac{\alpha}{r_{12}} - z\right)^{-1}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) - 2(T - z)^{-1}\left(-\frac{1}{r_1} - \frac{1}{r_2} + \frac{\alpha}{r_{12}}\right)\\
&= (T - z)^{-1}\frac{1}{r_1}\left(T - \frac{1}{r_1} - z\right)^{-1}\left(-\frac{1}{r_2} + \frac{\alpha}{r_{12}}\right)\\
&\quad + (T - z)^{-1}\frac{1}{r_2}\left(T - \frac{1}{r_2} - z\right)^{-1}\left(-\frac{1}{r_1} + \frac{\alpha}{r_{12}}\right)\\
&\quad + (T - z)^{-1}\frac{\alpha}{r_{12}}\left(T + \frac{\alpha}{r_{12}} - z\right)^{-1}\left(\frac{1}{r_1} + \frac{1}{r_2}\right).
\end{aligned}
$$

Consequences (4.4.6)

As shown above, J is compact for $d(z, \mathbb{R})$ sufficiently large. Moreover, its compactness extends by analyticity to the whole region $\mathbb{C}\backslash\mathbb{R}^+ \bigcup_{n=1}^{\infty} \{-1/2n^2\}$ (Problem 3). This means that $(1 - J(z))^{-1}$ has only isolated poles of finite multiplicity in the region of analyticity, and the only additional singularities of $R(z) = (1 - J(z))^{-1}D(z)$ are those of $D(z)$. This reasoning leads to a result due to Hunziker, Van Winter, and Zhislin, generalizing (4.3.5) for not necessarily positive α.

The HVZ Theorem (4.4.7)

$$
\sigma_{\mathrm{ess}}(H(\alpha)) = \sigma_{\mathrm{ess}}\left(T - \frac{1}{r_1}\right) \cup \sigma_{\mathrm{ess}}\left(T - \frac{1}{r_2}\right) \cup \sigma_{\mathrm{ess}}\left(T + \frac{\alpha}{r_{12}}\right).
$$

Remark (4.4.8)

This result casts more light on Remark (4.3.6; 1). The essential spectrum describes particles that escape to infinity, so σ_{ess} begins at the various ionization energies.

In order to eliminate the possibility of σ_{sing}, we look at the $H(\alpha)$ dilated with a complex parameter τ as in (4.1.16):

$$H_\alpha(\tau) \equiv U(\tau)H(\alpha)U^{-1}(\tau) = \exp(2\tau)T + \exp(\tau)V,$$

$$(H_\alpha(\tau) - z)^{-1} = (\mathbf{1} - J)^{-1}D,$$

$$\begin{aligned} D = &\left(\exp(2\tau)T - \frac{\exp(\tau)}{r_1} - z\right)^{-1} + \left(\exp(2\tau)T - \frac{\exp(\tau)}{r_2} - z\right)^{-1} \\ &+ \left(\exp(2\tau)T + \frac{\alpha\exp(\tau)}{r_{12}} - z\right)^{-1} - 2(\exp(2\tau)T - z)^{-1}, \end{aligned}$$

$$\begin{aligned} \exp(2\tau)J = &(T - \exp(-2\tau)z)^{-1}\frac{1}{r_1}\left(T - \frac{\exp(-\tau)}{r_1} - \exp(-2\tau)z\right)^{-1} \\ &\times \left(-\frac{1}{r_2} + \frac{\alpha}{r_{12}}\right) + (T - \exp(-2\tau)z)^{-1}\frac{1}{r_2} \\ &\times \left(T - \frac{\exp(-\tau)}{r_2} - \exp(-2\tau)z\right)^{-1}\left(-\frac{1}{r_1} + \frac{\alpha}{r_{12}}\right) \\ &+ (T - \exp(-2\tau)z)^{-1}\frac{\alpha}{r_{12}}\left(T + \frac{\alpha\exp(-\tau)}{r_{12}} - \exp(-2\tau)z\right) \\ &\times \left(\frac{1}{r_1} + \frac{1}{r_2}\right). \end{aligned} \tag{4.4.9}$$

The operator J is again compact, so $(\mathbf{1} - J)^{-1}$ affects only the point spectrum of $H_\alpha(\tau)$. The essential spectrum originates from D, which, however, contains only the sorts of expressions encountered in (4.1.16). Since

$$\sigma(A \otimes \mathbf{1} + \mathbf{1} \otimes B) = \sigma(A) + \sigma(B)$$

(see [3], section XIII.9) and

$$\sigma\left(\exp(2\tau)\frac{|\mathbf{p}|^2}{2} - \frac{\exp(\tau)}{r}\right) = \bigcup_{n\geq 1}\left\{\frac{-1}{2n^2}\right\} \cup \exp(2\tau)\mathbb{R}^+$$

(see (4.1.17; 2)),

$$\begin{aligned} &\sigma\left(\exp(2\tau)\frac{1}{2}(|\mathbf{p}_1|^2 + |\mathbf{p}_2|^2) - \frac{\exp(\tau)}{r_1}\right) \\ &\quad = \bigcup_{n\geq 1}\left\{\frac{-1}{2n^2} + \exp(2\tau)\mathbb{R}^+\right\} \cup \exp(2\cdot\ \mathbb{R}^+. \end{aligned}$$

This means that the continuum starting at each energy $-1/2n^2$ gets swung out into the complex plane by the dilatation (see Figure 20):

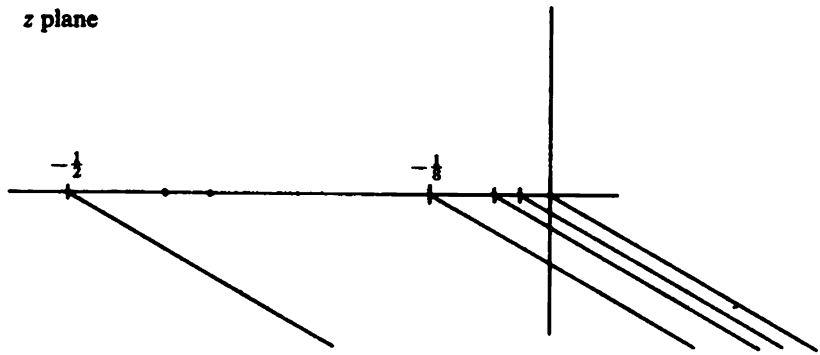


Figure 20 $\mathrm{Sp}(\exp(2\tau)\frac{1}{2}(|\mathbf{p}_1|^2 + |\mathbf{p}_2|^2) - \exp(\tau)/r_1)$ when $\mathrm{Im}\exp(2\tau) < 0$.

As a consequence, the matrix elements of the resolvent in the dense set D of entire vectors with respect to $U(\tau)$ can be continued analytically past the real axis, since it intersects σ_{ess} only at $\bigcup_n \{-1/2n^2\} \cup \{0\}$. As in (4.1.16), we conclude the

Absence of Singular Spectrum (4.4.10)

$$\sigma_{\mathrm{sing}}(H_\alpha) = \varnothing, \text{ so } \sigma_{\mathrm{ess}}(H_\alpha) = \sigma_{\mathrm{ac}}(H_\alpha).$$

Because $\langle U^{-1}(\tau^*)\varphi | (H_\alpha - z)^{-1} U^{-1}(\tau)\psi\rangle = \langle \varphi | (H_\alpha(\tau) - z)^{-1}\psi\rangle$, the spectrum of $H_\alpha(\tau)$ reflects the singularities that occur when matrix elements of the resolvent are continued analytically. The next topic to investigate is how the eigenvalues in the continuum of H_0 move onto the second sheet of z when the perturbation α/r_{12} is switched on after this analytic continuation. We start by noting the

Spectrum of $H_0(\tau)$ (4.4.11)

$$\sigma_p(H_0(\tau)) = \sigma_p(H_0(0)) = \bigcup_{n,m\geq 1} \left\{ -\frac{1}{2n^2} - \frac{1}{2m^2} \right\},$$

$$\sigma_{\mathrm{ac}}(H_0(\tau)) = \bigcup_{n\geq 1} \left\{ -\frac{1}{2n^2} + \exp(2\tau)\mathbb{R}^+ \right\} \cup \{\exp(2\tau)\mathbb{R}^+\}.$$

As to the eigenvalues of the non-Hermitian operator $H_\alpha(\tau)$, if $\mathrm{Im}\exp(2\tau) < 0$, then some of them may have negative imaginary parts. The argument of (4.1.17), by which the eigenvalues were analytic in τ and invariant for real τ, and therefore constant, works only assuming that they remain isolated. But σ_{ess} sweeps over the eigenvalues with negative imaginary parts as $\mathrm{Im}\,\tau \to 0$, invalidating the argument. In fact, the eigenvalues $\bigcup_{n,m\geq 2} \{-1/2n^2 - 1/2m^2\}$ of $H_0(\tau)$ move to complex positions as α/r_{12} is turned on with τ fixed, unless their movement is prevented by some selection rule. Since the

continuum of $H_0(\tau)$ swings out of the way, the eigenvalues are isolated for $\operatorname{Im}\tau < 0$ and $\alpha = 0$, and lowest-order perturbation theory (3.5.18) can be used to compute their displacement as α/r_{12} is turned on (the derivation of the perturbation-theoretic formula (3.5.18) did not require the operator to be Hermitian). As expected, the position of an eigenvalue is independent of τ, which merely specifies which complex half-plane the limit to real values is to be taken from.

Perturbation Theory of the Complex Eigenvalues (4.4.12)

Let $|\tau\rangle = U(\tau)|0\rangle$ *in the notation of* (3.5.18), *taking* $|0\rangle$ *and* $E(0)$ *as the eigenvector and eigenvalue of* $H_0(\tau)$. *Then the eigenvalue of* $H_\alpha(\tau)$ *is*

$$\begin{aligned} E(\alpha) &= E(0) + \alpha\langle\tau|\frac{\exp(\tau)}{r_{12}}|\tau\rangle - \alpha^2\langle\tau|\frac{\exp(\tau)}{r_{12}}P_\perp(H_0(\tau) \\ &\quad - E(0))^{-1}P_\perp\frac{\exp(\tau)}{r_{12}}|\tau\rangle + o(\alpha^2) \\ &= E(0) + \alpha\langle 0|\frac{1}{r_{12}}|0\rangle - \alpha^2\lim_{\varepsilon\downarrow 0}\langle 0|\frac{1}{r_{12}}P_\perp(H_0(0) \\ &\quad - E(0) - i\varepsilon)^{-1}P_\perp\frac{1}{r_{12}}|0\rangle + o(\alpha^2). \end{aligned}$$

Remarks (4.4.13)

1. To $o(\alpha^2)$, the imaginary part of $E(\alpha)$ is

$$\operatorname{Im} E(\alpha) = -\pi\alpha^2\langle 0|\frac{1}{r_{12}}P_\perp\,\delta(H_0 - E(0))P_\perp\frac{1}{r_{12}}|0\rangle,$$

a formula known as **Fermi's golden rule**. Although this is certainly an eigenvalue of $H_\alpha(\tau)$ for sufficiently large $\operatorname{Im}\tau$, the Hermitian operator $H_\alpha(0)$, of course, has no complex eigenvalues. They only appear when the matrix elements of the resolvent are continued analytically (see Figure 21).

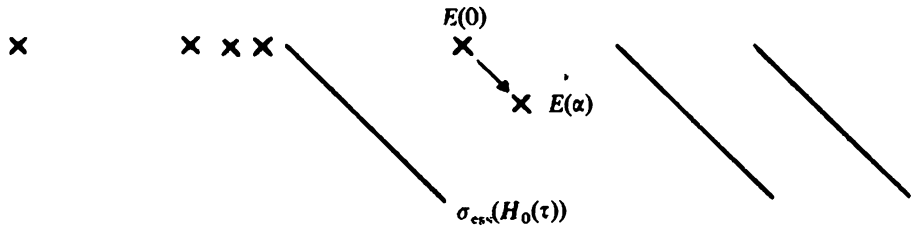


Figure 21 The motion of the eigenvalues of $H_\alpha(\tau)$ for $\alpha > 0$.

2. The interpretation of the poles as resonances is based on the lifetime (4.2.11) as well as on the scattering operator $V - V(H - E)^{-1}V$. If α is small, they are the dominant contribution to the resolvent at $E = \mathrm{Re}(E(\alpha))$, and in that case Im $E(\alpha)$ determines the probability of decay.
3. For the states of unnatural parity, $H_0(0)$ has no continuum in the subspace of equal quantum numbers, so $P_\perp \delta(H(0) - E_0)P_\perp$ vanishes, and thus so does Im $E(\alpha)$. However, for the other states, Im $E(\alpha) < 0$; this answers the question that arose earlier about $\sigma_p(H(\alpha))$ embedded in the continuum. For sufficiently small α, it develops continuously out of the eigenvalues $-1/2n^2 - 1/2m^2$ of $H(0)$, which have Im $E(\alpha) = 0$.

The next problem is to show that the vectors associated with $\sigma_{ac}(H(\alpha))$ are scattering states, in order to be able eventually to calculate the relevant scattering parameters with accuracies good enough for comparison with experimental data. This is a formidable goal, so we shall content ourselves with the simplest nontrivial situation, where an electron e^- scatters from an atom consisting of a μ^- and a p. We consider only energies less than 1 KeV, so the muon remains in the ground state. If the energy is great enough to excite the muon to higher bound states, then the calculation is quite similar in principle, but much more complicated to write out. If the muon can be ionized, then the ordinary Møller operators do not exist, and recourse must be had to comparison with the kind of modified time-evolution of (4.1.19; 2). The Coulomb field is screened only provided that the muon remains bounded. Only then is the range of the interaction short enough for the scattering theory of §3.4 to work. As in (3.4.16) we shall study the

Channel Hamiltonian (4.4.14)

$$H = \frac{|\mathbf{p}_1|^2}{2\mu} + \frac{|\mathbf{p}_2|^2}{2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}},$$

$$H_1 = \frac{|\mathbf{p}_1|^2}{2\mu} - \frac{1}{r_1} + \frac{|\mathbf{p}_2|^2}{2}, \qquad I_1 = -\frac{1}{r_2} + \frac{1}{r_{12}},$$

$$P_1(E) \equiv \Theta(E - H_1) = |\varphi\rangle\langle\varphi| \otimes \Theta\left(E + \frac{\mu}{2} - \frac{|\mathbf{p}_2|^2}{2}\right) \quad \text{for } E < -\frac{\mu}{8},$$

$$Q_1(E) \equiv \Theta(E - H),$$

$\varphi(r_1) = 2\mu^{3/2} \exp(-\mu r_1)$ is the ground state of $\dfrac{|\mathbf{p}_1|^2}{2\mu} - \dfrac{1}{r_1}$.

