THE MECHANICS

OF THE ATOM

C. W. P. Palmer

Contents

Chapter 1

General Principles: I

1.1 What sort of theory is Classical Mechanics?

In this chapter we shall take a first look at some of the ideas and methods of quantum mechanics. Because quantum mechanics differs profoundly from classical mechanics it is valuable to start by taking a brief look at classical physics from a very general viewpoint, in order to delineate its main characteristics. By classical physics we include not only mechanics but also Newtonian gravitation, classical electromagnetism and special relativity.

Classical mechanics is fundamentally a theory of the motion of particles. In the *Opticks* Newton says:

> It seems probable to me that in the beginning God formed matter in solid, massy, hard, impenetrable moveable particles ... incomparably harder than any porous body compounded of them; even so very hard, as never to wear or break in pieces.

Similarly in the *Principia* he writes 'We conclude the least particles of all bodies to be also all extended, and hard, and impenetrable, and movable, and endowed with their proper inertia.' The accelerations of these particles are due to forces, which are conceived as either acting directly on contact, or are ascribed to *fields.* Classical physics recognizes two fields: Newton introduced the gravitational field, and Maxwell gave mathematical form to the electromagnetic field. The fields in turn arise from the positions and masses of the particles in the case of gravity, or their positions, motions and charges in the case of electromagnetism.

Two formulations of the laws of motion may be distinguished: the Newtonian and the Hamiltonian. The Newtonian form of the equation of motion for particle i with mass m_i at position $\mathbf{r}_i$ is the well-known

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i \tag{1.1}$$

where $\mathbf{F}_i$ is the total force on the particle. The fundamental concepts in this formulation are thus the concepts of particle, position, time, mass and force.

The conservation of momentum was known to Newton, but the full development of the principle of energy conservation did not occur until the nineteenth century. In Hamilton's formulation the momentum and energy play a more central rôle, while force plays a much less important part. This formulation applies mainly to systems for which the forces which can be derived from a potential function, which of course includes both the classical fields. A function of position and momentum is defined, the Hamiltonian $H(\mathbf{r}, \mathbf{p})$, from which the equations of motion can be derived:

$$\frac{d\mathbf{r}}{dt} = \nabla_p H \qquad \frac{d\mathbf{p}}{dt} = -\nabla H, \tag{1.2}$$

where ∇_p denotes the derivatives of H with respect to the three components of $\mathbf{p}$, just as ∇ denotes the derivatives with respect to the three components of $\mathbf{r}$. Normally the Hamiltonian is just the energy function; thus for a single particle subject to an external field with potential energy $V(\mathbf{r})$ the Hamiltonian is given by :

$$H(\mathbf{r}, \mathbf{p}) = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \tag{1.3}$$

where the first term is the kinetic energy and the second term is the potential energy. Substitution into the equations of motion gives

$$\frac{d\mathbf{r}}{dt} = \frac{\mathbf{p}}{m} \qquad \frac{d\mathbf{p}}{dt} = -\nabla V \tag{1.4}$$

which is obviously equivalent to the Newtonian form provided that the force $\mathbf{F}$ can be written as $-\nabla V$. The fundamental concepts in this formulation clearly include momentum and energy, while force becomes a quantity derived from the more fundamental ones.

We can identify three important characteristics of this theory common to both formulations. Firstly, the state of the system is conceived as the totality of sharply defined positions and momenta of all its constituent particles. Secondly, the theory is deterministic: the current state of the system determines its future behaviour. (It is now known that many classical systems are chaotic, for which determinism implies only limited predictability.) Finally, it is also time-symmetric, so that the current state also allows us to infer past states equally as well as future ones.

There is also a continuum form of classical physics, fluid mechanics, in which the matter is represented not as particles but as a continuum, but here again the same properties emerge, that in principle, given complete knowledge of the initial state in terms of the the motion of all the fluid elements, future or past states can be predicted.

There is a classical theory into which probabilities enter. Statistical mechanics deals with certain properties of very large assemblies of particles, such as a gas containing many molecules. For example we could consider the probability of finding a given number of gas molecules in a given volume with a velocities in a given range. However, these probabilities are thought of as expressing ignorance of the true situation (these are termed *epistemic probabilities* — see the discussion of epistemology below). One distinguishes between the micro-state (positions and momenta of all particles) and the macro-state (the macroscopic variables defining the system, such as volume and internal energy); the probability enters as the fraction of all micro-states consistent with the macro-state in which the given condition occurs. The idea of a sharply-defined 'true' or 'actual' state is still present.

To some degree the physical characteristics of determinism and time-symmetry are shared by quantum mechanics, but the state of the system is no longer defined as the positions and momenta of all the particles. To clarify the divergence between classical and quantum physics we have to look at some of the metaphysical elements in the two theories. The Greek prefix 'meta' is often translated 'beyond', but in this context it perhaps denotes 'before': we need to examine the often implicit assumptions about the world that underlie the theories.

The fundamental concepts of classical mechanics include Newtonian particles, with positions at a given time, and possessing inertia. Time and, at least in non-relativistic quantum mechanics, mass play much the same rôles in classical and quantum theory, but the concept of a particle occupying a position in space undergoes a profound change. Indeed it is debatable whether quantum mechanics is a theory of particles at all.

Another area to be contrasted is the degree of physical existence, or the *ontological status,* of the elements of the two theories. Many different philosophical positions are possible, which we can approximate by a realist/anti-realist spectrum. Physicists of the 'classical centuries' were generally realists, in that they assumed that their theories described what was actually happening — real particles moving from one position to another. The ontological statuses of the fields are not so easily decided, but the conservation laws of energy and momentum tend to result in the conserved quantities being thought of as real, which entails that the potentials as well as the force fields have some physical reality, even though they are not uniquely defined — for example the potential energy has an arbitrary zero. The situation in quantum mechanics is far more complex: the ontological status of the central element of the theory, the wavefunction, has always been controversial, but one dominant viewpoint is that it has no reality, and is just a mathematical device. This calls into question the ontological status of all other elements of the theory.

A third area of contrast is in *epistemology,* or the theory of how we obtain knowledge. Broadly speaking classical physics assumes that we have direct access to knowledge of the positions of particles (or at least of compound particles large enough to be 'viewed' in some sense). Another way of putting this is that the variables that enter the theory (positions, momenta) are the same as the ones of which we have knowledge. There is also no evident limitation to the accuracy of this knowledge within classical theory, although in a given case our knowledge may only be approximate. The ontological framework already mentioned leads us to the assumption that even in the case of incomplete knowledge, the position and momentum are still really existing quantities with definite values, and that it is only our ignorance that leads us to be uncertain. We shall find in quantum mechanics that the variable that enters the theory (the wavefunction) is rather distantly related to observations, and we shall need a complete quantum theory of measurement which has no classical counterpart. We shall also find that there are significant constraints on what knowledge we can obtain, and even on what facts can be said to exist even though we have no knowledge of them.

1.2 Schroedinger's Equation

Quantum theory began in 1900 with Planck's study of the theory of the black-body spectrum, which he was able to explain only by assuming that radiation was emitted and absorbed by matter in quanta proportional to the frequency:

$$E = h\nu. \tag{1.5}$$

In this equation E is the quantum energy, ν is the frequency of the radiation and h is Planck's constant. Modern usage tends towards the use of the angular frequency $\omega = 2\pi\nu$, so we shall more often use the reduced Planck's constant $\hbar = h/2\pi$ and write (1.5) as

$$E = \hbar\omega. \tag{1.6}$$

It is interesting to look at this equation from a relativistic perspective: E is the time-like component of a four-vector $(E, c\mathbf{p})$ where $\mathbf{p}$ is the momentum and c the speed of light. (This simply means that the Lorentz transformation relates E and $c\mathbf{p}$ in different reference frames in exactly the same way as ct and $\mathbf{r}$.) Similarly ω is the time-like component of the four-vector $(\omega, c\mathbf{k})$ where $\mathbf{k}$ is the wave-vector; this is the case for any wave, not just waves travelling at the speed of light. Equation (1.6) is thus a relation between the time-like components of two four-vectors; for it to be valid in all reference frames we must also assume that the space-like components are similarly related:

$$\mathbf{p} = \hbar\mathbf{k}. \tag{1.7}$$

Initially these relations were applied only to the quanta of the radiation field, which are now termed photons, while the theory of atomic spectra developed independently, from Bohr's 1913 theory of the hydrogen atom, which is now referred to as semi-classical, or old quantum theory. The main theoretical problem was to predict the energy states of atoms as observed by spectroscopy, and the method which was developed was to find a principle for selecting those classical motions of the system that were allowed to occur. This was the Wilson-Sommerfeld quantisation rule, which generalised the rule used by Bohr for hydrogen. For a one-dimensional system this rule is

$$J = \oint p\,dx = nh. \tag{1.8}$$

Here J is defined by the integral, and is called the action; the integral is taken around one period of the motion, for example from the minimum value of the x co-ordinate to the maximum and back again, and the integrand is the value of the momentum p at the corresponding place in the motion. Classically the action integral can take any value, but the quantisation rule restricts it to multiples of Planck's constant, which is therefore sometimes referred to as the quantum of action. (The account of Hamiltonian mechanics given in section 1.1 is necessarily simplified, so that the importance of the action cannot be appreciated, and we cannot discuss its generalisation to systems with more degrees of freedom; suffice it to say that this rule is in fact a natural generalisation of Bohr's quantisation rule that in a circular orbit the angular momentum is given by $2\pi l = nh$.)

These two developments, the photon theory of radiation and semi-classical atomic theory, were united by a remarkable suggestion by de Broglie, of a general wave-particle duality. Again the argument depends on relativistic considerations. (It is remarkable how important these are in the origin of quantum mechanics, even the non-relativistic quantum mechanics which we shall discuss.) The first part of this hypothesis was the suggestion that the Planck relation $E = h\nu$ applied equally to particles: E would be the relativistic energy including the rest mass energy, and ν was the frequency of some unspecified phenomenon associated with the particle. In the rest frame of a free particle E is given by mc^2, and in a frame where the particle has velocity v it is given by γmc^2 where γ is the usual relativistic factor $1/\sqrt{1 - v^2/c^2}$. The relativistic consideration is that in order for the frequency ν to transform in the same way as E, the periodic process has to be a spatially extended *wave* and not simply defined at the point-like particle. The argument is not difficult, and is given in Box 1.1

This leads to the idea of a wave associated with the particle whose frequency and wave-vector satisfy the relations which are now postulated to be universal, $E = \hbar\omega$ and $\mathbf{p} = \hbar\mathbf{k}$. This idea has some obviously satisfactory features: if by superposing waves of this sort with a range of wave-vectors around $\mathbf{k}$ we make a pulse of small spatial extent, or wave-packet, then the wave packet will travel with the group velocity $\mathbf{v}_g = \frac{\partial\omega}{\partial\mathbf{k}}$ which the universal relations give as $\frac{\partial E}{\partial\mathbf{p}}$. For a free particle this is equal to the particle velocity:

$$E = \sqrt{m^2c^4 + \mathbf{p}^2c^2} \qquad \rightarrow \qquad \frac{\partial E}{\partial\mathbf{p}} = \frac{c^2\mathbf{p}}{E} = \frac{c^2\gamma m\mathbf{v}}{\gamma mc^2} = \mathbf{v}.$$

Hence a wave-packet associated with a free particle will travel at the same velocity, and thus remain associated with it. More significantly, the equation $\mathbf{v}_g = \frac{\partial E}{\partial\mathbf{p}}$ is strikingly similar to the Hamilton's equation $\frac{d\mathbf{x}}{dt} = \frac{\partial H}{\partial\mathbf{p}}$, since H is usually the energy function, which suggests that the scheme could apply quite generally. Indeed, it works equally well if we use a non-relativistic relationship between mass and energy (see problem 1.1), essentially because Hamilton's equations apply equally to both viewpoints. (This is actually very puzzling, since it means that the wave associated with a non-relativistic particle could have two very different phase velocities, depending on whether we use relativistic or non-relativistic kinematics. This is the first hint that the phase of these waves is going to be both ill-defined and to some degree non-physical.) Finally, the wave-particle duality may provide an understanding of the quantisation rule (1.8): if we divide both sides of the equation by $\hbar$, and remember that $h/\hbar = 2\pi$ and $p/\hbar = k$, we obtain

$$\oint k\,dx = 2n\pi.$$

However $k\,dx$ is an element of wave phase, so the equation states that the round trip phase is a multiple of 2π; obviously the wave-particle duality may be able to interpret this in terms of a standing wave pattern.

From here it is a short step to Schrodinger's equation. Accepting de Broglie's hypothesis, Schrodinger set out to find the wave equation for de Broglie's waves. He first tried to use relativistic relations between energy and momentum, but failed and reverted to non-relativistic relations. (Or at least he thought he had failed: the relativistic wave equation he came up with is now known as the Klein-Gordon equation.) The problem is thus to find a wave equation which predicts waves

A periodic process associated with a particle is essentially a clock which ticks once per period. We can transform the clock ticks from the reference frame $\mathcal{S}'$ in which the particle is at rest at the origin ($x' = 0$) to the frame $\mathcal{S}$ in which $\mathcal{S}'$ moves with velocity v along the x axis. The n'th clock tick occurs at a time $t' = n/\nu_0$ where ν_0 is the rest-frame frequency, which according to the de Broglie hypothesis is mc^2/h. The transformation to the frame $\mathcal{S}$ is given by

$$t = \gamma(t' + vx'/c^2)$$

which, with $x' = 0$, gives $t = \gamma t' = n(\gamma/\nu_0)$. Thus the clock frequency in $\mathcal{S}$ is $\nu = \nu_0/\gamma$, *smaller* than the freqency in $\mathcal{S}'$, whereas the energy in $\mathcal{S}$ is *greater,* γmc^2. An equivalent approach would be to define the phase of the periodic process to be $\omega_0 t'$ in $\mathcal{S}'$. Phase is Lorentz-invariant; thus the phase in $\mathcal{S}$ is also $\omega_0 t' = (\omega_0/\gamma)t$, using the same time transformation. This implies that the angular frequency in $\mathcal{S}$ is *smaller* than in $\mathcal{S}'$ by a factor γ. Thus for this periodic process the equation $E = h\nu = \hbar\omega$ is not covariant.

If on the other hand we postulate a spatially extended periodic wave in $\mathcal{S}'$, with a spatially-uniform phase (in other words a non-travelling wave, with zero wave-vector), then the frequency transforms differently. Suppose the phase in $\mathcal{S}'$ is $\omega_0 t'$, independent of x'. Then using the equivalent reverse transformation

$$t' = \gamma(t - vx/c^2)$$

we find the phase in $\mathcal{S}$ is $\omega_0\gamma(t - vx/c^2) = (\gamma\omega_0)t - (\gamma\omega_0 v/c^2)x$. This is the phase of a *travelling* wave with angular frequency $\omega = \gamma\omega_0$ and wave-vector $(\gamma\omega_0 v/c^2)\hat{\mathbf{x}}$. This is the same transformation as for the energy and momentum: in the rest frame $\mathcal{S}'$ the energy is $E_0 = mc^2$ and the momentum is zero, while in $\mathcal{S}$, where the particle is moving with speed $v\hat{\mathbf{x}}$, the energy is γE_0 and the momentum is $\mathbf{p} = \gamma mv\hat{\mathbf{x}} = (\gamma E_0 v/c^2)\hat{\mathbf{x}}$.

The reason for the difference in transformation of what appears to be the same quantity, frequency, can be traced to the different definition of the two frequencies. The first is associated with a point, and if that point is moving we define the frequency following the motion. The second is defined over a spatially-extended region, and we define the frequency in each frame at a fixed point in that frame; the relativity of simultaneity then introduces an extra time-variation which changes the frequency transformation.

Box 1.1 Lorentz Transformation of Clocks and Waves with $E = \hbar\omega$ and $\mathbf{p} = \hbar\mathbf{k}$ when E and $\mathbf{p}$ are related by

$$E = H(\mathbf{r}, \mathbf{p}) \tag{1.9}$$

where H is the (non-relativistic) Hamiltonian. Suppose H is independent of $\mathbf{r}$ in some region: then classically the momentum of particles in this region is constant, and so is their energy. In this region the wave can therefore be written as

$$\psi(\mathbf{r}, t) = A \exp i(\mathbf{k} \cdot \mathbf{r} - \omega t) \tag{1.10}$$

where $\mathbf{k}$ and ω are constants, independent of $\mathbf{r}$ and t. This represents a plane wave in the direction $\mathbf{k}$. Partial differentiation with respect to t brings out a factor of $-i\omega$:

$$\frac{\partial\psi}{\partial t} = -i\omega\psi$$

and partial differentiation with respect to any one of the components of $\mathbf{r}$ brings out a factor of i and the corresponding component of $\mathbf{k}$

$$\nabla\psi = i\mathbf{k}\psi.$$

Multiple differentiations with respect to $\mathbf{r}$ will obviously produce multiple factors of $i\mathbf{k}$. Using the universal relations we see that for this plane wave we can define operators (denoted by a caret) which bring out factors of E and $\mathbf{p}$:

$$\hat{E} = i\hbar\frac{\partial}{\partial t} \qquad \hat{\mathbf{p}} = -i\hbar\nabla. \tag{1.11}$$

(Note that in (1.10) the choice of sign for the phase was arbitrary: we could equally well have chosen the exponent to be $i(\omega t - \mathbf{k} \cdot \mathbf{x})$, as this still represents a wave in the direction $\mathbf{k}$. This arbitrary choice has produced the signs in (1.11): the signs have to be opposite, one plus and one minus, but could have been chosen the other way round. However this choice is the conventional one.)

To enforce the correct relationship (1.9) between E and $\mathbf{p}$ in this plane wave region we simply require

$$\hat{E}\psi = \hat{H}(\mathbf{r}, \hat{\mathbf{p}})\psi \tag{1.12}$$

where we have created a Hamiltonian operator $\hat{H}$ by substituting the momentum operator $\hat{\mathbf{p}}$ for the momentum in the classical Hamiltonian $H(\mathbf{r}, \mathbf{p})$. This is a partial differential equation which ψ must satisfy in order that its ω and $\mathbf{k}$ have the correct E, $\mathbf{p}$ relationship.

This was derived for a plane wave region; we now assume that it is generally valid even when H varies with $\mathbf{r}$. Equation (1.12) is then a statement of Schrodinger's Equation, also known as

Schrodinger's time-dependent equation. To take a specific example, we consider a single particle subject to a potential $V(\mathbf{r})$, for which the Hamiltonian was given above, in (1.3):

$$H(\mathbf{r},\mathbf{p}) = \frac{p^2}{2m} + V(\mathbf{r}).$$

Replacing $\mathbf{p}$ with the operator $\hat{\mathbf{p}} = -i\hbar\nabla$ as in (1.12) and inserting the explicit form of the $\hat{E}$ operator, we obtain

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r})\psi \tag{1.13}$$

which is the general form for Schrodinger's equation for a single particle subject to a potential V.

One very important feature of Schrodinger's equation is its *linearity.* This has the mathematical consequence that if ψ_1 and ψ_2 are both valid solutions, so is $c_1\psi_1 + c_2\psi_2$ for any complex constants c_1 and c_2. The physical significance of this is that it permits the typical wave phenomena of diffraction and interference. For example if ψ_1 represents the wave associated with particles from one slit of a double slit arrangement, and ψ_2 the wave from the other, then the superposition of both is the valid solution when both slits are open. Right from the outset, therefore, wave-particle duality envisages new physics.

However it is worth emphasizing that what we have at this point is theoretical speculation of a rather ill-defined nature. There are many important questions which are not yet answered. What is the wave and how are we to interpret ψ? What is the nature of the 'association' — is the particle to be replaced by the wave, or do both exist? How does the suggestion that we can replace the Wilson-Sommerfeld quantisation rule work out in practice? Some of these questions we will be able to address in subsequent sections; others are surprisingly difficult.

The first question, relating to the interpretation of ψ, we can to some extent address immediately. The analogy with radiation is very helpful here. The classical radiation fields ($\mathbf{E}$ and $\mathbf{B}$) satisfy linear equations and exhibit interference and diffraction phenomena, whereas the energy density is quadratic in the fields: $u = \frac{1}{2}(\epsilon_0\mathbf{E}^2 + \mathbf{B}^2/\mu_0)$. The photons are quanta of energy and therefore the photon density is related to the squares of the fields. If we assume the same sort of relationship between particle and wavefunction we would surmise that the square modulus of ψ is related to the density of particles, since this is also a sum of squares:

$$|\psi|^2 = \psi\psi^\star = (\Re e\,\psi)^2 + (\Im m\,\psi)^2.$$

In the case of what we are used to thinking of as particles rather than fields (wave-particle duality enforces some such circumlocution upon us!) we need to be able to discuss the motion of a *single* particle. In this case we have to interpret $|\psi(\mathbf{r},t)|^2$ in terms of the *probability* of finding the particle at $\mathbf{r}$ at time t. However, because $\mathbf{r}$ is a continuous rather than a discrete variable we have to use a probability density. The suggestion is thus that $|\psi(\mathbf{r},t)|^2$ is equal to the probability density for finding the particle at $\mathbf{r}$ at time t.

This suggestion raises at least two separate problems. The first and easier problem is what to call ψ if $|\psi|^2$ is a probability (in this case a probability density). This is a new, non-classical, concept which requires a new name. The analogy with radiation, where the fields define the wave amplitude, suggested the term *probability amplitude* for a complex number whose square modulus is a probability or a probability density. The wavefunction $\psi(\mathbf{r})$ is thus the probability amplitude for finding the particle at $\mathbf{r}$ at time t; in this case its square modulus is a probability density, but we shall also meet probability amplitudes whose square modulus is a probability. The more difficult question is: what sort of probability is this? Is it a classical probability expressing ignorance of the actual situation, or does it represent a fundamental indeterminacy? Ultimately it will appear that the answer is closer to the second alternative, but here we approach one of the most difficult issues in quantum mechanics, which we must postpone until after our discussion of quantum theory is more complete.

1.3 Solution of Schrodinger's Equation

Schrodinger's equation is a partial differential equation in some number of space dimensions and time. A very useful approach to solving equations of this sort is separation of variables, and this is applicable to Schrodinger's equation in the very important case that the Hamiltonian $H(\mathbf{r},\mathbf{p})$ does not depend explicitly on the time. (In fact we have not so far indicated the possibility of H depending explicitly on t, but there exist classical and quantum-mechanical problems for which an explicit time argument is appropriate also.) In the case that H does *not* depend on t, the form of the equation

$$\hat{H}\psi(\mathbf{r},t) = i\hbar\frac{\partial\psi}{\partial t} \tag{1.14}$$

suggests the use of the separation of variables, since the operations involving space and time are already separated on the two sides of the equation. The method involves the use of a separated product solution:

$$\psi(\mathbf{r},t) = u(\mathbf{r})T(t).$$

If we substitute this into (1.14) and divide by ψ we obtain

$$\frac{\hat{H}u(\mathbf{r})}{u(\mathbf{r})} = \frac{i\hbar}{T(t)}\frac{\partial T}{\partial t}. \tag{1.15}$$

The left-hand side of (1.15) is independent of t, while the right-hand side is independent of $\mathbf{r}$; their equality is only possible if both sides are independent of $\mathbf{r}$ and t, in other words a constant. Because the original equation (1.12) was an energy equation we shall call the separation constant E. We have therefore separated the Schrodinger equation (1.14) into two equations

$$\hat{H}u(\mathbf{r}) = Eu(\mathbf{r}) \tag{1.16}$$

$$i\hbar\frac{\partial T}{\partial t} = ET(t). \tag{1.17}$$

The second of these is very easy to solve:

$$T(t) = C\exp(-iEt/\hbar)$$

with one arbitrary complex constant C. The function we are really interested in is ψ, which is the product uT; the separation into two factors is slightly undefined in the sense that any *constants* such as C can be moved between u and T without changing the definitions of u and T as functions of $\mathbf{r}$ and t respectively. To put it another way, the space function u is also the solution of a linear equation, so that one of the arbitrary constants in its solution will be an overall multiplicative constant D say, and only the product CD enters ψ. Thus without loss of generality we can set $C = 1$ (or any other convenient number, but this choice turns out to be the most convenient as we shall see). The solution to the time equation is therefore $T = e^{-iEt/\hbar}$.

Equation (1.16), $\hat{H}u = Eu$, is known as the *time-independent Schrodinger equation.* This is an equation of a type which we shall see frequently: an *eigenvalue equation,* in which the result of an operator operating on a function is a multiple of the same function. We shall solve this in a very simple case below, and discuss it in more detail in the next chapter. For the moment we simply note that in general this has not one but a set of solutions u_n, each with an eigenvalue E_n. The end result of separation of variables is thus a *set* of separated solutions $\psi_n = u_n(\mathbf{r})e^{-iE_nt/\hbar}$. The linearity of the Schrodinger equation then allows us to superpose these solutions, so that a general solution constructed out of the separated solutions can be written

$$\psi(\mathbf{r}, t) = \sum_n c_n u_n(\mathbf{r})\exp(-iE_nt/\hbar) \tag{1.18}$$

with arbitrary complex constants c_n. It turns out that this is not just a general solution, but *the* general solution: all solutions to (1.14) with time-independent Hamiltonians can be written in this form.

Before solving our first problem we should look briefly at the other conditions that apply to the wavefunction. The first is independent of the Schrodinger equation and derives from our interpretation of ψ. The linearity of the Schrodinger equation implies that if ψ is a solution then $c\psi$ is also a solution, for arbitrary complex constant c. If we write c in modulus/argument form $|c|e^{i\alpha}$ we see that the arbitrariness of c implies two sorts of arbitrariness about ψ: Schrodinger's equation can never determine the *scale* of the solution, which is altered by $|c|$, nor the *phase* of the solution, altered by α. However the first of these is determined by our physical interpretation of ψ: since we are interpreting $|\psi|^2$ as a probability density, we must set the scale such that

$$\int_{\text{all space}} |\psi(\mathbf{r},t)|^2 \, d^3\mathbf{r} = 1. \tag{1.19}$$

This process is called *normalisation*, and a wavefunction satisfying (1.19) is called *normalised to unity,* or simply normalised, since unity is by far the most common value for the normalisation integral. (Although not the only one: for particular purposes it can be useful to normalise wavefunctions or parts of wavefunctions in other ways.) Normalisation thus defines one of the two aspects of c, the modulus. However the phase remains arbitrary, and in general the absolute phase of the wavefunction at a given place has no meaning; however the phase is not without meaning, but its significance lies in its spatial and temporal variation, as we shall see.

The other condition on ψ relates to its continuity, and this derives from the equation itself. If we write Schrodinger's time-independent equation for a one-dimensional problem in the form

$$\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \Big(V(x) - E\Big)\psi$$

then we see that at a point where $V(x)$ is continuous then ψ must be continuous and have continuous first and second derivatives. Even at a point where $V(x)$ has a finite discontinuity ψ is still continuous with a continuous first derivative, and the discontinuity is only in the second derivative. It is only at a point where there is an infinite discontinuity in V that the first derivative becomes discontinuous. (This argument is given in slightly more detail in Box 1.2.) In solving the time-independent Schrodinger equation it quite frequently happens that we find solutions of different forms in two or more regions; these must be made to match on the boundary by equating the values of ψ and its first derivative.

There is a (fairly obvious) theorem which states that if $\frac{d\psi}{dx}$ is defined for a function $\psi(x)$ at x then ψ is continuous at x. The existence of the second derivative at any point thus ensures the continuity of ψ and $\frac{d\psi}{dx}$. At a point where $V(x)$ is continuous Schrodinger's equation therefore implies that the second derivative is also continuous.

A discontinuous potential $V(x)$ is to some extent a mathematical fiction, since it implies an infinite force at the discontinuity. We can think of it as an idealisation of a real situation in which $V(x)$ changes rapidly from V_1 to V_2 as x changes from $a-\delta$ to $a+\delta$, obtained by taking the limit $\delta \to 0$. Integrating the Schrodinger equation across this region we obtain

$$\frac{\hbar^2}{2m}\left(\left.\frac{d\psi}{dx}\right|_{a+\delta} - \left.\frac{d\psi}{dx}\right|_{a-\delta}\right) = \int_{a-\delta}^{a+\delta} (V(x)-E)\psi(x)\,dx.$$

Provided V remains finite the integral on the right-hand side tends to zero as $\delta \to 0$. The equation then states that first differential is continuous at $x = a$. It is only an infinite discontinuity in V that leads to a finite discontinuity in $\frac{d\psi}{dx}$.

Box 1.2 Continuity of the Wavefunction

1.4 The One-dimensional Box

We are now in a position to solve the simplest possible quantum-mechanical problem, a particle of mass m confined in a one-dimensional box of width a. This potential is often referred to as the infinite square well, referring to the appearance of a plot of V against x. The potential is defined by

$$V(x) = \begin{cases} 0 & \text{if } 0 \le x \le a; \\ \infty & \text{if } x < 0 \text{ or } x > a. \end{cases} \tag{1.20}$$

This represents a particle which is free to move in one dimension within the box, with no forces acting on it, but is confined within the region $0 \le x \le a$ by infinitely high potential barriers. The representation of the barriers has been simplified by making them of zero width.

The time-independent Schrodinger equation for this problem is

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} + V(x)u(x) = Eu(x) \tag{1.21}$$

In the region outside the box the only consistent solution is $u = 0$. Within the box we have to solve (1.21) with $V = 0$:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} = Eu(x). \tag{1.22}$$

with boundary conditions deriving from the continuity of u at $x = 0$ and $x = a$ (but not, in this case, continuity of $\frac{du}{dx}$). Thus the boundary conditions are $u(0) = 0$ and $u(a) = 0$. The general solution for $E > 0$ can be written in terms of trigonometric functions:

$$u(x) = A \sin kx + B \cos kx \qquad \text{with} \qquad k^2 = 2mE/\hbar^2. \tag{1.23}$$

For $E = 0$ or $E < 0$ we cannot find solutions that are zero in two places, and therefore we cannot satisfy the boundary conditions (see problem 1.2). Applying the boundary conditions to (1.23) we find

$$u(0) = 0 \quad \rightarrow \quad B = 0 \qquad\qquad u(a) = 0 \quad \rightarrow \quad \sin ka = 0.$$

This implies that $k = n\pi/a$ for integer n; however if $n = 0$ the solution is zero everywhere, and solutions with positive and negative n are related by $u_{-n} = -u_n$. Thus the allowed values of n are $1, 2, 3, \ldots$ If we substitute the allowed values of k into (1.23) we obtain the allowed values for E:

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \qquad n = 1, 2, 3, \ldots \tag{1.24}$$

These values are referred to as the *energy eigenvalues.* The corresponding u-functions, or *energy eigenfunctions* are given by

$$u_n(x) = A \sin \frac{n\pi x}{a} \tag{1.25}$$

where the constant A (or at least its modulus) has to be be determined by normalisation. The label n which distinguishes the eigenvalues and eigenfunctions is referred to as a quantum number.

There are several important points to note about this solution, both general and specific. The general point is the crucial rôle played by the boundary conditions. The one-dimensional time-independent Schrodinger equation (1.21) is a second order differential equation with an undetermined parameter E; it possesses two independent solutions for each value of the parameter, as given in (1.23) for the case $E > 0$. It is the boundary conditions that select the acceptable solutions, and thus determine the eigenvalues.

A further general point concerns notation. We have distinguished here rather carefully between the wavefunction $\psi(x, t)$ and the eigenfunction $u(x)$, which is the spatial part of a separated solution. However it is surprisingly easy to forget this distinction, and to think of $u(x)$ as the wave function, forgetting the time-dependence. The several reasons for this. Firstly $u(x)$ *is* a wavefunction, but only at $t = 0$ when the time part $T = 1$. Secondly, when separating the Schrodinger equation into space and time parts the equation for T is always the same, (1.17), whereas the time-independent Schrodinger equation (1.16) is different for every problem. In solving the time equation in the previous section we have solved it once and for all, whereas we shall have to expend a great deal of effort solving the space equation. Furthermore it is not uncommon to use the same symbol ψ for the eigenfunction and the wavefunction!

A third point relates to normalisation of the solution. If we take a single eigenfunction with quantum number n then the wavefunction ψ_n is given by

$$\psi_n(x,t) = u_n(x)T_n(t) = A\sin\frac{n\pi x}{a}\exp(-iE_nt/\hbar). \tag{1.26}$$

This must be normalised according to (1.19). We compute the square modulus of ψ_n by multiplying by the complex conjugate:

$$|\psi|^2 = \psi\psi^\star = (uu^\star)(TT^\star) = uu^\star$$

where the final step relies on the fact that $TT^\star = \exp(-iEt/\hbar)\exp(+iEt/\hbar) = 1$. This is the point at which the convenience of our choice of unity for the constant in T becomes apparent: it means that the time part is already normalised to unity, and to complete the normalisation we just have to normalise the space part $u(x)$. Thus the normalisation integral reduces to

$$AA^\star\int_0^a \sin^2\left(\frac{n\pi x}{a}\right)dx = 1 \tag{1.27}$$

which implies that the modulus of A is equal to $\sqrt{2/a}$ (see problem 1.3), and its phase is, as expected, undetermined. However it would be perverse to choose a complex A for an otherwise real eigenfunction, so we set $A = \sqrt{2/a}$. The eigenfunctions and probability densities for $n = 1$, 2, 3 and 8 are plotted in Figure 1.1. The general solution to the Schrodinger equation for this problem is thus

$$\psi(x,t) = \sum_{n=1}^{\infty} c_n\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\exp(-iE_nt/\hbar) \tag{1.28}$$

where the complex constants c_n are arbitrary apart from a normalisation constraint which we shall discuss in section 2.6.

The final point to make about this solution is its physical interpretation. We shall look at superposition states like (1.28) in the next chapter, but we can look at a single solution of the form (1.26) in terms of de Broglie waves. If we separate the sine function into two complex exponentials we can write this as

$$\psi_n(x,t) = \frac{i}{\sqrt{2a}}\left(e^{-i(k_nx+\omega_nt)} - e^{i(k_nx-\omega_nt)}\right)$$

where we have re-introduced $k_n = n\pi/a$ and also the angular frequency ω_n defined by $E_n = \hbar\omega_n$. This form makes it clear that the separated solutions ψ_n are standing waves, which we have here separated into two travelling waves. These two terms represent de Broglie waves associated with

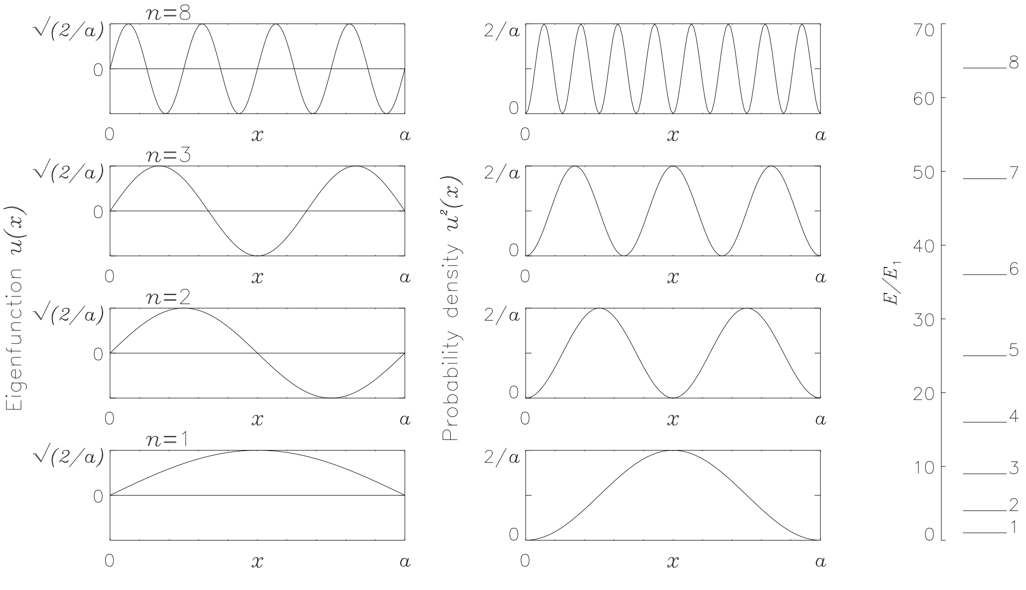


Figure 1.1: *Wavefunctions, Probability densities and Energy levels for the 1-D Box*

a particle with energy E_n, and momentum $-p_n$ and p_n respectively, where the momentum is given by $p_n = \hbar k_n$. Each of these waves has a uniform modulus, corresponding to a probability density $1/2a$, but the waves interfere constructively and destructively to give a standing wave, with zeros of probability density and peaks of $2/a$, four times the single-wave probability density, just as in any two-beam interference experiment. All of this is exactly the kind of behaviour we expected of our wave equation for de Broglie waves. Even the quantisation exactly reproduces the Wilson-Sommerfeld quantisation rule: when the classical particle has energy E the momentum is $p = \pm\sqrt{2mE}$, so the integrand in J in (1.8) is constant and positive as x goes from 0 to a, and then constant and negative as x goes from a to 0. The integral is therefore $J = 2a\sqrt{2mE}$, so that the quantisation rule gives

$$2a\sqrt{2mE} = nh = 2n\pi\hbar \quad \longrightarrow \quad E = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

in agreement with our result.

The probability densities shown in Figure 1.1 are the most detailed information available on the whereabouts of the particle in these states. However for some purposes we are satisfied with less detailed information. Any probability distribution can be crudely characterised by its mean and its width. In probability theory and in quantum mechanics the mean is usually referred to as the *expectation value,* and denoted by angle brackets. The position expectation value in one dimension is thus written $\langle x\rangle$ and is found by integrating x over the probability distribution:

$$\langle x\rangle = \int_{-\infty}^{\infty} xP(x)\,dx = \int_{-\infty}^{\infty} \psi^\star(x)x\psi(x)\,dx. \tag{1.29}$$

The second form for $\langle x\rangle$ looks rather perverse, in that we have split the two wavefunction factors and put the complex conjugate to the left of the x. It turns out that in this form we can generalise the expectation value to many other observables. We can evaluate this integral for the n'th state by inserting ψ_n. When we do this, just as in the case of the normalisation integral, the time factors cancel to leave a time-independent expectation value. Indeed, the whole probability distribution is time-independent, so that these separated solutions to the Schrodinger equation are often referred as *stationary states* because their quantum description contains no time evolution in the probability distribution. The result of the integration (see problem 1.4) is that $\langle x\rangle = a/2$ for all n.

In one sense this result looks reasonable enough. Looking at the wavefunctions in Figure 1.1 we see that they are alternately even and odd about the centre of the box ($\psi(x) = \pm\psi(a-x)$), so that the probability density is even about the centre of the box: $P(x) = P(a-x)$. It is easy to show that this implies the result we have obtained. Note however that the expectation value is the mean of the distribution; this is not to be confused with the most probable value, which is the mode. In the case of $n = 2$ the expectation value is actually the *least* likely place to find the particle, but it is the mean of a bi-modal distribution.