This notation allows the principal result to be stated:

The One-Channel Møller Operators (4.4.15)

If $E < -\mu/8$, *then the Møller operators*

$$\Omega_{1\pm} \equiv s\text{-}\lim_{t\to\pm\infty} Q_1(E)\exp(iHt)\exp(-iH_1t)P_1(E)$$

and

$$\Omega_{1\pm}^* \equiv s\text{-}\lim_{t\to\pm\infty} P_1(E)\exp(iH_1t)\exp(-iHt)Q_1(E)$$

exist and are complete,

$$\Omega_{1\pm}^*\Omega_{1\pm} = P_1(E), \qquad \Omega_{1\pm}\Omega_{1\pm}^* = Q_1(E).$$

Remarks (4.4.16)

1. It is crucial that the effective interaction between e^- and μ^-p falls off faster than $1/r$; if there were a nucleus of charge $Z > 1$ instead of p, it would be necessary to choose
$$H_1 = \frac{|\mathbf{p}_1|^2}{2\mu} + \frac{|\mathbf{p}_2|^2}{2} - \frac{Z}{r_1} - \frac{Z-1}{r_2}.$$
2. The scattering of e^+ from μ^-p is the same, with some changes of sign.
3. If the electronic spins are parallel, the scattering of e^- from a hydrogen atom is complicated by the Pauli principle: Since H_1 is not invariant under permutation of the two electrons, $\exp(iHt)\exp(-iH_1t)$ does not send the subspace of antisymmetric states to itself. It is necessary instead to take the limit of $\exp(iHt)\exp(-iH_1t)|\psi_1\rangle \pm \exp(iHt)\exp(-iH_2t)|\psi_2\rangle$, which is equivalent to an antisymmetrization of the scattering amplitude.
4. If the electronic spins are antiparallel, then H has a bound state, which must be known precisely to calculate the scattering length; if there is an eigenvalue at zero, the scattering length becomes infinite.
5. The S-matrix in the interaction representation, $S_{11} = \Omega_{1+}^*\Omega_{1-}$, satisfies the unitarity condition $S_{11}^*S_{11} = S_{11}S_{11}^* = P_1(E)$.

Proof of (4.4.15)

As in the proof of (3.4.11), we check whether

$$Q_1(E)\exp(iHt)I_1\exp(-iH_1t)P_1(E)$$

and

$$P_1(E)\exp(iH_1t)I_1\exp(-iHt)Q_1(E)$$

are integrable in time. The conditions of (3.4.11) for H and H_1 have to be met after multiplication by Q_1 and, respectively, P_1, so the supremum needs to be taken only over

$$\omega \in I \equiv \left(-\frac{\mu}{2} + \delta, -\frac{\mu}{8} - \delta\right), \quad \delta \downarrow 0.$$

(i) $\sup_{\omega \in I} \| \sqrt{I_1}\, \delta(H_1 - \omega) \sqrt{I_1} \|$. For this part it is intuitively clear that for $\omega < -\mu/8$,

$$\delta\left(\frac{|\mathbf{p}_1|^2}{2\mu} - \frac{1}{r_1} + \frac{|\mathbf{p}_2|^2}{2} - \omega\right) = |\varphi\rangle\langle\varphi| \otimes \delta\left(\frac{|\mathbf{p}_2|^2}{2} - \omega - \frac{\mu}{2}\right);$$

and this is derived formally in Problem 1. With $k^2/2 = \omega + \mu/2$, we find

$$\mathrm{Tr}(\sqrt{I_1}\, \delta(H_1 - \omega) \sqrt{I_1})^n$$

$$= \int d^3x_1 \cdots d^3x_n u(\mathbf{x}_1) g_k(\mathbf{x}_1 - \mathbf{x}_2) u(\mathbf{x}_2) g_k(\mathbf{x}_2 - \mathbf{x}_3) \cdots g_k(\mathbf{x}_n - \mathbf{x}_1),$$

where

$$g_k(\mathbf{x}) = \frac{1}{4\pi^2 r} \sin kr$$

and

$$u(\mathbf{x}) = \int d^3x' |\varphi(\mathbf{x}')|^2 |I_1(\mathbf{x}, \mathbf{x}')|$$

$$= \int d^3x' |\varphi(\mathbf{x}')|^2 \left| \frac{1}{|\mathbf{x}|} - \frac{1}{|\mathbf{x} - \mathbf{x}'|} \right|.$$

The potential u is larger than the potential

$$V(\mathbf{x}) = \int d^3x' |\varphi(\mathbf{x}')|^2 \left(\frac{1}{|\mathbf{x} - \mathbf{x}'|} - \frac{1}{|\mathbf{x}|} \right) = \left(\mu + \frac{1}{r}\right) \exp(-2\mu r) \quad (4.4.17)$$

(see (4.3.7)), which is the potential due to the proton shielded by the muon-cloud. However, the dipole expansion $1/|\mathbf{x} - \mathbf{x}'| = 1/r + (\mathbf{x} \cdot \mathbf{x}')/r^3 + O(r^{-3})$ shows that $\mu \sim r^{-2}$ as $r \to \infty$. We thus have a one-body situation of the kind treated in (3.4.11). Since u has only a $1/r$ singularity at the origin, (3.4.14; 1) shows that indeed

$$\sup_{\omega \in I} \| \sqrt{I_1}\, \delta(H_1 - \omega) \sqrt{I_1} \| < \infty.$$

(ii) $\sup_{\omega \in I} \| \sqrt{I_1}\, \delta(H - \omega) \sqrt{I_1} \|$.

$$\delta(H - \omega) = \frac{1}{2\pi i} \lim_{\varepsilon \downarrow 0} \left(\frac{1}{H - \omega - i\varepsilon} - \frac{1}{H - \omega + i\varepsilon} \right).$$

The resolvent still has the same structure as in (4.4.5) in the trivial generalization to $\mu > 1$, so

$$\sqrt{I_1}(H - z)^{-1}\sqrt{I_1} = (1 - \sqrt{I_1}J(z)(\sqrt{I_1})^{-1})^{-1}\sqrt{I_1}D(z)\sqrt{I_1},$$

and it is again a question of showing the boundedness of $\sqrt{I_1}\, D(z)\sqrt{I_1}$ and the compactness of $\sqrt{I_1}J(z)/\sqrt{I_1}$. We already know this if z is not real, and it only remains to see what happens for $z \in [-\mu/2 + \delta \pm i\varepsilon, -\mu/8 - \delta \pm i\varepsilon] = I$, $\delta > 0$, $\varepsilon \downarrow 0$. The only singular part of $D(z)$ is

$$\left(\frac{|\mathbf{p}_1|^2}{2\mu} - \frac{1}{r_1} + \frac{|\mathbf{p}_2|^2}{2} - z\right)^{-1} = |\varphi\rangle\langle\varphi| \otimes \left(\frac{|\mathbf{p}_2|^2}{2} - z - \frac{\mu}{2}\right)^{-1}$$

$$+ (1 - |\varphi\rangle\langle\varphi| \otimes 1)\left(\frac{|\mathbf{p}_1|^2}{2\mu} - \frac{1}{r_1} + \frac{|\mathbf{p}_2|^2}{2} - z\right)^{-1},$$

and in fact only the first term in this expression. If the muon is excited, its energy becomes $\geq -\mu/8$, and the second term is uniformly bounded by $1/\delta$ for all $z \in I$. In part (i) we found that

$$\sqrt{I_1}|\varphi\rangle\langle\varphi| \otimes \left(\frac{|\mathbf{p}_2|^2}{2} - \omega - \frac{\mu}{2} \pm i\varepsilon\right)^{-1}\sqrt{I_1}$$

is bounded (the proof also works for the term with $\delta(|\mathbf{p}|^2 - z)$ replaced by $(|\mathbf{p}|^2 - z)^{-1}$). Similarly, the only term in question in $\sqrt{I_1}J/\sqrt{I_1}$ is

$$\sqrt{I_1}(T - z)^{-1}\frac{1}{r_1}\left(T - \frac{1}{r_1} - z\right)^{-1}\sqrt{I_1},$$

and in fact again only the contribution from the muon in the ground state. To prove the compactness of

$$\sqrt{I_1(\mathbf{x}_1, \mathbf{x}_2)}(T - z)^{-1}\frac{1}{r_1}|\varphi(\mathbf{x}_1)\rangle\langle\varphi(\mathbf{x}_1)|$$

$$\otimes\left(\frac{|\mathbf{p}_2|^2}{2} - z - \frac{\mu}{2}\right)^{-1}\sqrt{I_1(\mathbf{x}_1, \mathbf{x}_2)}$$

we argue as in (3.4.13). It is rather easy (Problem 2) to convince oneself that $K = \sqrt{I_1(\mathbf{x}_1, \mathbf{x}_2)}(T - z)^{-1}(1/r_1)|\varphi(\mathbf{x}_1)\rangle\langle\varphi(\mathbf{x}_1)|\delta(|\mathbf{p}_2|^2 - \omega) \times \sqrt{I_1(\mathbf{x}_1, \mathbf{x}_2)}$ belongs to $\mathscr{C}_4$ and is Hölder continuous in ω. This guarantees the compactness of the operator in question for $z = x + iy$, $-\mu/2 < x < 0$, as $y \downarrow 0$ (Problem 2). The points z_i at which $J(z)$ has eigenvalue 1 are eigenvalues of H with finite multiplicity. The associated

eigenfunctions fall off exponentially (4.3.38), so $\sqrt{I_1}\psi$ is in $\mathscr{H}$. The operator $\sqrt{I_1}J(z)/\sqrt{I_1}$ also has eigenvalue 1 iff z equals one of the z_i. Since we know that there is no eigenvalue of H in the interval I, $(1 - \sqrt{I_1}J(z)/\sqrt{I_1})^{-1}$ is bounded uniformly on I, and thus so is

$$\sup_{\omega \in I} \| \sqrt{I_1}\, \delta(H - \omega) \sqrt{I_1} \| < \infty. \qquad \square$$

Once it is known that the Møller operators exist, and hence that the S-matrix is well defined, it becomes possible to calculate the scattering amplitude of e^- from μ^-p. This is a matter of finding the expectation value of $I_1 - I_1(H - E)^{-1}I_1$ with $E = -\mu/2 + k^2/2$ in the (unnormalizable) state $\varphi(\mathbf{x}_1)\exp(i\mathbf{k}\cdot\mathbf{x}_2)$. Physical intuition says that the large mass of the muon prevents an electron of low energy from having much influence on it. As a consequence, the electron should simply feel the familiar effective potential $V_t = 1 \otimes v$, where v is as in (4.4.17). This feeling can at least be tested by using V_t as the comparison potential in Kohn's variational principle (3.6.29) and substituting for Ω_t; setting $k = 0$ for this purpose, we get a

Variational Principle for the Scattering Length (4.4.18)

The scattering length is the expectation value of

$$T = T_t + T_t V_t^{-1}(I_1 - V_t)V_t^{-1}T_t - T_t V_t^{-1}(I_1 - V_t) \times \left(H + \frac{\mu}{2}\right)^{-1}(I_1 - V_t)V_t^{-1}T_t,$$

$$T_t = V_t - V_t\left(H_t + \frac{\mu}{2}\right)^{-1}V_t,$$

$$H_t = H + V_t - I_1 = \frac{|\mathbf{p}_1|^2}{2\mu} - \frac{1}{r_1} + \frac{|\mathbf{p}_2|^2}{2} + V_t(\mathbf{x}_2)$$

in the state $\varphi(\mathbf{x}_1) \otimes \mathbf{1}$.

Calculation of the Three Contributions to T (4.4.19)

(i) T_t. This amounts to the scattering of an electron by a short-range potential V_t. There is no interaction between the muon and the electron, so everything factorizes. Since V_t is radially symmetric, T_t could be evaluated numerically on a computer. However, it is hardly worth the

trouble, since with the actual value $\mu = 207$, V_t is such a small perturbation that the first Born approximation a_B has an accuracy measured in ‰. To see this, refer to (3.6.24) and calculate the quantity defined there,

$$\|K\|^2 \leq \|v\|_R^2 \equiv \int d^3x\, d^3x'\, v(\mathbf{x})v(\mathbf{x}')(4\pi|\mathbf{x}-\mathbf{x}'|)^{-2}$$

$$= \int \frac{d^3k}{(2\pi)^3}\left(\frac{\tilde{v}(\mathbf{k})}{4\pi}\right)^2 \frac{2\pi^2}{|\mathbf{k}|}$$

$$= \frac{1}{2}\int_0^\infty dk^2\, \frac{[|\mathbf{k}|^2+8\mu^2]^2}{[|\mathbf{k}|^2+4\mu^2]^4} = \frac{1}{4\mu^2}\frac{7}{6},$$

since the Fourier transform of $|\varphi(\mathbf{x})|^2$ is $(1+|\mathbf{k}|^2/4\mu^2)^{-2}$, so

$$\frac{\tilde{v}(\mathbf{k})}{4\pi} = \frac{-1}{|\mathbf{k}|^2}\left(1 - \frac{(4\mu^2)^2}{(|\mathbf{k}|^2+4\mu^2)^2}\right).$$

The scattering length a_t is thus equal to $a_B(1 \pm \|K\|/(1-\|K\|)) = a_B(1 \pm 0.002)$, and a calculation of a_B yields

$$a_B = \int \frac{d^3x}{4\pi}\, v(\mathbf{x}) = \frac{\tilde{v}(0)}{4\pi} = -\frac{1}{2\mu^2} = -\frac{1}{2}(206.8)^{-2}\cdot(\text{Bohr radius})$$

$$= -0.619 \times 10^{-13}\ \text{cm}.$$

(ii) The term linear in $I_1 - V_t$ vanishes: Clearly,

$$T_t\varphi(\mathbf{x}_1)\otimes\exp(i\mathbf{k}\cdot\mathbf{x}_2)$$

$$= \varphi(\mathbf{x}_1)\otimes\left(V_t - V_t\left(\frac{|\mathbf{p}_2|^2}{2} - |\mathbf{k}|^2\right)^{-1}V_t\right)\exp(i\mathbf{k}\cdot\mathbf{x}_2),$$

and $\int d^3x_1\,|\varphi(\mathbf{x}_1)|^2(I_1(\mathbf{x}_1,\mathbf{x}_2) - V_t(\mathbf{x}_2))$ is zero by definition. The V_t we have chosen is optimal in the sense that the difference between $\langle T\rangle$ and $\langle T_t\rangle$ is quadratic in $I_1 - V_t$.

(iii) To estimate the effect of $(H+\mu/2)^{-1}$ in the last term, recall from §4.3 that H has no bound state, so $H + \mu/2 \geq 0$. Indeed, H dominated a certain one-particle Hamiltonian with no bound states:

$$H + \frac{\mu}{2} \geq \left[\frac{|\mathbf{p}_2|^2}{2} - \frac{1}{r_2} + V_L(r_2)\right]P + \left(\frac{3\mu}{8} - \frac{1}{2\gamma} + \frac{1-\gamma}{2}|\mathbf{p}_2|^2\right)$$

$$\times (1-P) = H_L,$$

$$P = |\varphi\rangle\langle\varphi|\otimes 1,$$

where we used $|\mathbf{p}|^2/2 - 1/r \geq -1/2\gamma + (1-\gamma)|\mathbf{p}|^2/2$ for $0 < \gamma < 1$ in the last term. Let us finally choose γ to optimize the bound. If $a \geq b > 0$, then $a^{-1} \leq b^{-1}$ (2.2.38; 11), so we arrive at the upper bound

$$\left(H + \frac{\mu}{2}\right)^{-1} \leq H_L^{-1} = P\left(\frac{|\mathbf{p}_2|^2}{2} - \frac{1}{r_2} + V_L(r_2)\right)^{-1} + (1-P)\left(\frac{1-\gamma}{2}|\mathbf{p}_2|^2 - \frac{1}{2\gamma} + \frac{3\mu}{8}\right)^{-1}.$$

Zero would be a trivial lower bound for $(H + \mu/2)^{-1}$, but it is not good enough to assess how much difference the correction to T_t makes. For this purpose we can use the projection methods of (3.5.31), and take P' in $(H + \mu/2)^{-1} \geq P'(P'(H + \mu/2)P')^{-1} \cdot P'$ as the projection $|\varphi'\rangle\langle\varphi'| \otimes 1$ with some φ'. Then

$$P'\left(\frac{|\mathbf{p}_2|^2}{2} - \frac{1}{r_1} + \frac{1}{r_{12}}\right)P' \leq P'\frac{|\mathbf{p}_2|^2}{2},$$

since

$$\int \frac{d^3x'\rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} \leq \frac{1}{r}$$

for any spherically symmetric ρ. Let $P'(|\mathbf{p}_1|^2/2\mu - 1/r_1)P'$ be $\varepsilon_1 P'$. The not exactly known resolvent is thus finally bounded by the following one-particle operators:

$$\frac{2P'}{|\mathbf{p}_2|^2 + \kappa'^2} \leq \frac{1}{H + \mu/2} \leq \frac{P}{|\mathbf{p}_2|^2/2 - 1/r_2 + V_L(r_2)} + \frac{2}{1-\gamma}\frac{1-P}{|\mathbf{p}_2|^2 + \kappa^2},$$

$$\kappa'^2 = \mu + 2\varepsilon_1, \qquad \kappa^2 = \frac{2}{1-\gamma}\left[\frac{3\mu}{8} - \frac{1}{2\gamma}\right].$$

Since V_t has been chosen so that $P(I_1 - V_t)P = 0$, only the last term on the right contributes to T, and so the bounds on the scattering length are

$$\langle\psi|T_t|\psi\rangle - \|R(I_1 - V_t)V_t^{-1}T_t\psi\|^2 \leq \langle\psi|T|\psi\rangle \leq \langle\psi|T_t|\psi\rangle - \|P'R'(I_1 - V_t)V_t^{-1}T_t\psi\|^2,$$

$$R = \left[\frac{2/(\gamma-1)}{|\mathbf{p}_2|^2 + \kappa^2}\right]^{1/2}, \qquad R' = \left[\frac{2}{|\mathbf{p}_2|^2 + \kappa'^2}\right]^{1/2}, \qquad \psi = \varphi \otimes 1.$$

The term

$$V_t^{-1}T_t\psi = \varphi(\mathbf{x}_1) \otimes (1 + \tfrac{1}{2}|\mathbf{p}_2|^{-2}V_t(\mathbf{x}_2))^{-1} \cdot 1 \equiv \varphi(\mathbf{x}_1) \otimes \psi_t(\mathbf{x}_2)$$

factorizes as (ground state of the muon) $\otimes$ (scattering wave-function of the electron). The second factor can be evaluated by numerical

integration of the radial Schrödinger equation, but once more it is hardly worth the trouble, since the Born approximation $\psi_t \simeq 1$ is quite good. Specifically, the norm of $|\mathbf{p}|^{-2}V_t/2$ in L^∞ is

$$\|\tfrac{1}{2}|\mathbf{p}|^{-2}V_t\|_\infty = \frac{1}{8\pi}\sup_{\mathbf{x}}\int\frac{d^3x'\,V_t(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} = \frac{3}{8\mu},$$

so $\|\psi_t - 1\|_\infty \leq \|\tfrac{1}{2}|\mathbf{p}|^{-2}V_t\|_\infty = 0.001$. As a consequence, ψ_t can be replaced with 1 in the following integrals to an accuracy on the order of $\%_{00}$, after which they are all elementary by Fourier transformation:

$$\begin{aligned}\|R(I_1 - V_t)\psi_t\|^2 &= \int d^3x_1\,d^3x_2\,d^3x_2'\,\frac{\exp(-\kappa|\mathbf{x}_2-\mathbf{x}_2'|)}{2\pi(1-\gamma)|\mathbf{x}_2-\mathbf{x}_2'|}\psi_t(\mathbf{x}_2)\\
&\quad\times\left(-\frac{1}{|\mathbf{x}_2|}+\frac{1}{|\mathbf{x}_2-\mathbf{x}_1|}-V_t(\mathbf{x}_2)\right)\\
&\quad\times\left(-\frac{1}{|\mathbf{x}_2'|}+\frac{1}{|\mathbf{x}_2'-\mathbf{x}_1|}-V_t(\mathbf{x}_2')\right)\psi_t(\mathbf{x}_2')|\varphi(\mathbf{x}_1)|^2\\
&\overset{\psi_t\to 1}{\cong}\int\frac{d^3k}{(2\pi)^3}\frac{\kappa^2}{|\mathbf{k}|^2+\kappa^2}\left[2-\frac{2}{(1+|\mathbf{k}|^2/4\mu^2)^2}\right.\\
&\quad\left.-\left(1-\frac{1}{(1+|\mathbf{k}|^2/4\mu^2)^2}\right)^2\right]\frac{(4\pi)^2}{|\mathbf{k}|^4}\frac{2}{1-\gamma}\\
&= \frac{2}{1-\gamma}\int\frac{d^3k}{(2\pi)^3}\frac{\kappa^2}{|\mathbf{k}|^2+\kappa^2}\frac{(4\pi)^2}{|\mathbf{k}|^4}\left[1-\frac{1}{(1+|\mathbf{k}|^2/4\mu^2)^4}\right].\end{aligned}$$

The corresponding contribution to the upper bound is

$$\begin{aligned}&\int d^3x_1\,d^3x_1'\,d^3x_2\,d^3x_2'\,\varphi'(\mathbf{x}_1)\varphi(\mathbf{x}_1)\left(-\frac{1}{|\mathbf{x}_2|}+\frac{1}{|\mathbf{x}_1-\mathbf{x}_2|}-V_t(\mathbf{x}_2)\right)\\
&\quad\cdot\frac{\exp(-\kappa'|\mathbf{x}_2-\mathbf{x}_2'|)}{2\pi|\mathbf{x}_2-\mathbf{x}_2'|}\left(-\frac{1}{|\mathbf{x}_2'|}+\frac{1}{|\mathbf{x}_1'-\mathbf{x}_2'|}-V_t(\mathbf{x}_2')\right)\varphi'(\mathbf{x}_1')\varphi(\mathbf{x}_1').\end{aligned}$$

If φ' is now chosen as $(1+\alpha r)\exp(-\beta r)$ and the bounds are optimized in α, β, and γ, then there result the following

Bounds for the Scattering Length of $e^- - (p\mu)$ (4.4.20)

The scattering length $a = \langle\psi|T\psi\rangle/4\pi$ satisfies

$$\begin{aligned}-0.70\times10^{-13}\text{ cm} = a_t - \frac{\sqrt{3}}{2}\mu^{-5/2}\left(1-\frac{2}{\sqrt{3\mu}}\right)^{-1}\\
\leq a \leq -0.62\times10^{-13}\text{ cm}.\end{aligned}$$

Remarks (4.4.21)

1. Although muonium μ^-p is about $r_b/\mu \sim 2.4 \times 10^{-11}$ cm. across, the scattering length is smaller by a factor μ^{-1}: The kinetic energy prevents the wave-function from reacting much to a short-range potential. This explains why muonium diffuses through matter without significant interaction with the electrons.
2. The deviation from a_t can be interpreted as a virtual excitation of the muon. The lower bound shows that the ratio between the correction to a_t and a_t goes to 0 as $\mu^{-1/2}$ when $\mu \to \infty$. It is still on the order of 10% for the muon.
3. If $k > 0$, then $(H - E)^{-1}$ is no longer positive, and the resolvent must be analyzed more carefully.

Problems (4.4.22)

1. Prove that $\delta(|\mathbf{p}_1|^2/2\mu - 1/r_1 + |\mathbf{p}_2|^2/2 - \omega) = |\varphi\rangle\langle\varphi| \otimes \delta(|\mathbf{p}_2|^2/2 - \omega - \mu/2)$ for $\omega < 3\mu/8$ (see the proof of (4.4.15)).

2. Show that

$$K = \sqrt{I_1}\left(\frac{|\mathbf{p}_1|^2 + |\mathbf{p}_2|^2 - z}{2}\right)^{-1}\frac{1}{r_1}|\varphi(\mathbf{x}_1)\rangle\langle\varphi(\mathbf{x}_1)| \otimes \delta(|\mathbf{p}_2|^2 - \omega)\sqrt{I_1}$$

belongs to $\mathscr{C}_4$ if $z < 0$.

3. Show that if $I(z)$ is an analytic family of operators on a connected, open region G and $I(z)$ is compact in a neighborhood of $z_0 \in G$, then $I(z)$ is compact for all $z \in G$. (Hint: the series expansion

$$\sum_{n=0}^{\infty}\frac{(z - z_0)^n}{n!}I^{(n)}(z_0)$$

is convergent in norm on a sufficiently small neighborhood of z_0. Show that all $I^{(n)}(z_0)$ are compact and use the method of overlapping discs described, for example, in [17].

Solutions (4.4.23)

1. Use $\delta(a \otimes 1 + 1 \otimes b) = \int_{-\infty}^{\infty} d\alpha\, \delta(a - \alpha) \otimes \delta(\alpha + b)$:

$$\int_{-\infty}^{\alpha} d\alpha\, \delta\left(\frac{|\mathbf{p}_1|^2}{2\mu} - \frac{1}{r} - \alpha\right) \otimes \delta\left(\frac{|\mathbf{p}_2|^2}{2} - \omega + \alpha\right) = \int_{-\infty}^{\omega} d\alpha\, \delta \otimes \delta$$

$$= |\varphi\rangle\langle\varphi| \otimes \delta\left(\frac{|\mathbf{p}_2|^2}{2} - \omega - \frac{\mu}{2}\right).$$

2. The operator is of the form

$$\sqrt{I_1(\mathbf{x}_1, \mathbf{x}_2)}|\psi(\mathbf{x}_1)\rangle\langle\psi(\mathbf{x}_1)|\delta(|\mathbf{p}_2|^2 - \omega)\sqrt{I_1(\mathbf{x}_1, \mathbf{x}_2)},$$

where $\psi(\mathbf{x}_1) = ((|\mathbf{p}_1|^2 + \omega)/2 - z)^{-1}(1/r_1)\varphi(\mathbf{x}_1)$. If $z < 0$, then this function is as good as φ, since $\hat{u}(\mathbf{x}) = \int d^3x' |\psi(\mathbf{x}')|^2 |I_1(\mathbf{x}, \mathbf{x}')|$ has the same $1/r^2$ behavior as $u(\mathbf{x})$. Hence we conclude from (3.4.13; 2) that $\mathrm{Tr}(KK^*)^2 < \infty$.

3. $I^{(n)}(z_0) = (n!/2\pi i)\int_{C_0}(I(z)/(z-z_0)^{n+1})\,dz$ is the norm-limit of Riemann sums of compact operators and therefore compact, provided that C_0 is a circle in the region of compactness of z_0. However, the power series converges on the largest circle about z_0 completely contained in the domain of analyticity G. Hence compactness can be continued to the whole region G in analogy with analytic continuation through overlapping discs.

4.5 Complex Atoms

The motion of the inner electrons in a large atom can be approximated to within a few percent by motion in an averaged field.

The first genuinely many-body problem that we shall discuss in much depth is that of an infinitely heavy atomic nucleus of charge Z and N electrons. The methods will be the same as those developed for helium, though the Pauli exclusion principle will now emerge as the decisive fact. Insofar as the inter-electronic repulsion can be neglected, these ideas lead to the familiar shell structure of atoms, which is so evident in the periodic table of the elements. To date it has not been possible to determine whether electronic shells are also predicted by the Schrödinger equation including the effect of the electrons on one another. A derivation would require extraordinarily tight upper and lower bounds for the energy eigenvalues. It is easy to get upper bounds with variational procedures, elementary calculations providing about 10% accuracy and more elaborate ones attaining about 1%. The methods that have been presented for lower bounds break down, however, as the ground state is pushed well into the continuum of H_0 by the interelectronic repulsion, though lower bounds with an accuracy of a few percent are obtainable with another strategy. Unfortunately, the accuracy is with respect to the total energy, which goes as $Z^2N^{1/3}$ eV, amounting to MeV for large atoms, while the energy differences of importance for the shell structure and, for that matter, all of chemistry are only a few eV. The required precision is far too great, so we shall have to make do with the qualitative traits of the spectrum, which are due to various conserved quantities.