Obviously we can generalise this approach to any function of x:

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} \psi^{\star}(x) f(x) \psi(x)\, dx.$$

A simple example is the expectation value of x^2. This allows us to find a commonly-used measure of the width of the probability distribution Δ_x:

$$\Delta_x^2 = \langle (x - \langle x\rangle)^2\rangle = \langle x^2\rangle - \langle x\rangle^2.$$

The uncertainty Δ_x does vary with n, as shown in problem 1.5.

It is instructive to look at two variants of the problem of the particle in a box, which are both in some sense obviously physically equivalent to the original version, representing simply a shift in origin. The first is a shift in the x origin to the centre of the box, so that the walls of the box are at $x = \pm a/2$. The solution proceeds in exactly the same way down to (1.23), but the boundary conditions are now $u(-a/2) = u(a/2) = 0$. It is a simple exercise to show that there are now two sorts of solutions of the form (1.23) (see problem 1.6): either $A = 0$ and $k_n = n\pi/a$ for $n = 1, 3, 5\ldots$, or $B = 0$ and $k_n = n\pi/a$ for $k = 2, 4, 6\ldots$. The normalisation works in exactly the same way, so that the solutions for the lowest four states are

$$u_1(x) = \sqrt{\frac{2}{a}}\cos\frac{\pi x}{a} \qquad\qquad u_2(x) = \sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}$$

$$u_3(x) = \sqrt{\frac{2}{a}}\cos\frac{3\pi x}{a} \qquad\qquad u_4(x) = \sqrt{\frac{2}{a}}\sin\frac{4\pi x}{a}.$$

Taking both sine and cosine solutions together, the values of k_n and hence the eigenvalues E_n, are the same, as we would expect. The eigenfunctions are *nearly* the same: plots of u_1 and u_4 against x are identical to the previous case apart from the re-labelling of the x-axis, but the plots of u_2 and u_3 are inverted, reminding us of the arbitrary phase in the eigenfunctions. This is a more symmetrical placement for the origin, and the even and odd character of the solutions about the centre of the box is more apparent, because they are obtained separately.

The other kind of origin shift we could consider is a shift in the origin of V. In non-relativistic mechanics the potential energy is only defined as a difference in energy between two states, and some reference state is arbitrarily assigned the value zero. There is usually a natural choice of reference state (zero at infinity, zero at $x = 0$ or whatever) so that we can easily forget that V has this arbitrariness about it. Changing the reference state simply changes $V(x)$ by a constant, the potential energy difference between the old and new reference states. This leads to no change in the classical equations of motion: for example all the forces are the same, because they depend on the gradient of V. Suppose we have solved the time-independent Schrodinger equation for a potential $V(x)$. (The argument works equally well in three dimensions, but we use one for simplicity.) That is, we have a complete set of u_n and E_n satisfying

$$-\frac{\hbar^2}{2m}\frac{d^2u_n}{dx^2} + V(x)u_n(x) = E_n u_n(x). \tag{1.30}$$

We now look for solutions for the new potential $V'(x) = V(x) + V_0$, which satisfy the equation

$$-\frac{\hbar^2}{2m}\frac{d^2u'_n}{dx^2} + V'(x)u'_n(x) = E'_n u'_n(x). \tag{1.31}$$

If we subtract $V_0 u'_n$ from each side of (1.31) we obtain

$$-\frac{\hbar^2}{2m}\frac{d^2u'_n}{dx^2} + V(x)u'_n(x) = (E'_n - V_0)u'_n(x). \tag{1.32}$$

Comparing (1.32) with (1.30) we see that u'_n satisfies the same equation as u_n, but with a different definition of E_n. Thus the eigenfunctions are unchanged: $u_n(x) = u'_n(x)$, while the eigenvalues are simply shifted by V_0: $E'_n = E_n + V_0$. This means that the frequencies of the eigenfunctions are all changed: $\psi'_n(x,t) = \psi_n(x,t)\exp(-iV_0t/\hbar)$. However they are all changed by the same amount, so that when we make a superposition state such as (1.28) we can factor out the change in frequency and write $\psi'(x,t) = \psi(x,t)\exp(-iV_0t/\hbar)$. Again we are confronted by the unphysical nature of the phase of the wavefunction: we are describing the same physical system using two different but physically equivalent potential functions, and the wavefunctions differ not just by a phase but by a time-varying phase. And yet, as we shall see, the phase is telling us something!

We have now completed our initial look at a simple problem, and can take stock of the ground covered in the present chapter. The original concept of wave-particle duality has been clarified in some respects: we now have a wave equation for the wave aspect, Schrodinger's time-dependent equation, and an interpretation of the wavefunction as a probability amplitude for finding the particle. We have learned to solve Schrodinger's equation by separation of variables to give Schrodinger's time-independent equation, the eigenvalues of which give us the energy levels of the system. The corresponding eigenfunctions can then be superposed to give a wide range of solutions, and it has been asserted that this is in fact a general solution. We have not yet looked at the normalisation of the superposition solution, and it raises a puzzle. The probability densities in the stationary states, or energy eigenstates, are time-independent, because the time-dependence of the wavefunction is a pure phase which vanishes on calculating the square modulus. Hence the normalization integral (1.19) does not, in fact, depend on time. If we now superpose these eigenfunctions in the general solution this is no longer true: the probability density is obviously time-dependent, and yet we can only normalise the wavefunction once. We see that we cannot interpret $|\psi|^2$ as a probability density arbitrarily: it has to relate to some property of Schrodinger's equation in order that the normalisation is conserved. We also need to look at the interpretation of the superposition state: what, for example, can we say about the energy of the system?

One fairly obvious constraint on quantum mechanics, if we conceive it as a universally valid replacement for classical mechanics, is that it should reduce to classical mechanics in the appropriate limit. The classical limit of the problem we have discussed in this section is something like a billiard ball bouncing between the cushions of a billiard table (but only moving perpendicular to one set of cushions), with vanishingly small friction. It is not yet apparent how our eigenfunctions, which always fill the box, relate to this limit. This constraint is sometimes referred to as the correspondence principle, but at the moment it is not even clear what corresponds with what, since classical and quantum theories use different variables. Classical mechanics deals directly with position and momentum, whereas quantum mechanics gives us a wavefunction. We have seen how to extract a mean position $\langle x \rangle$ from ψ, but not yet how to obtain other variables like momentum, velocity or energy. These, then, are the issues to be taken up in chapter 2.

1.5 Problems

1.1 Show that, if the energy of a particle is given by the non-relativistic relation $E = p^2/2m + V$, then in a region where V is constant the group velocity of de Broglie waves is equal to the particle velocity. Show further that the phase velocity of these waves is $p/2m = v/2$, whereas in the relativistic case it is $E/p = c^2/v$.

1.2 Show that if $E = 0$, the general solution to (1.22) is $u = A + Bx$, and find the general solution if $E < 0$. Show further that these general solutions can only be zero for at most one value of x.

1.3 Evaluate the normalisation integral (1.27) and show that $AA^\star = 2/a$. (Appendix A contains some hints and methods for tackling typical quantum-mechanical integrals.)

1.4 Evaluate the expectation value $\langle x \rangle$ for ψ_n, using the techniques in Appendix A. Use the fact that $P(x) = P(a - x)$ to obtain the same result without integration. (Hint: use a substitution $x' = x - a/2$.)

1.5 Evaluate the expectation value $\langle x^2 \rangle$ for the state ψ_n and hence show that

$$\Delta_x^2 = a^2 \left(\frac{1}{12} - \frac{1}{2n^2\pi^2} \right)$$

1.6 Apply the boundary conditions for the symmetric box, $u(-a/2) = u(a/2) = 0$, to (1.23) and derive the results given in the text. Compare these eigenfunctions with the original ones and show that the odd n solutions are related by a factor of $\sin(n\pi/2a)$ and the even n solutions by a factor of $\cos(n\pi/2a)$.

Chapter 2

General Principles: II

2.1 Operators

In section 1.2 we introduced operators for momentum and energy:

$$\hat{\mathbf{p}} = -i\hbar\nabla \qquad \hat{E} = i\hbar\frac{\partial}{\partial t}. \tag{2.1}$$

Using these, the Schrodinger equation was introduced as a replacement of the classical equation $E = H(\mathbf{r}, \mathbf{p})$, which gives the energy as a function of position and momentum, by an operator equation operating on the wavefunction ψ:

$$\hat{E}\psi(\mathbf{r}, t) = \hat{H}(\mathbf{r}, \hat{\mathbf{p}})\psi(\mathbf{r}, t). \tag{2.2}$$

The Hamiltonian *operator* $\hat{H}$ is found from the classical Hamiltonan *function* $H(\mathbf{r}, \mathbf{p})$ by replacing the momentum $\mathbf{p}$ by the momentum operator $\hat{\mathbf{p}}$. It was this operator replacement that produced waves with the correct ω, $\mathbf{k}$ relationship to match the classical E, $\mathbf{p}$ relationship.

The operator concept is crucial in quantum mechanics: for every dynamical variable — like position, momentum, energy, angular momentum — there is a corresponding operator, and the operators for energy and momentum are those given in (2.1). The operator for position $\mathbf{r}$ is just $\hat{\mathbf{r}} = \mathbf{r}$; in other words the operation involved is not differentiation but just multiplication. Thus it is equally valid to write the equation for the Hamiltonian operator as

$$\hat{H} = H(\hat{\mathbf{r}}, \hat{\mathbf{p}}),$$

where the operator is given by the classical definition, but replacing *all* variables by operators. This gives a general rule for finding operators: they are related to each other in the same way as the corresponding classical variables. Thus for example the operator for velocity is $\hat{\mathbf{v}} = (1/m)\hat{\mathbf{p}}$.

There are several points to note here. Firstly mass is not a dynamical variable: for any given particle it is simply a constant, in non-relativistic quantum mechanics. (In relativistic quantum mechanics we would use the rest mass, which again is a constant.) Time is not a dynamical variable either: time in non-relativistic quantum mechanics is essentially Newtonian, providing a succession of instants at which the state of the system can be described. Thirdly, the rule about classical relationships between operators can be ambiguous: some classical equations can be translated into operators in several distinct ways depending on the order of factors. We shall discuss ways of handling such cases later (see **??**). Our simple Hamiltonian $H = \mathbf{p}^2/2m + V(\mathbf{r})$ contains no such ambiguity because the momentum and position dependence occur in separate terms. Finally the rule for classical relationships gives no guidance for finding the correct operators for non-classical degrees of freedom, like electron spin.

Having defined operators for all dynamical variables we can now generalise one of the results we obtained for the position variable, the expectation value. We wrote this in a special form (see 1.29) which we here generalise to three dimensions in a fairly obvious way:

$$\langle \mathbf{r}(t) \rangle = \int_{\text{all space}} \psi^\star(\mathbf{r},t)\,\mathbf{r}\,\psi(\mathbf{r},t)\,d^3\mathbf{r}. \tag{2.3}$$

(Like any vector equation, (2.3) is in fact three equations, for the x, y and z expectation values, each of which is found by integrating the corresponding variable over the probability distribution $|\psi(\mathbf{r},t)|^2$.) We noted previously that there was no obvious reason for separating the two wavefunction factors. The reason now becomes apparent: in (2.3) we can view the factor of $\mathbf{r}$ in the middle as the operator $\hat{\mathbf{r}}$, and *in this form* the equation generalises to the expectation value of any variable. Thus we can write the expectation value of A, whose operator is $\hat{A}$, as

$$\langle A(t) \rangle = \int_{\text{all space}} \psi^\star(\mathbf{r},t)\,\hat{A}\psi(\mathbf{r},t)\,d^3\mathbf{r}. \tag{2.4}$$

The operator $\hat{A}$ operates only on the ψ wavefunction factor and not the $\psi^\star$ factor; in the case of $\hat{\mathbf{r}}$ the operation is only multiplication and there is no distinction, but in the case of momentum, for example, $\hat{\mathbf{p}}$ involves differentiation, and the difference is crucial. (For some problems it is useful to express the wavefunction in co-ordinate systems other than Cartesian, for example spherical polar co-ordinates. In this case the volume element $d^3\mathbf{r}$ becomes $r^2 \sin\theta\, dr\, d\theta\, d\phi$, and it is important to remember that $\hat{A}$ operates *only* on ψ and not on the volume element!)

As a simple example of evaluating energy and momentum expectation values we shall find them for the eigenfunctions ψ_n of the one-dimensional box found in chapter 1:

$$\psi_n(x,t) = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a} \exp(-iE_nt/\hbar).$$

The energy expectation value is given by

$$\langle E\rangle = \frac{2}{a}\int_0^a e^{+iE_nt/\hbar} \sin^2\frac{n\pi x}{a}\, i\hbar\frac{\partial}{\partial t}\left(e^{-iE_nt/\hbar}\right) dx. \tag{2.5}$$

The time factors come out of the integral and the exponentials cancel; the integral is then the normalisation integral and gives 1, so that the result is simply E_n, the energy eigenvalue, rather as we might have expected. We note that the form of the eigenfunction u_n played no rôle here, so that this result is valid for any energy eigenfunction $\psi_n = u_n(\mathbf{r})\exp(-iE_nt/\hbar)$.

In the momentum expectation value the time factors cancel directly to leave

$$\langle p\rangle = \frac{2}{a}\int_0^a \left(\sin\frac{n\pi x}{a}\right)\left(\frac{-i\hbar n\pi}{a}\cos\frac{n\pi x}{a}\right) dx. \tag{2.6}$$

The integral can be evaluated in a number of ways: for example using the double angle formula $\sin 2A = 2\sin A\cos A$ we can write the integrand in terms of $\sin 2n\pi x/a$, which is integrated over exactly n wavelengths so that the result is $\langle p\rangle = 0$. This result also generalises to other eigenfunctions $u_n(\mathbf{r})$ as long as they are real functions, which is frequently but by no means always the case. If $u_n^\star = u_n$ then the integrand reduces to

$$-i\hbar u_n(\mathbf{r})\frac{\partial u_n}{\partial x} = \frac{-i\hbar}{2}\frac{\partial u_n^2}{\partial x}$$

which is a perfect differential and when integrated over x gives $u_n^2/2$ to be evaluated at the x limits. The boundary conditions invariably require u_n to vanish at these limits, so the integral is zero. The argument applies equaly to any component of momentum, so in an energy eigenfunction $\langle\mathbf{p}\rangle = 0$ provided u_n is real.

This calculation raises two points. The first is that the rôle played by *real* eigenfunctions in the last paragraph gives us the first hint of the significance of the phase of the wavefunction. We write a general wavefunction, not necessarily one of the separable ones, in modulus/argument form $\psi(\mathbf{r},t) = R(\mathbf{r},t)e^{iS(\mathbf{r},t)}$ where R and S are real functions. The modulus function R is obviously related to the probability density: $P = |\psi|^2 = R^2$. If we now operate on the wavefunction in this form with $\hat{\mathbf{p}}$ we get two terms:

$$\hat{\mathbf{p}}\psi(\mathbf{r},t) = \Big(-i\hbar\nabla R\Big)e^{iS} + Re^{iS}\Big(\hbar\nabla S\Big).$$

Inserting this into the expectation value we get two terms:

$$\langle p\rangle = -i\hbar\int_{\text{all space}} R\nabla R\, d^3\mathbf{r} + \hbar\int_{\text{all space}} \nabla S R^2\, d^3\mathbf{r}. \tag{2.7}$$

Both integrals are obviously real, so the two terms are respectively imaginary and real. The imaginary term is zero, by the same argument as for the separable wavefunction, so that the expectation value of the momentum is related to the gradient of the phase of the wavefunction.

The second point is that the result of the calculation *must* be real, and yet the ingredients of the calculation are all complex: the wavefunction is always complex, and both $\hat{E}$ and $\hat{\mathbf{p}}$ contain factors of i. This has not led to any problems so far, but we have to be sure that it can *never* do so — the sight of a term in $\langle \mathbf{p} \rangle$ equal to $-i$ multiplied by an obviously real integral which happens in this case to be zero is disturbing to say the least!. The operators must have some property which ensures that these results are always real. This forms the topic of the next section.

2.2 Hermitian Operators and their Properties

One of requirements we have imposed on the theory is that there should be a wave aspect to it. This has manifested itself in several ways, for example the oscillatory form of the wavefunction in space and time in a region where $V(\mathbf{r})$ is constant, and also in the linear form of Schrodinger's equation, which allows solutions to be superposed and therefore permits interference phenomena, such as the standing waves we saw for the one-dimensional box in section 1.4. Of these, the latter, linearity, turns out to have important and far-reaching consequences which we shall explore in this section. The results all depend on quite simple algebraic properties of the wavefunctions and operators, and it is therefore useful to consider in the abstract entities with these properties; this is particularly useful because when we introduce the spin of the electron in chapter 9 the wavefunction will look quite different, and so will operators, but these mathematical relations will persist unchanged.

The fundamental property of the wavefunction that permits interference is that if ψ_1 and ψ_2 are two possible wavefunctions for a given system then so is $c_1\psi_1 + c_2\psi_2$ for arbitrary complex numbers c_1 and c_2. It could be objected that the c's are subject to a normalisation constraint, and this is correct. For the straightforward applicability of the mathematical results we need, it is useful to adopt a slightly broader interpretation of the wavefunction, such that ψ and $c\psi$ are *equally* valid wavefunctions, both representing the same physical situation. The probability density is *proportional to* $|\psi|^2$ in both cases, and only equal to $|\psi|^2$ when ψ happens to be normalised. With this interpretation the above statement is true without constraint, and this is the key property of the wavefunction, which in fact defines the set of all wavefunctions for a given system to be a *complex vector space.*

A vector space $\mathbb{V}$ is defined to be a set of elements, called vectors $|\psi\rangle$, including a special vector $|0\rangle$, together with two operations of adding vectors and multiplication by a scalar, which satisfy the following axioms:

- Vector addition is commutative: $|\psi\rangle+|\phi\rangle = |\phi\rangle+|\psi\rangle$, and associative: $(|\psi\rangle+|\phi\rangle)+|\chi\rangle = |\psi\rangle + (|\phi\rangle + |\chi\rangle)$.
- The zero vector has no effect on vector addition: $|\psi\rangle + |0\rangle = |\psi\rangle$, and is the result of 'subtracting' any vector from itself: $|\psi\rangle + (-1)|\psi\rangle = |0\rangle$.
- Scalar multiplication compounds in the expected way: $a(b|\psi\rangle) = (ab)|\psi\rangle)$.
- Scalar multiplication is distributive over scalar or vector addition: $a(|\psi\rangle + |\phi\rangle) = a|\psi\rangle + a|\phi\rangle$, and $(a + b)|\psi\rangle) = a|\psi\rangle + b|\psi\rangle$.

If the numbers a, b are real then $\mathbb{V}$ is a real vector space, and if complex then $\mathbb{V}$ is a complex vector space.

Box 2.1 Definition of a Vector Space

A vector space $\mathbb{V}$ is defined to be a set of elements, called vectors $|\psi\rangle$, including a special vector $|0\rangle$, together with two operations of adding vectors and multiplication by a scalar. The formal axioms are given in box 2.1. It is obvious that these are all true for wavefunctions, if we allow for the possibility of a wavefunction that is zero everywhere, and that in combination these axioms permit exactly the superposition principle that we require.

The use of the word vector here calls for some comment: the axioms constitute a definition of a vector for these mathematical purposes, and the resulting concept is not necessarily related to vectors in the physics sense. However it is apparent that position vectors $\mathbf{r}$ or momentum vectors $\mathbf{p}$ do form a vector space, although in this case a real vector space. The vectors with which we are concerned here are not these vectors but wavefunctions, which are often called *state vectors.*

The other two mathematical concepts we require are the inner product and linear operators. The *inner product on a complex vector space* is a generalization of the scalar product of (physics) vectors, which we shall write as $\langle\psi|\phi\rangle$. The inner product is defined as a complex-valued function of two vectors with three properties: it preserves the linear relations of the vector space, so that if $|\chi\rangle = a|\psi\rangle + b|\phi\rangle$ then $\langle\zeta|\chi\rangle = a\langle\zeta|\psi\rangle + b\langle\zeta|\phi\rangle$; it has *conjugate-symmetry* in the two vectors, that is $\langle\psi|\phi\rangle = (\langle\phi|\psi\rangle)^\star$ where * denotes complex conjugate; and thirdly the inner product of any

The inner product $\langle\psi|\phi\rangle$ is a complex-valued function of two vectors $|\psi\rangle$ and $|\phi\rangle$ with the following properties:

- Conjugate-symmetry: $\langle\psi|\phi\rangle = (\langle\phi|\psi\rangle)^\star$ (note that this implies $\langle\psi|\psi\rangle$ is real);
- Linearity in the second vector: if $|\chi\rangle = a|\psi\rangle + b|\phi\rangle$ then $\langle\zeta|\chi\rangle = a\langle\zeta|\psi\rangle + b\langle\zeta|\phi\rangle$;
- Positive-definiteness: $\langle\psi|\psi\rangle \geq 0$ and $\langle\psi|\psi\rangle = 0$ if and only if $|\psi\rangle = |0\rangle$.

The first two properties imply that $\langle\psi|\phi\rangle$ depends *anti-linearly* on the first vector, that is for the given $|\chi\rangle = a|\psi\rangle + b|\phi\rangle$, $\langle\chi|\zeta\rangle = a^\star\langle\psi|\zeta\rangle + b^\star\langle\phi|\zeta\rangle$. The third property allows us to define the *norm* of a vector $|\psi\rangle$, written $||\psi||$, as the positive square root of the inner product of $|\psi\rangle$ with itself: $||\psi|| = \sqrt{\langle\psi|\psi\rangle}$. Normalization is thus the process of setting the norm to unity. A linear operator $\hat{A}$ acts on a vector $|\psi\rangle$ and transforms it into another $\hat{A}|\psi\rangle$ while preserving linear relations among vectors:

- If $|\chi\rangle = a|\psi\rangle$ then $\hat{A}|\chi\rangle = a\hat{A}|\psi\rangle$;
- If $|\chi\rangle = |\psi\rangle + |\phi\rangle$ then $\hat{A}|\chi\rangle = \hat{A}|\psi\rangle + \hat{A}|\phi\rangle$.

These imply that the scalar multiplication operation is an example of a linear operator, and also if $\hat{A}$ and $\hat{B}$ are linear operators, so are $a\hat{A} + b\hat{B}$, and $\hat{A}\hat{B}$ (meaning first operate with $\hat{B}$, then $\hat{A}$).

Box 2.2 The Inner Product, and Linear Operators

(non-zero) vector with itself is real and positive. The formal axioms of the inner product are given in box 2.2.

Strictly speaking we have not yet defined the inner product, only constrained it by these axioms. It would appear that we have to define it for a general pair of vectors, but in fact this is not so. It is a simple exercise in using these axioms to show that we can express an arbitrary inner product in terms of inner products of vectors with themselves, or *norms* (see problem 2.1). We have already identified the state vectors $|\psi\rangle$ with wavefunctions ψ, and we now identify the inner product $\langle\psi|\psi\rangle$ with the normalisation integral

$$\int_{\text{all space}} \psi^\star\psi \, d^3\mathbf{r}. \tag{2.8}$$

The result of problem 2.1 is then that the general inner product $\langle\phi|\psi\rangle$ is to be identified with the integral

$$\int_{\text{all space}} \phi^\star\psi \, d^3\mathbf{r} \tag{2.9}$$

and it can easily be checked that this satisfies all the requirements of an inner product.

A *linear operator* $\hat{A}$ transforms one state vector $|\psi\rangle$ into another, which for the moment we shall denote $|A\psi\rangle$ to emphasize that it is another state vector, while preserving linear relations between state vectors, so that if $|\chi\rangle = a|\psi\rangle + b|\phi\rangle$ then $|A\chi\rangle = a|A\psi\rangle + b|A\phi\rangle$. (We shall subsequently revert to the more standard notation $\hat{A}|\psi\rangle$ for the result of $\hat{A}$ operating on $|\psi\rangle$; also the use of the caret to denote operators is not universal, and we shall not continue with it when there is no risk of confusion.) It is apparent that the quantum-mechanical operators we have defined, $\hat{\mathbf{r}}$, $\hat{\mathbf{p}}$, $\hat{E}$ and $\hat{H}$ are all linear operators on wavefunctions. (Actually there are some technical issues here to do with the auxiliary conditions we may apply to wavefunctions: for example we may require that ψ is normalizable and twice differentiable; the result of $\hat{x}\psi$ or $\hat{H}\psi$ may exist but not satisfy these auxiliary constraints. We shall not go into detail here, but these issues do crop up in various guises subsequently.)

After this lengthy preamble we have now defined all the mathematical entities we require, and their properties. We first consider a general inner product between the result of $\hat{A}$ acting on $|\psi\rangle$ and another vector $|\phi\rangle$: $\langle\phi|A\psi\rangle$, and enquire whether we could obtain the same result (in other words the same complex number) by operating with a different operator on the state $|\phi\rangle$ and then taking the inner product with $|\psi\rangle$. We call this operator, if it exists, the *adjoint* of $\hat{A}$, which we write $\hat{A}^\dagger$; its defining property is thus

$$\langle A^\dagger\phi|\psi\rangle = \langle\phi|A\psi\rangle. \tag{2.10}$$

Both sides of this equation are linear in $|\psi\rangle$ and anti-linear in $|\phi\rangle$, so it is not impossible that such an operator may exist. It would have been impossible if we had written the left-hand side as $\langle\psi|A\phi\rangle$, because then the linear and anti-linear vectors are back-to-front, but an alternative definition is clearly

$$\langle\phi|A\psi\rangle = \Big(\langle\psi|A^\dagger\phi\rangle\Big)^\star. \tag{2.11}$$

In general such an operator does exist. As an example we consider the operator $\hat{A} = \frac{d}{dx}$ acting on a wavefunction $\psi(x)$. This is obviously a linear operator, and the two definitions of the adjoint are

$$\int_{-\infty}^{\infty} \left(\hat{A}^\dagger\phi\right)^\star \psi\,dx = \int_{-\infty}^{\infty} \phi^\star \frac{d\psi}{dx}\,dx = \left(\int_{-\infty}^{\infty} \psi\hat{A}^\dagger\phi\,dx\right)^\star \tag{2.12}$$

where the left-hand expression implements (2.10) and the right-hand expression (2.11). These two forms are obviously equivalent, as they must be, so we consider just the left-hand one. The central expression can be integrated by parts:

$$\int_{-\infty}^{\infty} \phi^\star \frac{d\psi}{dx}\,dx = \Big[\phi^\star\psi\Big]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \left(\frac{d\phi}{dx}\right)^\star \psi\,dx.$$

The integrated part vanishes at both limits to leave the integral, and comparing this with the left-hand expression of (2.10) we see that $\hat{A}^\dagger = -\frac{d}{dx}$.

Using the properties of linear operators and the defintion of the adjoint we can easily prove some elementary properties of it (see problem 2.2):

- The adjoint of the adjoint is the orginal operator: $\left(\hat{A}^\dagger\right)^\dagger = \hat{A}$;
- The adjoint of a sum is the sum of the adjoints: $(\hat{A} + \hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger$;
- If an operator is multiplied by a complex number, the adjoint is multiplied by the complex conjugate: $(c\hat{A})^\dagger = c^\star \hat{A}^\dagger$;
- The adjoint of a product is the product of the adjoints in the reverse order: $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger$.

Having defined the adjoint of a linear operator, we now consider the possibility that the adjoint is equal to the operator, $\hat{A}^\dagger = \hat{A}$. Such an operator is called *self-adjoint* or *Hermitian.* The defining property of a Hermitian operator can be written in two forms derived from (2.10) and (2.11):

$$\langle\phi|A\psi\rangle = \langle A\phi|\psi\rangle = \Big(\langle\psi|A\phi\rangle\Big)^\star \tag{2.13}$$

where the middle and right-hand expressions are related by the conjugate-symmetry of the inner product. An immediate consequence of this definition is found by taking the vector $|\phi\rangle$ to be the same as $|\psi\rangle$: we find that $\langle\psi|A\psi\rangle$ is equal to its complex conjugate, and so is real. This result is of profound importance, because it clarifies the puzzle referred to at the end of section 2.1 as to how expectation values could be guaranteed real: reverting to wavefunction language we find that

$$\langle A\rangle = \int_{\text{all space}} \psi^\star \hat{A}\psi \, d^3\mathbf{r}$$

is guaranteed to be real provided the operator $\hat{A}$ is Hermitian. In fact the converse is also true: if $\hat{A}$ is not Hermitian then there is some wavefunction ψ for which $\langle A\rangle$ is complex.

It now becomes apparent that we can make the theory produce real answers for expectation values provided all observables have Hermitian operators. For a multiplicative operator, like $\mathbf{r}$ or $V(\mathbf{r})$, this is true provided the multiplying function is real, which in these cases it is. The case of $\mathbf{p}$ is not so obvious, but it follows from the properties of the adjoint already discussed (see problem 2.2). It thus becomes very important to know how we can combine operators in such a way as to form a Hermitian result. The properties of the adjoint listed above imply the following:

- For arbitrary $\hat{A}$ the operator $\hat{A}+\hat{A}^\dagger$ is Hermitan and $\hat{A}-\hat{A}^\dagger$ is *anti-Hermitian,* that is the adjoint is the negative of the operator; another way of expressing this is that $i(\hat{A}-\hat{A}^\dagger)$ is Hermitian;
- For Hermitian $\hat{A}$ and $\hat{B}$, $a\hat{A}+b\hat{B}$ is Hermitian for *real* a and b;
- For Hermitian $\hat{A}$ and $\hat{B}$, $\hat{A}^2$ is Hermitian but $\hat{A}\hat{B}$ is not necessarily so; however $\hat{A}\hat{B}+\hat{B}\hat{A}$ and $i(\hat{A}\hat{B}-\hat{B}\hat{A})$ are Hermitan.

Taken together these imply that our single-particle Hamiltonian $\hat{H}=\mathbf{p}^2/2m+V(\mathbf{r})$ is Hermitian.

Since most of the operators we are going to deal with are Hermitian we can without (much) ambiguity use a notation introduced by Dirac (referred to above and already used in box 2.2) whereby the vector obtained by operating on $|\psi\rangle$ with operator A is denoted $A|\psi\rangle$ and its inner product with $|\phi\rangle$ is denoted $\langle\phi|A|\psi\rangle$ where the operator stands between the two vectors. Dirac referred to this inner product expression as a bracket, and the two vectors as bra and ket vectors (the ket vector being the right-hand or linear, vector, and the bra vector being the left-hand, or anti-linear, vector). If A is Hermitian then we can view this bracket as either the inner product of $|\phi\rangle$ with $A|\psi\rangle$ or $A|\phi\rangle$ with $|\psi\rangle$ — the two are equivalent; in other words we can allow the operator to act either way, forwards or backwards. If A is not Hermitian then these two are not equivalent, and the notation is potentially misleading: the correspondence between Dirac's notation and the one we orignally used is as follows:

$$\langle A^\dagger\phi|\psi\rangle = \langle\phi|A|\psi\rangle = \langle\phi|A\psi\rangle;$$

in other words if A is not Hermitian then when it operates backwards it has to be replaced with its adjoint.

The fact that the Hamiltonian is Hermitian clarifies another puzzle, one of the ones mentioned at the end of chapter 1: how can we guarantee that the wavefunction remains normalised? Suppose we have a wavefunction $\psi(\mathbf{r},t)$ which is normalised at $t=0$:

$$\int_{\text{all space}} \psi^\star(\mathbf{r},0)\psi(\mathbf{r},0)\,d^3\mathbf{r} = 1 \tag{2.14}$$

and whose time development satisfies the Schrodinger equation,

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi. \tag{2.15}$$

Since the time-development is prescribed by (2.15) we cannot force the wavefunction to remain normalised at later times, so the normalisation has to be a conserved property under the time development. To show this we consider the time-derivative of the normalisation integral:

$$\frac{d}{dt}\int_{\text{all space}} \psi^\star\psi\, d^3\mathbf{r} = \int_{\text{all space}} \frac{\partial\psi^\star}{\partial t}\psi + \psi^\star\frac{\partial\psi}{\partial t}\, d^3\mathbf{r}.$$

We can substitute for the time-derivatives from the Schrodinger equation and its complex conjugate

$$-i\hbar\frac{\partial\psi^\star}{\partial t} = \left(\hat{H}\psi\right)^\star$$

to give

$$\frac{d}{dt}\int_{\text{all space}} \psi^\star\psi\, d^3\mathbf{r} = i\hbar\int_{\text{all space}} \left(\left(\hat{H}\psi\right)^\star\psi - \psi^\star\hat{H}\psi\right)\, d^3\mathbf{r}. \tag{2.16}$$

However the integral vanishes because of the Hermitian property of the Hamiltonian, so the normalisation integral is in fact a constant. Thus the requirement that all observables have Hermitian operators solves two of the problems we have so far identified.

This does not exhaust the special properties of Hermitian operators: we can also prove important results concerning their eigenvalues and eigenvectors. These play a rôle in the further development of quantum mechanics, as we shall see in section 2.4. We have already met the concept of eigenvalues and eigenvectors in the context of the Schrodinger time-independent equation, which was introduced as the eigenvalue equation of the Hamiltonian operator H. We can consider however consider the eigenvalue equation of any Hermitian operator A:

$$A|n\rangle = a_n|n\rangle \tag{2.17}$$

where $|n\rangle$ is one of a set of eigenvectors, and has the eigenvalue a_n. We consider two such eigenvectors, $|n\rangle$ and $|m\rangle$, with eigenvectors a_n and a_m, and take the inner product of (2.17) with the other eigenvector $|m\rangle$: $\langle m|A|n\rangle$. We can transform this in two different ways to obtain two different expressions. Firstly we can use the eigenvalue equation directly, replacing $A|n\rangle$ with $a_n|n\rangle$, obtaining

$$\langle m|A|n\rangle = a_n\langle m|n\rangle.$$

Alternatively we can use the Hermitian property of A to obtain $(\langle n|A|m\rangle)^\star$, and then the eigenvalue equation for $|m\rangle$ to obtain $(a_m\langle n|m\rangle)^\star$ and finally the conjugate-symmetry of the inner product to write the complex conjugate as $a_m^\star\langle m|n\rangle$. The second equivalent expression is thus

$$\langle m|A|n\rangle = a_m^\star\langle m|n\rangle,$$

and if we equate these two equivalent forms we obtain

$$(a_n - a_m^\star)\langle m|n\rangle = 0. \tag{2.18}$$

Thus (at least) one of the two factors in (2.18) must be zero. We first consider the case $|m\rangle = |n\rangle$, and hence $a_n = a_m$; the result simplifies to $(a_n - a_n^\star)\langle n|n\rangle = 0$. However the inner product is now the square of a norm, and hence positive-definite, so that $a_n = a_n^\star$; thus *all eigenvalues of Hermitian operators are real.* In making further use of (2.18) we can ignore the complex conjugate, since the eigenvalues are real.

Secondly we consider the case of different eigenvalues $a_n \neq a_m$. In this case the first factor in (2.18) is non-zero by hypothesis, so that the second factor must be zero. By analogy with scalar products of (physics) vectors we call state vectors with vanishing inner product *orthogonal.* We have therefore proved that *any pair of eigenvectors of a Hermitan operator belonging to different eigenvalues is orthogonal.*

These two cases are not exhaustive: there is a third possibility, that $|m\rangle \neq |n\rangle$ but $a_m = a_n$. This is the case where the two state vectors are distinct but share the same eigenvalue. The only eigenvalue equation we have so far solved, the time-independent Schrodinger equation for the one-dimensional box, produced only one eigenfunction for each eigenvalue, but this is a special case, and multiple eigenfunctions for each eigenvalue are not uncommon. Such an eigenvalue and its eigenvectors are referred to as degenerate, and the phenomenon is known as degeneracy. In the case of degenerate eigenvectors (2.18) does not tell us anything: the first factor is zero by hypothesis, so we can conclude nothing about the second factor. We shall study the phenomenon of degeneracy more in **??**; for the moment we simply note that there is normally only a finite (usually small) number of linearly independent eigenvectors belonging to a degenerate eigenvalue, and these can be chosen to be orthogonal. Thus either naturally (because they belong to different eigenvalues) or by choice we can make all eigenvectors orthogonal to all other eigenvectors. If we also normalise them then we can summarise all their inner products by the simple equation

$$\langle m|n\rangle = \delta_{mn} \tag{2.19}$$

where the symbol on the right-hand side is a Kronecker delta, and denotes 1 if $n = m$ and zero if $n \neq m$. Such a set of eigenvectors is referred to as an *orthonormal set.*

We shall make repeated use of all of these important properties of Hermitian operators and their eigenvalues and eigenvectors. We therefore repeat all the essential properties explicitly for wavefunctions instead of the more general state vectors which we have used in this section. The adjoint of an operator A has the defining property

$$\int_{\text{all space}} \phi^\star A\psi \, d^3\mathbf{r} = \int_{\text{all space}} \left(A^\dagger \phi\right)^\star \psi \, d^3\mathbf{r}$$

for *any* pair of valid wavefunctions ϕ and ψ (where valid usually means continuous and square-integrable). If $A^\dagger = A$ then A is Hermitian: the defining property of a Hermitian operator is thus

$$\int_{\text{all space}} \phi^\star\, A\psi\, d^3\mathbf{r} = \int_{\text{all space}} (A\phi)^\star\ \psi\, d^3\mathbf{r}.$$

The eigenvalues of a Hermitian operator are real: if $A\psi_n = a_n\psi_n$ then the eigenvalue a_n is real. Eigenfunctions belonging to distinct eigenvalues are orthogonal: if $A\psi_n = a_n\psi_n$ and $A\psi_m = a_m\psi_m$, and $a_n \neq a_m$ then

$$\int_{\text{all space}} \psi_m^\star\, \psi_n\, d^3\mathbf{r} = 0.$$

Distinct eigenfunctions belonging to the same eigenvalue can be expressed in terms of a linearly independent set of eigenfunctions which can be chosen to be orthogonal, so that all eigenfunctions are then orthogonal. If in addition all eigenfunctions are normalised:

$$\int_{\text{all space}} \psi_n^\star\, \psi_n\, d^3\mathbf{r} = 1.$$

then the eigenfunctions form an *orthonormal set.* It is to the properties of such a set that we now turn.

2.3 Expansion in terms of a Basis

In the last section we defined an orthonormal set of wavefunctions $\{\psi_n\}$ with the equation

$$\int_{\text{all space}} \psi_m^\star\, \psi_n\, d^3\mathbf{r} = \delta_{mn}.$$

One way of finding such a set is to use the eigenfuntions of a Hermitian operator, but here we consider such a set regardless of where it came from. In this section, and the next, we are generally concerned with analysing a wavefunction in terms of other wavefunctions at a given time, rather than with questions of how the analysis might be different at different times. It is therefore useful to consider a time-independent set $\{\psi_n\}$.

An important technique which we shall use frequently is to represent an arbitrary wavefunction ϕ in terms of this set, that is we write ϕ as a linear superposition of the ψ_n:

$$\phi = \sum_n c_n \psi_n. \tag{2.20}$$

Obviously at this point the question arises as to whether all valid wavefunctions ϕ can be written in such a way in terms of the set $\{\psi_n\}$. If this is the case then the set $\{\psi_n\}$ is called a *complete* set, or *basis.* A basis is a set of wavefunctions in terms of which any valid wavefunction can be expanded; if the set is also orthonormal then we refer to it as an *orthonormal basis.* Thus provided the orthonormal set $\{\psi_n\}$ is an orthonormal basis the expansion (2.20) is indeed generally possible. Given the wavefunction ϕ and the orthonormal basis $\{\psi_n\}$ we ought to be able to determine the expansion coefficients c_n. In fact this is very straightforward. We multiply both sides of (2.20) by an arbitrary member of the basis (complex conjugated) and integrate over all space:

$$\int_{\text{all space}} \psi_m^\star \phi \, d^3\mathbf{r} = \sum_n c_n \int_{\text{all space}} \psi_m^\star \psi_n \, d^3\mathbf{r}.$$

Using the orthonormal property of the basis, the integral on the right vanishes except when $m = n$, in which case it is unity, so that the sum reduces to a single term c_m:

$$c_m = \int_{\text{all space}} \psi_m^\star \phi \, d^3\mathbf{r}. \tag{2.21}$$

This integral defines each of the expansion coefficients in turn, depending on which basis function is included in the integrand.

If the resulting wavefunction ϕ, now represented as a superposition of ψ_n wavefunctions, is normalised then this represents a constraint on the coefficients c_n. The normalisation integral is

$$\int_{\text{all space}} \phi^\star \phi \, d^3\mathbf{r} = 1.$$

If we substitute for both ψ and $\psi^\star$ the superposition summation we can write this as

$$\int_{\text{all space}} \left(\sum_m c_m \psi_m \right)^\star \left(\sum_n c_n \psi_n \right) \, d^3\mathbf{r} = 1$$

where we have given the two sums different dummy indices m and n to distinguish them. We can now rearrange the terms into a double sum:

$$\int_{\text{all space}} \sum_m \sum_n c_m^\star c_n \psi_m^\star \psi_n \, d^3\mathbf{r} = 1$$

and then take the constants and summation out of the integral to leave

$$\sum_m \sum_n c_m^\star c_n \int_{\text{all space}} \psi_m^\star \psi_n \, d^3\mathbf{r} = 1.$$

All the integrals are now seen to be either normalisation integrals if $n = m$ or zero by orthogonality if $n \neq m$, so the expression simplifies to

$$\sum_n c_n^\star c_n = \sum_n |c_n|^2 = 1 \tag{2.22}$$

which is the required normalisation constraint on the c_n.

If we substitute the explicit expression for c_n from (2.21) back into the expansion (2.20) we obtain

$$\phi(\mathbf{r}) = \sum_n \left(\int_{\text{all space}} \psi_n^\star(\mathbf{r}')\phi(\mathbf{r}')\, d^3\mathbf{r}' \right) \psi_n(\mathbf{r})$$

where we have changed the (dummy) variable of integration to $\mathbf{r}'$ to distinguish it from the independent variable $\mathbf{r}$ which occurs on both sides of the equation. If we reverse the order of summation and integration we can factor out the common $\phi(\mathbf{r}')$ from the sum to obtain

$$\phi(\mathbf{r}) = \int_{\text{all space}} \left(\sum_n \psi_n^\star(\mathbf{r}')\psi_n(\mathbf{r}) \right) \phi(\mathbf{r}')\, d^3\mathbf{r}' \tag{2.23}$$

The structure of this epression becomes clearer if we define the contents of the bracket, involving a sum over all the basis functions evaluated at two points $\mathbf{r}$ and $\mathbf{r}'$, as a function $g(\mathbf{r}, \mathbf{r}')$:

$$g(\mathbf{r}, \mathbf{r}') = \sum_n \psi_n^\star(\mathbf{r}')\psi_n(\mathbf{r}).$$

In terms of g we can write (2.23) as

$$\phi(\mathbf{r}) = \int_{\text{all space}} g(\mathbf{r}, \mathbf{r}')\phi(\mathbf{r}')\, d^3\mathbf{r}' \tag{2.24}$$

and this equation has to be true for any ϕ at all points $\mathbf{r}$.

This is a very puzzling equation: what sort of function g, which depends only on the orthonormal basis $\{\psi_n\}$, could make this equation true? It states that the arbitrary function ϕ evaluated at any point $\mathbf{r}$ can be expressed in terms of ϕ evaluated at *all* points, but weighted in each case by the value of g. It is perhaps helpful to recall that the function ϕ is not totally arbitrary, but is required to be twice-differentiable, so that it is in some sense a smooth function. Perhaps we can use this fact to define a length-scale for change, L, such that over distances less than L the function ϕ can be considered roughly constant, while over larger distances it can, of course, vary arbitrarily. By choosing L small enough we can presumably make the error in assuming that ϕ is constant over the region as small as we please. For functions ϕ for which such a length scale L can be defined we can make (2.24) generally true provided g vanishes at all points outside the region $\mathcal{L}$ defined by $|\mathbf{r} - \mathbf{r}'| < L$, while within the region $\mathcal{L}$ it is non-zero, not necessarily positive everywhere but on average positive, and integrates to one:

$$g(\mathbf{r}, \mathbf{r}') = 0 \quad \text{for} \quad |\mathbf{r} - \mathbf{r}'| < L \quad \text{and} \quad \int_{\mathcal{L}} g(\mathbf{r}, \mathbf{r}')\, d^3\mathbf{r}' = 1. \tag{2.25}$$

Using these properties we of g we can now evaluate the integral in (2.24) by splitting it into two parts: the part outside $\mathcal{L}$, where it is zero, and the part inside $\mathcal{L}$, over which $\phi(\mathbf{r}')$ is constant and equal to $\phi(\mathbf{r})$:

$$\int_{\text{all space}} g(\mathbf{r}, \mathbf{r}')\phi(\mathbf{r}')\, d^3\mathbf{r}' = \int_{\mathcal{L}} g(\mathbf{r}, \mathbf{r}')\phi(\mathbf{r}')\, d^3\mathbf{r}' = \phi(\mathbf{r}) \int_{\mathcal{L}} g(\mathbf{r}, \mathbf{r}')\, d^3\mathbf{r}' = \phi(\mathbf{r}).$$

To sum up, for any function ϕ with a length-scale for change equal to (or indeed greater than) L, any function g with the properties (2.25) will have the required effect.

The length-scale for change L introduced in the last paragraph is related to the momentum of the particle through the de Broglie relation: if system described by ϕ has momentum $\lesssim p$ then the shortest wavelength present is $\lambda = h/p$, so if we take $L = \epsilon h/p$ where ϵ is a small number then the error in assuming that ϕ is constant over $\mathcal{L}$ is small number depending on ϵ. The problem with this is that there is no upper bound for p, so there is no universal length-scale L which will always be short enough. This implies that the function $g(\mathbf{r}, \mathbf{r}')$ must have a vanishingly small L, and hence that within the region $\mathcal{L}$, now vanishingly small, the function must be not just positive on average, but infinitely positive, since it must integrate to one over the region $\mathcal{L}$. The function g is thus an infinitely sharply peaked function, which is generally known as the Dirac delta-function, and written $\delta(\mathbf{r} - \mathbf{r}')$. We can view it as a product of three one-dimensional delta-functions $\delta(\mathbf{r} - \mathbf{r}') = \delta(x - x')\delta(y - y')\delta(z - z')$. The formal properties of the delta-function are as follows:

- Symmetry: $\delta(x - x') = \delta(x' - x)$;
- Peaked: $\delta(x - x') = 0$ if $x \neq x'$;
- Unit area:
$$\int \delta(x)\, dx = 1;$$
- The defining property of filtering out a single value from an integral:
$$\int f(x')\, \delta(x - x')\, dx' = f(x)$$
where the range of the integral includes x.

Another way of writing the filtering property is $f(x')\delta(x - x') = f(x)\delta(x - x')$; this substitution allows $f(x)$ to be taken as a constant factor out of the integral over x', which then becomes one. This last relation implies, taking $f(x) = x$ as a special case, $x'\delta(x - x') = x\delta(x - x')$.

Returning finally to (2.23) we now see that this equation requires that the bracket be a delta function:

$$\sum_n \psi_n^\star(\mathbf{r}')\psi_n(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}') \tag{2.26}$$

which is a formal statement of the completeness property of an orthonormal basis.

2.4 The Measurement Postulate

We have now introduced all the necessary techniques to enable us to state the interpretative postulate of quantum mechanics, which defines the connection between the wavefunction describing a system and the results of observation, or measurements. We have already introduced two specific assumptions along these lines: that the wavefunction $\psi(\mathbf{r}, t)$ is the probability amplitude for position measurements at time t, (in other words $|\psi(\mathbf{r})|^2$ is the probability density), and that the expectation value for any other observable A with operator $\hat{A}$ is, as given by (2.4),

$$\langle A \rangle = \int \psi^\star \hat{A} \psi \, d^3\mathbf{r} = \langle \psi | A | \psi \rangle. \tag{2.27}$$

The measurement postulate subsumes both of these as special cases, and gives predictions for all observables in the same form, as a probability distribution for the possible results of measurement, just as we have for position.

Suppose we have a system which is described by a known wavefunction $\psi(t)$, and at time t_0 we make a measurement of an observable A. The wavefunction will in general be time-dependent, as shown; it will also depend on position variables which are not shown. The postulate refers to the eigenvalues and eigenfunctions of A: the eigenfunctions satisfy

$$A\phi_n = A_n \phi_n$$

where A_n are the eigenvalues, and ψ can be expanded in terms of ϕ_n as

$$\psi(t) = \sum_n c_n \phi_n.$$

Where the time-dependence goes on the right-hand side here is a matter of choice: the eigenfunctions of A can be chosen to be time-independent, in which case the c_n may be time-dependent, but if the measurement is of energy, so that A is the Hamiltonian H, then the eigenfunctions ϕ_n can be chosen to be either the time-independent functions u_n or the time-dependent functions $u_n e^{-iE_n t/\hbar}$, and in the latter case the c's are constant, as we have already seen. The time-dependence is not essential to this discussion, which concerns a measurement made at a specific time t_0, the result of which depends on the wavefunction at that time $\psi(t_0)$, which we now call ψ.

The complete prediction of quantum mechanics for the result of the measurement is as follows: the result of the measurement of A on a system with normalised wavefunction ψ is:

(i) One of the eigenvalues of A, A_n

(ii) With probability $|c_n|^2$.

(iii) Immediately after the measurement $\psi = \phi_n$.

The postulate has three parts, as indicated. The first is that *the eigenvalues of an observable are the possible results of measurement.* This is an extrapolation of our experience wth the Hamiltonian, where we interpreted the energy eigenvalues as the possible energy states of the system, since we know from spectroscopy that atomic systems can only have certain energies.

This identification of the eigenvalues as the possible results of measurement could be taken to imply that if the wavefunction were equal to an eigenfunction then the measurement would certainly produce the corresponding eigenvalue. This in turn makes it plausible that in a superposition state the result of the measurement is not predictable with certainty, but that the larger the admixture of a given eigenfunction in the superposition state, the greater the liklihood of measuring the corresponding eigenvalue. The second part of the postulate implements this idea, using the fact (see equation 2.22) that the sum of the square moduli of the c_n is one. (The probability cannot be proportional to c_n as c_n is complex, whereas a probability is real and lies between 0 and 1.) We noted in section 1.2 when we introduced the term probability amplitude that we would be meeting probability amplitudes whose square modulus was a probability rather than a probability density, and this is the case here: c_n *is the probability amplitude for obtaining the result* A_n.

The third and final part of the postulate follows from an assumption that if we re-measured the same observable instantly we ought to obtain the same result. The first two parts then imply that, since the result of this second measurement is A_n with certainty, the wavefunction must now be ϕ_n. This is referred to as the *collapse* or *reduction of the wavefunction;* those parts of the wavefunction which are inconsistent with the result of the measurement are, as it were, erased and the remaining part re-normalised.

It should be apparent that we have not derived these results from other principles, but merely made them appear plausible in the light of some legitimate considerations, rather as we did with the Schrodinger equation in section 1.2, and they are normally viewed as a separate postulate of quantum mechanics. At this point there is enormous amount that could be said, as this postulate has been and continues to be the focus of immense controversy; without going into great detail we shall indicate the reasons for this.

However we must first show that the postulate does, as claimed, include the two assumptions already made about measurements as special cases. Firstly the expectation value: if the complete probability distribution of the results of measurement is the set $\{A_n\}$, each with probability $|c_n|^2$, then the mean or expectation value is

$$\langle A \rangle = \sum_n A_n |c_n|^2, \tag{2.28}$$

and we must show that (2.27) is equivalent to this result. In the integral in (2.27) we introduce the expansion of ψ in terms of the eigenfunctions of A, ϕ_n:

$$\langle A \rangle = \int \left(\sum_m c_m^\star \phi_m^\star \right) A \left(\sum_n c_n \phi_n \right) \, d^3\mathbf{r}.$$

If we take the coefficients out of the integral we obtain

$$\langle A \rangle = \sum_{m,n} c_m^\star c_n \int \phi_m^\star A \phi_n \, d^3\mathbf{r}.$$

In the integral we use the eigenvalue equation $A\phi_n = A_n \phi_n$ to give

$$\langle A \rangle = \sum_{m,n} c_m^\star c_n A_n \int \phi_m^\star \phi_n \, d^3\mathbf{r}.$$

But the integral is now simply an inner product of eigenfunctions, which is one if $n = m$ and zero otherwise, so that

$$\langle A \rangle = \sum_n A_n |c_n|^2$$

in agreement with (2.28).

The other result we must re-derive from the measurement postulate is the interpretation of the wavefunction as the probability amplitude for position measurements. We shall consider the application of the postulate to the measurement of position (for simplicity in one dimension, x). We first need the eigenfunctions $\phi_a(x)$ of the position operator x:

$$x\phi_a(x) = a\phi_a(x) \tag{2.29}$$

where a is the eigenvalue. If we re-arrange this as $(x - a)\phi_a(x) = 0$ then we immediately see a problem: ϕ_a must be zero everywhere except at $x = a$. There are several possible reactions to this observation. One can take the view that the position operator has no eigenfunctions; this makes the application of the measurement postulate impossible for position measurements. A different approach would be that there are eigenfunctions, but that they are not physically realisable; the reason for this is that they represent the state 'the particle is exactly at a' which is obviously a limiting case of possible states in which the particle's position is more and more closely defined.

On this viewpoint there is a physical reason for the special treatment that these eigenfunctions require, which is the continuous rather than discrete nature of the eigenvalue a. (Of course this is an assumption: whether space is really a three-dimensional continuum is open to question, but for the moment we are asuming that it is.) There are also other approaches which use a rather different mathematical formalism for quantum theory in order to circumvent these problems.

If we take the practical view that eigenfunctions can be defined, but only as limiting cases of physically realisable wavefunctions, then we can solve the eigenvalue equation (2.29) by noting that it is an equation satisfied by the delta-function (see the discussion on page 36), so that $\phi_a(x) = \delta(x-a)$. This makes physical sense: the delta-function was introduced in section 2.3 as a limiting case of a sharply peaked function, which would correspond to the expected wavefunction for the state 'the particle is at a'. However there is a problem with its normalisation: applying the usual rule one would want to specify a normalising factor N such that

$$N^\star N \int \delta(x-a)\delta(x-a)\,dx = 1.$$

However this is not possible: if we use the filtering property of one of the delta functions then the integral becomes $\delta(0)$ which is infinite. Thus the delta function is not square-integrable. (In fact since it is not continuous or differentiable either it is quite obvious that we are extending the normal rules for wavefunctions quite a lot!) This is a general feature of eigenfunctions whose eigenvalues lie in a continuous rather than a discrete set of values, and in these cases we have to change the normalisation condition for eigenfunctions (which we now write as $(\phi(x,a)$ to indicate that a is a continuous rather than a discrete variable):

$$\int \phi(x,a)^\star \phi(x,a')\,dx = \delta(a-a'). \tag{2.30}$$

When the two eigenvalues are not equal, $a \neq a'$, this expresses the expected orthogonality of the eigenfunctions, but when $a = a'$ the integral becomes the normalisation integral, which diverges in such a way that the dependence on a becomes a delta-function. This equation is satisfied by the delta-function eigenfunctions:

$$\int \delta(x-a)\delta(x-a')\,dx = \delta(a-a')$$

where the result is found by using the filtering property of one of the delta-functions, say $\delta(x-a)$, which replaces x by a in the argument of the other. Thus with this change in the normalisation rule for these eigenfunctions they are already correctly normalised without any factor N.

Having by way of preamble found the eigenfunctions of x we can now apply the measurement postulate to a measurement of position. The result of the measurement is one of the eigenvalues

a: which is to say, any value, since the eigenvalues form a continuous set covering the real line $(-\infty, \infty)$. To find the probability of obtaining a given result we need to find the coefficients for expanding the wavefunction ψ in terms of the eigenfunctions. Because the eigenvalues now form a continuous set we cannot sum over them, but must integrate:

$$\psi(x) = \int c(a)\phi(x, a)\, da = \int c(a)\delta(x - a)\, da = c(x).$$

From this we deduce that wavefunction $\psi(x)$ is also the expansion coefficient in terms of x eigenfunctions, so that the measurement postulate states that the probability amplitude for measuring a position x is $\psi(x)$, or in other words, $|\psi(x)|^2$ is the probability density for position measurements. This completes the derivation of our interpretation of the wavefunction from the measurement postulate.

The position operator is not the only one with continuous eigenvalues: the momentum operator also has this property, as we shall see in **??**. For future reference the properties of eigenfunctions with discrete and continuous eigenvalues are compared in table 2.4.

One problem with the measurement postulate as it stands is that it gives a very crude account of the results of physical measurement: a rather more realistic form might be that the result lay in a certain range $A \pm \delta A$, where the experimental uncertainty δA is compounded from the various errors and uncertainties of the measurement method. A still more realistic representation would involve a probabilistic statement about the result, for example that there is a 63% chance that it lies in the interval $A \pm \sigma_A$, but we shall work with the simple error bar δA. If the error bar is sufficiently small that only one eigenvalue of the operator A is consistent with the result, then we can still use the measurement postulate as it stands. However if, as will invariably be the case for measurements on macroscopic systems or of variables with a continuous range of eigenvalues, the error bar encompasses more than one eigenvalue then we need to generalise the postulate. The generalised statement is that the probability of obtaining a result $A \pm \delta A$ is the sum of $|c_n|^2$ for eigenvalues A_n lying in this interval (or the integral of $|c(a)|^2$ over this interval), and that after the measurement we find the new wavefunction by erasing those parts of the wavefunction which are inconsistent with the result, and re-normalising the rest. So in the discrete case, for example, $\psi = \sum c_n\phi_n$ becomes $N\sum' c_n\phi_n$ where the prime indicates that the sum is restricted to n such that A_n lies in the within the error bar $A \pm \delta A$, and N is a constant which re-normalises the wavefunction.

We now briefly turn to the question of why this postulate has been so controversial. One reason is that the evolution implied by the postulate from the wavefunction ψ to the wavefunction ϕ_n

A complete set of eigenfunctions	
$\phi_n(x)$	$\phi(x,a)$
satisfying the eigenvalue equation	
$A\phi_n = A_n\phi_n$	$A\phi(x,a) = a\phi(x,a)$
where the eigenvalues lie in a	
discrete range	continuous range
have orthogonality and normalisation properties	
$\int \phi_m^\star \phi_m \, dx = \delta_{mn}.$	$\int \phi^\star(x,a)\phi(x,a')\, dx = \delta(a-a').$
They can be used to expand an arbitrary wavefunction $\psi(x)$:	
$\psi(x) = \sum c_n\phi_n(x)$	$\psi(x) = \int c(a)\phi(x,a)\, da$
where the expansion coefficients c are found as	
$c_n = \int \phi_n^\star(x)\psi(x)\, dx.$	$c(a) = \int \phi^\star(x,a)\psi(x)\, dx.$
If $\psi(x)$ is normalised to unity then the c satisfy	
$\sum \lvert c_n\rvert^2 = 1.$	$\int \lvert c(a)\rvert^2 \, da = 1.$
In a measurement of the observable A, the coefficient c is the probability amplitude for obtaining the corresponding eigenvalue; in other words	
$\lvert c_n\rvert^2$ is the probability	$\lvert c(a)\rvert^2$ is the probability density
that the measurement will yield the result	
$A_n.$	$a.$

Table 2.1: Comparison of discrete and continous eigenfunctions

is a form of time-dependence, but it is not the result of time-evolution described by the time-dependent Schrodinger equation. This is clear because the wavefunction after the measurement does not depend linearly on the wavefunction before the measurement, so it cannot be the result of acting on ψ with a linear operator H. (In fact the wavefunction after the measurement hardly depends on ψ at all — only to the extent that the result of the measurement is a possible result.) We can summarise the situation by saying that in quantum mechanics there are two types of time-dependence of the wavefunction: that described by the time-dependent Schrodinger equation, which occurs when a measurement is not being made, and that described by the measurement postulate during a measurement. Unfortunately quantum mechanics cannot supply a definition of what exactly constitutes a measurement, and therefore cannot predict the time t_0 at which the wavefunction reduction will take place, although it is known that for all practical purposes one can choose one of several different times t_0 with equivalent results. There are a number of different positions that have been taken with regard to this state of affairs.

- **Orthodoxy.** The 'conventional view' set out above is also known as the 'Copenhagen interpretation' after the Institute for Theoretical Physics at Copenhagen, founded by Bohr after he was awarded the Nobel prize in 1920, whence it originated in the period 1925–35. On this view the wavefunction is a mathematical device which expresses our knowledge of the system, and any measurement necessarily changes that knowledge. The problem with this viewpoint is that by denying the wavefunction any real existence we have to some degree disconnected our theory from the external world — the theory serves to correlate observations without explaining them, since any putative explanation could only be in wavefunction terms. To put it crudely, if the wavefunction is not what is going on 'out there', we have no picture of what is going on 'out there'.
- **Objective Collapse.** This view tends to give more 'reality' to the wavefunction, but still accepts the reduction as a correct account of measurement. This entails that some reason must be found for it, to supply the definition of what constitutes a measurement. Actual measuring systems differ from atomic systems in several important respects, all of which have been put forward as the cause of the reduction at different times and in different combinations. Measuring apparatus is *macroscopic*, containing $\sim 10^{23}$ atoms and therefore $\sim 10^{25}$ particles; it is also *thermal*: there are degrees of freedom which are randomly and thermally excited, such thermal vibrations of solids, or blackbody radiation, so that there is a stochastic element in the state of the apparatus; at some stage in the measurement process there is usually *irreversibility*, in writing or erasing a computer memory location, or in putting ink on paper; and for a measurement to be of any use to a scientist there is the involvement of a *mind* at some point.
- **No Collapse.** This viewpoint is rather more subtle, in asserting that the reduction of the wavefunction is just a useful rule which gives the right answer, but that looked at in the right way the quantum mechanics of the measuring process would produce the same result. Various ways of bringing this about have been suggested, including the famous (or notorious) *many-worlds interpretation* according to which all possible outcomes to a measurement actually occur, but we only perceive one of them, and there exist alternative worlds in which alternative observers see other outcomes. Another approach is to assert that the wavefunction does not strictly describe a single system at all, but correctly predicts the statistical properties

of measurements made on each of an ensemble of identical systems; on this viewpoint the constants $|c_n|^2$ in the postulate are not so much probabilities but relative frequencies of occurrence, and all possible outcomes of the measurement occur in the ensemble.

- **Additional Variables.** Another approach, also in a sense a no-collapse view, is to reintroduce causality by asserting that the outcome of the measurement is causally dependent on other variables than those contained in the wavefunction. The most successful of these is due to Bohm, going back to the original concept of de Broglie, that the 'de Broglie waves' are in fact 'pilot waves', that is the wavefunction and the particles both exist, and the motion of the particles is dependent on the wavefunction. This can be developed into a complete alternative interpretation of quantum mechanics, which reproduces all the same predictions, but has a different set of conceptual difficulties.

2.5 Probability Flow

One of the difficulties listed at the end of chapter 1 was the problem of normalisation: how can we be sure that having normalised the wavefunction at some time it will remain normalised? One answer to this difficulty was given in section 2.2: the Hermitian property of the Hamiltonian implies that the time-derivative of the normalisation integral is in fact zero; this we might term *global* conservation of probability. However this does not altogether dispose of the question: within the constraint of global conservation one could imagine that probability could vanish from some region of space while simultaneously appearing at a distant region. (Perhaps more to the point, one can find a Hermitian Hamiltonan with this property.) An obviously desireable property in the theory would be *local* conservation of probability, which would rule out such non-local behaviour.

Many different systems, having a law of global conservation of some 'stuff' S also exhibit local conservation of S. The pre-requisites are that the stuff should be both distributed in space, but also localisable, so that there is a definite amount of S in any spatial region; these enable a density of S, which we term ρ, to be defined. Examples of S would be electric charge, or mass in a non-relativistic context, and in the present example, probability. The density ρ is therefore charge density, or mass density (for example in a fluid), or in this case probability density, $|\psi(\mathbf{r},t)|^2$. We can compute the amount of S in a arbitrary region V, S_V, by integrating the density over V:

$$S_V(t) = \int_V \rho(\mathbf{r},t)\,d^3\mathbf{r}.$$

If we extend V to all space then this is the global quantity of S, which is by hypothesis constant; however we are concerned with the case where V is a fixed and finite region. In this case S_V need not be constant, but could depend on time as shown. However if S is locally conserved then the only way in which $S_V(t)$ could change would be if some S were to flow through the bounding surface A. We therefore define $\mathbf{J}$, the flux or current density of S, as the flow of S per unit time per unit area perpendicular to $\mathbf{J}$. Thus if we take an arbitrarily-oriented element of area at $\mathbf{r}$, $d\mathbf{A}$, the rate at which $\mathbf{J}$ transports S across $d\mathbf{A}$ in the direction of the normal is $\mathbf{J}(\mathbf{r},t) \cdot d\mathbf{A}$. We can interpret the cosine in the dot product either as the component of the flow normal to the surface, or the projected area of the surface normal to the flow.

A statement of local conservation of probability is thus that rate of decrease of S_V is equal to the rate at which S is transported out of V acrosss the bounding surface A:

$$-\frac{dS_V}{dt} = \int_A J(\mathbf{r},t) \cdot d\mathbf{A}. \tag{2.31}$$

On the left-hand side of (2.31) we can insert the definition of S_V:

$$-\frac{dS_V}{dt} = -\frac{d}{dt}\int_V \rho(\mathbf{r},t)\, d^3\mathbf{r} = \int_V -\frac{\partial\rho}{\partial t}\, d^3\mathbf{r}.$$

On the right-hand side we can use the divergence theorem to transform the surface integral to a volume integral:

$$\int_A J(\mathbf{r},t) \cdot d\mathbf{A} = \int_V \nabla \cdot \mathbf{J}(\mathbf{r},t)\, d^3\mathbf{r}.$$

With these two substitutions (2.31) becomes

$$\int_V -\frac{\partial\rho}{\partial t}\, d^3\mathbf{r} = \int_V \nabla \cdot \mathbf{J}(\mathbf{r},t)\, d^3\mathbf{r}$$

which we can combine under a single integral as

$$\int_V \left(\frac{\partial\rho}{\partial t} + \nabla \cdot \mathbf{J}\right) d^3\mathbf{r} = 0.$$

For this to be true for an arbitrary volume V the integrand must be zero at all times and in all places, so local conservation of S requires

$$\frac{\partial\rho}{\partial t} + \nabla \cdot \mathbf{J} = 0 \tag{2.32}$$

and there is a law of this form for each of the three examples referred to above.

In order for quantum mechanics to have this property we have to find a probability flux $\mathbf{J}$ which satisfies (2.32) when ρ is the probability denity $|\psi|^2$. The time-derivative is given by

$$\frac{\partial|\psi|^2}{\partial t} = \psi^\star\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^\star}{\partial t}.$$

We can substitute for the time-derivatives from the Schrodinger equation:

$$\frac{\partial|\psi|^2}{\partial t} = \frac{1}{i\hbar}\Big(\psi^\star H\psi - \psi(H\psi)^\star\Big). \tag{2.33}$$

Thus far we have simply reproduced the working in section 2.2 leading to (2.16). At this point the two discussions diverge, as we have now to manipulate this expression into a divergence, and this requires an explicit form for H. We take our standard example of a single particle subject to a potential $V(\mathbf{r})$:

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}).$$

If we substitute this into (2.33) we obtain

$$\frac{\partial|\psi|^2}{\partial t} = \frac{i\hbar}{2m}\Big(\psi^\star\nabla^2\psi - \psi\nabla^2\psi^\star\Big) + \frac{1}{i\hbar}\Big(\psi^\star V\psi - \psi V\psi^\star\Big).$$

The potential terms cancel, and the two terms involving the Laplacian ∇^2 can be combined as

$$\psi^\star\nabla^2\psi - \psi\nabla^2\psi^\star = \nabla\cdot\Big(\psi^\star\nabla\psi - \psi\nabla\psi^\star\Big)$$

because the extra $\nabla\psi^\star\cdot\nabla\psi$ terms on the right-hand side cancel. Thus (2.33) reduces to the required local conservation form

$$\frac{\partial|\psi|^2}{\partial t} + \nabla\cdot\mathbf{J} = 0 \tag{2.34}$$

where the probability flux $\mathbf{J}(\mathbf{r}, t)$ is given by

$$\mathbf{J}(\mathbf{r}, t) = \frac{-i\hbar}{2m}\Big(\psi^\star\nabla\psi - \psi\nabla\psi^\star\Big). \tag{2.35}$$

The existence of this probability flux or probability current density ensures that probability is locally as well as globally conserved, that is the density can only change because the probability has flowed somewhere else.

This particular combination of derivatives looks rather obscure, but it can be written in an interesting way if we put the wavefunction in modulus-argument form, as in section 2.1: $\psi(\mathbf{r}, t) = R(\mathbf{r}, t)\, e^{iS(\mathbf{r},t)}$ where R and S are real functions. In this form $\psi^\star$ is $R\,e^{-iS}$, and the probability density is just R^2. Obviously

$$\nabla\psi = \nabla(R\,e^{iS}) = (\nabla R)\; e^{iS} + i\,(\nabla S)\,Re^{iS}$$

and if we substitute this into $\mathbf{J}$ together with the corresponding result for $\nabla\psi^\star$ the terms involving ∇R cancel while those involving ∇S add, so that

$$\mathbf{J} = R^2\frac{\hbar\nabla S}{m} = |\psi|^2\mathbf{V} \quad \text{where} \quad \mathbf{V} = \frac{\hbar\nabla S}{m}. \tag{2.36}$$

The quantity $\mathbf{V}$ has a simple interpretation: if the probability density is $|\psi|^2$ and the flux is $|\psi|^2\mathbf{V}$ then $\mathbf{V}$ is the velocity with which the probability is flowing. In simple cases this is equal to the local classical particle velocity. For example consider a plane de Broglie wave $\psi = Ne^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$; S is given by $\mathbf{k}\cdot\mathbf{r}-\omega t$ so $\mathbf{V} = \hbar\mathbf{k}/m$. But since for such a wave $\hbar\mathbf{k} = \mathbf{p}$ this is equal to the particle velocity $\mathbf{p}/m$.

We should enter one caveat at this point. This example involved only a single particle, as indeed have all our examples up to this point. When we come to consider multi-particle systems the wavefunction will become a function of all the particle positions, in other words a function not in three-dimensional space but in configuration space, the space of possible positions of all the particles. The 'local' conservation equation then works in exactly the same way *but in configuration space.* This does not embody the same physics as in the single-particle example, as the probability is only localised in configuration space and not in three-dimensional space, so that we cannot identify a given amount of probability as existing in a given spatial region, as required for the local conservation concept to be applicable.

2.6 The Classical Limit

We have now a sufficient theoretical framework to examine how the quantum-mechanical description of a simple system — the one-dimensional box — relates to the classical description. One of the constraints on the development of quantum theory was that it should reproduce classical predictions in the appropriate limit; this constraint is often referred to as the *correspondence principle.* The discussion prior to the introduction of the Schrodinger equation in section 1.2 suggested that correspondence would be possible if we used wavepacket solutions, which ought to follow classical trajectories. The method followed here is therefore to establish what is the classical trajectory for this system, to review the general quantum-mechanical solution, and finally to see how they agree in the appropriate limit.

The classical system we have in mind is a particle bouncing to and fro between perfectly elastic walls separated by a distance a. The energy of the system E is entirely kinetic, $\frac{1}{2}mv^2$, so the velocity v is $\pm\sqrt{2E/m}$. If for simplicity we set the time to 0 as the particle bounces off the wall at $x = 0$ then it will travel at velocity $v_+ = \sqrt{2E/m}$ to the other wall, arriving there at time $a/v_+ = a\sqrt{m/2E}$, and then travel with velocity $v_- = -\sqrt{2E/m}$ back to the starting point, arriving there at time $T = 2a\sqrt{m/2E} = a\sqrt{2m/E}$. This motion is illustrated in Figure 2.1: it

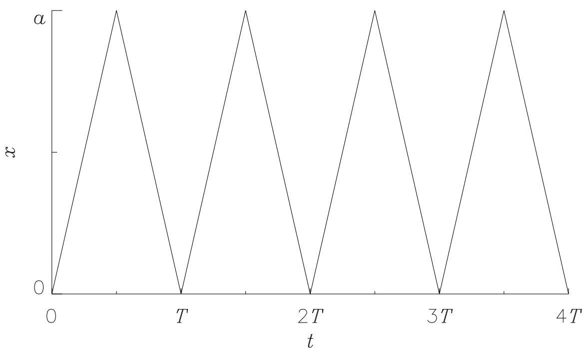


Figure 2.1: *Classical Motion in the 1-D Box*

is periodic with time period T, or frequency $F = 1/T = \sqrt{E}/a\sqrt{2m}$. This completes the clasical description of the system: for given initial conditions (in this case, energy E, and position $x = 0$ at $t = 0$) we have the position $x(t)$ at all later times.

The eigenvalues E_n and normalised eigenfunctions $u_n(x)$ of the quantum-mechanical Hamiltonian were found in section 1.4 to be

$$\begin{aligned} E_n &= \frac{n^2 E_1 \quad \text{where} \quad \pi^2\hbar^2}{2ma^2} \\ u_n(x) &= \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}. \end{aligned}$$

Using these we can construct the general time-dependent solution to the Schrodinger equation, as in (1.28),

$$\psi(x,t) = \sum_{n=1}^{\infty} c_n u_n(x)\, e^{-iE_n t/\hbar}. \tag{2.37}$$

The c_n are arbitrary complex constants, although they are subject to an overall normalisation constraint. If we require that the wavefunction in (2.37) is normalised to unity then we have

$$1 = \int_0^a \psi^\star \psi \, dx = \sum_{m,n} c_m^\star c_n \exp i(E_m - E_n)t/\hbar \int_0^a u_m^\star u_n \, dx.$$

However, because the Hamiltonian is Hermitian its eigenfunctions are orthogonal, and the u_n are normalised. The integral is therefore 1 if $n = m$ and zero otherwise, so that the normalisation constraint reduces to

$$\sum_n |c_n|^2 = 1. \tag{2.38}$$

(This illustrates in a slightly different way the connection between the Hermitian property of the Hamiltonian and the conservation of normalisation which we discussed in section 2.2. In 2.2 we showed that the time-dependence induced by H for an arbitrary wavefunction led to the conservation of normalisation. Here we express the arbitrary wavefunction in terms of eigenfunctions of

H, and the normalisation integral splits up into time-independent and time-dependent terms; the orthogonality of the eigenfunctions, which follows from the Hermitian property of H, ensures that the time-dependent terms are all zero, so that again the normalisation is preserved.)

Given the general solution to the Schrodinger equation (2.37), we must enquire what sort of coefficients c_n we need in order to make the quantum-mechanical solution correspond to the classical solution. The simplest connection would be to pick a single eigenfunction with the right E, that is we take $c_n = 1$ for the E_n closest to E, and set all the other c's to zero. If we are discussing a macroscopic system, with m, a and E all of macroscopic size (within a few orders of magnitude of 1 kg, 1 m and 1 J) then since $\hbar$ is of order 10^{-34} Js the quantum number for this E_n is of order 10^{+34}, and the eigenfunction spreads across the whole box with 10^{+34} maxima and zeros. This is obviously a very non-classical state: the ‘particle’ is not localised at all and the probability distribution is time-independent. Indeed, this is generally true of energy eigenfunctions of all systems: they fill the classically-allowed space, and have time-independent probability distributions; it is quite clear that we will never obtain a correspondence between a classical system exhibiting time-dependent behaviour (in other words, dynamics) and a quantum-mechanical energy eigenfunction. It is also clear that an eigenfunction is never a wave-packet; this follows from the very first line of our solution of the Schrodinger equation by separation of variables $\psi = u(x)T(t)$: such a solution has a time-independent spatial distribution $u(x)$, which obviously cannot represent a moving wave-packet.

We are therefore led to consider superposition states, in which more than one of the c_n are non-zero. We can arrive at the same conclusion from a quite different consideration, by considering the results of measurements of energy. Bearing in mind the enormous quantum number $N \sim 10^{34}$ in the macroscopic limit, we note that the energy levels are exceedingly closely spaced: if we write $E_N = N^2 E_1$ then the energy difference for a small change in N is $\delta E = 2NE_1\delta N$, or $\delta E/E = 2\delta N/N$. The theory of measurement then tells us that a measurement of energy on the single eigenfunction produces E_N with certainty, and has a zero probability of producing $E_{N\pm1}$, which differ by only parts in 10^{34} from E_N. If we take the view that the wavefunction represents our knowledge of the system. then it is obviously the case that the single eigenfunction ψ_N represents far more knowldge of the energy than we could imagine possessing, while as we have just seen it represents far too little knowledge of the position x. Both these considerations point to the use of superposition states to represent the classical limit. Indeed the densely packed levels allow us to use very large superpositions: even a superposition of 10^{17} states would still define the energy to parts in 10^{17}!

Directly computing these very large superposition wavefunctions from eigenfunctions is clearly not a sensible approach, but it instructive to consider two cases: firstly a superposition of just two eigenfunctions, which illustrates a number of general properties of superpositions, and secondly a moderately large superposition which we can generate in a computer, and compare with the classical limit.