We follow the steps of §4.3.

The Normal Form H_N of the Hamiltonian (4.5.1)

$$H = \frac{1}{2m}\sum_{i=1}^{N}|\mathbf{p}_i|^2 - Ze^2\sum_{i=1}^{N}\frac{1}{|\mathbf{x}_i|} + e^2\sum_{i>j}\frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}$$

can be transformed to $Z^2e^4mH_N$, where

$$H_N(\alpha) = \frac{1}{2}\sum_{i=1}^{N}\left(|\mathbf{p}_i|^2 - \frac{1}{|\mathbf{x}_i|}\right) + \alpha\sum_{i>j}\frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} = H_0 + \alpha H', \qquad \alpha = \frac{1}{Z},$$

by a dilatation of the coordinates.

Remarks (4.5.2)

1. The potential energy is once again ε-bounded relative to the kinetic energy, and H is self-adjoint on the domain of the kinetic energy and bounded from below.
2. The analysis of the resolvent in (4.4.5) can be adapted for the many-electron Hamiltonian. All the connected graphs in the expansion of the resolvent are compact, and the noncompact parts correspond to distributions of the nucleus and electrons into groups within which the particles interact, but which are not bound together. The clusters determine where the essential spectrum of the overall Hamiltonian begins, and if $\alpha > 0$, Theorem (4.4.7) generalizes:

The HVZ Theorem (4.5.3)

$$\sigma_{\text{ess}}(H_N(\alpha)) = \bigcup_{M=2}^{N-1} \text{Sp}(H_M(\alpha)).$$

The point spectrum also resembles that of (4.3.10) and (4.3.19); the effect of dilatations on the Hamiltonian implies the

Concavity of the Ground-State Energy (4.5.4)

The functions $E_1(\alpha)$ and also $-\sqrt{-E_1(\alpha)}$ are concave in α.

The Virial Theorem (4.5.5)

If $(H(\alpha) - E)\psi = 0$, then

$$E = -\langle\psi| \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2} |\psi\rangle = \frac{1}{2}\langle\psi| - \sum_{i=1}^{N} \frac{1}{|\mathbf{x}_i|} + \alpha \sum_{i>j} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} |\psi\rangle.$$

Remarks (4.5.6)

1. As before, it follows that there are no eigenvalues $E \geq 0$.
2. If $E(\alpha)$ is known, then (4.5.5) together with

$$\frac{\partial E}{\partial \alpha} = \langle\psi| \sum_{i>j} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} |\psi\rangle$$

allows the expectation values of $1/|\mathbf{x}_i|$ to be determined, too.

It is furthermore true that positive ions and atoms have infinitely many bound states. Because of the symmetry requirements on the wave-function the proof is more difficult than for helium.

The Infinitude of the Point Spectrum (4.5.7)

If $\alpha < 1/(N-1)$, then $H_N(\alpha)$ has an infinite point spectrum.

Proof

We follow the time-honored recipe of the proof of (4.3.8), but this time the exclusion principle comes into play. To take care of the symmetry, assume a trial function

$$\Psi_{n,\tau}(\mathbf{x}_1 \cdots \mathbf{x}_N) = \mathcal{N} \sum_{j=1}^{N} \varphi_n(r_j\tau)\chi(\mathbf{x}_1, \ldots, \hat{\mathbf{x}}_j, \ldots, \mathbf{x}_N), \qquad \tau \in \mathbb{R}^+, r_j \equiv |\mathbf{x}_j|,$$

where χ is the antisymmetrized, normalized ground state of H_{N-1}, with energy E_{N-1}. The symbol $\hat{\mathbf{x}}_j$ is used to indicate the absence of the coordinate $\mathbf{x}_j$, which stands for both the spatial and the spin coordinates of the j-th particle. For the present we assume only that $\varphi \in C^\infty$ and $\varphi_n(r) \neq 0$ only for $n < r < n+1$, $n = 1, 2, \ldots$. The $\mathcal{N}$ is a normalization constant. Since H is real, we may suppose that φ and χ are real:

$$\mathcal{N}^2 \sum_{j=1}^{N} (-1)^j \sum_{k=1}^{N} (-1)^k \int d^3x_1 \cdots d^3x_N \, \varphi_n(\tau r_j)\varphi_n(\tau r_k)\chi(\mathbf{x}_1 \cdots \hat{\mathbf{x}}_j \cdots \mathbf{x}_N)$$
$$\times \chi(\mathbf{x}_1 \cdots \hat{\mathbf{x}}_k \cdots \mathbf{x}_N) = 1.$$

The mixed terms like $\int d^3x_1 \cdots d^3x_N \varphi_n(\tau r_1)\varphi_n(\tau r_2)\chi(\mathbf{x}_2 \cdots \mathbf{x}_N)\chi(\mathbf{x}_1, \mathbf{x}_3, \ldots, \mathbf{x}_N)$ cause trouble. However, we know that the functions χ fall off exponentially, as the argument leading to (4.3.39) does not depend on the number of particles: consider the group generated by $\exp(isr_1)$; by analytic continuation, for some $\delta > 0$, $\exp(sr_1)\chi(x_1, \ldots, x_{N-1}) \in \mathscr{H}$ for all s, $|s| < \delta$. It then follows that the mixed term is $O(\exp(-2\tau\,\delta))$ as $\tau \to \infty$, because $\|\exp(-sr)\varphi_n(r\tau)\| \leq \exp(-ns\tau)$, and so $\mathcal{N}^2 = N + O(\exp(-2\tau\,\delta))$. If $\langle\psi|H_N\psi\rangle$ is calculated next, there are some more mixed terms:

$$O(\exp(-2\tau\,\delta)) + \langle\varphi|\frac{|\mathbf{p}|^2}{2} - \frac{1}{r} + \alpha V(r)|\varphi\rangle + E_{N-1}(\alpha),$$

$$V(r_1) = (N-1)\int d^3x_2 \cdots d^3x_N \frac{1}{r_{12}} |\chi(\mathbf{x}_2 \cdots \mathbf{x}_N)|^2.$$

Because of the exponential fall-off, $V(r) = (N-1)/r + O(\exp(-2r\,\delta))$ as $r \to \infty$. All told, if τ is sufficiently large and $\alpha < 1/(N-1)$, then

$$\langle\Psi_{n,\tau}|H_N|\Psi_{n,\tau}\rangle = E_{N-1} + \tau^{-2}\langle\varphi_n|\frac{|\mathbf{p}|^2}{2}\varphi_n\rangle - (1 - \alpha(N-1))$$
$$\times \langle\varphi_n|\frac{1}{r}|\varphi_n\rangle\tau^{-1} + O(\exp(-2\tau\,\delta)) < E_{N-1}.$$

Although the functions Ψ_n are not orthogonal, it is still true that $\langle \Psi_n | \Psi_{n'} \rangle = \delta_{n,n'} + O(\exp(-2\tau\,\delta))$. They can thus be orthogonalized in the limit $\tau \to \infty$ without affecting the inequality $\langle H_N \rangle \leq E_{N-1}$. The off-diagonal matrix elements $\langle \Psi_{n,\tau} | H_N | \Psi_{n',\tau} \rangle$ are all likewise $O(\exp(-2\tau\delta))$. If τ is sufficiently large, then for any $n \in \mathbb{Z}^+$ there is an n-dimensional subspace on which all eigenvalues of H_N lie below E_{N-1}, which proves (4.5.7) □

Bound States within the Continuum (4.5.8)

The continuous spectrum between E_{N-1} and 0 usually has embedded eigenvalues, of states whose decay is forbidden by conservation laws. Consider as an example lithium, $N = 3$. The ground state is the $(1s)^2(2s)$ configuration $^2S^+$. The lowest state with spin $\frac{3}{2}$ is $(1s)(2s)(2p)$, i.e., $^4P^-$, which is well within the continuum of the $^2S^+$ states $(1s)^2(\infty s)$. Moreover, the states of unnatural parity $^4P^+$ of the $(1s)(2p)^2$ configuration are within the continuum of the $^2S^+$ states. (The notation is $^{(2S+1)}L^P$.)

It would take us too far afield to go into great detail about the host of energy levels. To gain an overview of the dependence of the energy on N, it is most convenient to investigate the ground states of atoms with full shells. They are milestones in the periodic table, and their theoretical analysis is relatively straightforward.

Upper Bounds for $E_1(\alpha)$ Using Eigenfunctions of $H(0)$ (4.5.9)

The most primitive estimate is the expectation value of H in the ground state of $H(0)$, which is easy to find; the Balmer levels are simply filled up with the available electrons in accordance with the exclusion principle. If the states with quantum numbers (n, l, l_3, s) are enumerated with the index j, then the wave-function of the N noninteracting particles is

$$\Psi(\mathbf{x}_1 \cdots \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \prod_{j=1}^{N} \psi_j(\mathbf{x}_{p_j}), \tag{4.5.10}$$

where p_j is a permutation of $1 \cdots N$. Since the levels of energy $-1/2n^2$ are $2n^2$-fold degenerate, the eigenvalue of $H(0)$ with this eigenfunction and filled n-shells for $n \leq n_0$ is

$$E = -\frac{1}{2} \sum_{n=1}^{n_0} \frac{2n^2}{n^2} = -n_0,$$

where

$$N = 2 \sum_{n=1}^{n_0} n^2 = \frac{2n_0^3 + 3n_0^2 + n_0}{3}$$

(see Problem (4.5.29)). The calculation of $\langle\psi|H|\psi\rangle$ requires in addition the evaluation of

$$\begin{aligned}\langle\Psi|H'|\Psi\rangle &= \frac{N(N-1)}{2}\langle\Psi|\frac{1}{r_{12}}|\Psi\rangle \\ &= \frac{1}{2}\int\frac{d^3x_1\,d^3x_2}{|\mathbf{x}_1-\mathbf{x}_2|}\sum_{j,j'}(|\psi_j(\mathbf{x}_1)|^2|\psi_{j'}(\mathbf{x}_2)|^2 \\ &\quad -\psi_j(\mathbf{x}_1)\psi_{j'}(\mathbf{x}_2)\psi_j^*(\mathbf{x}_1)\psi_{j'}^*(\mathbf{x}_2)).\end{aligned} \tag{4.5.11}$$

The latter part of this, known as the **exchange term**, only occurs if ψ_j and $\psi_{j'}$ have the same spin, since the scalar product includes the scalar product in spin space as a factor. The exchange term is ≤ 0 for all j and j':

$$\int\frac{d^3x_1\,d^3x_2}{|\mathbf{x}_1-\mathbf{x}_2|}\rho^*(\mathbf{x}_1)\rho(\mathbf{x}_2)\geq 0$$

holds because the Fourier transform $1/2\pi^2k^2$ of $1/|\mathbf{x}|$ is positive.

The exchange term was calculated for the simplest states in §4.3 and was about 10% as large as the first term. If it is ignored when $j\neq j'$, then at any rate there results an upper bound. The remaining term simplifies for closed L-shells when it is noted that

$$\frac{1}{|\mathbf{x}_1-\mathbf{x}_2|}=\frac{1}{r_2}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left(\frac{r_1}{r_2}\right)^l\frac{4\pi}{2l+1}Y_l^m(\Omega_1)Y_l^{-m}(\Omega_2) \tag{4.5.12}$$

for $r_2>r_1$, and otherwise $r_1\leftrightarrow r_2$. Since $\sum_{m=-l}^{l}|Y_l^m(\Omega)|^2$ is independent of the angles, it is clear that the first contribution to the sum $\sum_{j,j'}$ is spherically symmetric, and when the angular integration is done, the term with $l\neq 0$ in the decomposition (4.5.12) cancels out:

$$\begin{aligned}\langle\Psi|H'|\Psi\rangle &\leq \frac{1}{2}\int d^3x_1\,d^3x_2\sum_{j\neq j'}|\psi_j(\mathbf{x}_1)|^2|\psi_{j'}(\mathbf{x}_2)|^2 \\ &\quad\times\left(\frac{\Theta(r_1-r_2)}{r_2}+\frac{\Theta(r_2-r_1)}{r_1}\right) \\ &\leq \frac{1}{2}\sum_{j\neq j'}\min\left\{\langle\psi_j|\frac{1}{r}|\psi_j\rangle,\langle\psi_{j'}|\frac{1}{r}|\psi_{j'}\rangle\right\}.\end{aligned} \tag{4.5.13}$$

Because of the virial theorem, $\langle\psi_j|1/r|\psi_j\rangle=1/n^2$, $j=(n,l,l_3,s)$, so

$$\begin{aligned}\langle\Psi|H'|\Psi\rangle &\leq \frac{1}{2}\sum_{n,n'=1}^{n_0}2n^2 2n'^2\min\left\{\frac{1}{n^2},\frac{1}{n'^2}\right\}=\sum_{n=1}^{n_0}4\sum_{n'=1}^{n}n'^2 \\ &=\frac{1}{3}[n_0^4+4n_0^3+5n_0^2+2n_0]\end{aligned}$$

(see the Problem). The net result is that

$$\langle \Psi | H | \Psi \rangle \leq -n_0 + \frac{\alpha}{3}[n_0^4 + 4n_0^3 + 5n_0^2 + 2n_0].$$

As $N \to \infty$, $n_0 = (3N/2)^{1/3} + O(1)$, and if $\alpha = O(1/N)$, then

$$E \leq -N^{1/3}\left(\frac{3}{2}\right)^{1/3}\left(1 - \frac{\alpha N}{2}\right) + O(1). \tag{4.5.14}$$

Because of (4.5.4), Equation (4.5.13) can be bettered with a parabolic bound, as before, and since $H' > 0$, we obtain

Rough Bounds for E_N for Neutral Atoms (4.5.15)

If $\alpha N = N/Z = 1$, then to $O(N^{-1/3})$ the lowest eigenvalue E_N of H_N is

$$-\left(\frac{3}{2}\right)^{1/3} = -1.145 \leq \frac{E_N}{N^{1/3}} \leq -\left(\frac{3}{2}\right)^{1/3}\left(1 - \frac{1}{4}\right)^2 = -0.6439.$$

Remarks (4.5.16)

1. This eigenvalue E_N is $Z^{-2}e^{-4}m^{-1}$ times the eigenvalue of the H of (4.5.1), so the dependence on N and Z anticipated in (1.2.11) is verified.
2. An estimate $O(N^{-1/3})$ is useless for actual atoms, since the corrections neglected in (4.5.14) with the replacement of $\sum_{n'=1}^{n} (n')^2$ by $n^3/3$ are still about 50% for $n_0 = 10$, which makes $N = 770$.
3. The estimate (4.5.13) is not very good for electrons within the same shell. For instance, the right side is 1 for $(1s)^2$, while in reality the left side is only $\frac{5}{8}$ (see (4.3.22; 1)). However, it is pretty accurate for electrons in different shells; for $(1s)(2s)$ it gives 0.25 instead of 0.2318. In all the error is not so bad for large atoms, since it is the interaction between shells that causes E_N to be $\sim N^{1/3}$.
4. If α is arbitrary, then the upper bound is $-(\frac{3}{2})^{1/3}N^{1/3}(1 - \alpha N/4)^2$, which has the maximum $(\frac{6}{7})^{7/3}\alpha^{-1/3}$ when $N\alpha = \frac{4}{7}$. Thus a more favorable trial function when $N > 4Z/7$ is the one having all additional electrons at infinity with energy 0; with it, $E/N^{1/3} \leq -(\frac{6}{7})^{7/3} = -0.6978$. According to Thomas–Fermi theory (see volume IV) the correct asymptotic value is -0.77.