We start by considering an equal superposition of just two adjacent eigenfunctions, N and $N+1$:

$$\psi(x,t) = c_N\sqrt{\frac{2}{a}}\sin\frac{N\pi x}{a}e^{-iE_N t/\hbar} + c_{N+1}\sqrt{\frac{2}{a}}\sin\frac{(N+1)\pi x}{a}e^{-iE_{N+1}t/\hbar}. \tag{2.39}$$

The complex coefficients satisfy the normalisation constraint (2.38): $|c_N|^2+|c_{N+1}|^2 = 1$, so that for an equal superposition we have $|c_N| = |c_{N+1}| = 1/\sqrt{2}$. However the phases are arbitrary: suppose the two coefficients have phases that differ by ϕ (where $-\pi \le \phi \le \pi$), so that the phases are $\alpha+\phi/2$ and $\alpha-\phi/2$. We can multiply by an arbitrary overall phase $e^{-i\alpha}$ without changing the physics, so that without loss of generality we can take the phases to be equal and opposite: $c_N = (e^{i\phi/2})/\sqrt{2}$ and $c_{N+1} = (e^{-i\phi/2})/\sqrt{2}$. We shall consider two aspects of this system: the energy E and the position x.

The energy of the system with this wavefunction can be found in a number of ways. We already have the wavefunction as a superposition of energy eigenfunctions, so the theory of measurement tells us that the possible results of an energy measurement are E_N and E_{N+1}, each with probability $|c_N|^2 = |c_{N+1}|^2 = \frac{1}{2}$. The average energy of this probability distribution, or expectation value, is thus

$$\langle E\rangle = \frac{1}{2}(E_N + E_{N+1}) = \left(N^2 + N + \frac{1}{2}\right)E_1. \tag{2.40}$$

This expectation value can also be found by evaluating

$$\langle E\rangle = \int_0^a \psi^\star(x,t)\hat{E}\psi(x,t)\,dx = \int_0^a \psi^\star(x,t)\,i\hbar\frac{\partial\psi}{\partial t}\,dx \tag{2.41}$$

or by evaluating

$$\langle E\rangle = \int_0^a \psi^\star(x,t)H\psi(x,t)\,dx = -\frac{\hbar^2}{2m}\int_0^a \psi^\star(x,t)\,\frac{\partial^2\psi}{\partial x^2}\,dx. \tag{2.42}$$

The equality of (2.41) and (2.42) follows from the Schrodinger equation $\hat{E}\psi = H\psi$, and their equivalence to (2.40) follows from the general proof of equivalence in section 2.4. Direct evaluation of these expressions in left to problem 2.3.

In order to find the probability distribution for measurements of position we must find an expression for the probability density $|\psi(x,t)|^2$. There are quite a number of equivalent ways of writing this, but the following approach seems to give the most insight into how the wavefunction works. Each energy eigenfunction is a standing wave, representing the both the forwards and backwards motion of the particle in the box, and like any standing wave it can be decomposed into two travelling waves:

$$\psi_N(x,t) = \psi_N^+(x,t) + \psi_N^-(x,t) = -\frac{i}{\sqrt{2a}}\Big(\exp i(k_N x - \omega_N t) - \exp i(-k_N x - \omega_N t)\Big)$$

where $k_N = N\pi/a$ and $\omega_N = E_n/\hbar = N^2\pi^2\hbar/2ma^2$. The first term, ψ_N^+, represents the wave travelling in the positive direction and the second term, ψ_N^-, in the negative direction. We now note that $\psi_N^+(x,t) = -\psi_N^-(-x,t)$, which simply expresses the fact that the positive-going wave is a reflection, with π phase change because of the zero boundary condition, of the negative-going wave incident on the $x = 0$ boundary. This means that we can work with just ψ_+ over the interval $[-a,a]$, and re-construct the full wavefunction at the end of the calculation using $\psi(x,t) = \psi^+(x,t) - \psi^+(-x,t)$.

We now superpose the two eigenfunctions using our values for the c coefficients, but keeping only the ψ^+ parts:

$$\psi^+(x,t) = \frac{-i}{2\sqrt{a}}\Big(\exp i(k_N x - \omega_N t + \phi) + \exp i(k_{N+1} x - \omega_{N+1} t - \phi)\Big).$$

We can combine these two terms if we make the substitutions $k_{N+1} = \bar{k} + \delta k$ and $k_N = \bar{k} - \delta k$, where $\bar{k} = (N + \frac{1}{2})\pi/a$ and $\delta k = \pi/2a$, and similarly $\omega_{N+1} = \bar{\omega} + \delta\omega$ and $\omega_N = \bar{\omega} - \delta\omega$, where $\bar{\omega} = (E_N + E_{N+1})/2\hbar$ and $\delta\omega = (E_N - E_{N+1})/2\hbar$. These substitutions allow us to factor out a common exponential from both terms:

$$\psi^+(x,t) = \frac{-i}{2\sqrt{a}}\exp i(\bar{k}x - \bar{\omega}t)\Big(\exp i(-\delta k\, x + \delta\omega\, t + \phi) + \exp i(\delta k\, x - \delta\omega\, t - \phi)\Big).$$

The two terms in the bracket can now be combined as a cosine:

$$\psi^+(x,t) = \frac{-i}{\sqrt{a}}\exp i(\bar{k}x - \bar{\omega}t)\cos(\delta k\, x - \delta\omega\, t - \phi).$$

The superposition of the two travelling waves produces the well-known beats phenomenon, where the envelope factor is the cosine, with peak amplitudes and nulls separated by $\pi/\delta k = 2a$. The peak amplitude is located at zero phase of the beat, which is at $x = \phi/\delta k = (\phi/\pi)a$ at $t = 0$, and travelling with the group velocity $v_g = \delta\omega/\delta k$. Having combined the two eigenfunctions we can now re-introduce the standing wave by adding in ψ^-; the two travelling waves now produce a standing wave but modified by the beat which relects to and fro between the walls. (The explicit expression is complicated, but embodies this description.) There is always exactly one beat in the box, which at $t = 0$ is located at $x = (|\phi|/\pi)a$ and travelling either forwards or backwards depending on the sign of ϕ. The round trip time is $2a/v_g = 2\pi\hbar/(E_{N+1} - E_N)$, or alternatively the frequency is $(E_{N+1} - E_N)/h$. The evaluation of the expectation value $\langle x(t)\rangle$ is left to problem 2.4.

Now that we have looked in detail at a two-state superposition we can see how to make a many-state superposition which describes a localised wave-packet: we simply have to ensure that all the 'beat' positions between every adjacent pair of eigenfunctions are coincident: that is, there is a constant phase difference ϕ between every adjacent c_N and c_{N+1}. Figure **??** shows the probability distribution at various times for a medium-sized wave-packet created in this way. The figure shows a superposition of 15 eigenfunctions with quantum numbers from 209 to 223, centred on $N = 216$. The c_N vary smoothly: they are all real (that is, $\phi = 0$), with $c_n = (1\sqrt{6})\cos^2(n - N)\pi/16$. This form gives a smooth variation of c, from a single maximum at $n = N = 216$ to zero at $n = 208$ and 224, so that the non-zero c's are 209 – 223 as indicated; the factor of $1/\sqrt{6}$ normalises the c_n to 1, as shown in problem 2.5. The first panel of Figure **??** show the probability distribution $\psi(x)^2$ at $t = 0$. Because the coefficients were defined with $\phi = 0$ the wave-packet is locatd at $x = 0$, and the reflection of the front half interferes with the rear half to generate the short section of standing wave. The next two panels show the wavepacket at two later times: it moves steadily across the box and then reflects and returns. The final panel shows $\langle x\rangle$ as a function of t: the similarity with the classical behaviour shown in Figure 2.1 is obvious.

2.7 Problems

2.1 Show using the properties of the inner product that

$$4\langle\psi|\phi\rangle = \Big(\langle\psi+\phi|\psi+\phi\rangle - \langle\psi-\phi|\psi-\phi\rangle\Big) + i\Big(\langle\psi-i\phi|\psi-i\phi\rangle - \langle\psi+i\phi|\psi+i\phi\rangle\Big).$$

This expresses a general inner product in terms of inner products of vectors with themselves. Hence derive (2.9) from (2.8).

2.2 Prove the properties of the adjoint listed in section 2.2. Using these, and the fact that the adjoint of $\frac{d}{dx}$ is $-\frac{d}{dx}$ (as shown in the text), prove that the momentum operator is self-adjoint.

2.3 Show that both the expressions (2.41) and (2.42) for $\langle E\rangle$ of the two-state superposition are identical to the result (2.40).

2.4 Show that $\langle x(t)\rangle$ for the two-state superposition (2.39) is

$$\langle x(t)\rangle = \frac{a}{2} - \frac{2a}{\pi^2}\left(1 - \frac{1}{(2N+1)^2}\right)\cos\left(\frac{E_{N+1}-E_N}{\hbar} - \phi\right).$$

2.5 The cosine-squared coefficients of the wave-packet state in section 2.6 are a particular instance of a general set of coefficients defined by

$$c_n = K\cos^2\frac{(n-N)\pi}{2\Delta N+2}e^{-i(n-N)\phi} \quad \text{for} \quad n = N-\Delta N \ldots N+\Delta N.$$

with the parameters set to $N = 216$, $\Delta N = 7$ and $\phi = 0$. Show that $\sum |c_n|^2 = 1$ implies $K^2 = 4/3(\Delta N + 1)$, which for the given parameters gives $K = 1/\sqrt{6}$. (Hint: show that $\cos^4\theta = \frac{3}{8} + \frac{1}{2}\cos 2\theta + \frac{1}{8}\cos 4\theta$, and then show that the sums over the cosines are zero if the sum is extended to include the zero contribution from $n = N - \Delta N - 1$.)

Chapter 3

The Uncertainty Principle and Commuting Operators

3.1 Commutators

One of the most fundamental aspects of quantum theory, and perhaps the most radically non-classical, is the non-commutation of operators. By this we mean that if $\hat{A}$ and $\hat{B}$ are two operators (which may or may not be Hermitian, and may or may not represent physical observables), the operators $\hat{A}\hat{B}$ and $\hat{B}\hat{A}$ are not necessarily equivalent, and the difference between them is defined to be the *commutator of* $\hat{A}$ *and* $\hat{B}$*,* written with square brackets as follows:

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{3.1}$$

If $\hat{A}\hat{B} = \hat{B}\hat{A}$, so that $[\hat{A}, \hat{B}] = 0$, then $\hat{A}$ and $\hat{B}$ commute. There are cases where $\hat{A}\hat{B}$ is more closely related to $-\hat{B}\hat{A}$, and in these cases an *anti-commutator* is sometimes defined: $\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$. In this chapter we shall examine some of the important consequences of commutation and non-commutation of operators: the uncertainty principle (section 3.2), the existence of simultaneous eigenfunctions (section 3.5) and the time-development of expectation values (section 3.6). Sections 3.3 and 3.4 form a slight digression on the existence and time-development of wavefuctions with minimum uncertainty. In this section we shall look at some elementary properties of commutators.

As a first simple example we consider the commutator $[x, p_x]$, between one component of the position vector of a particle, and the corresponding component of the momentum vector. Recalling that p_x is given by $-i\hbar\frac{\partial}{\partial x}$ we obtain

$$[x, p_x] = xp_x - p_x x = -i\hbar \left(x\frac{\partial}{\partial x} - \frac{\partial}{\partial x}x \right). \tag{3.2}$$

In the evaluation of the second term we have to remember that we are dealing with an operator, so that the differential acts not just on the x but also on any following operator or wavefunction. It may be helpful to insert an arbitrary wavefunction ψ for this purpose; the second term then becomes

$$\frac{\partial}{\partial x}x\psi = \psi + x\frac{\partial \psi}{\partial x}$$

which implies that as regards the operator part we can write

$$\frac{\partial}{\partial x}x = 1 + x\frac{\partial}{\partial x}.$$

Substituting this into 3.2 we obtain

$$[x, p_x] = -i\hbar \left(x\frac{\partial}{\partial x} - 1 - x\frac{\partial}{\partial x} \right) = i\hbar.$$

Clearly the non-commutation arises because the differentiation in the p_x operator acts on the x position operator, so that if we consider a commutator of non-corresponding components, such as $[x, p_y]$, it will vanish:

$$[x, p_y] = [x, p_z] = [y, p_x] = [y, p_z] = [z, p_x] = [z, p_y] = 0$$

whereas any of the corresponding components have the same non-vanishing commutator

$$[x, p_x] = [y, p_y] = [z, p_z] = -i\hbar.$$

The factor of i in the $[x, p_x]$ commutator is at first sight surprising, but in fact this is quite a general property of commutators. If A and B are Hermitian operators, then the product operator AB is *not* necessarily Hermitian, as we discussed in section 2.2. In fact the Hermitian property implies that $AB + BA = \{A, B\}$ is Hermitian, and that $AB - BA = [A, B]$ is anti-Hermitian, that is a Hermitian operator multiplied by i. (An equivalent statement would be $i[A, B]$ is Hermitian.) In the case of the $[x, p_x]$ commutator, where the result is simply a constant, the anti-Hermitian property implies that the constant is purely imaginary, as we observe.

In section 2.1 it was asserted that (in general) operators were related in the same way as classical observables. The phenomenon of non-commutation clearly raises problems: if the classical observable Q involves a product of observables AB with non-commuting operators then the quantum operator $\hat{Q}$ can be defined in two inequivalent ways depending on whether we use $\hat{A}\hat{B}$ or

$\hat{B}\hat{A}$. For example, the component of momentum in the radial direction is $(1/r)\mathbf{r}\cdot\mathbf{p}$, but this has several different operator forms depending on the order of the factors. The fact that $AB + BA$ is Hermitian means that this is normally the correct form for a observable constructed out of a product of non-commuting operators. If the operators commute then the order is immaterial and both $\hat{A}\hat{B}$ and $\hat{B}\hat{A}$ are Hermitian operators as required.

There are a number of simple properties of commutators which can be used to simplify complex expressions, which we collect here for reference.

- $[A, A] = 0$ and $[A, B] = -[B, A]$: these follow directly from 3.1;
- Multiplication by a (complex) number c can be factored out: $[cA, B] = [A, cB] = c[A, B]$;
- Operator sums can be split up: $[A + B, C] = [A, C] + [B, C]$;
- An operator commutes with any power of itself: $[A, A^n] = 0$, and by extension any function of itself $[A, f(A)] = 0$;
- A commutator involving an operator product can be split up by adding and subtracting a term: $[A, BC] = ABC - BCA = ABC - BAC + BAC - BCA = [A, B]C + B[A, C]$;
- In the previous example, combining the same terms in a different way yields anti-commutators: $[A, BC] = ABC - BCA = ABC + BAC - BAC - BCA = \{A, B\}C - B\{A, C\}$.

3.2 The Uncertainty Principle

In this section we shall derive what is commonly known as the uncertainty principle, although obviously the fact that we are deriving it implies that the uncertainty theorem would be a more appropriate name. This is an important result which sharply distinguishes quantum mechanics from classical mechanics in that it prohibits the existence of states with well-defined values of certain pairs of non-commuting observables such as position and momentum, in contrast with the classical description where all observables simultaneously have precise values.

The theorem involves a pair of observables A and B, and an arbitrary normalised wavefunction ψ, which we shall write as a ket vector $|\psi\rangle$. The measurement postulate (section 2.4) gives the prediction of the result of a precise measurement of A or B in terms of a probability distribution, either continuous or discrete, of possible measurement outcomes, and the mean of this distribution is equal to the expectation value $\langle A\rangle$ or $\langle B\rangle$. (Note that here, and throughout this section, we are using angle brackets to denote the expectation value taken with the wavefunction ψ: $\langle A\rangle \equiv \langle\psi|A|\psi\rangle$.) The theorem constrains the degree to which this mean can be sharply-defined for two observables simultaneously, and for this purpose we need to consider the dispersion of possible results relative to the mean. We have already considered this quantity in the case of the position variable in section 1.4 where we defined the dispersion Δx in terms of its square:

$$(\Delta x)^2 = \langle\psi|(x-\langle x\rangle)^2|\psi\rangle = \langle x^2\rangle - \langle x\rangle^2.$$

This definition means that $(\Delta x)^2$ is the mean square deviation from the expectation value of many measurements of x performed on systems each with wavefunction ψ, and we shall define the positive square root, or root-mean-square deviation Δx, to be the dispersion. We can apply the definition equally well to another observable:

$$(\Delta A)^2 = \langle\psi|(A-\langle A\rangle)^2|\psi\rangle = \langle A^2\rangle - \langle A\rangle^2.$$

This defines the dispersion of the observable A in the state ψ.

The theorem gives an upper limit to the product of the dispersions of two observables, A and B

$$\Delta A\,\Delta B \geq |\langle\frac{i}{2}[A,B]\rangle|. \tag{3.3}$$

(Note that the factor of i inside the modulus sign on the right-hand side is strictly unnecessary, but is simply to remind us that the expectation value of the commutator is purely imaginary, so that $\langle i[A,B]\rangle$ is real. However it may not be positive, so that the modulus sign is not redundant.) The proof of (3.3) uses the Cauchy-Schwartz inequality, a general property of vector spaces, including the wavefunction space discussed in section 2.2. A simple proof of the inequality is given in box 3.1.

We can use the Cauchy-Schwartz inequality if we define two auxiliary ket vectors

$$|\alpha\rangle = (A-\langle A\rangle)|\psi\rangle \qquad \text{and} \qquad |\beta\rangle = (B-\langle B\rangle)|\psi\rangle.$$

We can then write $(\Delta A)^2$ in terms of $|\alpha\rangle$:

$$(\Delta A)^2 = \langle\alpha|\alpha\rangle$$

and similarly for $(\Delta B)^2$. The product of these can then be transformed using the inequality:

$$(\Delta A)^2(\Delta B)^2 \geq \langle\alpha|\beta\rangle\langle\beta|\alpha\rangle. \tag{3.4}$$

The Cauchy-Schwartz inequality is an upper bound for a inner product of two arbitrary vectors $|\psi\rangle$ and $|\phi\rangle$ in a complex vector space:

$$|\langle\phi|\psi\rangle|^2 = \langle\phi|\psi\rangle\langle\psi|\phi\rangle \leq \langle\phi|\phi\rangle\langle\psi|\psi\rangle.$$

Here the middle expression is a re-writing of the square modulus on the left-hand side using the conjugate symmetry of the inner product, and the result we wish to prove is the following inequality. Although it involves both vectors symmetrically the result is most easily proved in a slightly asymmetrical way, using a decomposition of one vector, $|\phi\rangle$, into a multiple of $|\psi\rangle$ and a vector orthogonal to $|\psi\rangle$:

$$|\phi\rangle = |\phi\rangle_\psi + |\phi\rangle_\perp = \left(\frac{\langle\psi|\phi\rangle}{\langle\psi|\psi\rangle}|\psi\rangle\right) + \left(|\phi\rangle - \frac{\langle\psi|\phi\rangle}{\langle\psi|\psi\rangle}|\psi\rangle\right).$$

Here $|\phi\rangle_\psi$ is a multiple of $|\psi\rangle$, and $|\phi\rangle_\perp$ is orthogonal to $|\psi\rangle$, as we can easily check:

$$\langle\psi|\phi\rangle_\perp = \langle\psi|\phi\rangle - \langle\psi|\phi\rangle\langle\psi|\psi\rangle/\langle\psi|\psi\rangle = 0.$$

The norm of $|\psi\rangle_\perp$, like the norm of any vector, is greater than or equal to zero:

$$0 \geq \langle\phi|\phi\rangle - 2\langle\psi|\phi\rangle\langle\phi|\psi\rangle/\langle\psi|\psi\rangle + \langle\psi|\phi\rangle\langle\phi|\psi\rangle/\langle\psi|\psi\rangle$$

which simplifies to

$$\langle\phi|\phi\rangle - \langle\psi|\phi\rangle\langle\phi|\psi\rangle/\langle\psi|\psi\rangle \geq 0.$$

This expression can be re-arranged to give the required result:

$$\langle\phi|\phi\rangle\langle\psi|\psi\rangle \geq \langle\phi|\psi\rangle\langle\psi|\phi\rangle.$$

Equality can only occur when $|\phi\rangle_\perp = 0$, that is when $|\phi\rangle$ is a multiple of $|\psi\rangle$.

Box 3.1 Cauchy-Schwartz Inequality

The right-hand side of this expression is the square modulus of the complex number

$$\langle\alpha|\beta\rangle = \langle\psi|(A - \langle A\rangle)(B - \langle B\rangle)|\psi\rangle.$$

We can expand this expression:

$$\langle\alpha|\beta\rangle = \langle\psi|AB|\psi\rangle - \langle\psi|A|\psi\rangle\langle B\rangle - \langle A\rangle\langle\psi|B|\psi\rangle + \langle A\rangle\langle B\rangle = \langle AB\rangle - \langle A\rangle\langle B\rangle.$$

The expectation values of A and B are real, but if the operators A and B do not commute then AB is not Hermitian, so that $\langle AB\rangle$ is not necessarily real. However, $\{AB + BA\}$ is Hermitian, while $[A,B]$ is anti-Hermitian. Thus if we write

$$AB = \frac{1}{2}\{A,B\} + \frac{1}{2}[A,B]$$

then this splits $\langle AB\rangle$ into its real and imaginary parts, so that we can write

$$\langle\alpha|\beta\rangle = \left(\langle\frac{1}{2}\{A,B\}\rangle - \langle A\rangle\langle B\rangle\right) - i\left(\langle\frac{i}{2}[A,B]\rangle\right)$$

where both terms in parentheses are real. The second factor in (3.4) can be treated similarly using

$$BA = \frac{1}{2}\{A,B\} - \frac{1}{2}[A,B]$$

to give

$$\langle\beta|\alpha\rangle = \left(\langle\frac{1}{2}\{A,B\}\rangle - \langle A\rangle\langle B\rangle\right) + i\left(\langle\frac{i}{2}[A,B]\rangle\right)$$

which is the complex conjugate of $\langle\alpha|\beta\rangle$ as expected. If we substitute these into (3.4) it becomes

$$(\Delta A)^2(\Delta B)^2 \geq \left(\langle\frac{1}{2}\{A,B\}\rangle - \langle A\rangle\langle B\rangle\right)^2 + \left(\langle\frac{i}{2}[A,B]\rangle\right)^2 \tag{3.5}$$

which is very close to the desired result apart from the first term on the right-hand side. Both terms on the right-hand side are positive, so it is the case that

$$(\Delta A)^2(\Delta B)^2 \geq \langle\frac{i}{2}[A,B]\rangle^2 \tag{3.6}$$

and hence $\Delta A\,\Delta B \geq |\langle\frac{i}{2}[A,B]\rangle|$. However, unless we can show that the omitted term can be zero we are not really justified in omitting it from the inequality. To put it another way, equality is true in (3.5) under the usual condition for equality in the Cauchy-Schwartz inequality, namely $|\beta\rangle = \lambda|\alpha\rangle$ for some complex λ, whereas the equality is only satisfied in (3.6) if in addition

$$\langle\frac{1}{2}\{A,B\}\rangle = \langle A\rangle\langle B\rangle, \tag{3.7}$$

and if this is not possible then the lower bound on $\Delta A\,\Delta B$ cannot be attained. We shall defer further discussion of this point for arbitrary operators A and B to the next section, where the physical significance of the term $\langle\frac{1}{2}\{A,B\}\rangle - \langle A\rangle\langle B\rangle$ is explored for the position/momentum uncertainty relation. In this case we can show that there do exist states for which (3.7) holds, and the physical interpretation makes it plausible that this is true for arbitrary operators A and B.

To discuss the significance of the uncertainty relation we shall therefore start with the position/momentum case. The true lower bound in this case is indeed

$$\Delta x\,\Delta p_x \geq |\langle\frac{i}{2}[x,p_x]\rangle = |\langle -\frac{\hbar}{2}\rangle|.$$

The constant in the expectation value can be factored out to give $|(-\hbar/2)\langle\psi|\psi\rangle| = \hbar/2$, since $|\psi\rangle$ is normalised. Thus the position-momentum uncertainty relation is

$$\Delta x\, \Delta p_x \geq \frac{\hbar}{2}. \tag{3.8}$$

This prohibits the existence of wavefunctions with arbitrarily small dispersions for both position and momentum simultaneously. If we imagine a situation in which we can create multiple copies of a system, each described by the same wavefunction, and we carry out a set of position measurements on some and momentum measurements on others, then the product of the dispersions of the two sets of measurements will never be less than the lower bound of $\hbar/2$. This means that initial conditions of the sort required by classical mechanics (position and momentum at $t = 0$) are in principle unattainable. Note that it does not preclude measurements of arbitrary accuracy of either x or p, but only the existence of states with well-defined vales of both simultaneously.

Many textbook discussions of the uncertainty principle proceed at this point to discuss sequential measurements of position and momentum. The principle does not in fact apply to such cases, because the two measurements are made on systems with different wavefunctions, since the first measurement causes a reduction of the wavefunction. It is in fact possible to derive a different lower bound for sequential (x and then p) measurements on the same system

$$\Delta x\, \Delta p \geq \hbar.$$

The superficial similarity to (3.8) is misleading as the symbols have somewhat different interpretations: Δx and Δp are now the dispersion of the measured results, which in the case of the x measurement includes a contribution from measurement error in addition to the underlying spread of values from the input state $|\psi\rangle$, and in the case of the p measurement includes the disturbance to the momentum caused by the position measurement.

We finally return to the general case described by (3.5), and consider what we obtain if we evaluate both sides for a normalisable eigenfunction of one of the operators, for example A, with eigenvalue a:

$$A|\psi\rangle = a|\psi\rangle.$$

This implies that $\langle A\rangle = a$, and hence $|\alpha\rangle = A|\alpha\rangle - a|\alpha\rangle = 0$, and hence $\Delta A = 0$, which is the expected result for an eigenfunction in which observable A has the value a with certainty. Thus in a normalisable A-eigenfunction the dispersion of A is zero. On the right-hand side we obtain $\langle AB\rangle = a\langle B\rangle$ and hence

$$\langle \frac{1}{2}\{A, B\}\rangle = \langle A\rangle\langle B\rangle \qquad \text{and} \qquad \langle \frac{i}{2}[A, B]\rangle = 0$$

so that in a normalisable A-eigenfunction condition 3.7 is always true and the expectation value of all commutators with A vanish. The consequence of these two results is that the uncertainty principle becomes trivial: $0 = 0$. A slightly more interesting consequence is that a constant commutator, $[A, B] = iC$ for some real non-zero C, is inconsistent with the existence of an A-eigenfunction, since the expectation value of C is just is the non-zero C, whereas for an eigenfunction the commutator has zero expectation value as we have just seen. Thus the $[x, p_x] = i\hbar$ commutator prohibits the existence of normalisable eigenfunctions of either x or p_x. We have already observed the absence of normalisable x eigenfunctions in section 2.3, and we shall consider the momentum eigenfunctions in the section 3.4.

A final consequence of the uncertainty principle is that there appears to be no lower bound on the dispersion product of commuting operators. This has interesting implications which we shall consider further in section 3.5.

3.3 The Minimum Uncertainty Wavefunction

This section and the next constitute a slight digression in which we shall find what sort of wavefunction achieves the lower bound in the uncertainty principle for x and p. We shall consider both the forms given in the previous section, the extended form (3.5):

$$(\Delta x)^2 \, (\Delta p)^2 - \left(\frac{1}{2}\langle xp + px\rangle - \langle x\rangle\langle p\rangle\right)^2 = \left(\frac{\hbar}{2}\right)^2 \tag{3.9}$$

and the usual form (3.6):

$$\Delta x \, \Delta p = \frac{\hbar}{2}. \tag{3.10}$$

This will lead on to a discussion of the meaning of the extra term in (3.9).

We start with wavefunctions satisfying the extended uncertainty principle (3.9). This inequality is solely based on the use of the Cauchy-Schwartz inequality, which becomes an equality when the two kets involved are proportional to each other; that is, in the notation of section 3.2, when $|\alpha\rangle = \lambda|\beta\rangle$ for some constant λ (possibly complex). Taking the case of operators x and p this becomes

$$(\hat{x} - \langle x\rangle)\,\psi = \lambda\,(\hat{p} - \langle p\rangle)\,\psi. \tag{3.11}$$

Bearing in mind that

$$\langle x\rangle = \int \psi^* \hat{x} \psi \, d\tau$$

and similarly for $\langle p \rangle$, (3.11) appears to be a non-linear equation, with ψ appearing both explicitly and under the integral sign. Fortunately ths is not the case; if we re-write the equation as

$$(\hat{x} - X)\,\psi = \lambda\,(\hat{p} - P)\,\psi \tag{3.12}$$

where X and P are constants, then it can easily be shown (**??**) that for any normalisable solution $X = \langle x \rangle$ and $P = \langle p \rangle$. Equation (3.12) is therefore the equation we have to solve. Replacing the operator $\hat{p}$ with $-i\hbar\partial/\partial x$, and $\hat{x} = x$ we obtain

$$\frac{d\psi}{dx} = -\frac{(x-X)}{i\lambda\hbar}\psi - \frac{iP}{\hbar}\psi = -\left(\frac{x-\chi}{s}\right)\psi, \tag{3.13}$$

where in the second form we have defined $s = i\lambda\hbar$ and $\chi = X + isP/\hbar$. This is a linear first-order equation, and the general solution is

$$\psi(x) = A\,\exp -\frac{(x-\chi)^2}{2s}. \tag{3.14}$$

This is a very compact form, but because both χ and s are complex it is not very obvious what shape the wavefunction has. We need to separate real and imaginary parts in the exponent to obtain the modulus and phase of the wavefunction explicitly. The modulus then tells us where the probability is concentrated, and the phase tells us about the motion. To this end we partially expand the exponent, substituting for χ:

$$\frac{(x-\chi)^2}{2s} = \frac{(x-X)^2}{2s} - \frac{iP(x-X)}{\hbar} - \frac{sP^2}{2\hbar^2}.$$

Here the middle term is imaginary, while the first and last terms are complex if s is complex. We introduce the real and imaginary part of s explicitly: $s = s_1 + is_2$, so that

$$\frac{1}{s} = \frac{s_1}{s_1^2 + s_2^2} - i\frac{s_2}{s_1^2 + s_2^2}.$$

These enable us to complete the separation of real and imaginary parts in the exponent:

$$\psi(x) = A\,\exp i\left(\frac{s_2(x-X)^2}{2(s_1^2+s_2^2)} + \frac{P(x-X)}{\hbar} + \frac{s_2P^2}{\hbar^2}\right)\exp -\left(\frac{s_1(x-X)^2}{2(s_1^2+s_2^2)} - \frac{s_1P^2}{\hbar^2}\right). \tag{3.15}$$

This form is known as a Gaussian wavepacket, since the probability density is Gaussian in shape:

$$\psi^*\psi = |B|^2 \exp -\frac{(x-X)^2}{a^2}$$

where $B = A\exp\left(s_1P^2/\hbar^2\right)$ and $a^2 = (s_1^2 + s_2^2)/s_1$. (Obviously a requirement for the solution to be normalisable is that the coefficient of $(x-X)^2$ in the exponent is negative, so we have assumed $s_1 > 0$.)

The modulus of B is determined by the normalisation condition:

$$\int_{-\infty}^{\infty} \psi^* \psi \, dx = |B|^2 \sqrt{\pi} a = 1. \tag{3.16}$$

(Integrals involving Gaussian functions are discussed in appendix A, section A.1.) The Gaussian form makes it obvious that the mean position is, as expected, $\langle x \rangle = X$, since the probability distribution is symmetric about $x = X$. The width of the packet is controlled by a;

$$(\Delta x)^2 = \int_{-\infty}^{\infty} \psi^* (x - X)^2 \psi \, dx = \frac{a^2}{2} = \frac{s_1^2 + s_2^2}{2 s_1}. \tag{3.17}$$

The Gaussian wavepacket is thus located at $x = X$ with uncertainty $\Delta x = a/\sqrt{2}$.

The momentum uncertainty $(\Delta p)^2$ can be derived from $(\Delta x)^2$ as follows:

$$(\Delta p)^2 = \int_{-\infty}^{\infty} \psi^* (\hat{p} - P)^2 \psi \, dx = \int_{-\infty}^{\infty} |(\hat{p} - P)\psi|^2 \, dx$$

where we have used the Hermitian property of $\hat{p} - P$. But the defining equation tells us that $(\hat{p} - P)\psi = i\hbar(\hat{x} - X)\psi/s$, so that

$$(\Delta p)^2 = \frac{\hbar^2}{|s|^2} \int_{-\infty}^{\infty} |(\hat{x} - X)\psi|^2 \, dx = \frac{\hbar^2}{s_1^2 + s_2^2} (\Delta x)^2 = \frac{\hbar^2}{2 s_1}. \tag{3.18}$$

We can also evaluate the expectation value of $(xp + px)/2$ using a similar trick, obtaining

$$\frac{1}{2}\langle xp + px \rangle - \langle x \rangle \langle p \rangle = \frac{\hbar s_2}{s_1^2 + s_2^2} (\Delta x)^2 = \frac{\hbar s_2}{2 s_1}. \tag{3.19}$$

Putting together (3.17), (3.18) and (3.19) we obtain, as expected, the defining minimum uncertainty property:

$$(\Delta x)^2 (\Delta p)^2 - \left(\frac{1}{2}\langle xp + px \rangle - \langle x \rangle \langle p \rangle \right)^2 = \frac{\hbar^2}{4} \left(\frac{(s_1^2 + s_2^2}{s_1^2} - \frac{s_2^2}{s_1^2} \right) = \frac{\hbar^2}{4}. \tag{3.20}$$

Thus any Gaussian wavepacket, with any finite values of X, P and s_2, and any positive value of s_1 is a minimum uncertainty wavepacket in this sense.

However the usual form of the uncertainty principle, (3.10), requires in addition that (3.19) vanishes, which obviously entails $s_2 = 0$. Thus the true minimum uncertainty wavefunction requires that s is real, $s = s_1$. Many derivations of the uncertainty principle make this assumption at the outset, and thus never obtain the extended form of the principle. The Gaussian wavepacket (3.15) is then simpler:

$$\psi(x) = \left(\frac{1}{\pi s_2} \right)^{1/4} e^{iP(x-X)} e^{-(x-X)^2/2 s_2}. \tag{3.21}$$

This has three factors: the normalisation constant, the phase term and the modulus term. The modulus term and normalisation constant are still Gaussian, and centred on the point $x = X$, but now with $a^2 = s_1$, giving $\Delta x = \sqrt{s_1/2}$. However the phase term is significantly different, having lost the quadratic term, and this change alters the momentum dispersion: $\Delta p = \hbar/\sqrt{2s_1}$. The product of these dispersions is $\hbar/2$ as required, and any wavepacket with this form, for any finite values of X and P, and any positive value of s_1, is a true minimum uncertainty wavefunction.

We now briefly consider the significance of the vanishing or otherwise of $\frac{1}{2}\langle xp + px\rangle - \langle x\rangle\langle p\rangle$. We recall that in section 3.1 we noted that a product of Hermitian operators AB is not in general Hermitian, but that the symmetrized product $AB+BA$ is, and is normally the appropriate quantum form for the operator for a classical product. Thus $(1/2)(xp+px)$ is simply a Hermitian form of the classical product xp. The non-vanishing of the whole expression thus implies that the expectation value of this product, xp, is *not* equal to the product of the separate expectation values of x and p. In a classical probability distribution this would indicate a degree of correlation between the variables x and p. The formalism of quantum mechanics requires us to make a rather complicated statement: measurement of the observable xp would have a range of possible outcomes, the expectation value of which would not be equal to the product of the expectation values of x and p if measured in separate experiments on systems with the same wavefunction. The fact that measurement changes the wavefunction always introduces long circumlocutions of this type; however this is saying much the same as that in a system with a non-zero value of this term there is correlation between x and p.

As we noted above, the significant difference between (3.15) and (3.21) is the absence of the quadratic term in the phase in (3.21). We saw in section 2.1 that the momentum expectation value is related an average value of the gradient of the wavefunction phase, and in the absence of the quadratic term this gradient is a constant. We can thus see exactly how the correlation between x and p manifests itself in the wavefunction: a Gaussian wavepacket with non-zero s_2 has a quadratic term in the wavefunction phase, which implies that different spatial parts of the wavefunction have different momenta, which leads to the non-vanishing of the correlation $\frac{1}{2}\langle xp+px\rangle - \langle x\rangle\langle p\rangle$. We have therefore linked the physical interpretation of the extra term in the extended uncertainty principle with the corresponding difference in the wavefunction.

3.4 The Free Particle with Minimum Uncertainty

In this section we shall find how a a minimum uncertainty wavefunction evolves in time in the case of a free particle. However we shall start with a brief look at the free particle in classical

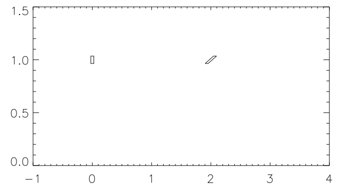


Figure 3.1: *Phase Space for the Free Particle*

mechanics, because there is a relevant aspect which may well be unfamiliar, which is the motion in *phase space*. Phase space is a multi-dimensional space labelled with co-ordinate axes for both position and momentum; for a free particle it thus has six dimensions, while a free particle moving in one dimension has a two-dimensional phase space, with points labelled by x and p. The important feature of phase space is that a single point represents both the configuration and motion of the whole system. Consider a free particle located at $x = 0$ at time $t = 0$, and having momentum p. Obviously at $t = 0$ the representative point in phase space is $(0, p)$, and at time t it will have moved to $(pt/m, p)$, because the particle has moved to $x = pt/m$ but its momentum is still p. Now consider what happens to the classical uncertainty in these quantities. Figure 3.1 shows a rectagular uncertainty box surrounding the phase space point $(0, p)$, with uncertainty d in position and q in momentum. We shall suppose that the classical probability distribution is uniform within these limits and zero outside. Thus at $t = 0$ the representative point has a uniform probability of being found anywhere within the rectangle. After time t the corners of the box have moved to $x = (p \pm q/2)t/m \pm d/2$, keeping the same momentum, producing the parallelogram uncertainty box. Direct calculation shows that the area of the uncertainty box has not changed: it was qd at time $t = 0$, and the parallelogram uncertainty box at time t has area qd as well.

Given the classical uncertainty we can also compute classical dispersion statistics for these probability distributions. Direct calculation gives the following results at time $t = 0$.

$$\begin{array}{ll} \langle x \rangle = 0 & \langle p \rangle = p \\ \langle x^2 \rangle = d^2/12 & \langle p \rangle = p^2 + q^2/12 \\ (\Delta x)^2 = d^2/12 & (\Delta p)^2 = q^2/12 \\ \langle xp \rangle = 0 & \end{array} \tag{3.22}$$

With rather more effort the following results can be derived for time t.

$$\begin{aligned} \langle x \rangle &= pt/m & \langle p \rangle &= p \\ \langle x^2 \rangle &= (pt/m)^2 + (q^2t^2/12m^2) + d^2/12 & \langle p \rangle &= p^2 + q^2/12 \\ (\Delta x)^2 &= (q^2t^2/12m^2) + d^2/12 & (\Delta p)^2 &= q^2/12 \\ \langle xp \rangle &= p^2t/m + q^2t/12m \end{aligned} \tag{3.23}$$

We can combine then combine these dispersion statistics in the form of the extended uncertainty principle to show that

$$(\Delta x)^2 (\Delta p)^2 - (\langle xp \rangle - \langle x \rangle \langle p \rangle)^2 = \text{constant, independent of } t. \tag{3.24}$$

To summarise, we have shown that both the phase space area represented by the classical uncertainty in position and momentum, and the combination of classical dispersion statistics in the form of the extended uncertainty principle remain constant during the motion. They also change in such a way that the initially uncorrelated uncertainties in position and momentum become correlated, as indicated by the skewed shape, and the non-zero value of $\langle xp \rangle - \langle x \rangle \langle p \rangle$. The reason for the emerging correlation is dynamically obvious: the uncertainty in momentum is an uncertainty in velocity, which creates a subsequent and correlated uncertainty in position. These two conservation laws, of area and the uncertainty product, are in fact essentially the same. Phase space area only has a straightforward meaning with the rather artificial uniform probability distribution we are using, whereas the combination of dispersion statistics is a generalization of the concept of 'area covered by the distribution in phase space' (or strictly the square of the area) which can be evaluated for any probability distribution.

Although we have only shown these results for the free particle, the area conservation holds true for any system evolving under Hamilton's equations of motion, but the conservation of the uncertainty product only approximately. Some developments along these lines are suggested in problems **??**. In the light of these classical results, the extended form of the uncertainty principle appears to act as a quantum-mechanical constraint on the possible values of the classical constant in (3.24): it has to be greater than or equal to $\hbar^2/4$. The standard method of classical mechanics is to specify a system by its initial conditions, and the uncertainty principle totally undermines this as a procedure with arbitrary accuracy. Conversely, the classical results also suggest that the quantum-mechanical constant in the extended form of the uncertainty principle will be conserved in the subsequent motion, a significant clue which we shall use in finding the time-development of the minimum uncertainty wavepacket. (It turns out that, while this is true for the free particle, this result does *not* generalize to systems with general Hamiltonians even hough the corresponding classical result is still true!)

We next examine wavefunctions for the free particle. The Hamiltonian is simply $H = p^2/2m$, so that the time-dependent Schrodinger equation for the free particle is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = i\hbar\frac{\partial\Psi}{\partial t} \tag{3.25}$$

Since H is independent of time we can follow the standard method of solution by separation of variables described in chapter 1, according to which the eigenfunctions will satisfy the time-independent Schrodinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2u_k}{dx^2} = E_k u_k(x).$$

This has real solutions of the form $u_k = A\cos kx$ or $v_k = B\sin kx$, or complex solutions of the form $w_k = e^{ikx}$, where $E_k = \hbar^2k^2/2m$. In the real case, k can be chosen to be positive (since solutions with negative k are linearly dependent on solutions with positive k), while in the complex case the solutions with positive and negative k are independent, so in either case we have two solutions for each E. Following the normal method we now look for solutions satisfying boundary conditions, and we find that there are none: all solutions continue to oscillate indefinitely, so that no solutions satisfy zero boundary conditions at infinity. Furthermore, for the same reason no solutions are normalizable.

A very similar situation arose when we tried to find eigenfunctions of x in section 2.4: eigenfunctions can be found for eigenvalues forming a continuous rather than a discrete set, and no eigenfunctions are normalisable to unity. We follow the same approach and consider the eigenfunctions as a basis which is not physically realisable, but from which we can make physically realisable wavefunctions by superposition. The appropriate normalisation is then δ-function normalisation. However there is an additional complexity in this case, which is that we have found not one but two eigenfunctions for each eigenvalue: either the two real functions u_k and v_k, or the two complex functions w_k and w_{-k}. This is an example of degeneracy, which we shall discuss in more detail in the next section, but for the moment we simply note that if we pick the functions w then they are also eigenfunctions of the momentum p:

$$\hat{p}w_k(x) = -i\hbar\frac{d}{dx}e^{ikx} = \hbar k\, w_k(x). \tag{3.26}$$

This immediately gives us an interpretation of the two solutions for each energy: they represent a particle with momentum either $p = \hbar k$ or $-\hbar k$, in each case having the same kinetic energy

$\hbar^2 k^2/2m$. We therefore choose to label the eigenfunctions by the momentum eigenvalue p rather than k, and we define our set of eigenfunctions as

$$w(x,p) = C\, \exp ipx/\hbar \tag{3.27}$$

where we have replaced the suffix label by an argument, since the p eigenvalue is continuous rather than discrete. The normalisation requirement is

$$\int_{-\infty}^{\infty} w(x,p)^*\, w(x,p')\, dx = \delta(p-p'), \tag{3.28}$$

which expresses the fact that every eigenfunction is orthogonal to every other, but that all have infinite normalisation. (The absence of normalisable eigenfunctions of $\hat{p}$ was predicted in the discssion of the uncertainty principle in section 3.2, on the basis of its commutator with x.) The constant C has to have the value $(2\pi\hbar)^{-1/2}$ (see problem **??**). These eigenfunctions represent a particle whose location is totally unknown (uniform probability density filling all space) but with momentum exactly p. We can use these eigenfunctions in the same way as any other set of eigenfunctions, for example to predict the possible results of a momentum measurement of a particle with wavefunction ψ, as described in section 2.4. To do this have to represent ψ as a superposition of the w (see Table 2.1):

$$\psi(x) = \int \phi(p)\, w(x,p)\, dx$$

where the coefficients of the superposition are the function $\phi(p)$, and are given by

$$\phi(p) = \int w^\star(x,p)\psi(x)\, dx.$$

The probability of measuring the momentum to be in the interval p, $p+dp$ is given by $|\phi(p)|^2\, dp$, and we can use this probability distribution to find $\langle p\rangle$, $\langle p^2\rangle$ and similar expectation values, as an alternative to integrating over the wavefunction with the appropriate operator. There is thus a symmetry between the use of $\psi(x)$ to find expectation values depending on x and the use of $\phi(p)$ to find expectation values depending on p, so $\phi(p)$ is called the wavefunction in the momentum representation.

If we multiply by the usual time-dependent T depending on the eigenvalue $E(p) = p^2/2m$ we obtain the complete set of time-dependent eigenfunction solutions of (3.25):

$$\Psi(x,p,t) = \frac{1}{\sqrt{2\pi\hbar}} e^{i(px - p^2 t/2m)/\hbar}. \tag{3.29}$$

One approach to the minimum uncertainty problem is now to superpose these eigenfunctions at $t=0$ to obtain the minimum uncertainty wavefunction

$$\Psi_{\text{min}}(x,0) = \int \phi(p)\, w(x,p)\, dx$$

and then put back in the time dependence to find out how it evolves in time:

$$\Psi_{\min}(x,t) = \int \phi(p)\, \Psi(x,p,t)\, dx.$$

This approach is taken further in the problems, but the integrals involved are not straightforward.

We shall take a more direct approach, using the clue offered above that a minimum-uncertainty wavefunction in the extended sense should remain so. We found in section 3.3 that these could be written in the form

$$\psi(x) = A \exp - \left(\frac{(x-\chi)^2}{2s} \right)$$

and if it is to remain a minimum-uncertainty wavefunctions then the only possible time-dependence is that the three coefficients A, s and χ are functions of time. We can thus form both sides of the time-dependent Schrodinger equation (3.25) and equate them. If we differentiate the defining equation (3.12) we find the second derivative with respect to x:

$$\frac{\partial^2 \psi}{\partial x^2} = \left(\frac{x-\chi}{s} \right)^2 \psi - \frac{1}{s}\, \psi$$

while if we differentiate with respect to t we find

$$\frac{\partial \psi}{\partial t} = \left(\frac{1}{A}\frac{dA}{dt} \right) \psi + \left(\frac{(x-\chi)^2}{2s^2}\frac{ds}{dt} \right) \psi + \left(\frac{(x-\chi)}{s}\frac{d\chi}{dt} \right) \psi.$$

The Schrodinger equation thus takes the form:

$$-\frac{\hbar^2}{2m} \left(\frac{(x-\chi)^2}{s^2} - \frac{1}{s} \right) \psi = i\hbar \left(\frac{1}{A}\frac{dA}{dt} + \frac{(x-\chi)^2}{2s^2}\frac{ds}{dt} + \frac{(x-\chi)}{s}\frac{d\chi}{dt} \right) \psi. \tag{3.30}$$

We now equate coefficients of powers of $x - \chi$ to obtain

$$\frac{ds}{dt} = i\frac{\hbar}{m} \tag{3.31}$$

$$\frac{d\chi}{dt} = 0 \tag{3.32}$$

$$\frac{1}{A}\frac{dA}{dt} = -\frac{1}{2s}\frac{i\hbar}{m} = -\frac{1}{2s}\frac{ds}{dt} \tag{3.33}$$

Equation (3.32) tells us directly that χ is constant. Equation (3.31) implies that the imaginary part of s is changing linearly with time, while the real part is constant. There is thus a unique time t_0 at which the imaginary part vanishes, so that we can write $s = s_1 + i\hbar(t - t_0)/m$. Finally, (3.33) tells us that A is inversely proportional to $\sqrt{s}$, $A = C/\sqrt{s}$, where the constant C is determined by normalisation and turns out to be

$$C = \left(\frac{s_1}{\pi} \right)^{1/4} \exp(-s_1 P^2/\hbar^2).$$

$c/\sqrt{s}$ differs from the constant $|A|$ found in the previous section only by a time-dependent phase, which gives an extra $\pi/2$ of phase change between $t \ll t_0$ and $t \gg t_0$. The complete time-dependent minimum uncertainty wavepacket is thus

$$\psi(x,t) = \frac{C}{\sqrt{s}} \exp - \left(\frac{(x-\chi)^2}{2s} \right) \quad \text{where} \quad s = s_1 + \frac{i\hbar}{m}(t - t_0), \quad \chi = X + \frac{isP}{\hbar}. \tag{3.34}$$

This confirms the suggestion from the classical solution that a free particle minimum-uncertainty wavepacket in the extended sense remains one during subsequent time evolution.

We shall briefly consider the significance of some of the last few results, starting with the constant χ. This is complex, $\chi = \chi_1 + i\chi_2$, and if we substitute the explicit form of s into the equation for χ we find $\chi = (X - (P/m)(t - t_0)) + is_1P/\hbar$. Thus the imaginary part of χ is $\chi_2 = s_1P/\hbar$, which, given that s_1 and χ are constant, implies that P is constant, as we would expect for a free particle. The real part of χ is $\chi_1 = X - (P/m)(t - t_0)$, which we can re-arrange to be an equation for X as

$$X = \chi_1 + \frac{P}{m}(t - t_0).$$

Thus X, the expectation value of the position x, is time-dependent, moving with speed P/m, the classical particle velocity, and χ_1 is the value of X at time $t = t_0$, the time at which s is real.

The constant s controls the width of the wavepacket in position and momentum, as we found in the previous section; in particular the imaginary part s_2 introduces correlation between x and p, and means that the wavepacket is only minimum uncertainty in the extended sense. The fact that there is a time at which s_2 vanishes therefore implies that the true minimum-uncertainty wavefunction and the extended minimum-uncertainty wavefunction represent the same system at different times, and the correlation represented by s_2 has built up from the time t_0 when it was zero. This is very reminiscent of the classical situation we described above, and we can make the two sets of results appear identical. We now bring together the dispersion statistics we have found. In the quantum case, equations (3.17), (3.18) and (3.19), we put $t_0 = 0$ to match the classical case, $s_1/2 = \Delta x^2(0)$ and $\hbar^2/2s_1 = \Delta p^2(0)$. In the classical case, (3.23), we put $q^2/12 = \Delta x^2(0)$ and $p^2/12 = \Delta p^2(0)$. In either case we find the following:

$$\begin{aligned} \Delta x^2(t) &= \Delta x^2(0) + (\Delta p^2(0)t^2/m^2) && (3.35) \\ \Delta p^2(t) &= \Delta p^2(0) && (3.36) \\ \frac{1}{2}\langle xp + px\rangle - \langle x\rangle\langle p\rangle &= (\Delta p^2 t/m) && (3.37) \end{aligned}$$

The growth in the position uncertainty and the emergence of correlation are entirely classical given the non-zero momentum uncertainty: the only non-classical feature in this problem is the linkage between $\Delta x(0)$ and $\Delta p(0)$ represented by the uncertainty principle.

3.5 Simultaneous Eigenfunctions

The uncertainty principle indicates a connection between a non-vanishing commutator, $[\hat{A},\hat{B}] \neq 0$, and a necessary uncertainty in the value of the corresponding observables A and B, whereas if the commutator vanishes, $[\hat{A},\hat{B}] = 0$, the uncertainty principle places no lower limit n the accuracy with which we can predict their values. In this section we shall discuss a theorem which addresses this case.

The theorem states the complete equivalence of three apparently distinct statements:

(a) The operators $\hat{A}$ and $\hat{B}$ commute, $[\hat{A},\hat{B}] = 0$;

(b) $\hat{A}$ and $\hat{B}$ have a complete set of simultaneous eigenfunctions;

(c) The observables A and B can be measured compatibly.

Statement (a) appears to be about operators, (b) about their eigenfunctions, and (c) about the measurement of observables. The phrase simultaneous eigenfunctions in statement (b) refers to a set of eigenfunctions ϕ_n which are eigenfunctions of both $\hat{A}$ and $\hat{B}$:

$$\hat{A}\phi_n = a_n\phi_n \qquad \text{and} \qquad \hat{B}\phi_n = b_n\phi_n.$$

The word compatibly in statement (c) refers to the possibility that a measurement of B may change the wavefunction following a prior measurement of A in such a way that a second A measurement yields a different value. In this case A and B can *not* be measured compatibly; if they can be measured compatibly then any wavefunction change induced by the B measurement is not such as to alter the value of A already established.

The complete equivalence of (a), (b) and (c) means in principle that any one of them can be used to deduce the other two. Our strategy in proving this is to start by showing the equivalence of (b) and (c), and then discuss the relation of (b) and (a). The definition of the word compatibly, which obviously involves the quantum theory of measurement discussed in section 2.4, provides the clue as to the equivalence of (b) and (c). The first measurement of A leaves the system in an eigenfunction of $\hat{A}$, while the following measurement of B leaves the system in an eigenfunction of $\hat{B}$. If the final repeated A measurement is still bound to yield the same result as the first measurement then the $\hat{B}$ eigenfunction must also be an A eigenfunction, and if this is so for any possible measurement outcome of the A and B measurements then there must be a complete set of such states. This proves that (c) implies (b). The converse is also straightforward: if there is a complete set of simultaneous eigenfunctions then the wavefunction following the B measurement will be formed from those eigenfunctions whose A and B eigenvalues correspond to the measured ones, and the outcome of the final A measurement will indeed be the same as outcome of the first A measurement, which s the requirement for compatible measurement. Thus statements (b) and (c) are equivalent.

We can also show that (b) implies (a). We can expand an arbitrary wavefunction ψ in terms of the complete set of simultaneous eigenfuctions:

$$\psi = \sum_n c_n \phi_n$$

and if we operate on this with, for example, $\hat{A}$ we obtain

$$\hat{A}\psi = \sum_n c_n a_n \phi_n.$$

The effect of operating on ψ wth the commutator is thus

$$\hat{A}\hat{B}\psi - \hat{B}\hat{A}\psi = \sum_n c_n (a_n b_n - b_n a_n)\phi_n = 0$$

since the eigenvalues are just numbers and hence commute. Thus the effect of operating with the commutator on any function is zero, and so the commutator itself is just the zero operator.

To complete the proof we just need to show that (a) implies (b). This is slightly more difficult. We start with one of the eigenstates of one of the commuting operators, $\hat{A}$:

$$\hat{A}\phi_n = a_n \phi_n$$

and we operate on this equation with $\hat{B}$:

$$\hat{B}\hat{A}\phi_n = a_n \hat{B}\phi_n.$$

But by hypothesis $\hat{B}\hat{A} = \hat{A}\hat{B}$ so we find

$$\hat{A}\,\hat{B}\phi_n = a_n\,\hat{B}\phi_n \tag{3.38}$$

which implies that $\hat{B}\phi_n$ is also an eigenfunction of $\hat{A}$ wth eigenvalue a_n. At this point there are two possibilities we must consider. The first is that there is only one eigenfunction of $\hat{A}$ with this eigenvalue. Most of the cases we have looked at so far are of this sort, but this is because we are mostly solving one-dimensional problems; in general this situation is by no means inevitable. However in this case the function $\hat{B}\phi_n$ must be essentially the same function: it can differ only by a multiplicative constant:

$$\hat{B}\phi_n = b_n\phi_n.$$

But this says that ϕ_n is also an eigenfunction of $\hat{B}$, and b_n is its eigenvalue. (Incidentally this shows that the multiplicative constant must in fact be real because it is the eigenvalue of a Hermitian operator.)

The other possibility we must consider is that there are several eigenfunctions of $\hat{A}$ with the same eigenvalue. This phenomenon is known as degeneracy, and adjective degenerate is applied to the set of eigenfunctions with the same eigenvalue. (The case we have just considered is therefore described as non-degenerate.) We found an example of degeneracy in the previous section when discussing energy eigenfunctions for a free particle: there were two eigenfunctions for every eigenvalue. This case illustrated an important feature of degenerate eigenfunctions: any linear superposition of them is also an eigenfunction. If ϕ_1 and ϕ_2 are eigenfunctions of $\hat{A}$ with eigenvalue a

$$\begin{aligned}\hat{A}\phi_1 &= a\phi_1\\ \hat{A}\phi_2 &= a\phi_2\end{aligned}$$

then any linear combination of eigenfunctions $c_1\phi_1 + c_2\phi_2$ is also an eigenfunction with eigenvalue a. In the case of the free particle we could take $\phi_1 = e^{ikx}$ and $\phi_2 = e^{-ikx}$ as eigenfunctions with eigenvalue $\hbar^2k^2/2m$; the two linear combinations

$$\begin{aligned}\phi_c = \cos kx &= \frac{1}{2}\phi_1 + \frac{1}{2}\phi_2\\ \phi_s = \sin kx &= \frac{-i}{2}\phi_1 + \frac{i}{2}\phi_2\end{aligned}$$

are also eigenfunctions with the same eigenvalue.

The other important property of degenerate eigenfunctions is that they are not necessarily orthogonal. The orthogonality of eigenfunctions of a Hermitian operator depends on them having distinct eigenvalues (see secction 2.2), and so it does not apply to degenerate eigenfunctions. To construct a complete orthonormal basis of eigenfunctions we therefore have to know how many of this infinite number of distinct eigenfunctions we can include. It can be shown that in any particular case there is a fixed number of linearly independent eigenfunctions belonging to any eigenvalue, and these can be chosen to be orthogonal. To continue the example, the functions ϕ_1

and ϕ_c are linearly independent, and ϕ_2 and ϕ_s can be expressed in terms of them, but they are not orthogonal. Either the pair ϕ_1 and ϕ_2, or the pair ϕ_c and ϕ_s can be chosen as members of an orthogonal basis. There is thus an additional degree of freedom about the basis in the case of degeneracy; the only choice we have to make for a non-degenerate eigenfunction is the arbitrary overall phase factor, but in the case of degeneracy we can select any orthogonal combination of the eigenfunctions.

To return to our proof that commuting operators have simultaneous eigenfunctions, we now suppose that all the $\hat{A}$-eigenvalues a_m, $a_{m+1} \dots a_n$ are equal, so that the $\hat{A}$-eigenfunctions ϕ_m to ϕ_n are degenerate, and that these are the the only orthogonal eigenfunctions with this eigenvalue. Under these circumstances the result proved above (3.38), that if ϕ is an eigenstate of A then so is $\hat{B}\phi$, does not now imply that $\hat{B}\phi$ is the same as ϕ, but instead that it is a linear combination of the basis set of $\hat{A}$-eigenfunctions, and this is equally true for all the functions $\hat{B}\phi_m$ to $\hat{B}\phi_n$:

$$\hat{B}\phi_q = \sum_{p=m}^{n} b_{pq}\phi_p \quad \text{for } q = m,\, m+1\dots, n. \tag{3.39}$$

As with any other wavefunction we can find the expansion coefficients b_{pq} by taking the inner product with the basis set (see section 2.3):

$$b_{pq} = \int \phi_p^{\star}\hat{B}\phi_q \, d\tau. \tag{3.40}$$

We now consider the action of $\hat{B}$ on a linear combination of the $\hat{A}$-eigenfunctions, by multiplying these equations by constants c_q and summing:

$$\hat{B}\sum_{q=m}^{n} c_q\phi_q = \sum_{p=m}^{n}\left(\sum_{p=m}^{n} b_{pq}c_q\right)\phi_p = \sum_{p=m}^{n} d_p\phi_p.$$

At this point it is extremely useful to adopt a matrix notation. If we write the coefficients c_q as a column vector

$$\mathbf{c} = \begin{pmatrix} c_m \\ c_{m+1} \\ \vdots \\ c_n \end{pmatrix}$$

then (3.40) says that the operation of $\hat{B}$ on the function with coefficients $\mathbf{c}$ produces a function with coefficients $\mathbf{d}$ such that

$$\mathbf{d} = \mathbf{Bc} \quad \text{where } \mathbf{B} = \begin{pmatrix} b_{mm} & \dots & b_{mn} \\ \vdots & & \vdots \\ b_{nm} & \dots & b_{nn} \end{pmatrix}.$$

This is our first example of a connection between matrices and our use of ideas from linear vector spaces, but the connection is very deep, and many problems have a matrix formulation. In this case the Hermitian property of operator $\hat{B}$ implies that matrix $\mathbf{B}$ is also Hermitian. (A Hermitian matrix is one where $\mathbf{B}^T = \mathbf{B}^\star$.) But it is well known that a Hermitian matrix has a compete set of eigenvectors, so that there exist a set of linear coefficients vectors $\mathbf{c}^{(r)}$ for which $\mathbf{B}\mathbf{c}^{(r)} = B^{(r)}\mathbf{c}^{(r)}$ where $B^{(r)}$ are the eigenvalues of $\mathbf{B}$. So finally we have proved that among the eigenfunctions of $\hat{A}$ with a given eigenvalue we can always find a basis whose members are also eigenfunctions of B.

This completes our discussion of the equivalence of the three statements above, except to remark that the theorem is of extraordinary importance in atomic physics. Typically we are trying to find eigenfunctions of a difficult operator $\hat{H}$, and our task is considerably simplified if we know that we can restrict ourselves to eigenfunctions of some much simpler operator $\hat{A}$ because $[\hat{A}, \hat{H}] = 0$.

3.6 Dynamics of Expectation values

Chapter 4

The Harmonic Oscillator

4.1 Introduction and Classical Treatment

The harmonic oscillator is one of the most widely studied systems in elementary physics, and it plays a correspondingly important rôle in quantum mechanics. The importance accorded to it is not altogether misplaced, as a number of real quantum systems can be modelled with more or less accuracy as harmonic oscillators. In this section we briefly review the classical results, and in section 4.2 we solve the Schrodinger time-independent wave equation to find eigenfunctions for the oscillator. In section 4.3 we look at a purely algebraic approach to finding eigenstates and eigenvalues, and in section 4.4 we find an interesting solution of the time-dependent Schrodinger equation.

The harmonic oscillator is the name given to a (one-dimensional) system subject to a restoring force which is linear in the displacement from equilibrium, $F = -kx$. In quantum mechanics we need the potential function from which this is derived, which, to within an arbitrary additive constant, is $V(x) = \frac{1}{2}kx^2$. If the system consists of a particle of mass m, then the angular frequency of the oscillation turns out to be $\omega = \sqrt{k/m}$, and we therefore choose to write the potential in terms of ω and not k:

$$V(x) = \frac{1}{2}m\omega^2 x^2. \tag{4.1}$$

Application of Newton's second law of motion then gives

$$m\frac{d^2x}{dt^2} = -\frac{dV}{dx}.$$

If we multiply by the velocity, both terms become perfect time differentials:

$$m\frac{d^2x}{dt^2}\frac{dx}{dt}+\frac{dV}{dx}\frac{dx}{dt}=\frac{d}{dt}\left\{\frac{1}{2}m\left(\frac{dx}{dt}\right)^2+V(x)\right\}=0.$$

Integrating with respect to time, we arrive at a statement of energy conservation, so we call the constant of integration E:

$$\frac{1}{2}m\left(\frac{dx}{dt}\right)^2+V(x)=E$$

which we can re-arrange as

$$1=\frac{\frac{dx}{dt}}{\sqrt{2(E-V(x))/m}}.$$

This development works for any potential $V(x)$; we now insert the specific form of V for the harmonic oscillator, and multiply both sides by ω:

$$\omega=\frac{\frac{dx}{dt}}{\sqrt{\frac{2E}{m\omega^2}-x^2}}.$$

For the harmonic oscillator, E is a sum of squares, and thus positive definite. We can therefore define $2E/m\omega^2=a^2$, and integrate again with respect to time:

$$\omega t-\phi=\int\frac{dx}{\sqrt{a^2-x^2}}$$

where we have defined the constant of integration to be $-\phi$. The integral is an inverse sine or cosine (the two differ only in the value assigned to ϕ); we choose the inverse cosine to give

$$x=a\cos(\omega t-\phi). \tag{4.2}$$

This describes harmonic motion with amplitude a, angular frequency ω and phase ϕ. The important property of this motion (which is, of course, the reason for the name 'harmonic') is that the frequency does not depend on the energy (or amplitude) of the motion. The correspondence principle argument of **??** thus predicts that the eigenvalues must satisfy

$$\frac{dE_n}{dn}=\hbar\omega\quad\rightarrow\quad E_n=n\hbar\omega+c$$

in the limit of large quantum numbers n.

The above is the standard 'Newtonian' treatment of the problem. The 'Hamiltonian' treatment is slightly more direct, and the momentum plays a more significant rôle. We start from the Hamiltonian:

$$H=\frac{p^2}{2m}+\frac{1}{2}m\omega^2x^2 \tag{4.3}$$

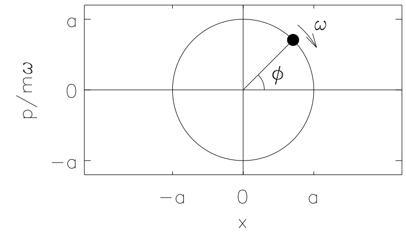


Figure 4.1: *Phase Space for the harmonic oscillator, and the motion of a representative point*

and differentiate to find the equations of motion:

$$\begin{aligned} \frac{dx}{dt} &= \frac{\partial H}{\partial p} = p/m \\ -\frac{dp}{dt} &= \frac{\partial H}{\partial x} = m\omega^2 x. \end{aligned}$$

These are now first-order instead of second-order with respect to time, and also exhibit a certain symmetry between x and p. This becomes more apparent if we scale p to have the same dimensions as x, defining $p' = p/m\omega$. The equations of motion become

$$\frac{dx}{dt} = \omega p' \tag{4.4}$$

$$\frac{dp'}{dt} = -\omega x. \tag{4.5}$$

We now define the complex variable $\mathbf{a} = x + ip/m\omega = x + ip'$; the equation of motion for $\mathbf{a}$ is given by (4.4) plus i times (4.5):

$$\frac{d\mathbf{a}}{dt} = \omega(p' - ix) = -i\omega\mathbf{a}. \tag{4.6}$$

This can be solved directly to give

$$\mathbf{a}(t) = \mathbf{a}(0)\exp(-i\omega t) \tag{4.7}$$

where $\mathbf{a}(0)$ is given in terms of the initial conditions at time $t = 0$: $\mathbf{a}(0) = x(0) + ip(0)/m\omega$. The relationship of (4.7) to the Newtonian solution (4.2) is obvious: a and ϕ are the modulus and phase of $\mathbf{a}(0)$. (This is the reason for the non-standard use of boldface type to denote the complex variable $\mathbf{a}$.) The use of a complex variable in this classical treatment is simply a convenient algebraic device; however the quantum analogue of $\mathbf{a}$ plays a surprisingly important rôle in the quantum theory in section 4.3.

Finally in this summary of classical treatments we mention phase space. The instantaneous state of motion of any classical system is given by the current values of x and p, which can be represented as a point in phase space, where each position and momentum is plotted on a separate axis. For this one-dimensional system, phase space is two-dimensional (and it is also the complex plane for the variable **a**). The Hamiltonian defines surfaces of constant H in this space, and Hamilton's equations of motion define the motion of the representative point in time. In terms of the scaled momentum p' we can write the Hamiltonian as $H = (m\omega^2/2)(x^2 + (p')^2)$, so that the curves of constant H are circles. The equations of motion imply that the point representing the state of the system rotates clockwise with angular velocity ω. Figure 4.1 shows contours of H in phase space, and the initial state of the oscillator at $t = 0$, $\mathbf{a}(0)$.

4.2 Solution of Schrodinger Equation for the Harmonic Oscillator

We shall begin our study of the harmonic oscillator in quantum mechanics with the solution of the time-independent Schrodinger equation to find the eigenvalues and eigenfunctions of the Hamiltonian. In the eigenvalue equation

$$Hu_n(x) = E_n u_n(x) \tag{4.8}$$

the Hamiltonian is given by the classical Hamiltonian (4.3) with the usual replacement $p \rightarrow -i\hbar\partial/\partial x$:

$$-\frac{\hbar^2}{2m}\frac{d^2u_n}{dx^2} + \frac{1}{2}m\omega^2 x^2 u_n = E_n u_n. \tag{4.9}$$

Our first step in the solution is one that can be applied in many problems in quantum mechanics, and indeed in most physical problems of any sort, which is the identification of the appropriate scales for the variables involved. As it stands the Schrodinger equation contains three constants, $\hbar$, m and ω, and the values of these control the length and energy scale of the solutions. We can find these scales by dimensional analysis: the three constants are just sufficient to define a unique set of values for a mass, length and time, which in combination define unique values for any mechanical quantity, including energy. The dimensions of the constants are as follows:

$$\begin{array}{ll} \hbar & [\mathrm{ML^2T^{-1}}] \\ m & [\mathrm{M}] \\ \omega & [\mathrm{T^{-1}}] \end{array}$$

It is clear that the combinations with dimensions of mass and time are m and ω^{-1}, and hence that the length is $L_{\mathrm{HO}} = \sqrt{\hbar/m\omega}$. These form a 'natural' set of units for discussing this problem. Since energy has dimensions $[\mathrm{ML^2T^{-2}}]$, its unit in this system is $E_{\mathrm{HO}} = (m)(\hbar/m\omega)(\omega^2) = \hbar\omega$. In order to use these units we have to change the variables. We define ξ (Greek xi) to be the displacement

x in units of $L_{\rm HO}$: $\xi = x/L_{\rm HO}$, and $\epsilon_n = E_n/E_{\rm HO}$ represents the energy eigenvalue in units of $E_{\rm HO}$. To convert the differentials we use the chain rule:

$$\frac{d}{dx} = \frac{d\xi}{dx}\frac{d}{d\xi}. \tag{4.10}$$

The effect of this substitution on the normalisation of u is discussed in problem 4.1. Carrying out the substitution in (4.9) we obtain

$$-\frac{\hbar^2}{2mL_{\rm HO}^2}\frac{d^2u_n}{d\xi^2} + \frac{1}{2}m\omega^2 L_{\rm HO}^2\xi^2 u_n = E_{\rm HO}\epsilon_n u_n. \tag{4.11}$$

Inserting the values of $E_{\rm HO}$ and $L_{\rm HO}$ we obtain

$$-\frac{\hbar\omega}{2}\frac{d^2u_n}{d\xi^2} + \frac{\hbar\omega}{2}\xi^2 u_n = \hbar\omega\epsilon_n u_n. \tag{4.12}$$

Every term contains the factor $\hbar\omega$, which thus cancels throughout. In a sense this is obvious, since the original Schrodinger equation is an energy equation, derived from the classical Hamiltonian, so that each term must have dimensions of energy, but the result is that in these natural units all the constants disappear from the problem, to leave

$$\frac{d^2u}{d\xi^2} = (\xi^2 - 2\epsilon)u \tag{4.13}$$

This is the differential equation we must solve, with boundary conditions $u(\xi) \to 0$ as $\xi \to \pm\infty$. We have dropped the suffix n from u and ϵ: the eigenvalues ϵ_n are those values of ϵ for which we can find solutions $u(\xi)$ satisfying the boundary conditions; these solutions are then the eigenfunctions $u_n(\xi)$.

We follow the procedure outlined in Appendix **??**. We first look at the indices (power of ξ − order of differentiation) of the three terms and find that they are -2, $+2$ and 0. Direct solution in series is not therefore appropriate, since it will not give a two-term recursion relation. We therefore look at the asymptotic form of the solution as $\xi \to \infty$. For any finite ϵ_n there is a ξ so large that the last term is negligible compared to the middle term, so that in this limit the equation becomes

$$\frac{d^2u}{d\xi^2} = \xi^2 u. \tag{4.14}$$

This is the same as the differential equation for $\exp(\pm\xi^2/2)$ in this limit:

$$\frac{d^2}{d\xi^2}\exp(\pm\xi^2/2) = (\xi^2 \pm 1)\exp(\pm\xi^2/2). \tag{4.15}$$

It therefore seems likely that the solution will take one or other of these forms at large ξ — clearly we require the form with the negative exponent in order to satisfy the boundary conditions. This argument works equally well with $\xi^k \exp(\pm\xi^2/2)$, since the dominant term in the second differential comes from differentiating the exponent each time, rather than the power of ξ, as long as $\xi \gg \sqrt{k}$. We therefore try a solution of the form $u(\xi) = H(\xi)\exp(-\xi^2/2)$; provided the polynomial H does not diverge at large ξ as fast as $\exp(\xi^2/2)$ this solution will satisfy the boundary conditions. With this substitution the equation for H becomes

$$\frac{d^2H}{d\xi^2} = 2\xi\frac{dH}{d\xi} + (1-2\epsilon)H. \tag{4.16}$$

The term on the left has index -2, and the two terms on the right have index 0, so solution in series is now possible. We make the standard substitution:

$$H(\xi) = \sum_{p=0}^{\infty} a_p \xi^{p+c} \qquad a_0 \neq 0. \tag{4.17}$$

Substituting this, and re-numbering the summation on the left-hand side, we obtain

$$\sum_{p=-2}^{\infty} a_{p+2}(p+c+1)(p+c+2)\xi^{p+c} = \sum_{p=0}^{\infty} a_p(2p+2c+1-2\epsilon)\xi^{p+c}. \tag{4.18}$$

Setting the coefficient of each power of ξ to zero we obtain the following set of equations.

$$\begin{aligned} c-2: &\quad a_0(c-1)c = 0 \\ c-1: &\quad a_1 c(c+1) = 0 \\ p+c: &\quad a_{p+2}(p+c+1)(p+c+2) = a_p(2p+2c+1-2\epsilon) \end{aligned} \tag{4.19}$$

The first equation is the indicial equation, and gives us $c = 0$ or 1. The roots of the indicial equation differ by an integer, whereas the recurrence relation (the third equation above) relates powers differing by 2. In this circumstance the series solution method generates one of the two independent solutions in two different ways: the first solution is given with $c = 0$ and $a_1 = 0$ (and hence all odd powers of ξ vanish), while the second solution can be obtained either by setting $c = 1$, $a_0 \neq 0$ and $a_1 = 0$ or by setting $c = 0$, $a_0 = 0$ and $a_1 \neq 0$. The latter option is non-standard, in the sense that the standard substitution specifies $a_0 \neq 0$, but it is convenient in this case because we can discuss both solutions with the same recurrence relation.

The recurrence relation is then, with $c = 0$

$$\frac{a_{p+2}}{a_p} = \frac{2p+1-2\epsilon}{(p+1)(p+2)} = \frac{2(p-p_0)}{(p+1)(p+2)} \tag{4.20}$$

where we have defined the zero of the numerator to be $p_0 = \epsilon - \frac{1}{2}$. The two linearly independent solutions are obtained as a sum of even powers beginning with a_0, and a sum of odd powers beginning with $a_1\xi$. Questions of convergence of this series are discussed in Box 4.1. The conclusion of this discussion is that for an eigenfunction satisfying the boundary conditions we need $H(\xi)$ to

There are in principle two separate convergence issues to be examined. The first is the convergence of the infinite series in the function $H(\xi)$ at finite ξ. The requirement for convergence of an infinite sum of terms T_n is $\lim_{n\to\infty} |T_{n+1}/T_n| < 1$. In this case the ratio of adjacent terms is

$$\frac{a_{p+2}\xi^{p+2}}{a_p\xi^p} = \frac{2(p-p_0)\xi^2}{(p+1)(p+2)}$$

and for any finite ξ this is not only less than unity but actually tends to zero at sufficiently large p. The infinite series thus defines a finite function $H(\xi)$ for any finite ξ.

The second issue is the behaviour of this function as $\xi \to \infty$. Bearing in mind that our general analysis suggests that at large ξ the eigenfunction u varies like $\xi^n e^{\pm\xi^2/2}$ we compare the $H(\xi)$ series with the series for e^{ξ^2} (or, in the case of the odd series, $\xi\, e^{\xi^2}$), which is the sort of behaviour H would have if u had the *wrong* sort of behaviour at large ξ. These series are

$$e^{\xi^2} = \sum_n \frac{\xi^{2n}}{n!} \qquad \xi\, e^{\xi^2} = \sum_n \frac{\xi^{2n+1}}{n!}$$

which gives the coefficient ratio as

$$\frac{a_{p+2}}{a_p} = \frac{2}{p+2} \qquad \frac{a_{p+2}}{a_p} = \frac{2}{p+1}$$

in the two cases. Comparing these with (4.20) we see that the $H(\xi)$ recursion relation differs only by a factor of $(p-p_0)/(p+1)$ or $(p-p_0)/(p+2)$. In the limit of large p this tends to 1, so the recursion relation becomes asymptotically identical with that for the diverging solution. This indicates that the general solution for $u(\xi)$ with an *infinite* series for $H(\xi)$ diverges as $\xi \to \infty$ in spite of the converging factor in our substitution, so that satisfactory solutions are only obtained if the series for $H(\xi)$ terminates.

Box 4.1 Convergence of the series solution.

be a finite polynomial; in other words, the series must terminate. The condition for termnation is $a_{p+2}/a_p = 0$ for some p. The function on the right of (4.20) only has a single zero, at $p = p_0$, and if p_0 is an even (or odd) integer n the even (or odd) series will terminate at the term $a_n\xi^n$. Hence this termination can only apply to one of the two solutions. The eigenvalues are thus

$$\epsilon_n = n + \frac{1}{2} \qquad n = 0, 1, 2 \ldots \tag{4.21}$$

If n is even, then H_n is an even polynomial with first term a_0 and last term $a_n\xi^n$, while if n is odd, H_n is an odd polynomial with first term $a_1\xi$ and last term $a_n\xi^n$; in both cases the recursion relation for the coefficients is (4.20), with p_0 set to n. These polynomials are known as Hermite polynomials, and we shall discuss some of their properties shortly.