$E_1(\alpha)$ Estimated with Trial Functions having Two Parameters (4.5.17)

In the effort to improve eigenvalue bounds, we recall that the parabolic bounds corresponded to the use of trial functions $\exp(id\tau)\Psi$ with an optimized dilatation parameter τ. This takes the partial screening of the field of the nucleus into account, which is clearly most significant for the external electrons. It would thus make more sense to stretch the different ψ_j with different τ_j. Although this would ruin the orthogonality of the ψ_j, which

is essential for the calculation, it is still compatible with orthogonality to dilate the ψ's with different l independently. In order to have more flexibility in the choice of trial functions, let us use eigenfunctions of a Hamiltonian containing an additional $1/r^2$ potential, since the eigenvalues are known in that case. If the angular momentum is l, we shall take

$$H_l = \frac{p_r^* p_r}{2} + \frac{(l + \delta_l)(l + \delta_l + 1)}{r^2} - \frac{\tau_l}{r},$$

which has eigenvalues

$$E_{n_r, l} = -\frac{\tau_l^2}{2}(n_r + l + \delta_l + 1)^{-2}.$$

Later, τ_l and δ_l will be optimized. The expectation values of $1/r$ and $1/r^2$, and therefore of $|\mathbf{p}|^2$ can be calculated by taking derivatives of E by τ and, respectively, δ: with $n = n_r + l + 1$,

$$\left\langle \frac{1}{r} \right\rangle = \tau_l (n + \delta_l)^{-2},$$

$$\langle |\mathbf{p}|^2 \rangle = \tau_l^2 (n + \delta_l)^{-3} \left(n - \frac{\delta_l (l + \frac{1}{2})}{\delta_l + l + \frac{1}{2}} \right).$$

To fill the shells in order, the sets of quantum numbers (n, l, l_3, s) will be enumerated with an index j. Each l-shell must be filled with $2l + 1$ or $2(2l + 1)$ electrons to be spherically symmetric. In that case,

$$\langle H \rangle = \sum_l \sum_n \nu(n, l) \left\{ \frac{\tau_l^2}{2} (n + \delta_l)^{-3} \left[n - \frac{\delta_l (l + \frac{1}{2})}{\delta_l + l + \frac{1}{2}} \right] - \frac{\tau_l}{(n + \delta_l)^2} (1 - \alpha N(n, l)) \right\},$$

$$N(n, l) = \sum_{j' < j} \nu(n(j), l(j')),$$

where $\nu(n, l)$ is the occupation number, and δ_l is allowed to vary only as long as $n + \delta_l$ is monotonic in j. The optimal value of $\langle H \rangle$ as a function of τ is attained when

$$\tau_l = \sum_n \nu(n, l) \frac{1 - \alpha N(n, l)}{(n + \delta_l)^2} \left[\sum_{n'} \frac{\nu(n', l)}{(n + \delta_l)^3} \left(n' - \frac{\delta_l (l + \frac{1}{2})}{\delta_l + l + \frac{1}{2}} \right) \right]^{-1},$$

i.e.,

$$\langle H \rangle = -\frac{1}{2} \sum_l \left\{ \sum_n \nu(n, l) \frac{1 - \alpha N(n, l)}{(n + \delta_l)^2} \right\}^2 \left\{ \sum_{n'} \frac{\nu(n', l)}{(n + \delta_l)^3} \left(n' - \frac{\delta_l (l + \frac{1}{2})}{\delta_l + l + \frac{1}{2}} \right) \right\}^{-1}. \tag{4.5.18}$$

The optimization by δ_l has to be done on a computer, and improves the result of our earlier ansatz that $\delta_l = 0$ by several percent. The table given below contains calculations of energies for several typical atoms, along with the

screening constants and the δ_l. Note that because of (4.5.13), Formula (4.5.18) is still a strict upper bound even for a spherical configuration plus one more electron.

Z	configuration of non-filled n-shells	δ_0 τ_0	δ_1 τ_1	δ_2 τ_2	δ_3 τ_3	δ_4 τ_4	δ_5 τ_5	$EN^{-7/3}$ by (4.5, 18)	$EN^{-7/3}$ by Hartree-Fock
10	$2s^2p^33p^3$	−0.03 0.86	−0.39 0.28	—	—	—	—	−0.524	−0.594
20	$3d^54d^5$	−0.01 0.94	0 0.69	−0.82 0.17	—	—	—	−0.562	−0.620
40	$3p^6d^{10}4f^{14}$	−0.01 0.96	−0.11 0.72	0 0.48	0 0.19	—	—	−0.591	−0.646
60	$4d^5f^75g^96h^{11}$	−0.02 0.94	−0.09 0.78	−0.19 0.53	0 0.40	0 0.27	0 0.10	−0.607	−0.648
80	$4s^1p^6d^{10}f^{14}5d^5f^7g^9$	−0.02 0.94	−0.17 0.73	−0.59 0.41	−0.86 0.20	0 0.06	—	−0.613	−0.656

Remarkably, this simple analytical ansatz arrives nearly within 10% of the correct values. The road to greater precision is rocky, but the trip is made easier by the reasonable assumption of a

Self-Consistent Field (4.5.19)

Hartree and Fock discovered one of the favorite methods for inventing good trial functions. The first step is to take the infimum of $\langle \Psi | H\Psi \rangle$ when Ψ is a product or determinantal trial function (4.5.10). The question immediately arises of whether the infimum is actually a minimum, i.e., whether there are minimizing ψ_j. If so, they satisfy the appropriate variational equations,

$$(H_\Psi \varphi_i)(\mathbf{x}) = \sum_{j=1}^{N} e_{ij}\varphi_j(\mathbf{x}), \qquad i = 1 \cdots N,$$

$$(H_\Psi \varphi)(\mathbf{x}) = \left\{ -\frac{\Delta}{2} - \frac{1}{|\mathbf{x}|} + \alpha U_\Psi(\mathbf{x}) \right\} \varphi(\mathbf{x}) - \alpha(K_\psi \varphi)(\mathbf{x}),$$

$$U_\Psi(\mathbf{x}) = \sum_{i=1}^{N} \int d^3x' \, \frac{|\varphi_i(\mathbf{x}')|^2}{|\mathbf{x} - \mathbf{x}'|},$$

$$(K_\psi \varphi)(\mathbf{x}) = \sum_{i=1}^{N} \varphi_i(\mathbf{x}) \int d^3x' \, \varphi(\mathbf{x}')\varphi_i^*(\mathbf{x}') \frac{1}{|\mathbf{x} - \mathbf{x}'|};$$

where e_{ij} are the Lagrange multipliers due to the orthonormalization. Since H_Ψ is self-adjoint, e_{ij} is a Hermitian matrix, and can thus be put into diagonal form $e_{ij} = \delta_{ij} e_i$. Hence we look for the N lowest eigenvalues of H_Ψ. If $\alpha \lesssim 1/N$ (positive ions and neutral atoms), then, as has recently been proved in [18], minimizing solutions exist, but an analytical solution of this system of nonlinear equations is hardly to be hoped for. An iterative procedure on a computer is called for, and even if this also fails to find exact solutions, $\langle \psi | H\psi \rangle$ is at least still an upper bound for the lowest eigenvalue. The procedure is unfortunately very cumbersome, especially because of the exchange terms $K\varphi$. The upper bounds obtained are also shown in the table for comparison. It is assumed that these values are within a few percent of the exact values. Granting that accuracy, the product ansatz of (4.5.10) is not at all bad, which suggests looking for lower bounds by using effective one-particle potentials approaching the Coulombic repulsion of the electrons from below. The principal theoretical shortcoming so far is the lack of a good lower bound; great refinement of the upper bound does not help much. The methods used in §4.3 are of no value because of the huge number of levels of $H(0)$. Some help is provided by the

Lower Bound for Interactions of Positive Type (4.5.20)

Let $V(x)$ be a potential of positive type (i.e., with a Fourier transform $\tilde{V}(k) \geq 0$, $V(0) < \infty$), and suppose $\Phi(\mathbf{x}) \in L^1(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$, so that $\tilde{\Phi}(\mathbf{k})$ exists. Then

$$\sum_{n>m} V(\mathbf{x}_n - \mathbf{x}_m) \geq \sum_{n=1}^{N} \Phi(\mathbf{x}_n) - \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} \left[\frac{|\tilde{\Phi}(\mathbf{k})|^2}{\tilde{V}(\mathbf{k})} + N\tilde{V}(k) \right].$$

Proof

It follows from

$$0 \leq \int d^3x\, d^3x' \left(\sum_{n=1}^{N} \delta(\mathbf{x} - \mathbf{x}_n) - \rho(\mathbf{x}) \right) V(\mathbf{x} - \mathbf{x}') \left(\sum_{m=1}^{N} \delta(\mathbf{x}' - \mathbf{x}_m) - \rho(\mathbf{x}') \right)$$

that

$$\sum_{n>m} V(\mathbf{x}_n - \mathbf{x}_m) \geq \sum_{n=1}^{N} \int d^3x\, \rho(\mathbf{x}) V(\mathbf{x} - \mathbf{x}_n) - \frac{N}{2} V(0)$$
$$- \frac{1}{2} \int d^3x\, d^3x'\, \rho(\mathbf{x}) \rho(\mathbf{x}') V(\mathbf{x} - \mathbf{x}').$$

Now set $\Phi(\mathbf{x}) = \int d^3x'\, \rho(\mathbf{x}') V(\mathbf{x} - \mathbf{x}')$; the proposition then follows by Fourier transformation. □

Remarks (4.5.21)

1. The significance of (4.5.20) is that a pair interaction is bounded by an effective one-particle potential Φ.
2. The degree to which Φ is arbitrary may seem surprising. A poor choice of Φ, however, renders (4.5.20) a triviality, saying that something positive is greater than something negative.

The Atomic Potential Bounded Below (4.5.22)

We have seen that a V of positive type can be estimated from below with arbitrary one-particle potentials, at the cost of a constant. Since the Coulomb potential becomes infinite at 0, it is first necessary to find a smaller function finite at 0 and with a positive Fourier transformation;

$$V(\mathbf{x}) \equiv \frac{1 - \exp(-\mu r)}{r} \leq \frac{1}{r}, \quad \tilde{V}(k) = \frac{4\pi\mu^2}{k^2(k^2 + \mu^2)}, \tag{4.5.23}$$

will do. The effective repulsive potential

$$\Phi(\mathbf{x}) = \int d^3x' \, \frac{n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|},$$

where $n(\mathbf{x})$ is the electron density, should be fairly realistic and lead to the best result. Then (transforming back to x-space),

$$H' \geq \sum_{n=1}^{N} \Phi(\mathbf{x}_n) - \frac{1}{2}\left\{\int d^3x \, \Phi(\mathbf{x}) n(\mathbf{x}) + 4\pi\mu^{-2} \int d^3x \, n(\mathbf{x})^2 + N\mu\right\}. \tag{4.5.24}$$

Since μ appears only in the constants, it can be optimized immediately, so we may set

$$\mu = \left[\frac{8\pi}{N} \int d^3x \, n(\mathbf{x})^2\right]^{1/3}.$$

As an analytically convenient approximation to $n(\mathbf{x})$ we use the semi-empirical expression (for $N = Z$),

$$\Phi(\mathbf{x}) = N \frac{r + 2(9/2N)^{1/3}}{[r + (9/2N)^{1/3}]^2}, \qquad n(\mathbf{x}) = \frac{N^{2/3}}{4\pi r} \frac{6(9/2N)^{1/3}}{[r + (9/2N)^{1/3}]^4},$$

$$\frac{1}{2}\{\quad\} = \frac{2}{5}\left(\frac{2}{9}\right)^{1/3} N^{7/3} + \frac{3}{2}\left(\frac{2}{7}\right)^{1/3} N^{5/3}. \tag{4.5.25}$$

Although the Schrödinger equation can not be solved analytically with this potential, the solution of a radial equation poses no difficulty for a computer. The following one-particle levels are found for

$$H_N \equiv Z^{-2}\left[-\frac{\Delta}{2} - \frac{Z}{r} + \Phi_N(\mathbf{x}) - \frac{\{\ \}}{2N}\right]:$$

n	l	H_0	$\hat{H}_{10}$	$\hat{H}_{20}$	$\hat{H}_{40}$
1	0	−0.5	−0.395	−0.412	−0.436
2	0	−0.125	−0.112	−0.084	−0.083
2	1	−0.125	−0.103	−0.077	−0.079
3	0	−0.055	−0.097	−0.053	−0.036
3	1	−0.055	—	−0.051	−0.034
3	2	−0.055	—	−0.051	−0.031
4	0	−0.031	—	−0.051	−0.028
4	1	−0.031	—	—	−0.028
4	2	−0.031	—	—	−0.028

After these levels have been filled up, the resultant lower bounds compare with the Hartree–Fock upper bounds as follows:

N	$\leq EZ^{-2}N^{-1/3} \leq$	
10	−0.761	−0.594
20	−0.730	−0.620
40	−0.715	−0.646
60	−0.712	−0.648
80	−0.711	−0.656

(4.5.26)

Remarks (4.5.27)

1. This method works better for larger N. Indeed, one of the most important results of Thomas–Fermi theory (see volume IV) is that the product ansatz for the wave-functions in an averaged field becomes exact as $N \to \infty$.
2. The potential (4.5.25) guessed here is still not the best possible. If $n(\mathbf{x}) = c\exp(-1.56r)$, then the lower bound one gets is -0.698 for $Z = N = 36$.
3. In volume IV, (4.5.24) will be recognized as a special case of a family of inequalities of Thomas–Fermi theory. In this case all the inequalities are, however, numerically about equally accurate.
4. Unlike the upper bounds, these lower bounds work just as well for the individual excited states; the n-th eigenvalue of the lower-bound Hamiltonian lies below the true n-th eigenvalue.