Thus the eigenfunctions are given by $u_n(\xi) = N_n H_n(\xi)\exp(-\xi^2/2)$, where H_n is the n'th Hermite polynomial, N_n is a normalising constant, and the corresponding eigenvalue is $\epsilon_n = n + \frac{1}{2}$. (In a sense N_n could be made unnecessary by a proper choice of the coefficients in the polynomial; however there is a standard definition of H_n, which we shall explain shortly, so that N_n is also required.) These eigenfunctions are in fact real, so we shall ignore the complex conjugate in the discussion of normalization.

The lowest few eigenfunctions can be derived very simply on a case-by-case basis. For the ground state $n = 0$ we have $\epsilon_0 = \frac{1}{2}$ and H_0 consists of the single term $H_0 = a_0$; the polynomial is cut off by the recursion relation which gives $a_2/a_0 = 0$. The eigenfunction is thus $u_0(\xi) = N_0 a_0 \exp(-\xi^2/2)$. The normalisation constant is found from the normalisation integral:

$$N_0^2 a_0^2 \int_{\infty}^{\infty} \exp(-\xi^2)\, d\xi = 1.$$

The integral is well known and is given by $\sqrt{\pi}$, so that $N_0 a_0 = \pm 1/\pi^{1/4}$.

For the first excited state $n = 1$ we have $\epsilon_1 = \frac{3}{2}$, and again the polynomial consists of a single term $H_1 = a_1\xi$. The eigenfunction is thus $u_1(\xi) = N_1 a_1 \xi \exp(-\xi^2/2)$, and the normalisation integral is

$$N_1^2 a_1^2 \int_{\infty}^{\infty} \xi^2 \exp(-\xi^2)\, d\xi = 1.$$

This integral can be reduced to the earlier one (see Appendix A, section A.1), and has the value $\sqrt{\pi}/2$, so that $N_1 a_1 = \pm\sqrt{2}/\pi^{1/4}$.

For the second excited state, $n = 2$ and $\epsilon_2 = \frac{5}{2}$. The recursion relation gives $a_2/a_0 = -2$ and $a_4/a_2 = 0$ so that $H_2(\xi) = a_0(1 - 2\xi^2)$, and $u_2(\xi) = N_2 a_0 (1 - 2\xi^2)\exp(-\xi^2/2)$. The normalisation integral now has three terms:

$$N_2^2 a_0^2 \int_{-\infty}^{\infty} (1 - 4\xi^2 + 4\xi^4)\exp(-\xi^2)\, d\xi = 1.$$

The integral can be evaluated using the techniques described in Appendix A, section A.1, giving $\sqrt{\pi}(1 - 2 + 3) = 2\sqrt{\pi}$, so that $N_2 a_0 = \pm\sqrt{2}/\pi^{1/4}$. (While in the former cases the standard phase choice is given by the plus sign, in this case it is the minus sign, as we shall see below.) However it is apparent that this procedure rapidly becomes tedious, and that to use eigenstates of much larger n we require a more powerful technique, which we shall discuss shortly.

Before doing that we show plots of the eigenfunctions just derived. The $n = 0, 1, 2$ eigenfunctions are shown in Figure 4.2. Each plot also shows the classical amplitude for motion with energy equal

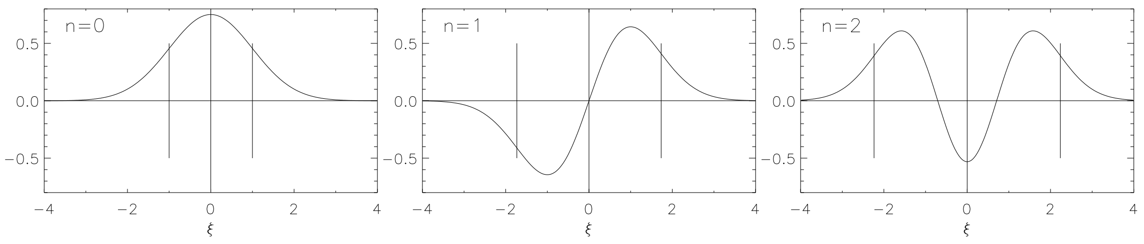


Figure 4.2: *The $n = 0$, 1, and 2 eigenfunctions for the harmonic oscillator*

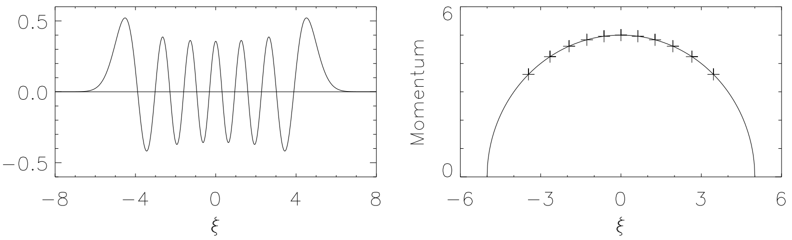


Figure 4.3: *The $n = 12$ eigenfunction, and the variation of wavelength with position*

to the corresponding eigenvalue. For the eigenstate with quantum number n the eigenvalue is (reverting to 'unscaled' units) $E_n = (n + \frac{1}{2})\hbar\omega$, and the corresponding amplitude is $a = \sqrt{2E/m\omega^2}$ (see Section 4.1) which gives the amplitude as $a = \sqrt{(2n+1)\hbar/m\omega}$, or $\sqrt{2n+1}$ in 'natural' units. Each successive eigenfunction has one more zero, and these all occur between the classical turning points $\pm a$. For comparison we show in Figure 4.3 the eigenfunction for $n = 12$; the classical turning points are marked, and the eigenfunction has twelve zeros between the turning points. In this case we can start to relate the wavelength of the oscillations in the eigenfunction to the de Broglie wavelength $\lambda = h/p$: it is apparent from the plot in the left-hand panel that the wavelength is shorter near $\xi = 0$ than it is near the turning point, corresponding to the faster classical motion in the centre, and the slowing down further out. The right-hand panel makes this correspondence explicit: the solid line shows the classcal momentum as a function of position with energy $(25/2)\hbar\omega$, and the plotted points are the momenta inferred from the de Broglie relation. These are generated by taking the wavelength to be twice the distance between the zeros of the eigenfunction, and plotting the point halfway between the zeros used to define it, giving a total of eleven plotted points. The correspondence is clearly extremely close.

Finally in this section we turn to a more powerful algebraic technique for handling Hermite polynomials, applicable to many sets of functions, the use of a *generating function.* To generate a set of functions of *one* variable, for example $H_n(\xi)$, we can use a function of *two* variables, $G(t, \xi)$, such that if G is expanded as a power series in t the coefficient of t^n, which will depend on ξ, is related to $H_n(\xi)$. This approach defines explicitly the normalisation of the functions, and allows us to prove relations between them. For the case of the Hermite polynomials the generating function is $G(t,\xi)=\exp(2\xi t-t^2)$, and the definition of the polynomials is

$$G(t,\xi)=\exp(2\xi t-t^2)=\sum_{n=0}^{\infty}H_n(\xi)\frac{t^n}{n!}. \tag{4.22}$$

If we expand up to terms of order t^2 we can easily find the first couple of Hermite polynomials: $\exp(-t^2)\approx(1-t^2)$ and $\exp(2\xi t)\approx 1+2\xi t+4\xi^2t^2/2$. Multiplying these together and keeping only terms up to t^2 we obtain

$$\Big(1\Big)+\Big(2\xi\Big)\,t+\Big(4\xi^2-2\Big)\,\frac{t^2}{2}=H_0(\xi)+H_1(\xi)\,t+H_2(\xi)\,\frac{t^2}{2}. \tag{4.23}$$

The polynomials in brackets are consistent with our forms for H_0, H_1 and H_2 derived above, but this approach supplies a specific value for a_0 or a_1 for the polynomial (and we observe that the sign of H_2 is as noted above). However, although these first three polynomials agree with our earlier results, we have not shown that the polynomials defined by the generating function are in general consistent with the H_n defined by the differential equation (4.16) for all n.

There are two ways of doing this. One is to find an explicit expression for the polynomial coefficients from the generating function, and then show that it is consistent with the recurrence relation required to satisfy the differential equation; this approach is explored in problem 4.2. An alternative approach is to show directly that the H_n defined by the generating function satisfy the differential equation. To do this we first prove two recursion relations between H_n of different orders. If we differentiate (4.22) with respect to ξ we obtain

$$2t\,\exp(2\xi t-t^2)=\sum_{n=0}^{\infty}\frac{dH_n}{d\xi}\frac{t^n}{n!}. \tag{4.24}$$

But the left-hand side of (4.24) can be written in terms of the original expansion:

$$2t\,G(t,\xi)=\sum_{n=0}^{\infty}2H_n(\xi)\frac{t^{n+1}}{n!}.$$

Changing the definition of n we can re-write this as

$$\sum_{n=0}^{\infty}2H_n\frac{t^{n+1}}{n!}=\sum_{n=1}^{\infty}2H_{n-1}\frac{t^n}{(n-1)!}=\sum_{n=1}^{\infty}2nH_{n-1}\frac{t^n}{n!}.$$

Equating this to the right-hand side of (4.24) we obtain

$$\sum_{n=1}^{\infty}2nH_{n-1}\frac{t^n}{n!}=\sum_{n=0}^{\infty}\frac{dH_n}{d\xi}\frac{t^n}{n!}.$$

Finally we can equate powers of t to obtain $dH_0/d\xi=0$ from the coefficient of t^0, and in general

$$\frac{dH_n}{d\xi}=2nH_{n-1}(\xi). \tag{4.25}$$

If we differentiate the Hermite generating function (4.22) with respct to t we obtain

$$(2\xi - 2t)G(t,\xi) = \sum_{n=1}^{\infty} H_n(\xi)\frac{t^{n-1}}{(n-1)!}$$

where the term in t^0 vanishes on the right-hand side after differentiation. Introducing the original expansion of $G(t,\xi)$ on the left-hand side we obtain

$$\sum_{n=0}^{\infty} 2\xi H_n\frac{t^n}{n!} - 2H_n\frac{t^{n+1}}{n!} = \sum_{n=1}^{\infty} H_n(\xi)\frac{t^{n-1}}{(n-1)!}.$$

Re-numbering the second term on the left, and also the right-hand side we obtain

$$\sum_{n=0}^{\infty} 2\xi H_n\frac{t^n}{n!} - \sum_{n=1}^{\infty} 2nH_{n-1}\frac{t^n}{n!} = \sum_{n=0}^{\infty} H_{n+1}\frac{t^n}{n!}.$$

Equating coefficients of t^n we obtain $2\xi H_0 = H_1$ from the coefficient of t^0, and in general

$$2\xi H_n = 2nH_{n-1} + H_{n+1}$$

We can substitute for $2nH_{n-1}$ from the first recursion relation (4.25) to obtain instead

$$2\xi H_n = \frac{dH_n}{d\xi} + H_{n+1}$$

which is the required result.

Box 4.2 Derivation of a recursion relation for Hermite polynomials

In a similar but slightly more complicated way we can derive

$$2\xi H_n = \frac{dH_n}{d\xi} + H_{n+1}; \tag{4.26}$$

the details are given in Box 4.2. We can combine these two relations to derive the differential equation satisfied by the Hermite polynomials. In (4.25) we replace n by $n+1$ so that both relations refer to the same pair of polynomials:

$$\frac{dH_{n+1}}{d\xi} = 2(n+1)H_n(\xi).$$

We can then eliminate H_{n+1} by differentiating (4.26) with respect to ξ and substituting from above:

$$2\xi\frac{dH_n}{d\xi} + 2H_n = \frac{d^2H_n}{d\xi^2} + 2(n+1)H_n;$$

which can be re-arranged to give

$$\frac{d^2H_n}{d\xi^2} = 2\xi\frac{dH_n}{d\xi} - 2nH_n$$

which is equivalent to (4.16) when $\epsilon = n + \frac{1}{2}$. Thus we have proved that the Hermite polynomials defined through the generating function $G(t, \xi)$ satisfy the same differential equation and are thus equivalent to the terminating polynomial solutions found above. This approach does not quite supercede our rather more labour-intensive approach based on solving (4.16) in series, since we would not otherwise have found out that these are the only possible solutions that satisfy the boundary conditions.

The generating function is a very powerful tool for deriving general results. As an example we can derive an explicit form for the normalization constant N_n for the n'th eigenfunction, such that $u_n = N_n H_n \, e^{-\xi^2/2}$ is normalised to unity. If we multiply the generating function expansion (4.22) by $\exp -\xi^2/2$ we obtain

$$G(t, \xi) \exp(-\xi^2/2) = \exp(-t^2 + 2\xi t - \xi^2/2) = \sum_{n=0}^{\infty} \frac{t^n}{n!} \Big(H_n(\xi) \exp -\xi^2/2 \Big) \tag{4.27}$$

where the coefficient of $t^n/n!$ is the unnormalised eigenfunction u_n/N_n. We now multiply together two of these expansions with different auxiliary variables s and t:

$$\exp(-t^2 + 2\xi t - s^2 + 2\xi s - \xi^2) = \sum_{m,n} \frac{s^m t^n}{m!n!} \frac{u_m u_n}{N_m N_n}.$$

If we now integrate over ξ we obtain on the left a function of s and t, whose series expansion on the right gives us all possible normalisation and overlap integrals between the eigenfunctions u_n:

$$\int_{-\infty}^{\infty} \exp(-t^2 + 2\xi t - s^2 + 2\xi s - \xi^2) \, d\xi = \sum_{m,n} \frac{s^m t^n}{m!n!} \frac{1}{N_m N_n} \int_{-\infty}^{\infty} u_m(\xi) u_n(\xi) \, d\xi. \tag{4.28}$$

The exponent on the left-hand side of (4.28) is nearly a perfect square:

$$-t^2 + 2\xi t - s^2 + 2\xi s - \xi^2 = -(\xi - s - t)^2 + 2st$$

so that the integral on the left is

$$e^{2st} \int_{-\infty}^{\infty} e^{-(\xi - s - t)^2} \, d\xi = \sqrt{\pi} e^{2st} = \sqrt{\pi} \sum_n \frac{(2st)^n}{n!}. \tag{4.29}$$

Comparing cofficient of of $s^m t^n$ on the right-hand side of (4.28) with the corresponding coefficient on the right-hand side of (4.29), we see that the integrals in (4.28) are all zero unless $m = n$: thus the eigenfunctions u_n form an orthogonal set, as expected. Looking at the $m = n$ terms we find

$$\frac{1}{N_n^2} \int_{-\infty}^{\infty} u_n^2(\xi) \, d\xi = \sqrt{\pi} \, 2^n \, n!$$

The integral is defined to be one, since u_n is normalised, so the normalisation constant is given by $N_n = (\sqrt{\pi} 2^n n!)^{-1/2}$.

This completes our discussion of the eigenfunctions of the harmonic oscillator Hamiltonian. Reverting to 'unscaled' units we have eigenvalues $E_n = (n + \frac{1}{2})\hbar\omega$, and time-independent eigenfunctions

$$u_n(x) = \left(\frac{m\omega}{\hbar}\right)^{1/4} N_n \, H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-m\omega x^2/2\hbar}, \tag{4.30}$$

where we have used the results of problem 4.1 to re-normalize the eigenfunction as a function of x instead of ξ. The time-dependent eigenfunctions are thus $\psi_n(x,t) = u_n(x)e^{-E_n t/\hbar}$ and the general solution to the time-dependent Schrodinger equation is, as usual,

$$\psi(x,t) = \sum_n c_n \psi_n(x,t)$$

where the complex constants c_n are arbitrary except for the normalisation condition $\sum_n |c_n|^2 = 1$. We shall consider an interesting example of a superposition state of this sort in section 4.4.

4.3 Algebraic Treatment of the Harmonic Oscillator

In this section we shall discuss a completely different approach to finding the eigenstates of the harmonic oscillator, a wholly algebraic approach in which finding a solution of a differential equation appears to play no part. We shall also discuss a hidden assumption in this approach, which means that it is not quite as independent of the differential equations as it appears.

Our starting point is the same as in section 4.2: we have a Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

and we wish to find the eigenvalues of H. We shall also make some use of the scaled variables introduced in section 4.2: $\xi = \sqrt{m\omega/\hbar}x$ and $\rho = p/\sqrt{m\omega\hbar}$ are dimensionless position and momentum variables, scaled by the'natural' units of length and momentum $\sqrt{\hbar/m\omega}$ and $\sqrt{m\omega\hbar}$. We start by defining two operators:

$$a = \frac{1}{\sqrt{2}}(\xi + i\rho) = \sqrt{\frac{m\omega}{2\hbar}}x + \frac{i}{\sqrt{2m\omega\hbar}}p \tag{4.31}$$

$$a^\dagger = \frac{1}{\sqrt{2}}(\xi - i\rho) = \sqrt{\frac{m\omega}{2\hbar}}x - \frac{i}{\sqrt{2m\omega\hbar}}p. \tag{4.32}$$

These are related to the classical $\mathbf{a} = x - ip/m\omega$ which we found useful in section 4.1: a here is the operator equivalent of $\mathbf{a}/\sqrt{2}$ in 'natural' units. Because of the presence of the imaginary i, neither of these operators is Hermitian, but they form an adjoint pair, which is the reason for the dagger superscript to the second operator. We can also invert these equations to give x and p in terms of a and $a^\dagger$:

$$\begin{aligned} x &= \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger) && (4.33) \\ p &= i\sqrt{\frac{m\omega\hbar}{2}}(a^\dagger - a). && (4.34) \end{aligned}$$

Substituting these into the Hamiltonian we can find H in terms of a and $a^\dagger$:

$$H = -\frac{1}{2m}\frac{m\omega\hbar}{2}(a - a^\dagger)^2 + \frac{m\omega^2}{2}\frac{\hbar}{2m\omega}(a + a^\dagger)^2 = \frac{\hbar\omega}{2}(aa^\dagger + a^\dagger a). \tag{4.35}$$

The algebraic method relies on the use of commutators, so we first derive the relevant results. Using the fundamental commutator $[x, p] = i\hbar$ we can quickly derive

$$[a, a^\dagger] = \frac{[x, -ip] + [ip, x]}{2\hbar} = 1. \tag{4.36}$$

(The difference of $\sqrt{2}$ between the classical $\mathbf{a}$ and the operator a is purely to ensure that this commutator is unity.) The other commutator required is between a and the Hamiltonian H:

$$[a, H] = \frac{\hbar\omega}{2}\Big([a, aa^\dagger] + [a, a^\dagger a]\Big) = \hbar\omega a \tag{4.37}$$

where we have used the $[a, a^\dagger]$ commutator to evaluate the two commutators in (4.36). The commutator of $a^\dagger$ with H is very similar:

$$[a^\dagger, H] = \frac{\hbar\omega}{2}\Big([a^\dagger, aa^\dagger] + [a^\dagger, a^\dagger a]\Big) = -\hbar\omega a^\dagger. \tag{4.38}$$

We can also use the $[a, a^\dagger]$ commutator to eliminate one or other of the terms in H, and so derive two other forms equivalent to (4.35):

$$H = \frac{\hbar\omega}{2}(aa^\dagger + a^\dagger a) = \hbar\omega\Big(aa^\dagger - \frac{1}{2}\Big) = \hbar\omega\Big(a^\dagger a + \frac{1}{2}\Big) \tag{4.39}$$

With these results we can very quickly derive the set of eigenvalues of H. The only explicit assumption that we make is that there exists at least one eigenstate ψ, with eigenvalue E:

$$H\psi = E\psi. \tag{4.40}$$

We now consider the wavefunction obtained by operating on ψ with a, $a\psi$. We can use the $[H, a]$ commutator (4.37) to show that this state is also a solution of the Schrodinger equation:

$$H\,a\psi = a\,H\psi - \hbar\omega a\psi = (E - \hbar\omega)a\psi. \tag{4.41}$$

Similarly we can use the $[H, a^\dagger]$ commutator (4.38) to show that the wavefunction obtained by operating on ψ with $a^\dagger$ is also a solution of the Schrodinger equation:

$$H\, a^\dagger\psi = a^\dagger\, H\psi + \hbar\omega a^\dagger\psi = (E + \hbar\omega)a^\dagger\psi. \tag{4.42}$$

Thus the existence of the state ψ with eigenvalue E appears to imply the existence of two more states with eigenvalues $E+\hbar\omega$ and $E-\hbar\omega$. Obviously we can now repeat the argument on these new states to derive further states, so that the existence of the state ψ appears to imply the existence of a infinite ladder of states $E + n\hbar\omega$ for all integer n. The operators a and $a^\dagger$ are often referred to as ladder operators, or altenatively as lowering and raising operators, because of their effect on the eigenvalue.

However, this infinite ladder of eigenstates of H cannot all exist, because this particular H has positive eigenvalues. This is because H is a sum of squares of Hermitian operators, having two terms involving x^2 and p^2 with positive coefficients. Any operator which can be written as the square of a Hermitian operator is positive definite in the sense that all expectation values of it are positive; the eigenvalues are special cases of expectation values, obtained when the wavefunction is the corresponding eigenfunction. The proof of this is straightforward: the expectation value of p^2, for example, can be written

$$\langle p^2\rangle = \int \psi^* p^2 \psi\, d\tau = \int (p\psi)^*\; p\psi\, d\tau = \int |p\psi|^2\, d\tau \geq 0$$

where the first equality is the definition of the expectation value, the second uses the Hermitian property of p, and the final equality expresses the result as an integral with a positive definite integrand, which gives the final inequality. Thus $\langle p^2\rangle \geq 0$, and similarly $\langle x^2\rangle \geq 0$, so that $\langle H\rangle \geq 0$. Hence all eigenvalues are also positive, and the infinite set of states with negative eigenvalues of H simply does not exist. Hence we must have made an error above.

The error lies in the assumption that the equation $H\, a\psi = (E-\hbar\omega)a\psi$ (4.41 above) implies that there exists a state with wavefunction $a\psi$ and eigenvalue $E-\hbar\omega$. Another possiblity is that $a\psi = 0$; the equation is still true, but only in the trivial sense $0 = 0$, which does *not* imply the existence of such a state, since the wavefunction vanishes. Since all the eigenvalues of H are positive, there must be a least energy state ψ_0 with energy E_0, and we assume that for this state $a\psi_0 = 0$, in order to prevent the existence of a lower energy state, contrary to our assumption. Operating on this equation with $a^\dagger$ we obtain $a^\dagger a\psi_0 = 0$, which, using the third form for H in (4.39) we can write as

$$\left(\frac{H}{\hbar\omega} - \frac{1}{2}\right)\psi_0 = 0 \qquad \text{or} \qquad H\psi_0 = \frac{1}{2}\hbar\omega\psi_0. \tag{4.43}$$

Thus this method of cutting off the ladder of negative energy states only works for a state with eigenvalue $E_0 = \frac{1}{2}\hbar\omega$. There is thus a single set of eigenvalues built on this unique eigenvalue: $E_n = (n + \frac{1}{2})\hbar\omega$, $n = 0, 1, 2, \ldots$. We haven't yet proved that there is a unique *eigenfunction* ψ_0, but for every ψ_0 with the minimum eigenvalue we can generate the other eigenfunctions $\psi_n = (a^\dagger)^n\psi_0$.

We can also show quite simply that there is no maximum energy state, because the raising operator cannot give a zero eigenfunction. If we for some ψ we assume $a^\dagger\psi = 0$ then $aa^\dagger\psi = 0$, which we can write, using the second form for H in (4.39), as $H\psi = (-\hbar\omega/2)\psi$. This implies that such a ψ must have a negative eigenvalue of H, which is inconsistent with the fact that H is positive definite, so that such a ψ cannot exist. There is no upper limit to the range of eigenvalues.

This appears to be a very quick and straightforward way to derive the eigenvalue spectrum. However, after a bit of thought it appears to be *too* quick and straighforward. In the solution of the differential equation in section 4.2 the rôle of the boundary conditions is crucial: it is the boundary conditions which define the eigenfunctions, as the states which satisfy them. The algebraic approach appears to make no use of the boundary conditions at all, and yet still arrives at the eigenvalue spectrum. In fact there is an implicit assumption about boundary conditions. In saying, as we did above in our explicit assumption, that ψ is an eigenfunction with eigenvalue E, we imply that ψ satisfies the Schrodinger equation, is non-zero, and satisfies the boundary conditions. This, we showed, implied that $a\psi$ and $a^\dagger\psi$ satisfy the Schrodinger equation, and we then assumed that when they were non-zero they were also eigenfunctions. This obviously ignores another possibility: that $a\psi$ or $a^\dagger\psi$ is non-zero, satisfes the Schrodinger equation *but does not satisfy the boundary conditions.* The implicit assumption about boundary conditions is thus that we can operate on a function which satisfies them an arbitrary number of times with either a or $a^\dagger$ and still obtain a function which satisfies them. If, as is the case here, the boundary conditions are $\psi(x) \to 0$ as $x \to \pm\infty$ then the wavefunction is likely decay exponentially at large x. The operators a and $a^\dagger$ involve only x and p, that is multiplication by x or differentiation with respect to x, and it *is* the case that we can carry out these operations any number of times on a decaying exponential and still obtain a decaying exponential. Thus the implicit assumption is in fact true for the usual boundary conditions. However one can imagine model problems involving a harmonic oscillator Hamiltonian with different boundary conditions, for example $\psi(x_0) = 0$ for some x_0, and the implicit assumption may then not be true, and this method will fail. However in this case it does indeed yield the correct eigenvalue spectrum.

The eigenfunction obtained by raising or lowering a given eigenfunction ψ will not necessarily have the same normalisation as ψ: we have merely shown that it satisfies the Schrodinger equation, and this tells us nothing about normalisation. We can quite simply calculate the effect on the normalisation. We start from a normalised ψ_n and define ψ_{n+1} to be normalised also, so that the raised state has to be written

$$a^\dagger \psi_n = N_+(n)\psi_{n+1}$$

for some constant $N_+(n)$. Taking the square modulus and integrating over all space we obtain

$$\int_{-\infty}^{\infty} \left(a^\dagger \psi_n\right)^* \left(a^\dagger \psi_n\right)\, dx = |N_+(n)|^2 \int_{-\infty}^{\infty} |\psi_{n+1}|^2\, dx.$$

The integral on the right is defined to be one, and the integral on the left can be transformed using the adjoint operator a:

$$\int_{-\infty}^{\infty} \psi_n^* \left(a a^\dagger \psi_n\right)\, dx = |N_+(n)|^2.$$

We can now substitute for $aa^\dagger$ from the second form for H in (4.39):

$$\int_{-\infty}^{\infty} \psi_n^* \left(\frac{H}{\hbar\omega} + \frac{1}{2}\right) \psi_n\, dx = |N_+(n)|^2.$$

Substituting the eigenvalue $E_n = (n + \frac{1}{2})\hbar\omega$ we find $|N_+(n)|^2 = n + 1$. This defines the modulus of N_+; the phase is arbitrary, but we can choose the overall phases for our basis set ψ_n such that $N_+(n)$ is real, in which case $N_+(n) = \sqrt{n+1}$. We can thus write an explicit equation for ψ_n in terms of the ground state ψ_0:

$$\psi_n = \frac{a^\dagger \psi_{n-1}}{\sqrt{n}} = \frac{\left(a^\dagger\right)^2 \psi_{n-2}}{\sqrt{n(n-1)}} = \ \ldots \ = \frac{\left(a^\dagger\right)^n \psi_0}{\sqrt{n!}}. \tag{4.44}$$

We can repeat this argument to find the normalisation change introduced by the lowering operator a, but we can also find it without repeating the argument, but analysing the result we have just found. We introduce the correspnding constant $N_-(n)$, so that the two ladder operators satisfy

$$a^\dagger \psi_n = N_+(n)\psi_{n+1} \qquad \text{and} \qquad a\psi_n = N_-(n)\psi_{n-1}$$

where all the ψ are normalised. We now multiply these equations by ψ_{n+1}^* or ψ_{n-1}^* respectively and integrate over all x to obtain

$$\int_{-\infty}^{\infty} \psi_{n+1}^* a^\dagger \psi_n\, dx = N_+(n) \qquad \text{and} \qquad \int_{-\infty}^{\infty} \psi_{n-1}^* a \psi_n\, dx = N_-(n).$$

However the second integral is now related to the first: we take the complex conjugate of the second integral

$$\int_{-\infty}^{\infty} (a\psi_n)^* \psi_{n-1}\, dx = N_-^*(n)$$

and use the adjoint property

$$\int_{-\infty}^{\infty} (a\psi_n)^* \psi_{n-1}\, dx = \int_{-\infty}^{\infty} \psi_n^* a^\dagger \psi_{n-1}\, dx = N_+(n-1).$$

Thus $N_-^*(n) = N_+(n-1)$, or $N_-(n) = N_+^*(n-1) = \sqrt{n}$. In summary, the two ladder operators satisfy

$$a\psi_n = \sqrt{n}\psi_{n-1} \qquad \text{and} \qquad a^\dagger \psi_n = \sqrt{n+1}\psi_{n+1}. \tag{4.45}$$

The results of this section are fully consistent with the explicit expressions we found for the wavefunction in the previous section. To show this we need to show that the ground state wavefunction ψ_0 is the same, and that the raising and lowering operations (4.45) are also consistent. The ground state wavefunction is defined by $a\psi_0 = 0$. Inserting the definition of a from (4.31) we find

$$\sqrt{\frac{m\omega}{2\hbar}}\, x\psi_0 + \sqrt{\frac{\hbar}{2m\omega}}\, \frac{d\psi_0}{dx} = 0$$

which we can re-arrange to give

$$\frac{d\psi_0}{dx} = -\frac{m\omega x}{\hbar}\psi_0. \tag{4.46}$$

This integrates directly:

$$\ln(\psi_0) = -\ln\left(\frac{m\omega x^2}{2\hbar}\right) + \text{constant}$$

or $\psi_0 = A\exp(-m\omega x^2/2\hbar)$, which is the same form for ψ_0 found above. This also answers the query raised earlier as to whether the ground state is unique: the condition $a\psi_0 = 1$ does in fact define a unique wavefunction. To complete the consistency check we need to prove relations equivalent to the ladder operations (4.45) using the wavefunctions found in section 4.2; this is relatively straightforward and is left to problem 4.3. Using these algebraic results we can then quickly calculate any required expectation value or matrix element that involves only position and momentum operators; this topic is also explored further in the problems.

4.4 A Solution of the Time-Dependent Schrodinger Equation

In this section we shall derive a remarkable solution of the time-dependent Schrodinger equation for the harmonic oscillator. We have already given the general solution to the time-dependent equation at the end of section 4.2:

$$\Psi(x,t) = \sum_n c_n \psi_n(x,t)$$

with c_n equal to any set of complex constants, and the solution we are about to find can of course be written in this form. However it also has a remarkably simple analytic form as a moving wavepacket solution of the type we constructed numerically for the square well, and it connects very closely to the classical solution we found in section 4.1.

The solution has the form of a moving Gaussian wavepacket; the x-dependence is therefore in the form of the exponential of a quadratic form in x. A general solution of this type can in fact be found with modest difficulty (see problem 4.5) but the solution we shall look at is slightly simpler in that the quadratic term has a fixed coefficient, $-m\omega/2\hbar$. This gives the same $\exp(-m\omega x^2/2\hbar)$ factor that we found to be present in all the eigenstates, and produces the same cancellation of terms when substituted into the Schrodinger equation. Thus the solution we shall look at has the form

$$\Psi(x,t) = \exp\left(\frac{m\omega}{\hbar}\left(-x^2/2 + \mathbf{a}(t)x + \mathbf{b}(t)\right)\right) \tag{4.47}$$

where $\mathbf{a}$ and $\mathbf{b}$ are complex functions of t (and we are using boldface type to denote the complex variables, as in section 4.1).

We substitute this solution into the time-dependent Schrodinger equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{4.48}$$

and we obtain

$$\left(-\frac{m\omega^2}{2}(\mathbf{a}-x)^2 + \frac{\hbar\omega}{2} + \frac{m\omega^2}{2}x^2\right)\Psi = im\omega\left(x\frac{d\mathbf{a}}{dt} + \frac{d\mathbf{b}}{dt}\right)\Psi. \tag{4.49}$$

The terms involving $x^2\Psi$ on the left cancel, just as they did in the corresponding place in the solution of the time-independent Schrodinger equation, between equations (4.13) and (4.16). We can equate the terms in $x\Psi$ and Ψ on the two sides to give

$$\frac{d\mathbf{a}}{dt} = -i\omega\mathbf{a} \tag{4.50}$$

$$\frac{d\mathbf{b}}{dt} = \frac{i}{2}\omega\mathbf{a}^2 - i\frac{\hbar}{2m}. \tag{4.51}$$

We can immediately solve (4.50) to give $\mathbf{a} = \mathbf{a}(0)\,e^{-i\omega t}$ where $\mathbf{a}(0)$ is an arbitrary (complex) constant of integration, which we shall write as $a\,e^{i\phi}$. The solution for $\mathbf{a}(t)$ can thus be written $\mathbf{a}(t) = a\,e^{-i\chi}$ where the phase χ is given by $\chi = \omega t - \phi$.

In (4.51) we can substitute for $i\omega\mathbf{a}$ from (4.50) to give

$$\frac{d\mathbf{b}}{dt} = -\frac{\mathbf{a}}{2}\frac{d\mathbf{a}}{dt} - \frac{i\hbar}{2m}.$$

To normalise the wavefunction (4.53) we separate its modulus and phase, by separating the real and imaginary parts of the exponent. The exponent is equal to

$$-\frac{m\omega}{2\hbar}\left(x^2 - 2axe^{-i\chi} + (a^2/2)e^{-2i\chi}\right) - \frac{i\omega t}{2} + C$$

which separates into

$$\left(-\frac{m\omega}{2\hbar}(x^2 - 2ax\cos\chi + (a^2/2)\cos 2\chi) + C\right) - i\left(\frac{m\omega}{2\hbar}(2ax\sin\chi - (a^2/2)\sin 2\chi) + \frac{\omega t}{2}\right).$$

In the real part we can write $\cos 2\chi = 2\cos^2\chi - 1$ which enables the real part to be written $-(m\omega/2\hbar)(x - a\cos\chi)^2 + (C + m\omega a^2/4\hbar)$. The complex conjugate wavefunction will have the same modulus, determined by the real part of the exponent, and the opposite phase, determined by the imaginary part. The normalisation integral can thus be written

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,dx = 1 = e^{2C + m\omega a^2/2\hbar}\int_{-\infty}^{\infty} e^{-(m\omega/\hbar)(x - a\cos\chi)^2}\,dx.$$

A change of variable to $y = x - a\cos\chi$ reduces the integral to a standard Gaussian integral (see Appendix A, section A.1) to leave

$$1 = e^{2C + m\omega a^2/2\hbar}\sqrt{\frac{\pi\hbar}{m\omega}}.$$

Thus the normalisation constant is $e^C = (m\omega/\pi\hbar)^{1/4}e^{-m\omega a^2/4\hbar}$.

Box 4.3 Normalisation of the time-dependent solution

which integrates directly to give

$$\mathbf{b}(t) = -\frac{\mathbf{a}^2}{4} - \frac{i\hbar t}{2m} + \frac{\hbar C}{m\omega} \tag{4.52}$$

where the last term is a constant of integration, which we have written in this form so that C becomes a separate term in the exponent of the full solution.

The full solution can thus be written

$$\Psi(x,t) = e^C\, e^{-(m\omega/2\hbar)(x^2 - 2\mathbf{a}x + \mathbf{a}^2/2)}\, e^{-i\omega t/2} \qquad \text{where} \qquad \mathbf{a}(t) = \mathbf{a}(0)\, e^{-i\omega t} = a\, e^{-i\chi} \tag{4.53}$$

in terms of the two complex constants of integration $\mathbf{a}(0)$ and C. Of these two constants C is almost trivial: e^C is just an overall constant factor, so the real part of C is determined by the normalisation requirement, and the imaginary part of C is just an overall phase which does not affect the physics of the solution. We can therefore take C to be real, and from the normalisation integral we find $e^C = (m\omega/\pi\hbar)^{1/4}e^{-m\omega a^2/4\hbar}$ (see Box 4.3). The constant $\mathbf{a}(0) = a\, e^{i\phi}$, on the other

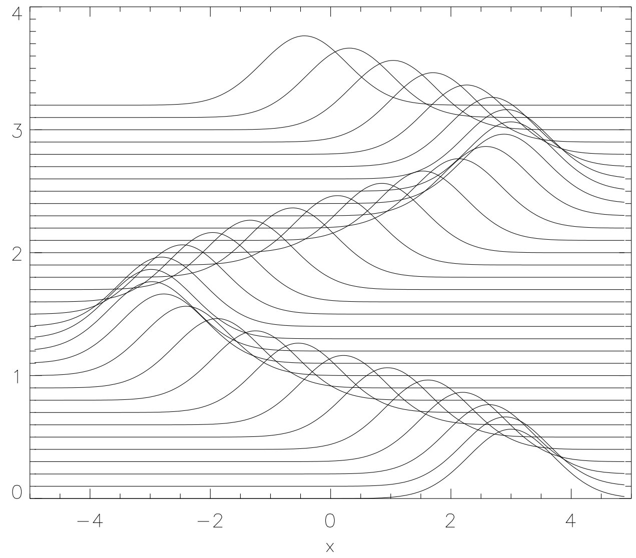


Figure 4.4: *The probability distribution* $|\Psi(x,t)|^2$ *for the coherent state*

hand, is not trivial, and is not determined by general considerations. Thus we have a whole family of solutions for different values of a and ϕ, each of the form

$$\Psi(x,t) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar}\left((x^2 - 2\mathbf{a}x + \mathbf{a}^2/2 + a^2/2\right) - \frac{i\omega t}{2}\right).$$

This set of solutions provides an interesting example of several of the ideas we looked at in earlier chapters. The first priority is simply to look at the probability distribution of position which these solutions have, in order to discover what sort of motion is being described. The probability distribution is given by the square modulus of the wavefunction, which we find by separating the real and imaginary parts of the exponent, as in box 4.3:

$$|\Psi(x,t)|^2 = \sqrt{\frac{m\omega}{\pi\hbar}} \exp\left(-\frac{m\omega}{\hbar}\left(x - a\cos(\omega t - \phi)\right)\right). \tag{4.54}$$

This is simply a Gaussian, or normal, distribution of probability, centred at $\langle x\rangle = a\cos(\omega t - \phi)$, with a constant width. This is illustrated in figure 4.4, which shows the probability distribution $|\Psi(x,t_n)|^2$ at times $t_n = n/4\omega$, from $t_0 = 0$ to $t_{32} = 8/\omega$, for a specific choice of $\mathbf{a}(0)$, given by $a = 3\sqrt{\hbar/m\omega}$ and $\phi = 0$. The probability distribution at each successive time is displaced upwards on the plot. The figure clearly shows a wavepacket of probability executing simple harmonic motion. This is like the wavepacket solution we constructed for the square well, except that in this case the width of the wavepacket is fixed — the only time-dependence in $|\Psi(x,t)|^2$ is in $\langle x\rangle$, and not in the width of the wavepacket. For this reason this family of solutions are known as coherent states, because the wavepacket maintains its structure over time.

The width corresponds to a mean square deviation of $\Delta x^2 = \langle (x - \langle x\rangle)^2\rangle$ of $\hbar/2m\omega$. Thus the solution represents a moving wave-packet executing simple harmonic motion with amplitude a and phase ϕ. The parameter $\mathbf{a} = a\,e^{i\phi}$ in the solution thus corresponds in an expectation-value sense to the classical complex variable $\mathbf{a}$ introduced in section 4.1, which is why they have been given the same symbol. The classical $\mathbf{a}$ was defined as $x + ip/m\omega$, and the correspondence extends to the imaginary part of $\mathbf{a}$ as well: it is not difficult to show that the expectation value of p is $m\omega a \sin(\omega t - \phi)$, just as in the classical case. A further calculation shows that the momentum probability distribution is also Gaussian, and has mean square width $\Delta p^2 = \hbar m\omega/2$. The wave-packet thus satisfies $\Delta x\,\Delta p = \hbar/2$ at all times, and is thus a minimum-uncertainty wave-packet.

lack of quantisation; classical limit; expansion in eigenstates using generating function; coherent state

4.5 Problems

4.1 The wavefunction (in one linear dimension) has dimensions of $[L]^{-1/2}$, since $|\psi(x)|^2$ is a probability density (per unit x). To change ψ to natural units $\xi = x/L_{\mathrm{HO}}$ we therefore have to multiply by $\sqrt{L_{\mathrm{HO}}}$. Show that if $\psi(x)$ is a normalised wavefunction, that is

$$\int_{-\infty}^{\infty} |\psi(x)|^2\,dx = 1$$

then $\phi(\xi) = \sqrt{L_{\mathrm{HO}}}\,\psi(L_{\mathrm{HO}}\xi)$ is a normalised wavefunction in natural units, in the sense that $|\phi(\xi)|^2$ is the probability per unit ξ:

$$\int_{-\infty}^{\infty} |\phi(\xi)|^2\,d\xi = 1.$$

4.2 (i) Using the expansions

$$\exp 2\xi t = \sum_{p=0}^{\infty} \frac{2^p \xi^p t^p}{p!} \qquad \text{and} \qquad \exp -t^2 = \sum_{r=0}^{\infty} \frac{(-1)^r t^{2r}}{r!}$$

and collecting terms in the generating function $G(t,\xi)$ with the same power of t, show that in the Hermite polynomials are $H_n(\xi) = \sum a_p^{(n)} \xi^p$ the polynomial coefficients are given by

$$a_p^{(n)} = \frac{(-1)^r 2^p n!}{r!\,p!} \qquad \text{where} \qquad 2r + p = n. \tag{4.55}$$

(ii) Show that this form for $a_p^{(n)}$, equation (4.55), satisfies the recurrence relation (4.20).

(iii) Show that (4.25) implies $pa_p^{(n)} = 2na_{p-1}^{(n-1)}$, and show that (4.55) satisfies this.

(iv) Show that (4.26) implies $a_p^{(n+1)} = 2a_{p-1}^{(n)} - (p+1)a_{p+1}^{(n)}$, and show that (4.55) satisfies this.

4.3 Using the definition $\xi = \sqrt{m\omega/\hbar}\,x$ and the form of the eigenfunction (4.30), which we can re-arrange as $H_n(\xi) = (\hbar/m\omega)^{1/4} u_n(x)\, e^{m\omega x^2/2\hbar}/N_n$, show that (4.25) is equivalent to $au_n = \sqrt{n}\,u_{n-1}$, and (4.26) is equivalent to $a^\dagger u_n = \sqrt{n+1}\,u_{n+1}$. This completes the proof of the equivalence of the algebraic approach of section 4.3 to the direct approach in terms of Hermite polynomials of section 4.2

4.4

4.5

Chapter 5

Perturbation Theory

The quantum mechanical problems we have so far studied have produced Schroedinger equations that were soluble in terms of relatively simple functions. Such problems are very few in number: the square well and harmonic oscillator in various numbers of dimensions and a fairly good approximation to a one-electron atom are the most important such solutions. Obviously this leaves a large range of systems for which the Schroedinger equation cannot be solved in terms of simple functions. In such cases there is a choice of two approaches: we can find the eigenfunctions and eigenvalues numerically, or we can resort to various approximations to simplify the problem to one which we have already solved. This latter approach sounds *ad hoc* and not very useful, but in fact it is one of the most important quantum mechanical techniques. There are two reasons for this: firstly, a surprising number of problems can be modelled as having a potential which is close to flat (square well), quadratic (harmonic oscillator) or reciprocal (one-electron atom), so that the perturbation approach is a natural one. Secondly, perturbation theory tells us how to evaluate the effect of *any* small additional term in the Hamiltonian, whether we can solve the unperturbed problem or not, and this allows us to make accurate calculations of small effects in complicated systems like real atoms even where we certainly cannot solve the unperturbed problem in general. The later chapters of the book contain many examples of such calculations.

So what is a perturbation? Formally it is a small term in a Hamiltonian, so that the Hamiltonian for the problem, H, can be written

$$H = H^{(0)} + H' \tag{5.1}$$

where $H^{(0)}$ is the unperturbed Hamiltonian, and H' is the perturbation, which in some sense (to be made more precise later) is small compared with $H^{(0)}$. It is perhaps helpful to discuss a few actual examples. In chapter 8 we shall solve the Schroedinger equation for the hydrogen atom, or more precisely for a simplified model of hydrogen, where the only interaction between the electron and nucleus is the Coulomb inverse square electrostatic attraction. In a real hydrogen atom there are also magnetic forces, generated by the motion of the particles, but these are much weaker than the Coulomb force, by a factor of order v^2/c^2 where v is a typical particle velocity and c is the velocity of light. In this case the Hamiltonian used in chapter 8 is $H^{(0)}$, and the perturbation is the additional term representing the magnetic interactions. This perturbation has a fixed size, but in other cases it may be under our control. In chapter **??** we shall consider the effect of an external magnetic field B on an atom, and in this case the perturbation is proportional to B, which we can vary over a large range including zero. Thus in each case there is a perturbation parameter β such that the perturbation is proportional to β: in the first case $\beta = 1/c^2$ and is fixed, and in the second case $\beta = B$ and is under our control. In either case, if we set $\beta = 0$ we recover the unperturbed Hamiltonian.

The question we wish to answer is: what is the effect of the perturbation H' on the energy levels and wavefunctions of the unperturbed system, that is, how do eigenvalues and eigenfunctions vary with β? In the second case we can vary β by varying the B field to verify the results of perturbation theory, but in the first case we only have actual data for the fixed value of β. However we can still examine the variation with β mathematically, and the fundamental assumption of perturbation theory is that we can represent this variation as a power series in β where each successive term is much smaller than its predecessor. We shall only consider the first few terms in the series, in particular the first order term, where the changes in eigenvalue and eigenfunction are proportional to β, and the second order term where they are proportional to β^2.

5.1 First-Order Perturbation Theory for a Non-degenerate Level

One of the more difficult aspects of perturbation theory is the notation, as it is necessary to indicate both the order of perturbation theory, and one or more quantum numbers for the state(s) being considered. The order of perturbation will be indicated by a number of primes, with an unprimed quantity being the exact result for the perturbed system. The exact result for the unperturbed system ought thus to be indicated by zero primes, so this will be shown as a superscript zero in brackets. All of these conventions are used in (5.1). Subscripts can then be used to indicate the quantum numbers in the usual way.

The exact wavefunction and eigenvalue thus satisfy

$$H\psi_n = E_n\psi_n. \tag{5.2}$$

The use of perturbation theory implies that we cannot solve this directly, but that we can separate H into an unperturbed part and a perturbation according to (5.1). We assume we have a complete solution for the unperturbed problem: in the unperturbed Schroedinger equation

$$H^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \tag{5.3}$$

all the eigenfunctions and eigenvalues are assumed known. We are going to concentrate initially on one, non-degenerate eigenvalue $E_n^{(0)}$ with wavefunction $\psi_n^{(0)}$; as mentioned above we are assuming that $\psi_n^{(0)}$ is a good approximation to the unknown exact wavefunction ψ_n. Before deriving the results of perturbation theory we want to make this fundamental assumption more explicit.

The set of unperturbed states $\psi_n^{(0)}$ is a complete set, so we can expand the exact ψ_n in terms of them:

$$\psi_n = \sum_m c_{mn}\psi_m^{(0)} \tag{5.4}$$

but of course we do not know the coefficients c_{mn} any more than we know ψ_n. However, if both ψ_n and all the $\psi_m^{(0)}$ are normalised to unity then we know that

$$\sum_m |c_{mn}|^2 = 1 \tag{5.5}$$

and we can always choose the phase of ψ_n such that c_{nn} is real and positive. Our fundamental assumption that $\psi_n^{(0)}$ is a good approximation to ψ_n can thus be stated as $c_{nn} \approx 1$, and $|c_{mn}| \ll 1$ for $m \neq n$; in other words, the terms in the summation (5.4) are all very small except for the main term, which we can separate out:

$$\psi_n = c_{nn}\psi_n^{(0)} + \sum_{m\neq n} c_{mn}\psi_m^{(0)}. \tag{5.6}$$

Next we define $a_{mn} = c_{mn}/c_{nn}$ for $m \neq n$, enabling us to factor out c_{nn}:

$$\psi_n = c_{nn}\left(\psi_n^{(0)} + \sum_{m\neq n} a_{mn}\psi_m^{(0)}\right). \tag{5.7}$$

This shows that apart from an overall normalisation factor c_{nn} the correction to the unperturbed wavefunction $\psi_n^{(0)}$ can be written entirely in terms of other wavefunctions, with $m \neq n$, and this is a result which we shall use repeatedly. Another way of stating this result is that the correction to the wavefunction (the second term in (5.7)) is orthogonal to the unperturbed wavefunction.

Finally we relax the requirement for ψ_n to be normalised, and note that a perfectly satisfactory but unnormalised wavefunction is given by

$$\psi_n = \left(\psi_n^{(0)} + \sum_{m\neq n} a_{mn}\psi_m^{(0)}\right). \tag{5.8}$$

Since by hypothesis $c_{nn} \approx 1$ the difference in normalisation is small; in fact from (5.7)

$$c_{nn} = \frac{1}{\sqrt{(1+\sum_{m\neq n}|a_{mn}|^2)}} \approx 1 - \frac{1}{2}\sum_{m\neq n}|a_{mn}|^2 \tag{5.9}$$

so that the error is at least second order in the perturbation, since the a_{mn} are at least first order. Equation (5.8) is the form we shall assume for our perturbed wavefunction.

We can now write down our order-by-order expansion of ψ_n and E_n:

$$\begin{aligned} \psi_n &= \psi_n^{(0)} + \psi_n' + \psi_n'' \dots \\ E_n &= E_n^{(0)} + E_n' + E_n'' \dots \end{aligned} \tag{5.10}$$

where, when necessary, each correction term in the wavefunction can be expanded like the second term in (5.8); for example

$$\psi_n' = \sum_{m\neq n} a'_{mn}\psi_m^{(0)}. \tag{5.11}$$

We substitute (5.10) into the Schroedinger equation (5.2), and collect together terms of the same order:

$$\left(H^{(0)}\psi_n^{(0)} - E_n^{(0)}\psi_n^{(0)}\right) + \left(H^{(0)}\psi_n' - E_n^{(0)}\psi_n' + H'\psi_n^{(0)} - E'\psi_n^{(0)}\right)\dots = 0. \tag{5.12}$$

Here the first bracket contains only unperturbed quantities (superscript (0)) and is therefore of zeroth order; the second bracket contains terms involving only one first-order (primed) quantity, and is therefore of first order. Second and higher-order terms are indicated by the ellipsis. The key step is the recognition that these brackets must separately equal zero. This is because our solution to the Schroedinger equation, if it is to be of any use, must be valid over a range of values of the perturbation parameter β, in which case the coefficient of each power of β in (5.12) must be zero. In the case of a genuinely variable perturbation parameter, like the external magnetic field example discussed above, it is obvious that we require solutions for a range of β; in the case of a fundamentally fixed parameter, like the $\beta = 1/c^2$ example, it is not so obvious, but it follows from the fact that we are starting from a valid wavefunction and eigenvalue in the unperturbed limit $\beta = 0$, and we are trying to correct this solution to the actual value of β.

Equating the first bracket in (5.12) to zero gives the unperturbed Schroedinger equation (5.3), which is already satisfied. Equating the next bracket to zero gives the equation which determines the first-order corrections to the eigenvalue and wavefunction:

$$\left(H^{(0)}\psi_n' - E_n^{(0)}\psi_n'\right) + \left(H'\psi_n^{(0)} - E_n'\psi_n^{(0)}\right) = 0. \tag{5.13}$$

The first two terms involve the unknown wavefunction correction ψ_n', and the last term the unknown eigenvalue correction E_n'. To separate these corrections we use the orthogonality properties of the unperturbed eigenfunctions. We first multiply by $\psi_n^{(0)\star}$ and integrate over all space; this function is orthogonal to the terms involving ψ_n', so these terms vanish, as we can quickly show. The first term gives the integral

$$\int \psi_n^{(0)\star} H^{(0)} \psi_n' \, d\tau = \int \left(H^{(0)}\psi_n^{(0)}\right)^\star \psi_n' \, d\tau = E_n^{(0)} \int \psi_n^{(0)\star} \psi_n' \, d\tau \tag{5.14}$$

where we have used the Hermitian property of $H^{(0)}$. This manipulation has reduced the first term to be identical with the second term, so that the terms cancel. In fact both terms are zero because, as shown above, the correction to the wavefunction can be written in terms of the unperturbed eigenfunctions $\psi_m^{(0)}$ with $m \neq n$, and these are all orthogonal to $\psi_n^{(0)}$. Thus only the last two terms remain:

$$E_n' \int \psi_n^{(0)\star} \psi_n^{(0)} \, d\tau = \int \psi_n^{(0)\star} H' \psi_n^{(0)} \, d\tau \tag{5.15}$$

which we can re-arrange to give an expression for the perturbation to the energy:

$$E_n' = \frac{\int \psi_n^{(0)\star} H' \psi_n^{(0)} \, d\tau}{\int \psi_n^{(0)\star} \psi_n^{(0)} \, d\tau} = \int \psi_n^{(0)\star} H' \psi_n^{(0)} \, d\tau. \tag{5.16}$$

The first equality gives E_n' as the expectation value of the perturbation H' in the unperturbed quantum state $\psi_n^{(0)}$, without making the assumption that $\psi_n^{(0)}$ is normalised to unity; if it is, then the denominator is just 1, giving the second equality. Thus the first-order shift in the eigenvalue is the expectation value of the perturbation in the unperturbed state.

To find the correction to the wavefunction we must eliminate the term involving E_n' from (5.13), which we can do by multiplying by any of the $\psi_m^{(0)\star}$ with $m \neq n$, and integrating. The term involving E_n' then vanishes by orthogonality to leave

$$\int \psi_m^{(0)\star} H^{(0)} \psi_n' \, d\tau - E_n^{(0)} \int \psi_m^{(0)\star} \psi_n' \, d\tau + \int \psi_m^{(0)\star} H' \psi_n^{(0)} \, d\tau = 0. \tag{5.17}$$

In the first term we can use the Hermitian property of $H^{(0)}$ as in (5.14) to give

$$\left(E_m^{(0)} - E_n^{(0)}\right) \int \psi_m^{(0)\star} \psi_n' \, d\tau + \int \psi_m^{(0)\star} H' \psi_n^{(0)} \, d\tau = 0. \tag{5.18}$$

We can re-arrange this to give

$$\int \psi_m^{(0)\star} \psi_n' \, d\tau = \frac{\int \psi_m^{(0)\star} H' \psi_n^{(0)} \, d\tau}{\left(E_n^{(0)} - E_m^{(0)}\right)}. \tag{5.19}$$

The integral on the left-hand side is just the overlap between the wavefunction correction ψ'_n and the unperturbed wavefunction $\psi^{(0)}_m$; substituting the expansion of ψ'_n in terms of the $\psi^{(0)}_m$ from (5.11) we find that this gives the expansion coefficient a'_{mn}:

$$a'_{mn} = \frac{\int \psi^{(0)\star}_m H' \psi^{(0)}_n \, d\tau}{\left(E^{(0)}_n - E^{(0)}_m\right)}. \tag{5.20}$$

Thus we can write an explicit equation for ψ'_n, substituting these coefficients into (5.11):

$$\psi'_n = \sum_{m \neq n} \left(\frac{\int \psi^{(0)\star}_m H' \psi^{(0)}_n \, d\tau}{E^{(0)}_n - E^{(0)}_m} \right) \psi^{(0)}_m. \tag{5.21}$$

Referring back to our fundamental assumption that the correction to the wavefunction is small we see that the requirement for the validity of the perturbation approach for a given state is $a'_{mn} \ll 1$ for all $m \neq n$. This in turn implies that the off-diagonal matrix elements of H' (the integrals appearing in the numerator of a'_{mn}) must be much less than the energy differences between $E^{(0)}_n$ and neighbouring states. Equations (5.16) for the energy perturbation and (5.19) for the coefficients of the wavefunction perturbation are the main results of first-order perturbation theory.

Orthogonality of wavefunctions belonging to different eigenvalues is a fundamental quantum-mechanical property, which we have used repeatedly in this argument, and it must also be true for the exact wavefunctions as well as the unperturbed ones. It is not difficult to show that the first-order mixing coefficients satisfy $a'_{mn} = -a'^{\star}_{nm}$, and that this is sufficient to ensure that orthogonality is maintained to first order (see question 5.1). This result also implies that the first-order mixing is equal and opposite: if the state m is mixed into the state n then the state n is equally mixed into the state m, but with the opposite phase.

5.2 Second-Order Perturbation Theory

The general approach to the first-order results in section 5.1 can be generalised to higher order in a fairly obvious way, and an expression for the general p'th order energy is not difficult to find (see question 5.2). In this section we shall simply derive the second-order correction to the energy E''_n, which we shall find is connected to the first-order correction to the wavefunction ψ'_n. We shall not pursue the second-order wavefunction correction, because it is of little practical use unless we need to use very high order perturbation theory for some problem, as the third-order correction to the energy E'''_n can also be written in terms of ψ'_n (see question 5.4) and in general a p'th order wavefunction correction is sufficient to calculate the energy to order $2p + 1$.

The second-order term, which was omitted from (5.12), is obviously

$$\left(H^{(0)}\psi_n'' - E_n^{(0)}\psi_n''\right) + \left(H'\psi_n' - E_n'\psi_n'\right) = E_n''\psi_n^{(0)}. \tag{5.22}$$

As with the terms involving ψ_n' in (5.13), the unknown terms involving ψ_n'' can be eliminated by multiplying by $\psi_n^{(0)\star}$ and integrating; since ψ_n' is also orthogonal to $\psi_n^{(0)}$ this also removes the last term on the left-hand side to leave

$$\int \psi_n^{(0)\star} H_n' \psi_n' \, d\tau = E_n'' \int \psi_n^{(0)\star} \psi_n' \, d\tau. \tag{5.23}$$

Again we recognise the normalisation integral on the right-hand side, giving

$$E_n'' = \int \psi_n^{(0)\star} H' \psi_n' \, d\tau \tag{5.24}$$

which shows the very close connection between the second-order perturbation to the energy and the first-order perturbation to the wavefunction: the first-order wavefunction change is a pre-requisite for a second-order energy change. Substituting for ψ_n' from (5.21) we obtain the explicit second-order energy correction:

$$E_n'' = \sum_{m \neq n} \frac{\int \psi_m^{(0)\star} H' \psi_n^{(0)} \, d\tau \int \psi_n^{(0)\star} H' \psi_m^{(0)} \, d\tau}{E_n^{(0)} - E_m^{(0)}} = \sum_{m \neq n} \frac{\left| \int \psi_m^{(0)\star} H' \psi_n^{(0)} \, d\tau \right|^2}{E_n^{(0)} - E_m^{(0)}} \tag{5.25}$$

where the final step uses the Hermitian property of H'.

In addition to (5.24) and (5.25) a third form for E_n'' can be given, substituting for the matrix elements in terms of a_{mn}':

$$E_n'' = \sum_{m \neq n} |a_{mn}'|^2 \left(E_n^{(0)} - E_m^{(0)}\right). \tag{5.26}$$

Bearing in mind the symmetry noted in the previous section between the magnitude of mixing of the state m into n and *vice versa*, we see that one way of describing this result is to say that all states that are intermixed in first order repel in second order. In other words, the total second-order energy shift is the sum of shifts away from the energies of admixed states. In particular the second-order shift of the ground state is always negative, because all other states lie above it.

This form also shows that not only is a wavefunction change a pre-requisite for a second-order shift, it almost inevitably produces one, since the only circumstance in which (5.26) could give zero for E_n'' with some non-zero a_{mn}' would be an accidental cancellation between the shifts induced by mixing of higher- and lower-energy states.

5.3 Discussion of Results

The derivation of the results in sections 5.1 and 5.2 is somewhat intricate, involving several manipulations of integrals. It is therefore particularly important, since the results are going to be used repeatedly, that they are understood as being, in some sense, obvious quite independently of their derivation. That is the aim of the current section.

We first return to the exact Schroedinger equation

$$H\psi_n = E_n\psi_n, \tag{5.27}$$

multiply by $\psi_n^\star$ and integrate over all space to obtain

$$E_n = \frac{\int \psi_n^\star H\psi_n \, d\tau}{\int \psi_n^\star \psi_n \, d\tau} = \langle H \rangle. \tag{5.28}$$

Thus the exact energy is the expectation value of the exact Hamiltonian in the exact eigenstate. If we recall the theory of measurement, this is an obvious result: on the one hand, a measurement of an observable on a system in an eigenstate results in the eigenvalue with certainty, and on the other hand the expectation value is the average of possible results of measurement. In an eigenstate there is but one value to average, and so the eigenvalue is also an expectation value.

We next introduce our fundamental assumption that the unperturbed wavefunction is a good approximation to the exact wavefunction:

$$\begin{aligned} E_n &\approx \frac{\int \psi_n^{(0)\star} H \psi_n^{(0)} \, d\tau}{\int \psi_n^{(0)\star} \psi_n^{(0)} \, d\tau} \\ &= \int \psi_n^{(0)\star} (H^{(0)} + H') \psi_n^{(0)} \, d\tau = E_n^{(0)} + E_n'. \end{aligned} \tag{5.29}$$

The final step here uses the expression derived above for the first-order perturbation to the energy. We have therefore shown that the form of the first-order perturbation to the energy is a straightforward consequence of the fundamental assumption that the unperturbed wavefunction is a good approximation to the exact wavefunction; essentially we are assuming that the wavefunction has not changed while the Hamiltonian has changed, and the energy difference is just the expectation value of this change in Hamiltonian.

This makes the relationship (5.24) between the change in the wavefunction and the second-order perturbation to the energy entirely natural: if there is no change in the wavefunction then the fundamental assumption is true without approximation, and there is no approximation in (5.29). Under these circumstances the second order perturbation to the energy is zero, so that a direct relationship between E_n'' and ψ_n' is inevitable.

We can extend this argument slightly by substituting the expansion $\psi_n = \psi_n^{(0)} + \psi_n' + \psi_n''$ into (5.28), as in (5.10), instead of the unperturbed function. At this point we are simply assuming that ψ_n' and ψ_n'' are first- and second order corrections to the wavefunction (that is, they vary linearly or quadratically with β) and that they are orthogonal to ψ_n. We collect together terms of the same order in numerator and denominator, and neglect those which vanish by orthogonality or are higher than second order (the details are left to question 5.3):

$$E_n = \frac{E_n^{(0)} + E_n' + \left(\int \psi_n'^\star H' \psi_n^{(0)}\, d\tau + \int \psi_n'^\star H^{(0)} \psi_n'\, d\tau + \int \psi_n^{(0)\star} H' \psi_n'\, d\tau\right)}{1 + \left(\int \psi_n'^\star \psi_n'\, d\tau\right)}. \tag{5.30}$$

(Note that all terms involving ψ_n'' have vanished at this stage.) Now we expand the denominator and retain terms up to second order; note that because of the orthogonality of $\psi_n^{(0)}$ and ψ_n' there are no first-order terms in the denominator, so that to second order we can approximate

$$\frac{1}{1 + \left(\int \psi_n'^\star \psi_n'\, d\tau\right)} \approx 1 - \int \psi_n'^\star \psi_n'\, d\tau. \tag{5.31}$$

Collecting terms and neglecting higher order terms again we find

$$E_n = E_n^{(0)} + E_n' + \left(\int \psi_n'^\star H' \psi_n^{(0)}\, d\tau + \int \psi_n'^\star \left(H^{(0)} - E_n^{(0)}\right) \psi_n'\, d\tau + \int \psi_n^{(0)\star} H' \psi_n'\, d\tau\right) \ldots \tag{5.32}$$

The second-order correction contains three terms. The first term in the bracket is clearly related to the third, and is in fact the complex conjugate of it, using the Hermitian property of H'. In fact, both terms are real, since the third term is equal to E_n'' by (5.24), which is necessarily real. The middle term is equal to $-E_n''$ by (5.26), so that the whole second order term reduces to $E_n'' - E_n'' + E_n'' = E_n''$. Thus while the first-order perturbation to the energy results from the change in Hamiltonian with no change in the wavefunction, the second-order perturbation combines a number of effects: the cross-terms involving the change in wavefunction combined with the change in Hamiltonian, the unperturbed energy of the wavefunction perturbation, and the normalisation change of the unperturbed part of the wavefunction.

5.4 A Worked Example

In this section the energy and wavefunction perturbations are found for a simple example, a perturbation to the infinite square well, which is chosen because of the simplicity of its eigenfunctions, so that all the integrals can easily be evaluated.

The unperturbed Hamiltonian is that for an infinite square well between 0 and b, with zero potential inside the well:

$$H^{(0)} = \frac{p^2}{2m} \qquad 0 < x < b \tag{5.33}$$

$$= \infty \qquad x < 0, \quad x > b. \tag{5.34}$$

The unperturbed wavefunctions and eigenvalues are given by (1.24) and (1.25):

$$\psi_n^{(0)} = \sqrt{\frac{2}{b}} \sin \frac{n\pi x}{b} \qquad n = 1, 2 \ldots \tag{5.35}$$

$$E_n^{(0)} = \frac{\hbar^2 \pi^2 n^2}{2mb^2}. \tag{5.36}$$

The perturbation we shall consider is given by an extra potential inside the well such that the bottom is not flat:

$$H' = V_0 \cos \frac{2\pi x}{b}. \tag{5.37}$$

This example has been chosen to give a simplification: the product $H'\psi_n^{(0)}$ can easily be written in terms of other unperturbed wavefunctions using trigonometric addition formulae:

$$H'\psi_n^{(0)} = V_0 \sqrt{\frac{2}{b}} \sin \frac{n\pi x}{b} \cos \frac{2\pi x}{b} = \frac{V_0}{2} \sqrt{\frac{2}{b}} \left(\sin \frac{(n+2)\pi x}{b} + \sin \frac{(n-2)\pi x}{b} \right) \tag{5.38}$$

$$= \frac{V_0}{2} \left(\psi_{n+2}^{(0)} + \psi_{n-2}^{(0)} \right). \tag{5.39}$$

Equation (5.38) has to be used with caution for $n = 1$ and $n = 2$, because of the occurence of $\psi_0^{(0)}$ and $\psi_{-1}^{(0)}$, which are not defined in (5.35). The case $n = 2$ is straightforward:

$$H'\psi_2 = V_0 \sqrt{\frac{2}{b}} \sin \frac{2\pi x}{b} \cos \frac{2\pi x}{b} = \frac{V_0}{2} \sqrt{\frac{2}{b}} \sin \frac{4\pi x}{b} = \frac{V_0}{2} \psi_4^{(0)} \tag{5.40}$$

so that, in effect, $\psi_0^{(0)} = 0$. The case $n = 1$ is not difficult:

$$H'\psi_1 = V_0 \sqrt{\frac{2}{b}} \sin \frac{\pi x}{b} \cos \frac{2\pi x}{b} = \frac{V_0}{2} \sqrt{\frac{2}{b}} \left(\sin \frac{3\pi x}{b} - \sin \frac{\pi x}{b} \right) = \frac{V_0}{2} \left(\psi_3^{(0)} - \psi_1^{(0)} \right) \tag{5.41}$$

so that in effect $\psi_{-1}^{(0)} = -\psi_1^{(0)}$. With these relations all the integrals can be reduced to overlap and normalisation integrals.

We first consider the first-order perturbation to the energy. This is given by (5.16):

$$E_n' = \int \psi_n^{(0)\star} H' \psi_n^{(0)} \, d\tau = \frac{V_0}{2} \int \psi_n^{(0)\star} \left(\psi_{n+2}^{(0)} + \psi_{n-2}^{(0)} \right) d\tau = 0 \tag{5.42}$$

where the last step follows from the orthogonality of the unperturbed wavefunctions. Thus the first-order energy perturbation is zero in all states, except for the special case of the ground state, $n = 1$:

$$E_1' = \int \psi_1^{(0)\star} H' \psi_1 \, d\tau = \frac{V_0}{2} \int \psi_1^{(0)\star} \left(\psi_3^{(0)} - \psi_1^{(0)} \right) d\tau = -\frac{V_0}{2} \tag{5.43}$$

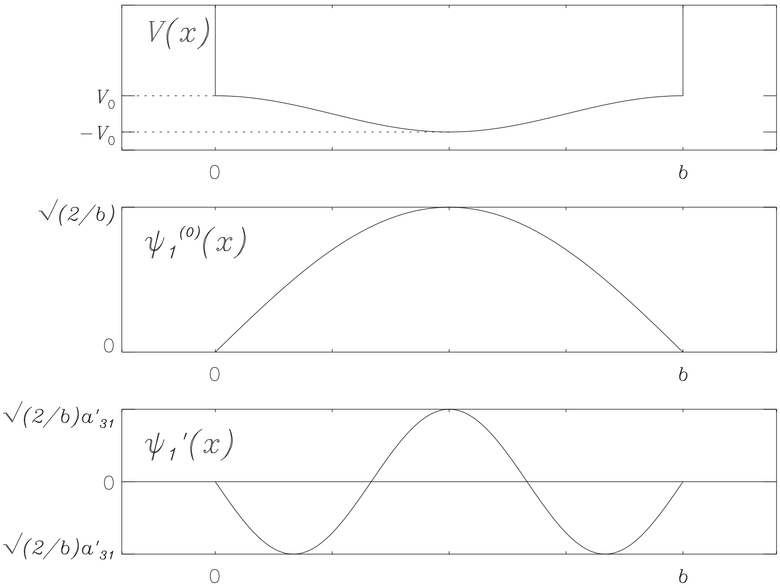


Figure 5.1: *The perturbed square well, ground state wavefunction and wavefunction perturbation*

where the final step follows from the normalisation of $\psi_1^{(0)}$.

We next consider the second-order perturbation to the energy, and the related first-order perturbation to the wavefunction. The expansion coefficients a'_{mn} of the wavefunction perturbation are given by (5.21):

$$a'_{mn} = \frac{\int \psi_m^{(0)\star} H' \psi_n \, d\tau}{E_n^{(0)} - E_m^{(0)}} = \frac{V_0}{2} \frac{\int \psi_m^{(0)\star} \left(\psi_{n+2}^{(0)} + \psi_{n-2}^{(0)} \right) \, d\tau}{E_n^{(0)} - E_m^{(0)}}. \tag{5.44}$$

Clearly the integral vanishes unless $m = n \pm 2$, in which case it is $V_0/2$. Thus the non-zero coefficients are given by $a_{n+2,n} = \frac{1}{2} V_0 / \left(E_n^{(0)} - E_{n+2}^{(0)} \right)$ and $a_{n-2,n} = \frac{1}{2} V_0 / \left(E_n^{(0)} - E_{n-2}^{(0)} \right)$ and in the cases $n = 1$ or 2 only the $n + 2$ coefficient exists. Similarly the second order perturbation to the energy is given by (5.24) or (5.25), which involve the same integral as the wavefunction, but squared:

$$E''_n = \frac{V_0^2}{4} \left(\frac{1}{E_n^{(0)} - E_{n-2}^{(0)}} + \frac{1}{E_n^{(0)} - E_{n+2}^{(0)}} \right) \tag{5.45}$$

where again only the $n + 2$ term exists for $n = 1$ or 2.

We shall look more closely at the case of the ground state, $n = 1$. Only a single expansion coefficient is non-zero:

$$a'_{31} = \frac{V_0}{2 \left(E_1^{(0)} - E_3^{(0)} \right)}. \tag{5.46}$$

The wavefunction perturbation is simply given by

$$\psi'_1 = a'_{31} \psi_3^{(0)}. \tag{5.47}$$

Our fundamental assumption that the perturbation to the wavefunction is small can be expressed as an inequality: $|a_{31}| \ll 1$ or

$$\frac{V_0}{2} \ll \left(E_3^{(0)} - E_1^{(0)}\right) \tag{5.48}$$

which must hold for the perturbation approach to be valid. Note that the inequality depends on the size of the perturbation V_0 in comparison with the difference of eigenvalues, rather than the absolute size of the eigenvalues. The perturbed well, unperturbed wavefunction and the perturbation are sketched in Figure 5.1; we see that the effect of the perturbation is to concentrate the wavefunction at the bottom of the potential well, and to diminish the wavefunction at the edges of the well where the potential energy is greater.

Finally we shall look at the wavefunction for states with large n. Using $E_n^{(0)} = n^2 E_1^{(0)}$ from (5.36), the energy differences are given by $E_n^{(0)} - E_{n-2}^{(0)} = (4n-4)E_1^{(0)}$ and $E_n^{(0)} - E_{n+2}^{(0)} = -(4n+4)E_1^{(0)}$. The wavefunction pertubation can thus be written

$$\begin{aligned}
\psi_n' &= \frac{V_0}{8E_1^{(0)}}\sqrt{\frac{2}{b}}\left(\frac{\sin(n-2)\pi x/b}{n-1} - \frac{\sin(n+2)\pi x/b}{n+1}\right) \\
&= \frac{V_0}{8(n^2-1)E_1^{(0)}}\sqrt{\frac{2}{b}}\left((n+1)\sin\frac{(n-2)\pi x}{b} - (n-1)\sin\frac{(n+2)\pi x}{b}\right) \\
&= \frac{V_0}{4(n^2-1)E_1^{(0)}}\sqrt{\frac{2}{b}}\left(\sin\frac{n\pi x}{b}\cos\frac{2\pi x}{b} - n\cos\frac{n\pi x}{b}\sin\frac{2\pi x}{b}\right).
\end{aligned}$$

Combining this with the unperturbed wavefunction we find the corrected wavefunction

$$\begin{aligned}
\psi_n^{(0)} + \psi_n' &= \sqrt{\frac{2}{b}}\left((1+\alpha(x))\sin\frac{n\pi x}{b} + \beta(x)\cos\frac{n\pi x}{b}\right) \\
&\approx \sqrt{\frac{2}{b}}\Big(1+\alpha(x)\Big)\sin\left(\frac{n\pi x}{b} + \beta(x)\right).
\end{aligned}$$

Here the final step is an approximation based on the fact that α and β are both small quantities much less than unity, so that we can neglect their products or squares. Thus the perturbed wavefunction has its amplitude re-distributed by the α term and its phase shifted by the β term. A physical interpretation of the form of α and β is given in question 5.5.

5.5 Degenerate Perturbation Theory.

In this section we consider the situation where one unperturbed eigenvalue $E_n^{(0)}$ is g-fold degenerate — the functions $\psi_{nk}^{(0)}$, $k = 1 \ldots g$, are all orthogonal eigenfunctions of $H^{(0)}$ with the same eigenvalue:

$$H^{(0)}\psi_{nk}^{(0)} = E_n^{(0)}\psi_{nk}^{(0)}. \tag{5.49}$$

This circumstance forces us to modify our approach to perturbation theory, because our fundamental assumption that we are starting from a known good approximation to the wavefunction is no longer necessarily valid. We shall start by examining the reasons for this.

In general the effect of the perturbation will be to lift the degeneracy — that is, the perturbed states will no longer be degenerate — although if $H^{(0)}$ and H' share some symmetry then this need not occur. Assuming for the moment that the degeneracy is lifted, we concentrate on just one of the perturbed states and consider what happens as the perturbation becomes vanishingly small ($\beta \to 0$). Obviously the energy of the state will tend to the unperturbed value $E_n^{(0)}$, but what about the wavefunction? It will tend to some definite superposition of the $\psi_{nk}^{(0)}$, but in general we do not know *a priori* what that superposition is. If we choose some other perturbed state, its wavefunction will tend to some other linear combination of the $\psi_{nk}^{(0)}$, orthogonal to the first one. In the limit $\beta \to 0$ there is thus a set of states with wavefunctions $\phi_{nl}^{(0)}$ defined by coefficients c_{kl}:

$$\phi_{nl}^{(0)} = \sum_k c_{kl} \psi_{nk}^{(0)}. \tag{5.50}$$

In order that these wavefunctions are orthonormal we require

$$\sum_k c_{kl'}^{\star} c_{kl} = \delta_{l'l}. \tag{5.51}$$

(This condition defines this transformation from the $\psi_{nk}^{(0)}$ basis to the $\phi_{nl}^{(0)}$ basis to be unitary.) Our fundamental assumption can now be re-stated in a form appropriate for degenerate states: the exact wavefunctions of the states which are degenerate in zeroth order can be written

$$\phi_{nl} = \phi_{nl}^{(0)} \ + \sum_{m \neq n} a_{m,nl} \psi_m^{(0)}. \tag{5.52}$$

Here the first term is the zeroth-order wavefunction just derived, with coefficients c_{kl} which are at present unknown, and the second term is the wavefunction perturbation induced by admixture of other states.

We note in passing that in writing (5.52) we have made a further assumption which does not follow from the discussion preceding it, which is that none of the other degenerate states is mixed in by the perturbation. The $m \neq n$ on the summation excludes not only the the first term $\phi_{nl}^{(0)}$ but also the other unperturbed states $\phi_{nl'}^{(0)}$ belonging to the same unperturbed eigenvalue. This assumption is valid: the $\phi_{nl}^{(0)}$ are not only the correct zeroth-order wavefunctions, they are also the correct wavefunctions to all orders within the degenerate set, and corrections to these wavefunctions only involve states of other energies. However the proof of this is left to question 5.6.

From this point we could proceed as before if we knew the correct zeroth-order wavefunctions $\phi^{(0)}_{nl}$. If for some reason we do know what these are — and we shall consider shortly how that might come about — then all of our previous results can be applied unchanged. The first-order energy shift is the expectation value of the perturbation in these states, and the second-order energy shift follows from the first-order wavefunction perturbation as before. However if we do not know the coefficients c_{kl} then we must proceed by a different route.