5. The lower bounds depend critically on the form of Ψ as an antisymmetrized product, whereas the upper bounds can be improved significantly by the use of linear combinations of determinants.
6. The bounds that have been derived reveal that the asymptotic value -0.77 is approached from above, but that the exact value is still not very close to -0.77 when $N = 80$.
7. The relativistic effects are comparable to the theoretical errors for heavy elements. The experimental values lie within the bounds found here, after relativistic corrections.

As to the properties of the electron density $\rho(\mathbf{x})$, there is an immediate generalization of the upper bounds of §4.3 as $r \to \infty$ and $r = 0$ to the case of N electrons. For the purposes of a qualitative discussion it suffices to have

Bounds for $\langle r^\nu \rangle$ (4.5.28)

In §1.2 it was explained why the average value of r should go as $N^{-1/3}$. This does not mean that heavier atoms are smaller than lighter ones. What is perceived as the size of an atom is the diameter of the outermost electronic orbital, whereas the mean value of r is dominated by the dense interior electron-cloud. In order to see whether the conjecture of §1.2 is a rigorous consequence of quantum mechanics, let us find some bounds for $\langle r^\nu \rangle^{1/\nu}$. If $\nu = -1$, then the virial theorem yields

$$\left\langle \frac{1}{r} \right\rangle^{-1} \leq \frac{NZ}{2|E_N|},$$

so if $N = Z$, then by (4.5.14),

$$\left\langle \frac{1}{r} \right\rangle^{-1} \leq N^{-1/3}(0.6978)^{-1}\frac{1}{2}(1 + O(N^{-1/3})).$$

On the other hand, for fermions with spin $\frac{1}{2}$,

$$\sum_{i=1}^{N}\left(\frac{|\mathbf{p}_i|^2}{2} - \beta\frac{1}{r_i}\right) \geq -\beta^2 N^{1/3}\left(\frac{3}{2}\right)^{1/3}(1 + O(N^{-1/3})), \qquad \beta > 0,$$

so

$$N\left\langle \frac{1}{r} \right\rangle \leq \frac{1}{\beta}\left\langle \sum_i \frac{|\mathbf{p}_i|^2}{2} \right\rangle + \beta\left(\frac{3N}{2}\right)^{1/3}(1 + O(N^{-1/3})).$$

If

$$\beta^2 = \left\langle \sum_i \frac{|\mathbf{p}_i|^2}{2} \right\rangle \left(\frac{3N}{2}\right)^{-1/3}$$

and

$$\sum_i \left\langle \frac{|\mathbf{p}_i|^2}{2} \right\rangle = |E_N| \leq \left(\frac{3}{2}\right)^{1/3} N^{7/3}(1 + O(N^{-1/3})),$$

then

$$\left\langle \frac{1}{r} \right\rangle^{-1} \geq N^{-1/3} \left(\frac{3}{2} \right)^{-1/3} \frac{1}{2} (1 + O(N^{-1/3})).$$

The result, to $O(N^{-1/3})$, is that $0.436 \leq N^{1/3} \langle 1/r \rangle^{-1} \leq 0.716$. The asymptotic Thomas–Fermi value is 0.556. If $v = 2$, then we obtain a lower bound by filling up the harmonic-oscillator levels:

$$\frac{1}{2} \sum_{i=1}^{N} (|\mathbf{p}_i|^2 + \omega^2 |\mathbf{x}_i|^2) \geq \omega N^{4/3} \frac{3^{4/3}}{4} (1 + O(N^{-1/3})),$$

so

$$\left\langle \sum_{i=1}^{N} |\mathbf{x}_i|^2 \right\rangle \geq \frac{(3N)^{8/3}}{16 \langle \sum |\mathbf{p}_i|^2 \rangle} \geq \frac{6^{1/3} 9 N^{1/3}}{32} \Rightarrow N^{1/3} \langle r^2 \rangle^{1/2} \geq 0.71 \text{ to } O(N^{-1/3}).$$

These rough numbers provide only an overview; for particular atoms one can do much better with the more accurate values of (4.5.26) for E.

Problem (4.5.29)

Calculate $\sum_{n=1}^{n_0} n^v$ for $v = 1, 2$, and 3.

Solution (4.5.30)

As a consequence of the binomial theorem,

$$(n_0 + 1)^{v+1} - 1 = (v + 1) \sum_n n^v + \binom{v+1}{2} \sum_n n^{v-1} + \cdots + \binom{v+1}{v} \sum_n n + n_0,$$

from which the individual sums can be determined recursively. The results are:

$$v = 1: \quad \tfrac{1}{2}(n_0^2 + n_0),$$

$$v = 2: \quad \tfrac{1}{6}(2n_0^3 + 3n_0^2 + n_0),$$

$$v = 3: \quad \tfrac{1}{4}(n_0^4 + 2n_0^3 + n_0^2).$$

4.6 Nuclear Motion and Simple Molecules

The large masses of atomic nuclei make them move so slowly within atoms and molecules that to a high degree of approximation they can be treated as static centers of force.

In the previous sections atomic nuclei were considered as fixed centers of force, but the validity of this approximation remains to be determined. The question is of central importance in molecular theory, which, as we shall see shortly, is based on the Born–Oppenheimer approximation (4.6.11),

in which the nuclei are at first regarded as fixed while the electrons move in the field of the static force centers. The energy of the system of electrons then serves as the potential in which the nuclei move. The intuition behind this approximation is that the light electrons move much more rapidly than the heavy nuclei, so from the standpoint of the electrons the potential is nearly static. Plausible as this may sound, it does not release us from the obligation to investigate whether this conceptual division of the action actually follows from an analysis of the Schrödinger equation of the whole atomic or molecular system.

Separation of the Center-of-Mass of an Atom (4.6.1)

We shall initially continue to investigate the case of an atom with N electrons. Let $(\mathbf{r}_0, \mathbf{k}_0)$ and $(\mathbf{r}_1, \mathbf{k}_1, \ldots, \mathbf{r}_N, \mathbf{k}_N)$ be the positions and momenta of the nucleus of mass M and, respectively, the electrons of mass m. (The symbols $\mathbf{x}_i$ are reserved for the relative coordinates below.) The kinetic energy is

$$T = \frac{|\mathbf{k}_0|^2}{2M} + \sum_{i=1}^{N} \frac{|\mathbf{k}_i|^2}{2m}.$$

In everything before now the limit $1/M \to 0$ was taken. Yet it is not possible to carry out any sort of perturbative expansion in $1/M$, at least directly. If $1/M = 0$, then the states are infinitely degenerate, and if $1/M < 0$, then T is not even positive definite. Let us introduce center-of-mass and relative coordinates $\mathbf{x}_0$ and $\mathbf{x}_1, \ldots, \mathbf{x}_N$:

$$\mathbf{x}_0 = \left(M\mathbf{r}_0 + m\sum_{i=1}^{N} \mathbf{r}_i\right)(M + Nm)^{-1}, \qquad \mathbf{x}_i = \mathbf{r}_i - \mathbf{r}_0, \qquad i = 1, \ldots, N.$$

In order to calculate the momenta conjugate to these coordinates, write T in terms of the velocities:

$$\begin{aligned} 2T &= M|\dot{\mathbf{r}}|^2 + m\sum_{i=1}^{N} |\dot{\mathbf{r}}_i|^2 \\ &= (M + Nm)|\dot{\mathbf{x}}_0|^2 + m\sum_{i=1}^{N} |\dot{\mathbf{x}}_i|^2 - \frac{m^2}{M + Nm}\left|\sum_{i=1}^{N} \dot{\mathbf{x}}_i\right|^2. \end{aligned}$$

The momenta are thus

$$\mathbf{p}_0 = \frac{\partial T}{\partial \dot{\mathbf{x}}_0} = (M + Nm)\dot{\mathbf{x}}_0, \qquad \mathbf{p}_i = \frac{\partial T}{\partial \dot{\mathbf{x}}_i} = m\left(\dot{\mathbf{x}}_i - \sum_{j=1}^{N} \dot{\mathbf{x}}_j \frac{m}{M + Nm}\right).$$

When substituted in above, this yields the

Kinetic Energy in Center-of-Mass and Relative Coordinates (4.6.2)

$$T = \frac{|\mathbf{p}_0|^2}{2(M + Nm)} + \frac{M + m}{2mM}\sum_{i=1}^{N} |\mathbf{p}_i|^2 + \frac{1}{M}\sum_{i>j>0} \mathbf{p}_i \cdot \mathbf{p}_j.$$

Remarks (4.6.3)

1. We see there are three terms, the kinetic energy of the center of mass with the total mass; the kinetic energy of the electrons, with reduced masses depending on the nuclear mass; and finally a correction on the order of $1/M$, known as the **Hughes–Eckart term**. Since it is obviously bounded relative to the second term, nothing prevents it from being handled with analytic perturbation theory. Note, however, that it can be either positive or negative.
2. Since the Hughes–Eckart term is not compact relative to T, it is a reasonable question whether it influences the essential spectrum. We have seen that without the correction the essential spectrum of H_N begins at the lowest point of the spectrum of H_{N-1}. This is physically reasonable, and is interpreted as the threshold of ionization. Expressed differently, we have proved that without the term on the order of $1/M$, $\inf \sigma_{ess}(T + V_N) = \inf \mathrm{Sp}(T + V_{N-1})$, where V_{N-1} is the potential neglecting the last particle. But this state of affairs should not be affected by the presence of the Hughes–Eckart term. Indeed, the compactness of the individual terms is not destroyed by a relatively bounded perturbation.

Estimate of the Effect of a Finite Nuclear Mass on the Energy Eigenvalues (4.6.4)

Since the center-of-mass motion separates off, we consider only the relative energy, which can also be written

$$H_r = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + \frac{|\sum_{i=1}^{N} \mathbf{p}_i|^2}{2M} + V.$$

Because mass has the dimensions of energy in units where $\hbar = e = 1$, and no other constants encumbered with dimensions appear, the ground-state energy must be of the form

$$E = mf\left(\frac{m}{M}\right) < 0.$$

The coefficient of $1/M$ in H_r is positive, so f increases monotonically. Since E must be concave in $(1/m, 1/M)$, it follows that

$$\frac{\partial^2 E}{\partial(1/m)^2}\frac{\partial^2 E}{\partial(1/M)^2} - \left(\frac{\partial^2 E}{\partial(1/m)\partial(1/M)}\right)^2 \geq 0,$$

so $f'' \leq 2(f')^2/f$, and $-1/f$ is concave. Since f is negative, this is a stronger concavity property than $f'' < 0$.

$$-\frac{1}{f(m/M)} \leq -\frac{1}{f(0)} + \frac{f'(0)}{f(0)^2}\frac{m}{M},$$

so

$$f\left(\frac{m}{M}\right) \leq \frac{f(0)}{1 - (f'(0)/f(0))(m/M)}. \tag{4.6.5}$$

We use the inequality $|\sum_{i=1}^{N} \mathbf{p}_i|^2 \leq N \sum_{i=1}^{N} |\mathbf{p}_i|^2$ to bound $f'(0)$: If the expectation value of H is calculated in the ground state for $m/M = 0$, then $\langle \sum_i |\mathbf{p}_i|^2 \rangle = 2m\, E(m/M = 0) = 2m|f(0)|$. As a consequence,

$$f(0) \leq f\left(\frac{m}{M}\right) \leq f(0)\left(1 - N\frac{m}{M}\right), \tag{4.6.6}$$

from which it follows that $0 \leq f'(0) \leq N\,|f(0)|$. With the aid of (4.6.5), Inequality (4.6.6) is refined to

$$f(0) \leq f\left(\frac{m}{M}\right) \leq \frac{f(0)}{1 + Nm/M}. \tag{4.6.7}$$

Remarks (4.6.8)

1. If $N = 1$, this method improves the upper bound $f(0)(1 - m/M)$ to $f(0)/(1 + m/M)$, which is the exact result for the correction due to the reduced mass.
2. If $N = 2$ and $Z = 1$, then the upper bound is good enough to prove the binding of $e^-\mu^+e^-$ but not of $e^-e^+e^-$. In that case $f(0)$ is the energy of H^-, -0.528, and it would be necessary to have

$$\frac{-0.528}{1 + 2(m/M)} < \frac{-0.5}{1 + (m/M)},$$

   i.e., $m/M < 0.06$. It requires highly sophisticated trial functions to show the existence of a bound state of $e^-e^+e^-$.
3. For neutral atoms, $M \geq N$ proton masses, and the correction for nuclear motion is less than 0.1 % of the energy for $M = \infty$. This means that the ratio of the nuclear velocity to the electronic velocities is $O(m/M)$.

We now take up the problem with $\mathcal{N}$ nuclei, the coordinates of which will be written as capital letters. We first write down the

Molecular Hamiltonian (4.6.9)

$$\begin{aligned} H &= \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + \sum_{k=1}^{\mathcal{N}} \frac{|\mathbf{P}_k|^2}{2M_k} - \sum_{i=1}^{N}\sum_{k=1}^{\mathcal{N}} \frac{\alpha Z_k}{|\mathbf{x}_i - \mathbf{X}_k|} \\ &\quad + \alpha \sum_{i<j} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} + \alpha \sum_{k<l} \frac{Z_k Z_l}{|\mathbf{X}_k - \mathbf{X}_l|} \\ &\equiv H_\infty + \sum_{k=1}^{\mathcal{N}} \frac{|\mathbf{P}_k|^2}{2M_k}. \end{aligned}$$

Remarks (4.6.10)

1. There are no new difficulties in verifying self-adjointness and semiboundedness.
2. The general conclusions that were drawn about the Coulomb potential from its behavior under dilatations are still valid.
3. The motion of the center of mass will henceforth be considered as separated off.

The Hamiltonian (4.6.9) describes a fairly intractable many-body problem. In order to be able to frame detailed propositions about it, we shall rely on the extreme ratio of the masses, $m/M_k < 0.001$, to break the motion into that of fast electrons and slow nuclei. The expectation is that the nuclei can be considered static for the motion of the electrons, so we next investigate the accuracy of this description.

The Born–Oppenheimer Approximation (4.6.11)

The first step is to find the energy eigenvalues $E_n(X)$, $X = (\mathbf{X}_1, \ldots, \mathbf{X}_\mathcal{N})$, of H_∞. These become the potentials for the motion of the nuclei, so the next step is to find the eigenvalues E_{nj} of

$$H_k \equiv \sum_{k=1}^{\mathcal{N}} \frac{|\mathbf{P}_k|^2}{2M_k} + E_n(X).$$

The Accuracy of the Born–Oppenheimer Approximation (4.6.12)

Let E_1 be the lowest eigenvalue of H, $\Psi_X(x)$ the ground state of H_∞, and $\Phi(X)$ that of H_k. Then, defining $x = (\mathbf{x}_1, \ldots, \mathbf{x}_N)$,

$$E_{11} \leq E_1 \leq E_{11} + \sum_k \frac{1}{2M_k} \int d^{3N}x \, d^{3\mathcal{N}}X \, |\Phi(X)\nabla_{\mathbf{X}_k}\Psi_X(x)|^2.$$

Proof

The lower bound follows from the operator inequalities

$$H \geq E_1(X) + \sum_{k=1}^{\mathcal{N}} \frac{|\mathbf{P}_k|^2}{2M_k} \geq E_{11}.$$

The upper bound. If $\Psi_X(x)\Phi(X)$ is used as a trial function, then clearly the expectation value of H_∞ is $E_1(X)$ and, on the one hand, H_k produces E_{11}. On

the other hand, since the electron wave-functions depend on the nuclear coordinates, the operator $\sum_{k=1}^{\mathcal{N}} |\mathbf{P}_k|^2/2M_k$ also acts on $\Psi_X(x)$;

$$P_k \Psi_X(x)\Phi(X) = -i\left[\Psi_X(x)\frac{\partial\Phi(X)}{\partial X_k} + \Phi(X)\frac{\partial\Psi_X(x)}{\partial X_k}\right].$$

When squared and combined with $\langle E_1(X)\rangle$ the first term yielded E_{11}, while the second term is the correction in (4.6.12). Because of the normalization of $\Psi_X(x)$ the mixed terms drop out when integrated by $d^{3N}x$:

$$\int d^{3N}x\left(\Psi_X^*(x)\frac{\partial\Psi_X(x)}{\partial \mathbf{X}_k} + \frac{\partial\Psi_X^*(x)}{\partial \mathbf{X}_k}\Psi_X(x)\right) = \frac{\partial}{\partial \mathbf{X}_k}\int d^{3N}x|\Psi_X(x)|^2 = 0. \quad \square$$

Remarks (4.6.13)

1. The only dependence on M_k in the integral is that of Φ. Provided that this quantity remains finite as $M_k \to \infty$, the difference between the bounds is $O(\max_k\{1/M_k\})$.
2. The vibrational energy of the nuclei is on the order of $(E(X)''/M_k)^{1/2} = O(M_k^{-1/2})$. The Born–Oppenheimer approximation is thus accurate enough that it makes sense to calculate this energy.
3. Rotational energy is inversely proportional to the moment of inertia, so for the nuclei it is $O(M_k^{-1})$. This is comparable to the error of the approximation, and it will thus not be possible to make any firm statements about it.

We shall now survey some general properties of $E(X)$.

Lower Bound: The Energy of the United Atom (4.6.14)

Disregarding the nuclear repulsion, $E(X)$ has its infimum when $\mathbf{X}_l = \mathbf{X}_k$ for all i and k.

Proof

$$H_\infty - \alpha\sum_{k>l}\frac{Z_kZ_l}{|\mathbf{X}_k - \mathbf{X}_l|} = \sum_{i=1}^{N}\frac{|\mathbf{p}_i|^2}{2m} - \sum_{i=1}^{N}\sum_{k=1}^{\mathcal{N}}\frac{\alpha Z_k}{|\mathbf{x}_i - \mathbf{X}_k|} + \alpha\sum_{i<j}\frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}$$

$$= \sum_{k=1}^{\mathcal{N}}\frac{Z_k}{Z}\left\{\sum_{i=1}^{N}\left(\frac{|\mathbf{p}_i|^2}{2m} - \frac{Z\alpha}{|\mathbf{x}_i - \mathbf{X}_k|}\right) + \sum_{i>j}\frac{\alpha}{|\mathbf{x}_i - \mathbf{x}_j|}\right\},$$

$$Z = \sum_{k=1}^{\mathcal{N}} Z_k,$$

and the expression in the curly brackets { } is precisely the Hamiltonian of an atom of charge Z. If its lowest eigenvalue is denoted $E(N, Z)$, then

$$E(X) \geq \alpha \sum_{k>l} \frac{Z_k Z_l}{|\mathbf{X}_k - \mathbf{X}_l|} + E(N, Z). \qquad \square$$

Remark (4.6.15)

Proposition (4.6.14) means that the electrons would prefer the nuclei to be all bunched together. To understand how molecules are formed it remains to be determined where this attraction balances the Coulombic repulsion of the nuclei.

The Effects of the Dilatation Group (4.6.16)

Let $\mathbf{X}_i = R\bar{\mathbf{X}}_i$. Consider the coordinates $\bar{\mathbf{X}}_i$ as fixed, so that the molecule preserves its shape as it expands or contracts as R varies. If $H_\infty = T + V$, where $T = \sum_i |\mathbf{p}_i|^2/2m$, then the expectation values with the electronic wavefunction $|\ \rangle$ such that $H_\infty|\ \rangle = E(R)|\ \rangle$ satisfy

$$\langle T \rangle = -E(R) - R\frac{\partial E(R)}{\partial R}$$

$$\langle V \rangle = 2E(R) + R\frac{\partial E(R)}{\partial R}.$$

Proof

The operator H_∞ is put into the form

$$H_\infty = \frac{1}{mR^2}\left(\sum_i |\mathbf{p}_i|^2 + mR\alpha V\right),$$

by a dilatation $\mathbf{x}_i \to R\mathbf{x}_i$, $\mathbf{p}_i \to R^{-1}\mathbf{p}_i$, where V depends on $\mathbf{x}_i$ and $\bar{\mathbf{X}}_i$, but not on R. Hence $E(R)$ is of the form $(1/mR^2)f(\alpha mR)$, where we will not bother to indicate the dependence on $\bar{\mathbf{X}}_i$. By the Feynman–Hellmann Theorem (3.5.19; 2), $\langle V \rangle = \alpha(\partial/\partial\alpha)E$ and $\langle T \rangle = E - \langle V \rangle = m\,\partial E/\partial(1/m)$, which shows (4.6.16). $\square$

Remarks (4.6.17)

1. At the equilibrium position, where $\partial E/\partial R = 0$, the virial theorem for the electrons as usual states that $\langle V \rangle = 2E = -2\langle T \rangle$. If $\partial E/\partial R \neq 0$, then the kinetic energy is less than $|E|$ when $\partial E/\partial R$ is greater than 0, and vice

versa. This agrees with physical intuition, according to which if R is too small the kinetic energy of the electrons is too large.

2. A false argument for the formation of molecules is sometimes advanced, that their greater volume allows some savings in the kinetic energy of the electrons. It is certainly true that $\langle T\rangle < |\langle V\rangle|/2$ as R is decreased from infinity to the region where $\partial E/\partial R > 0$. However, $\langle T\rangle = |E|$ at the equilibrium position, and is thus greater than in an atom if $|E|$ is to be greater than the energy of the isolated atoms.
3. Of course, the virial theorem also holds for H as a whole. If $\langle\!\langle \quad \rangle\!\rangle$ denotes the expectation value in the ground state E_1 of H, and T_k denotes the kinetic energy of the nuclei, then

$$|E_1| = \langle\!\langle T\rangle\!\rangle + \langle\!\langle T_k\rangle\!\rangle < |E_{11}| = \langle T\rangle,$$

so

$$\langle T\rangle - \langle\!\langle T\rangle\!\rangle > \langle\!\langle T_k\rangle\!\rangle.$$

This shows that the expectation value calculated in the Born–Oppenheimer approximation is within $O(M_k^{-1})$ of the exact expectation value.

4. Since V is bounded relative to T, isolated eigenvalues are analytic in α. Therefore f is analytic, so $E(R)$ is analytic in R for $R \neq 0$, provided that the eigenvalues remain isolated.

Upper Bound to $E_1(R)$ (4.6.18)

Let R_0 be the equilibrium position, i.e., $\partial E_1/\partial R|_{R=R_0} = 0$. Then for all $R > 0$,

$$E_1(R) \leq E_1(R_0)\frac{R_0^2}{R^2}\left(1 + 2\frac{R - R_0}{R_0}\right).$$

Proof

In the proof of (4.6.16) it was shown that $E_1 = (1/mR^2)f(\alpha mR)$, where f was some concave function by (3.5.23). Therefore $R^2E_1(R)$ is concave in R, and is always less than its tangent (see Figure 22):

$$R^2E(R) \leq R_1^2E(R_1) + (R - R_1)(2R_1E(R_1) + R_1^2E'(R_1))$$

for all R and R_1. Proposition (4.6.18) follows with $R_1 = R_0$. □

Application to Diatomic Molecules (4.6.19)

If there are two nuclei, R may be identified with $|\mathbf{X}_1 - \mathbf{X}_2|$, and the upper bound for the nuclear motion is

$$H_k \leq \frac{|\mathbf{P}_{cm}|^2}{2M_{cm}} + \frac{|\mathbf{P}|^2}{2M} + E(R_0)\frac{R_0^2}{R^2}\left(1 + 2\frac{R - R_0}{R}\right),$$

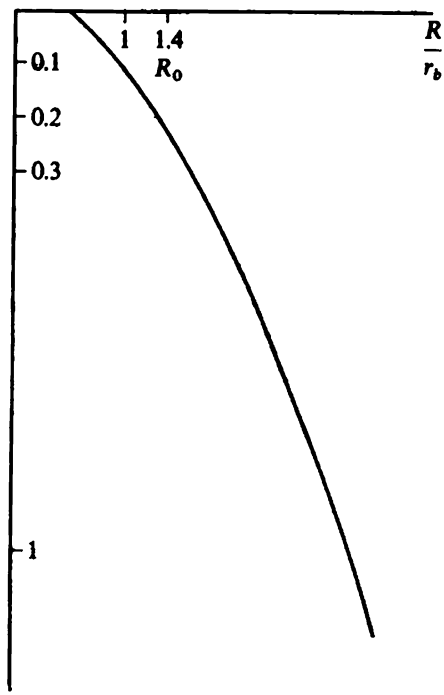


Figure 22 $E \cdot R^2$ in atomic units for H_2.

where $M_{cm} = M_1 + M_2, M = M_1M_2/(M_1 + M_2)$, and **P** is the momentum conjugate to $\mathbf{X}_1 - \mathbf{X}_2$. Since the potential is a superposition of $1/R$ and $1/R^2$ potentials, the Schrödinger equation can be solved analytically (Problem (4.6.29)), producing the general inequality

$$E(R_0) \leq E_{11} \leq \frac{E(R_0)}{(\sqrt{1+x} + \sqrt{x})^2}, \quad \text{where} \quad x = \frac{1}{4R_0^2 M|E(R_0)|}. \tag{4.6.20}$$

Remarks (4.6.21)

1. Since $|E_0(R)| \sim m$ and $R_0 \sim m^{-1}$, we see explicitly that $E_{11} - E(R_0) = O((m/M)^{1/2})$.
2. Inequality (4.6.20) is too general to be numerically accurate in special cases. For instance, for H_2^+ and H_2 it states that the zero-point energies of vibration, $E_{11} - E(R_0)$, are less than 0.24 and, respectively, 0.49 eV, whereas the observed values are roughly 0.14 and 0.26 eV.

As was shown in (4.6.14), $E_1(X)$ is always greater than the sum of the ground-state energy of the united atom and the Coulomb repulsion of the

nuclei. The amount by which the ground state of a diatomic molecule can exceed this lower bound can be estimated by a

Bound to $E_1(X)$ in terms of the Electron Density (4.6.22)

Let $\rho(\mathbf{x})$ be the electron density of the ground state of

$$H_{N,Z} = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} - Z \sum_{i=1}^{N} \frac{1}{r_i} + \sum_{i<j} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}, \qquad Z = Z_1 + Z_2,$$

and let $E(N, Z)$ be the ground-state energy. For a diatomic molecule,

$$E(N, Z) \leq E_1(R) - \frac{Z_1 Z_2}{R} \leq E(N, Z) + Z \int_{r \leq R/2} d^3x\, \rho(\mathbf{x}) \left(\frac{1}{r} - \frac{2}{R}\right),$$

$$R = |\mathbf{X}_1 - \mathbf{X}_2|.$$

Proof

Consider H_∞ as a function $H_{\mathbf{R}}$ of the vector variable $\mathbf{R} = \mathbf{X}_1 - \mathbf{X}_2$ and average over the angle. This affects only the potential

$$-\sum_{i=1}^{N} \left(\frac{Z_1}{|\mathbf{x}_i - \mathbf{R}/2|} + \frac{Z_2}{|\mathbf{x}_i + \mathbf{R}/2|} \right),$$

which is turned into the potential

$$-\sum_{i=1}^{N} \frac{Z}{r_i} + Z \sum_{i=1}^{N} \left(\frac{1}{r_i} - \frac{2}{R}\right) \Theta\left(\frac{R}{2} - r_i\right), \qquad R = |\mathbf{R}|, r_i = |\mathbf{x}_i|,$$

of a spherical shell of radius $R/2$ and charge Z. By the min-max principle, the expectation value of

$$\int \frac{d\Omega}{4\pi} H_{\mathbf{R}} = H_{N,Z} + \frac{Z_1 Z_2}{R} + Z \sum_{i=1}^{N} \left(\frac{1}{r_i} - \frac{2}{R}\right) \Theta\left(\frac{R}{2} - r_i\right)$$

in the ground state of $H_{N,Z}$ is an upper bound to $E_1(R)$. □

Remark (4.6.23)

As $R \to 0$ the bound reduces to

$$E(N, Z) \leq E_1(R) - \frac{Z_1 Z_2}{R} \leq E(N, Z) + \frac{Z\pi}{6} R^2 \rho(0).$$

Thus, after the Coulombic term Z_1Z_2/R is subtracted off, the energy $E(R)$ approaches $E(N, Z)$ with a horizontal tangent as $R \to 0$. This also follows from the fact proved in [19] with a somewhat more difficult argument, that, although $E(R)$ is not analytic at $R = 0$, it is at least C^2 there.

The rough outlines of the general features of the important observables are now known. We shall conclude by working out some of the finer details for especially simple molecules.

The Properties of $E_1(R)$ for H_2^+ (4.6.24)

If $\mathcal{N} = 2, N = 1, Z_1 = Z_2$, and $\mathbf{X}_1 - \mathbf{X}_2 = \mathbf{R}$, then H_∞ of (4.6.9) *is unitarily equivalent to $Z_1^2 mH$, where*

$$H = \frac{|\mathbf{p}|^2}{2} - \frac{\alpha}{|\mathbf{x} - \mathbf{R}/2|} - \frac{\alpha}{|\mathbf{x} + \mathbf{R}/2|} + \frac{\alpha}{R}.$$

If $E_1(R)$ is the lowest eigenfunction of H, then

(i) *$E_1(R) - \alpha/R$ increases monotonically in R; and*
(ii) *$R^2E_1(R) - R\alpha$ is concave and decreasing in R.*

Proof

(ii) This follows from (4.6.16). Since $H - \alpha/R$ decreases as a function of α,

$$\frac{\partial}{\partial R}\left(R^2\left(E_1 - \frac{\alpha}{R}\right)\right) = \frac{\alpha}{R}\frac{\partial}{\partial \alpha} f < 0,$$

where $f = R^2$ times the lowest eigenvalue of $H - \alpha/R$.

(i) This is less trivial, and requires a variant of (4.3.41) for not necessarily positive potentials:

Monotony of the Schrödinger Wave-Function in the Potential (4.6.25)

Let Ω be an open set $\subset \mathbb{R}^n$, and

(i) *$f, g \in C^0(\bar{\Omega}), f, g > 0$,*
(ii) *$f(\mathbf{x}), g(\mathbf{x}) \to 0$ as $|\mathbf{x}| \to \infty$,*
(iii) *$f(\mathbf{x}) \geq g(\mathbf{x})$ for all $\mathbf{x} \in \partial\Omega$,*
(iv) *$\Delta f, \Delta g \in L^1(\Omega)$,*
(v) *suppose that $V(\mathbf{x}) < W(\mathbf{x})$ for all $\mathbf{x} \in \Omega$ and that, in the sense of distributions, $-\Delta f + Vf \geq 0$ and $-\Delta g + Wg \leq 0$.*

Then $f(\mathbf{x}) \geq g(\mathbf{x})$ for all $\mathbf{x} \in \bar{\Omega}$.

Proof

To avoid some complications the proof will be sketched for sufficiently nice g, f, and Ω. Let $D = \{\mathbf{x} \in \Omega: g(\mathbf{x}) > f(\mathbf{x})\}$ as in the proof of (4.3.41). Assumptions (i), (ii), and (iii) imply that $g = f$ on ∂D. Because of (i) and (iv), with Green's theorem,

$$0 < \int_D (W - V) f g \, d^3x \leq \int_D (f \Delta g - g \Delta f) d^3x = \int_{\partial D} dS \, f \frac{\partial}{\partial n} (g - f),$$

where $\partial/\partial n$ is the derivative in the direction of the outward normal to ∂D. Since $g_{|\partial D} = f_{|\partial D}$ and $g > f$ on D, the difference $g - f$ can not increase in the outward direction, so we conclude that $D = \varnothing$. □

The proof of (4.6.24) can now be completed. The operator $H - \alpha/R$ is unitarily equivalent to

$$h = -\frac{\Delta}{2} - \frac{\alpha}{r} - \frac{\alpha}{[(x - R)^2 + y^2 + z^2]^{1/2}}.$$

By the Feynman–Hellmann theorem,

$$\begin{aligned} \frac{\partial e_1}{\partial R} &= \alpha \langle \psi | (R - x)[(x - R)^2 + y^2 + z^2]^{-3/2} \psi \rangle \\ &= \alpha \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dy \, dz \int_R^{\infty} dx (x - R)[(x - R)^2 + y^2 + z^2]^{-3/2} \\ &\quad \times [\psi^2(2R - x, y, z) - \psi^2(x, y, z)], \end{aligned}$$

where ψ is the ground-state eigenfunction of h and $e_1 = E_1 - \alpha/R$ is its eigenvalue. But now $\psi(2R - x, y, z) \geq \psi(x, y, z)$ for all $x > R$, since the assumptions of (4.6.25) are satisfied with $\Omega = \{(x, y, z): x > R\}$, $f = \psi(2R - x, y, z)$, and $g = \psi(x, y, z)$: As in (3.5.28), ψ is nonnegative, and it can in fact be proved strictly positive [3]. The functions f and g are equal on $\partial\Omega = \{(x, y, z): x = R\}$, and we take

$$W(x) \equiv -\frac{\alpha}{r} - \frac{\alpha}{[(x - R)^2 + y^2 + z^2]^{1/2}} - E_1(R) + \frac{\alpha}{R},$$

and

$$V \equiv \frac{-\alpha}{[(x - 2R)^2 + y^2 + z^2]^{1/2}} - \frac{\alpha}{[(x - R)^2 + y^2 + z^2]^{1/2}} - E_1(R) + \frac{\alpha}{R}.$$

Clearly, $W > V$ for all $x > R$. Therefore $\partial e_1/\partial R \geq 0$. □□

Remarks (4.6.26)

1. With (4.6.16) it now follows that $\langle V \rangle - 2E_1 \geq -\alpha/R$ for all R.
2. If H is of the form of (4.6.24), then

$$\frac{\partial}{\partial R}\left(E_1 - \frac{\alpha}{R}\right)$$
$$= \frac{\alpha}{4}\langle\psi|\left(\frac{R-2x}{[(x-R/2)^2+y^2+z^2]^{3/2}} + \frac{R+2x}{[(x+R/2)^2+y^2+z^2]^{3/2}}\right)$$
$$\times |\psi\rangle \geq 0$$

   means that the electron prefers to be between the two nuclei.
3. It is certainly not true that all eigenstates are monotonic in the internuclear separation. For example, as $R \to \infty$ the eigenvector with eigenvalue $e_2(R)$ that becomes the $2p$ state when $R = 0$ is asymptotically

$$\exp\left(-\left|x - \frac{R}{2}\right|\right) - \exp\left(-\left|x + \frac{R}{2}\right|\right),$$

   up to normalization. The corresponding eigenvalue is that of the ground state of the hydrogen atom, and thus the same as $e_2(0)$. Since $e_2(R)$ is not constant, it is definitely not monotonic in R.

Bounds for $E_1(R)$ for H_2^+ (4.6.27)

The most convenient methods are the Rayleigh–Ritz variational principle and Temple's inequality (3.5.32; 2). An accuracy of 0.1 % is attainable with the trial functions

$$\psi = \left(1 + \frac{\beta \hat{R}^2 \nu^2}{4}\right)\exp\left(-\frac{\alpha R \mu}{2}\right),$$
$$(\mu, \nu) = \frac{1}{2}\left(\left|\mathbf{x} - \frac{\mathbf{R}}{2}\right| \pm \left|\mathbf{x} + \frac{\mathbf{R}}{2}\right|\right),$$

by adjusting the parameters α and β (see the table and Figure 23).

Remarks (4.6.28)

1. For lack of a better lower bound, the value $-0.5 + 1/R$ was used for the energy $E_2(R)$ of the next higher gerade (even) state.
2. The bounds become inaccurate in the regime of large $\hat{R}$. It can be shown [20] that $E_1(R)$ goes asymptotically as $-9/4R^4$ as $R \to \infty$. The expressions for the gerade and ungerade states are the same to all orders in a formal $1/R$ expansion; however, it is feasible to calculate the gap between them [23].

R	$E_{1LB} \le E_1(R) \le E_{1UB}$ for H_2^+					
	Temple			Rayleigh–Ritz		
	E_{1LB}	α	β	E_{1UB}	α	β
0.2	−1.929	1.91	0.64	−1.929	1.94	0.67
0.4	−1.801	1.80	0.61	−1.801	1.84	0.61
0.6	−1.672	1.71	0.58	−1.671	1.75	0.57
0.8	−1.555	1.62	0.55	−1.554	1.67	0.54
1.0	−1.452	1.55	0.52	−1.451	1.59	0.52
1.2	−1.363	1.49	0.50	−1.362	1.53	0.50
1.4	−1.285	1.44	0.49	−1.284	1.48	0.48
1.6	−1.217	1.40	0.48	−1.216	1.43	0.46
1.8	−1.157	1.36	0.47	−1.156	1.39	0.45
2.0	−1.104	1.32	0.47	−1.102	1.35	0.45

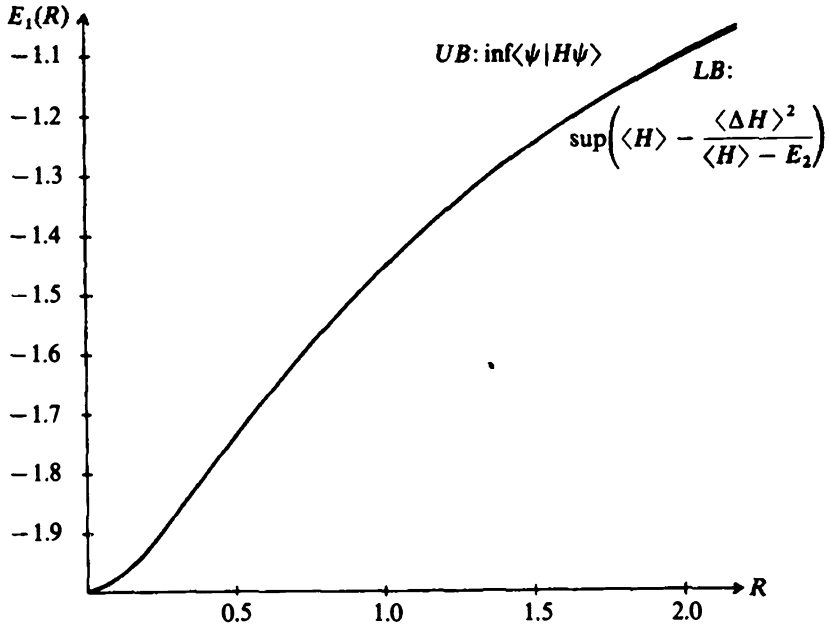


Figure 23 Bounds to $E_1(R)$ for H_2^+.

3. Since the relativistic corrections approach the level of 0.1%, it is not worthwhile to pursue greater accuracy within the framework of the Schrödinger equation.
4. The eigenvalues E_i of H_2^+ can be calculated to arbitrary accuracy as a continued fraction.
5. The increased density of states makes it more difficult to obtain accurate lower bounds when there are more electrons in the molecule. One first needs a rough lower bound for E_2 to get a better one for E_1. It takes a rather more laborious computation to reach the accuracy we have gotten for H_2^+ [21].

Problem (4.6.29)

Study the Schrödinger equation with $H = |\mathbf{p}|^2/2 + \alpha/r^2 - \beta/r$.

Solution (4.6.30)

Replace $\ell(\ell + 1)$ with $\ell(\ell + 1) + 2\alpha$ (cf. (I: 3.4.24; 6)).

Some Difficult Problems

1. Investigate the three-body Coulomb system with charges $+, -, -$, and masses m_1, m_2, 1. For what region of the m_1, m_2-plane does there exist a point spectrum (cf. (4.3.27))? In particular, is there a bound state of $e^+ H$?
2. Two helium atoms attract with a Van der Waals potential, $E_1(R) \sim -1/R^6$ as $R \to \infty$. Find a lower bound to $E_1(R)$ with a flat enough potential minimum to show that two helium atoms do not bind.
3. Find bounds for the imaginary parts of the resonances E of (4.4.13; 1).
4. Bound the scattering cross-section for $e^- - H$ near the resonances (4.4.13; 1).
5. Prove asymptotic completeness for the scattering of $e^- - H$ above the ionization energy.
6. Study the monotonic properties of $E_1(R) - Z_1Z_2/R$ for complicated diatomic molecules.
7. In what sense does the Born-Oppenheimer approximation converge? The operator $H \to H_\infty$ as $M_k \to \infty$, but how does $H_\infty(R)$ converge as $R \to \infty$ and to what?
8. The proof of (4.3.38) provides no numerical values for $c_\pm$ or r_0. Find some.
9. The upper bound (4.3.43) for $\rho(0)$ is the exact value if there is only one particle, while the lower bound is too small by a factor $\frac{3}{16}$. With more electrons the upper bound degrades somewhat and the lower bound gets much worse. Find better lower bounds.

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