We introduce an order-by-order expansion of the wavefunction and eigenvalue as in (5.10):

$$\begin{aligned}\phi_{nl} &= \phi^{(0)}_{nl} + \phi'_{nl}\dots && (5.53)\\ E_{nl} &= E^{(0)}_{n} + E'_{nl}\dots && (5.54)\end{aligned}$$

where $\phi^{(0)}_{nl}$ is given by (5.50) and ϕ'_{nl} by the first-order part of the wavefunction correction in (5.52):

$$\phi'_{nl} = \sum_{m\neq n} a'_{m,ln}\psi_m. \tag{5.55}$$

Substituting these into the Schrodinger equation gives us the zeroth-order equation which is already satisfied, and the first-order equation

$$\left(H^{(0)} - E^{(0)}_{n}\right)\phi'_{nl} + \left(H' - E'_{nl}\right)\phi^{(0)}_{nl} = 0. \tag{5.56}$$

This equation determines the coefficients c_{kl} which define the zeroth-order wavefunctions, the first-order energy shifts E'_{nl} and the first-order wavefunction perturbation ϕ'_{nl}. The wavefunction perturbation is discussed further in question refPert:Q5, and here we will concentrate on c_{kl} and E'_{nl}.

We multiply by one of the known unperturbed wavefunctions $\psi^{(0)}_{nk}$ and integrate over all space. The first two terms vanish in the same way as in the analogous first-order equation, between (5.13) and (5.15), to leave

$$\int \psi^{(0)\star}_{nk} H' \phi^{(0)}_{nl}\, d\tau = E'_{nl}\int \psi^{(0)\star}_{nk}\phi^{(0)}_{nl}\, d\tau. \tag{5.57}$$

We substitute the expansion of $\phi^{(0)}_{nl}$ in terms of $\psi^{(0)}_{nk}$ from (5.50) on each side. On the right-hand side the orthogonality of the $\psi^{(0)}_{nk}$ picks out a single term in the expansion, while on the left-hand side we obtain a sum of terms:

$$\sum_{k} c_{k'l}\int \psi^{(0)\star}_{nk} H' \psi^{(0)}_{nk'}\, d\tau = E'_{nl}c_{kl}. \tag{5.58}$$

The structure of this expression is much clearer if we adopt a matrix notation. We write the coefficients c_{kl} for a fixed state l as a vector

$$\mathbf{c}_l = \begin{pmatrix} c_{1l} \\ \vdots \\ c_{gl} \end{pmatrix} \tag{5.59}$$

and we define $\mathbf{H}'$ to be the matrix with elements

$$H'_{kk'} = \int \psi_{nk}^{(0)\star} H' \psi_{nk'}^{(0)}\, d\tau. \tag{5.60}$$

With these substitutions we can write (5.58) as

$$\mathbf{H}'\mathbf{c}_l = E'_{nl}\mathbf{c}_l. \tag{5.61}$$

This is simply an eigenvector equation. Since $\mathbf{H}'$ is a Hermitian matrix it has g orthogonal eigenvectors $\mathbf{c}_l$, and g eigenvalues E'_{nl} which may or may not be distinct, and these give the required coefficients c_{kl} and first-order energy shifts E'_{nl}. Note that the assumption which we made at the outset that the degeneracy is completely lifted turns out not to be crucial: if the assumption is not valid then we shall obtain repeated eigenvalues of $\mathbf{H}'$, but the method does not fail to work.

Thus finding the energy perturbations for a degenerate state involves finding the eigenvalues of a matrix, and if we need to know what the corresponding states are we need also the eigenvectors. This is a more complicated procedure than in the non-degenerate case, and the question naturally arises as to whether there is some other way of finding the correct zeroth-order wavefunctions. In general there is not, but in many cases there is. The criteria are firstly the existence of an Hermitian operator A which commutes with both $H^{(0)}$ and H', and secondly that the degenerate states belong to different eigenvalues of A. Suppose such an operator exists. The fact that $[A, H^{(0)}] = 0$ implies that we can choose the eigenfunctions of $H^{(0)}$ to be eigenfunctions of A also, while the fact that $[A, H^{(0)} + H'] = 0$ implies that the same is true of the exact eigenfunctions. This suggests that this basis is the right one to use to diagonalise $\mathbf{H}'$. It is easy to show that this is true: we suppose that this basis is the $\phi_{nl}^{(0)}$ basis, and consider a matrix element of the commutator between two different eigenstates of A.

$$\begin{aligned} 0 &= \int \phi_{nl'}^{(0)\star}(AH' - H'A)\phi_{nl}^{(0)}\, d\tau \qquad (5.62) \\ &= (A_{nl'} - A_{nl}) \int \phi_{nl'}^{(0)\star} H' \phi_{nl}^{(0)}\, d\tau \qquad (5.63) \end{aligned}$$

Here A_{nl} is the eigenvalue of A in the $\phi_{nl}^{(0)}$ state. This result shows that the matrix element of H' is zero unless the eigenvalues of A are equal. Thus if all the states which are degenerate in $H^{(0)}$ have different eigenvalues of A then all the off-diagonal matrix elements of H' are zero, and this basis is indeed the $\phi_{nl}^{(0)}$ basis for diagonalising the perturbation. This method for treating perturbations in degenerate states will be used several times in the following chapters. A very simple example is given in question 5.7.

5.6 Problems

5.1 Use the Hermitian property of H' to show that $a'_{mn} = -a'^{\star}_{nm}$. Evaluate the overlap integral for two first-order perturbed wavefunctions $\psi_n^{(0)} + \psi'_n$ and $\psi_m^{(0)} + \psi'_m$, retaining terms up to first-order, and show that this condition is sufficient to ensure that the perturbed wavefunctions are orthogonal to this order.

5.2 Show that the p'th order term in equation (5.12) is

$$\left(H^{(0)} - E_n^{(0)}\right)\psi_n^{(p)} + \left(H' - E'_n\right)\psi_n^{(p-1)} - E''_n\psi_n^{(p-2)} \ldots - E_n^{(p)}\psi_n^{(0)} = 0. \tag{5.64}$$

Adapt the method used to derive the second-order perturbation to the energy to derive

$$E_n^{(p)} = \int \psi_n^{(0)\star} H' \psi_n^{(p-1)}\, d\tau. \tag{5.65}$$

5.3 Fill in the steps leading to equation (5.32) and verify the equality of the three second-order terms as discussed in the text.

5.4 Show that the third-order perturbation to the energy is given by

$$E'''_n = \int \psi'^{\star}_n \left(H' - E'_n\right)\psi'_n\, d\tau. \tag{5.66}$$

This shows that it can be written in terms of the first-order wavefunction perturbation, as claimed in the text.

The methods used for the first- and second-order terms can be used, but a slightly more powerful approach is quicker. Using Dirac notation equations (5.13) and (5.22) can be written

$$\begin{aligned}\left(H^{(0)} - E_n^{(0)}\right)|n'\rangle &= -\left(H' - E'_n\right)|n^{(0)}\rangle & (5.67)\\ \left(H^{(0)} - E_n^{(0)}\right)|n''\rangle &= -\left(H' - E'_n\right)|n'\rangle + E''_n|n^{(0)}\rangle. & (5.68)\end{aligned}$$

We define the Hermitian operator R by

$$R = \sum_{m \neq n} |m^{(0)}\rangle \frac{1}{E_m^{(0)} - E_n^{(0)}} \langle m^{(0)}|. \tag{5.69}$$

Note that the operation of R on $|n^{(0)}\rangle$ gives zero. Operating on these equations with R gives directly

$$\begin{aligned}|n'\rangle &= -RH'|n^{(0)}\rangle & (5.70)\\ |n''\rangle &= -R\left(H' - E'_n\right)|n'\rangle. & (5.71)\end{aligned}$$

The first of these is simply equation (5.21) in this notation, while the second can be used in equation (5.65) with $p = 3$ to derive the required result.

Show that in the case of the perturbation (5.37) the third-order perturbation in zero in all states except $n = 1$ and $n = 3$, and that $E_1''' = -E_3''' = (1/8)V_0^3/(E_3 - E_1)^2$

5.5 The approximate first-order corrected wavefunction for the perturbed square well (5.49) can be interpreted physically using the probability flux. Like most one-dimensional wavefunctions this form represents a standing wave with zero net flux, but we can easily separate it into two travelling waves

$$\sqrt{\frac{2}{b}}\Big(1+\alpha(x)\Big)\sin\Big(\frac{n\pi x}{b}+\beta(x)\Big) = \sqrt{\frac{2}{b}}\Big(1+\alpha(x)\Big)\exp i\Big(\frac{n\pi x}{b}+\beta(x)-\frac{\pi}{2}\Big)+\text{c.c.} \quad (5.72)$$

and then discuss the probability flux associated with each. We found in **??** that wavefunctions of the form $\sqrt{P}e^{iS(x)}$ represented a probability density P travelling with the local particle velocity $(\hbar/m)\nabla S$, or $(\hbar/m)\frac{dS}{dx}$ in one dimension. Show that in this case

$$\frac{\hbar}{m}\frac{dS}{dx} = \sqrt{\frac{2E_n^{(0)}}{m}}\left(1-\frac{1}{2}V(x)\right) \quad (5.73)$$

and that this is equal to the local classical velocity of a particle with energy $E_n^{(0)}$, to first order in the perturbation $V(x)$. Then show that $\alpha = -\frac{d\beta}{dx}$ and that this result means that the flux variation due to the varying particle velocity is cancelled by a corresponding variation in the probability density, again to first order in the perturbation.

5.6 The statement in the text that (5.56) determines the perturbed wavefunction ϕ'_{nl} is not quite true. Include a term $a'_{nl,nl'}\phi'_{nl'}$ in the expansion of ϕ'_{nl}, and show by taking the matrix element with $\phi^{(0)\star}_{nl'}$ that (5.56) does not allow the coefficient $a'_{nl,nl'}$ to be determined.

That this coefficient is in fact zero follows from the second-order equation

$$\left(H^{(0)} - E_n^{(0)}\right)\phi''_{nl} + \left(H' - E'_{nl}\right)\phi'_{nl} = E''_{nl}\phi^{(0)}_{nl}. \quad (5.74)$$

By taking the matrix element with $\phi^{(0)\star}_{nl'}$, show that this implies $a'_{nl,nl'} = 0$ if $E'_{nl} \neq E'_{nl'}$. An extension of the to all orders of perturbation by induction can be constructed along similar lines: the p'th order equation leaves the coefficient $a^{(p)}_{nl,nl'}$ indeterminate, but the $(p+1)$'th order equation forces it to be zero. This proves the assertion made in the text — that the $\phi^{(0)}_{nl}$ are correct to all orders within the degenerate set of states — in the case that the degeneracy is completely lifted in first order.

5.7 *a)* Consider the rigid rotor discussed in **??**, subject to the perturbation $H' = V_0 \cos 2\phi$. The unperturbed energy levels are given by $E_n^{(0)} = n^2\hbar^2/(2I)$, $n = 0, 1, 2\ldots$, and all levels except $n = 0$ are doubly degenerate. In place of the nk pair of quantum numbers we can thus use a single quantum number n which can take all integer values, positive, negative and zero, with the degenerate pairs given by $\pm n$. As shown in **??**, the angular momentum operator commutes with $H^{(0)}$, so we shall use the angular momentum eigenfunctions $\psi_n^{(0)} = \exp(i\theta)/\sqrt{2\pi}$. Evaluate the elements of $\mathbf{H}'$ for $n = \pm 1$, and hence find the zeroth order eigenfunctions $\phi_{\pm 1}^{(0)}$, and show that the energy shifts are given by $E'_{\pm 1} = \pm V_0/2$.

b) Show that the reflection operator R which reflects an angular function about the $(0, \pi)$ line commutes with $H^{(0)}$ and H', and that the simultaneous eigenfunctions of $H^{(0)}$ and R are $\sin(n\theta)/\sqrt{\pi}$ and $\cos(n\theta)/\sqrt{\pi}$. Hence verify the results of part *a)* without diagonalisation.

Chapter 6

Angular Momentum

Chapter 7

Time-dependent Perturbation Theory

Chapter 8

The Hydrogen Atom

8.1 The Hamiltonian

In this chapter we turn from manifestly model systems, such as the particle in a one-dimensional box, to a real system, the hydrogen atom. In fact we shall treat all systems consisting of two oppositely charged particles bound by their mutual electrostatic attraction, which include hydrogen (proton and electron), but also *hydrogen-like ions*, consisting of a nucleus and a single electron, as well as a number of exotic systems containing muons and positrons which we shall discuss below. However it is important to note that even though we are now discussing a physically realizable quantum system, our discussion of it is still in terms of a model. We are not attempting an *exact* treatment of hydrogen — if indeed such a thing is possible. Essentially all calculations in physics are model calculations in the sense that some aspect of the system is treated approximately, or ignored altogether. We therefore start by briefly considering the approximations we are making in our Hamiltonian. We then go on to discuss the classical solution of the equations of motion, and then the quantum mechanical solution, and finally we examine some of the wavefunctions.

The Hamiltonian, as we have emphasized previously, is the energy function of the system, which in this case consists of kinetic energy T and potential energy V:

$$H = T + V.$$

We shall treat the system in the non-relativistic approximation, so the kinetic energy will be given by

$$T = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} \tag{8.1}$$

where the subscripts 1 and 2 label the two particles, with masses $m_1$and m_2. The particles interact in various ways: we have already mentioned the electrostatic interaction of their charges q_1 and q_2, but this is not the only possibility. If the charges move then they generate magnetic fields which give rise to an additional interaction, and both the electron and proton (and many of the other particles mentioned above) have magnetic moments which also generate and interact with magnetic fields. All of these smaller interactions we shall neglect for the moment, although some of them will be included in later chapters using perturbation theory. The systems we are going to consider all involve particles with integral multiples of the charge on the proton, e, and of opposite sign, so we can write $q_1 q_2 = -Ze^2$. In the case of a hydrogen-like atom, the nuclear charge is Ze, and the electron charge is $-e$. Thus, if the charges are point charges the interaction energy is given by

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \tag{8.2}$$

where r is the inter-particle separation, $r = |\mathbf{r}_1 - \mathbf{r}_2|$.

This however represents an additional approximation for most of the systems we are considering: while electrons, positrons and muons are point charges, the proton and other nuclei have extended charge distributions. If the charge distribution is spherical then (8.2) is still correct when the inter-particle separation is greater than the radius of the charge distribution r_N, but but over-estimates the magnitude of the potential at shorter distances. If the charge distribution is non-spherical then (8.2) is not valid anywhere. The charge distribution of nuclei has a radius of order $r_N = r_0 A^{1/3}$ where A is the mass number and r_0 is about 1.4 fm, that is 1.4×10^{-15} m. Thus for spherical nuclei the interior region where (8.2) is wrong is a very small volume around the origin, and in the case of non-spherical nuclei the corrections are smaller than (8.2) by a factor of r_N^2/r^2, which is also very small except very close to the origin. However our aim here is not to justify the approximations we are making, but simply to point out that they are being made. In principle we can always check *after* we have solved the model that the approximations made in setting it up are justified, even though this may not be apparent when they are made.

Thus our Hamiltonian for hydrogen-like systems is found by combining (8.1) and (8.2):

$$H = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} - \frac{Ze^2}{4\pi\epsilon_0 r} \tag{8.3}$$

8.2 The Classical Solution

The solution of the classical equations of motion derived from (8.3) proceeds in two stages. First we separate the external motion of the centre of mass of the system from the internal orbital motion of the particles about the centre of mass, and then we go on to solve the orbital motion, and find the conserved quantities or constants of the motion.

The separation of the centre of mass motion is not dependent on the specific form of the inter-particle potential provided it is a central potential, that is $V(r)$ not $V(\mathbf{r})$. The forces on the two particles can be found by differentiating with respect to their positions in the usual way:

$$\mathbf{F}_i = -\nabla_i V(r) \tag{8.4}$$

where ∇_i denotes the gradient with respect to the position vector $\mathbf{r}_i$, and the subscript i takes the values 1 or 2. Since V is a function of r we can evaluate the force in (8.4) with the chain rule:

$$\mathbf{F}_i = -\frac{dV}{dr}\nabla_i r. \tag{8.5}$$

The gradient of r we find from differentiating its definition as the modulus of $\mathbf{r}$:

$$\begin{aligned} \mathbf{r} &= \mathbf{r}_1 - \mathbf{r}_2 && (8.6)\\ r &= \sqrt{\mathbf{r}\cdot\mathbf{r}}. && (8.7) \end{aligned}$$

This gives $\nabla_1 r = \mathbf{r}/r = \hat{\mathbf{r}}$ and $\nabla_2 r = -\hat{\mathbf{r}}$. Equation (8.5) then becomes

$$\mathbf{F}_1 = -\frac{dV}{dr}\hat{\mathbf{r}} \qquad \mathbf{F}_2 = \frac{dV}{dr}\hat{\mathbf{r}}. \tag{8.8}$$

This simply states that the magnitude of the force on either particle is given by the derivative of the potential, that the force on particle 1 is directed along the line joining the particles, and that the force on particle 2 is equal in magnitude and opposite in direction; in other words Newton's third law of motion is satisfied by central potentials. Obviously the sign of the force (attractive or repulsive) depends on the sign of the derivative of V.

These forces give us the equations of motion of the two particles:

$$\begin{aligned} \frac{d\mathbf{p}_1}{dt} &= -\frac{dV}{dr}\hat{\mathbf{r}} && (8.9)\\ \frac{d\mathbf{p}_2}{dt} &= \frac{dV}{dr}\hat{\mathbf{r}}. && (8.10) \end{aligned}$$

If we add these two equations, and define the total momentum $\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2$, we obtain

$$\frac{d}{dt}(\mathbf{p}_1 + \mathbf{p}_2) = \frac{d\mathbf{P}}{dt} = 0 \tag{8.11}$$

which implies that the total momentum is conserved quantity, or a constant of the motion. The centre of mass of the system is located at

$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \tag{8.12}$$

so that $\mathbf{P} = M\frac{d\mathbf{R}}{dt}$ where M is the system mass $m_1 + m_2$. Thus the equation $\mathbf{P} =$ constant implies that $\mathbf{R}$ is a linear function of time, so that the centre of mass moves with constant velocity in a straight line, in accordance with Newton's first law of motion for the system as a composite body.

Having separated out the centre of mass motion, defined by the variables $\mathbf{R}$ and $\mathbf{P}$, we have now to find the equation for the internal motion relative to the centre of mass. To do this we find the momentum relative to the centre of mass $\mathbf{p}$. The velocity of the centre of mass is given by $\frac{d\mathbf{R}}{dt} = \mathbf{P}/M$, so that the velocity of particle 1 relative to the centre of mass is given by $\mathbf{p}_1/m_1 - \mathbf{P}/M$. We therefore define the momentum relative to the centre of mass to be m_1 multiplied by ths velocity:

$$\mathbf{p} = \mathbf{p}_1 - \frac{m_1\mathbf{P}}{M} = \frac{m_2\mathbf{p}_1 - m_1\mathbf{p}_2}{m_1 + m_2}. \tag{8.13}$$

A corresponding calculation for particle 2 gives its momentum relative to the centre of mass as $-\mathbf{p}$, which is not surprising, as the reference frame in which the centre of mass is at rest is also the zero-momentum frame. Another way of writing $\mathbf{p}$ is

$$\mathbf{p} = m_r\left(\frac{\mathbf{p}_1}{m_1} - \frac{\mathbf{p}_2}{m_2}\right) = m_r(\mathbf{v}_1 - \mathbf{v}_2) = m_r\frac{d\mathbf{r}}{dt} \tag{8.14}$$

where the reduced mass m_r is defined by $1/m_r = 1/m_1 + 1/m_2$. The internal momentum $\mathbf{p}$ thus has three interpretations: it is the momentum of particle 1 with respect to the centre of mass , as in (8.13); it is the negative of the momentum of particle 2 with respect to the centre of mass; and it is the momentum of a (fictitious) particle with the reduced mass moving with the inter-particle relative velocity, as in (8.14). To obtain an equation for $\mathbf{p}$ we multiply (8.9) by m_2/M and subtract (8.10) multiplied by m_1/M:

$$\frac{d\mathbf{p}}{dt} = m_r\frac{d^2\mathbf{r}}{dt^2} = -\frac{dV(r)}{dr}\hat{\mathbf{r}}. \tag{8.15}$$

Equation (8.15) is the equation of motion of a particle of mass m_r attracted to a fixed centre of force by the potential $V(r)$. We have thus separated the degrees of freedom of the system into the external degrees of freedom which satisfy (8.11) and the internal degrees of freedom which satisfy (8.15). If we express $\mathbf{p}_1$ and $\mathbf{p}_2$ in terms of $\mathbf{P}$ and $\mathbf{p}$ we can easily show that the total energy can be divided between the two systems:

$$H = \left(\frac{\mathbf{P}^2}{2M}\right) + \left(\frac{\mathbf{p}^2}{2m_r} + V(r)\right). \tag{8.16}$$

We can also describe this procedure as the replacement of the two equations of motion for the actual particles with equations of motion for two *quasi-particles*, useful dynamical fictions which obey simpler equations of motion, in this case a free particle of mass M, and a particle of mass m_r bound to a fixed centre.

We now proceed to solve the internal equation of motion, (8.15). We first form the vector product with $\mathbf{r}$ on the left, which gives zero on the right-hand side because $\mathbf{r} \wedge \hat{\mathbf{r}} = 0$:

$$\mathbf{r} \wedge \frac{d\mathbf{p}}{dt} = 0.$$

The left-hand side is in fact the time derivative of the angular momentum $\mathbf{r} \wedge \mathbf{p}$, because the other term in the derivative is $\frac{d\mathbf{r}}{dt} \wedge \mathbf{p} = 0$. We can therefore integrate this equation to obtain

$$\mathbf{r} \wedge \mathbf{p} = \boldsymbol{l} \tag{8.17}$$

where the three components of the vector $\boldsymbol{l}$ are all constants of the motion.

The next step involves the explicit form of the potential $V(r)$ from (8.2); to keep the number of symbols to a minimum we shall define $k = Ze^2/(4\pi\epsilon_0)$. Thus $V = -k/r$ and (8.15) can be written

$$\frac{d\mathbf{p}}{dt} = -\frac{k\,\hat{\mathbf{r}}}{r^2}.$$

We form the vector product with $\boldsymbol{l}$ on the left:

$$\boldsymbol{l} \wedge \frac{d\mathbf{p}}{dt} = -\frac{k\boldsymbol{l} \wedge \hat{\mathbf{r}}}{r^2}. \tag{8.18}$$

The left-hand side is again a complete time derivative, because the other term in the derivative of $\boldsymbol{l} \wedge \mathbf{p}$ involves the derivative of $\boldsymbol{l}$, which is zero. The right-hand side is also a complete time derivative, as can be seen by expanding the vector triple product:

$$-\frac{(\mathbf{r} \wedge \mathbf{p}) \wedge \hat{\mathbf{r}}}{r^2} = -\left(\frac{m_r}{r}\frac{d\mathbf{r}}{dt} - \frac{m_r\mathbf{r}}{r^3}\mathbf{r} \cdot \frac{d\mathbf{r}}{dt}\right) = -m_r\frac{d}{dt}\left(\frac{\mathbf{r}}{r}\right).$$

Equation (8.18) can thus be written

$$\frac{d}{dt}\left(\boldsymbol{l} \wedge \mathbf{p} + km_r\hat{\mathbf{r}}\right) = 0$$

which implies that the components of the vector in the bracket are also constants of the motion. This vector is called the Runge-Lenz vector, and for reasons which will become apparent shortly we will write it as $km_r\mathbf{e}$.

It is worth taking a moment to think about the geometrical significance of the constants of the motion we have found. The angular momentum vector $\boldsymbol{l}$ is orthogonal to both $\mathbf{r}$ and the velocity

$\mathbf{v}$ as a result of the vector product in its definition. The displacement of the particle in time δt is $\delta\mathbf{r} = \mathbf{v}\delta t$; the vector $\boldsymbol{l}$ is therefore orthogonal to both $\mathbf{r}(t)$ and $\delta\mathbf{r}$, and hence also to $\mathbf{r}+\delta\mathbf{r} = \mathbf{r}(t+\delta t)$. The vectors $\mathbf{r}(t)$ and $\mathbf{r}(t+\delta t)$ define the plane in which the orbit is being described at the instant t; the significance of the fact that $\boldsymbol{l}$ is constant is therefore that the plane of the orbit, the plane orthogonal to $\boldsymbol{l}$, is fixed. The Runge-Lenz vector, on the other hand, is in the plane of the orbit: the first term is orthogonal to $\boldsymbol{l}$ because of the vector product, and the second term, being parallel to $\hat{\mathbf{r}}$, is clearly in the plane of the orbit. The Runge-Lenz vector thus represents a fixed direction and magnitude in the plane of the orbit.

We have thus found six constants of the internal motion, the components of $\boldsymbol{l}$ and $\mathbf{e}$. This is already 'too many', since the internal motion is completely described by six variables, for example the components of $\mathbf{r}$ and $\mathbf{p}$, and if there are six independent constants then everything is constant and there is no motion! However the six constants we have found are not all independent, since there is an equation which relates them together. This derives from the fact that $\boldsymbol{l}$ and $\mathbf{e}$ are orthogonal:

$$\boldsymbol{l}\cdot\mathbf{e} = l_x e_x + l_y e_y + l_z e_z = 0. \tag{8.19}$$

This is the only relation between our constants of the motion, so that we have found five independent constants, which is therefore as many as we can hope to find. We expect the energy also to be a constant of the motion, so it must be expressible in terms of these five; indeed since the energy is independent of the orientation of the orbit with respect to the co-ordinate axes we expect it to be a function of the two scalars $l^2 = \boldsymbol{l}\cdot\boldsymbol{l}$ and $\varepsilon^2 = \mathbf{e}\cdot\mathbf{e}$. Forming the scalar product of the Runge-Lenz vector with itself we find

$$m_r^2k^2\mathbf{e}\cdot\mathbf{e} = l^2p^2 + 2km_r(\boldsymbol{l}\wedge\mathbf{p})\cdot\hat{\mathbf{r}} + m_r^2k^2 \tag{8.20}$$

which we can re-arrange to give the internal part of H from (8.16) in terms of l^2 and ε^2:

$$E = \frac{p^2}{2m_r} - \frac{k}{r} = -\frac{m_rk^2(1-\varepsilon^2)}{2l^2}. \tag{8.21}$$

We note that the sign of E depends on the magnitude of ε: if $\varepsilon > 1$ then $E > 0$.

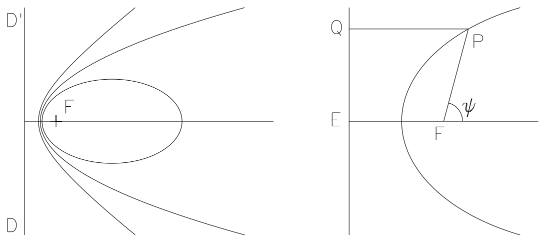
We next consider the significance of the Runge-Lenz vector. If we form the scalar product of $\mathbf{e}$ with $\mathbf{r}$ we obtain

$$\mathbf{e}\cdot\mathbf{r} = \frac{\boldsymbol{l}\wedge\mathbf{p}\cdot\mathbf{r}}{m_rk} + r. \tag{8.22}$$

If we interchange the dot and cross in the scalar triple product it becomes $-l^2$, while if the angle between $\mathbf{e}$ and $\mathbf{r}$ is ψ we can write $\mathbf{e}\cdot\mathbf{r} = \varepsilon r\cos\psi$. Thus

$$r = \frac{l^2/(m_rk)}{1-\varepsilon\cos\psi}. \tag{8.23}$$

This is the polar equation of a conic section with eccentricity ε and semi-latus rectum $h = l^2/(m_r k)$, with focus at the origin. (The relevant geometry is summarised in box 8.1.) The conic sections include the ellipse ($0 \le \varepsilon \le 1$), which corresponds to a regular orbital motion, and the parabola ($\varepsilon = 1$) and hyperbola ($\varepsilon > 1$), motions in which the two particles approach from infinite separation and scatter to infinity again. Bearing in mind the relation noted above between the magnitude of ε and the sign of E, these two types of motion also correspond to bound states (total energy $E < 0$) and unbound states.



One definition of a conic section is that it is the path of a point which moves such that its distance from a fixed point (the focus) stands in a constant ratio to its distance from a fixed line (the directrix). The ratio is the eccentricity ε. The left-hand figure shows three conic sections with the same focus F and directrix DD', with eccentricity $\varepsilon = 0.8$ (ellipse), $\varepsilon = 1$ (parabola) and $\varepsilon = 1.25$ (hyperbola). The perpendicular from F to DD' is called the axis. The right-hand figure shows one section in more detail: The conic section definition for the general point P is

$$PF = \varepsilon PQ. \tag{8.24}$$

We define $PF = r$ and $FE = d$; the distance PQ is thus given by $d + r\cos\psi$ where ψ is the angle between FP and the axis. Hence

$$r = \varepsilon(d + r\cos\psi) \qquad \text{or} \qquad r = \frac{h}{1 - \varepsilon\cos\psi} \tag{8.25}$$

where $h = \varepsilon d$, and is called the semi latus rectum. P crosses the axis twice, at $\psi = 0$, $r = h/(1-\varepsilon)$ and $\psi = \pi$, $r = h/(1+\varepsilon)$. The distance between these two points is called the major axis, and has length $2a = 2h/(1-\varepsilon^2)$.

Box 8.1 The Geometry of the Ellipse

To sum up, we have found that in bound states the relative co-ordinate $\mathbf{r}$ traces out an ellipse, with one focus at the origin. There are five constants of the motion, which we can choose to be three angles specifying the orientation of the orbit with respect to our co-ordinate system, and two scalar quantities specifying its size and shape. From the point of view of particle dynamics it would be natural to choose these scalars to be the internal energy E and the squared angular momentum l^2. These are directly related to the geometrical constants, the semi-latus rectum h and semi major axis a. Equation (8.23) gives $h = l^2/m_r k$, while (8.21) gives $E = -k(1-\varepsilon^2)/2h$, which in conjunction with the definition of a given in box 8.1 gives

$$E = -\frac{k}{2a}. \tag{8.26}$$

This is a surprising result — while we would expect the orientation of the orbit in space not to affect its energy, there is no obvious reason why the energy should not depend on the shape of the orbit as well as its size. There is a similar surprise in the dependence of the orbital period on the other parameters. We can show that the rate at which the radius vector sweeps out area is $l/2m_r$, so given that the area of the ellipse is $\pi a^2\sqrt{1-\varepsilon^2}$ we find the orbital period to be

$$T = \frac{2\pi m_r a^2\sqrt{1-\varepsilon^2}}{l}$$

which we can re-arrange to give the orbital frequency:

$$\nu(E,l) = \frac{l}{2\pi m_r a^2\sqrt{1-\varepsilon^2}} = \frac{(-2E)^{3/2}}{2\pi\sqrt{m_r k^2}}. \tag{8.27}$$

(The details here are left as a problem, 8.2, which also uses this equation in conjunction with the correspondence principle.) The surprise here is that ν, which is shown as depending on both dynamical variables, turns out only to depend on E and not l. Both of these surprises are special properties of the $1/r$ potential and the use of non-relativistic dynamics, and there are corresponding surprises in the quantum-mechanical description, to which we now turn.

8.3 The Quantum-Mechanical Solution

The quantum-mechanical treatment starts from Hamiltonian (8.3), with the usual interpretation of the operator $\mathbf{p}$ as $-i\hbar\nabla$. However this is the first situation we have encountered where we have a wavefunction describing more than one particle. The extension of the theory is straightforward, and analogous to the extension to a single particle in more than one spatial dimension in chapter **??**. The wave function has to define a probability amplitude for every possible *configuration* — that is every possible set of positions — of the two particles, and so it is a function in *configuration space*, which in this case has six dimensions: $\psi(\mathbf{r}_1, \mathbf{r}_2)$. Each momentum operator $\mathbf{p}_i$ involves the gradient with respect to the corresponding position vector $\mathbf{r}_i$. The Schrodinger equation can thus be written:

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi_T(\mathbf{r}_1,\mathbf{r}_2) - \frac{\hbar^2}{2m_2}\nabla_2^2\psi_T(\mathbf{r}_1,\mathbf{r}_2) - \frac{Ze^2}{4\pi\epsilon_0 r}\psi_T(\mathbf{r}_1,\mathbf{r}_2) = E_T\psi_T(\mathbf{r}_1,\mathbf{r}_2) \tag{8.28}$$

where the subscript T denotes Total, for the eigenfunction and energy of the whole system.

The separation of the Hamiltonian into the centre of mass and internal degrees of freedom is essentially identical to the classical treatment of the previous section, and the details are left to problem 8.3. In brief, we define the centre of mass according to (8.12), and the relative co-ordinate according to (8.6), and change to these variables. The Hamiltonian then splits up according to (8.16), where $\mathbf{P}$ involves the gradient with respect to the components of $\mathbf{R}$, and $\mathbf{p}$ involves the gradient with respect to the components of $\mathbf{r}$. As we have seen previously **??**, when the Hamiltonian can be written as a *sum* of terms acting on different variables, the wavefunction can be written as a *product* of wavefunctions of each variable: $\psi_T = \psi_C(\mathbf{R})\psi(\mathbf{r})$, and the eigenvalue becomes the sum of eigenvalues for the two systems:

$$\begin{aligned} -\frac{\hbar^2}{2M}\nabla_R^2\psi_C(\mathbf{R}) &= E_C\psi_C(\mathbf{R}) && (8.29)\\ -\frac{\hbar^2}{2m_r}\nabla^2\psi(\mathbf{r}) - \frac{Ze^2}{4\pi\epsilon_0 r}\psi(\mathbf{r}) &= E\psi(\mathbf{r}) && (8.30)\\ E_C + E &= E_T. && (8.31)\end{aligned}$$

As in the classical case, (8.29) is the equation for a free particle, with mass M, while (8.30) is the equation for a particle of mass m_r bound to a fixed centre, and (8.31) shows that the associated energies simply add. As we discussed in Chapter 1, the general solution to the Schroedinger equation is given by a superposition of time-dependent eigenfunctions, of which ψ_C and ψ give the spatial part. In the case of the free particle equation (8.29) this superposition is essential to obtain a normalisable wavefunction. However the equation which we are currently interested in solving is (8.30), since this determines the internal energy eigenvalues and eigenfunctions, which are independent of the external motion of the atom.

We begin our solution of (8.30), as we did the harmonic oscillator in chapter 4, by considering the physical constants which occur in the solution, in order to define physically relevant units of length and energy. As before the constants include Planck's constant $\hbar$ and the particle mass m_r, and in addition we have the constants in the potential energy. There appear to be several of these, but since they appear as a group we need not split them up, and we continue to refer to them as $k = Ze^2/4\pi\epsilon_0$. The dimensions of $\hbar$ and m_r are straightforward, while the fact that that $V = -k/r$ implies that the dimensions of k are energy × length.

$$\begin{array}{ll} \hbar & [\mathrm{ML^2T^{-1}}] \\ m_r & [\mathrm{M}] \\ k & [\mathrm{ML^3T^{-2}}] \end{array}$$

It is clear from this that to find a length we need two factors of $\hbar$ to cancel the time dependence in k, and then another factor of m_r to cancel the mass-dependence. Thus we obtain the length, a:

$$a = \frac{\hbar^2}{m_r k} = \frac{\hbar^2 4\pi\epsilon_0}{m_e Z e^2}. \tag{8.32}$$

As we mentioned in the section 8.1, we are actually considering a range of physical systems, with different values for m_r and k, although of course they all share the same value for $\hbar$. It is helpful to define reference values for these two quantities, to which the value in any given system is related by a dimensionless constant. We have already done this for k: $k = Z \times e^2/4\pi\epsilon_0$, and a sensible reference value for m_r is the electron mass m_e, since this is the value m_r would have if the nuclear mass were infinite: $m_r = \zeta \times m_e$. Thus the two dimensionless parameters are Z and ζ (Greek zeta). The length computed with the reference values of k and m_r is the Bohr radius:

$$a_0 = \frac{\hbar^2 4\pi\epsilon_0}{m_e e^2} = 0.529\,177\,2083(19) \times 10^{-10}\ \mathrm{m}$$

where the value comes from the CODATA 1998 Recommended Physical Constants, and the numbers in brackets are the estimated error in the last decimal place. In terms of a_0, the length in (8.32) can be written $a(Z,\zeta) = a_0/(Z\zeta)$.

The energy parameter follows directly from the length parameter, since k has dimensions of energy multiplied by length. We call the energy parameter $H(Z,\zeta)$:

$$H(Z,\zeta) = \frac{k}{a(Z,\zeta)} = \frac{m_r Z^2 e^4}{\hbar^2 (4\pi\epsilon_0)^2}.$$

Evaluating H with the reference values of k and m_r we obtain

$$H_0 = \frac{m_e e^4}{\hbar^2 (4\pi\epsilon_0)^2} = 4.359\,743\,81(34) \times 10^{-18}\ \mathrm{J}$$

The symbol H here does not, as so often, refer to Hamilton but Hartree, who was the first the person to use these atomic units in calculations, and H_0 is known as the atomic unit of energy, or the Hartree energy. In terms of H_0 we have $H(Z,\zeta) = Z^2\zeta\, H_0$.

We now define scaled length and energy variables in terms of these units:

$$\mathbf{r} = a(Z,\zeta)\boldsymbol{\rho} \tag{8.33}$$

$$E = H(Z,\zeta)\epsilon. \tag{8.34}$$

The substitution into (8.30) is straightforward, except in the differentials, but here we have $\nabla = (1/a(Z,\zeta))\nabla_\rho$. Each term in the equation has dimensions of energy, and, as we have seen, $H(Z,\zeta)$ is the only energy we can make with the physical constants involved. Hence every term involves a factor of $H(Z,\zeta)$, which we can cancel, leaving

$$-\frac{1}{2}\nabla_\rho^2\psi(\boldsymbol{\rho}) - \frac{1}{\rho}\psi(\boldsymbol{\rho}) = \epsilon\psi(\boldsymbol{\rho}). \tag{8.35}$$

The absence of any physical constants, including the dimensionless parameters Z and ζ, in (8.35) is significant, because it implies that the eigenfunctions and eigenvalues of (8.35) do not depend on these parameters. However the equation we started with, (8.30), could describe a number of different systems depending on the values taken by these parameters. We therefore arrive at the following important conclusion: *the eigenfunctions and eigenvalues for all the systems we are discussing are identical apart from the length- and energy-scaling implied by (8.33) and (8.34).* The range of systems involved is indicated by the following table. In this table, m_p is the proton mass, and m_α the mass of the He nucleus, or alpha particle. In each line the bracketed ratio is close to unity, so that we ignore this factor in the following order-of-magnitude discussion.

System	Z	ζ	Length Scale $a(Z,\zeta)/a_0$	Energy Scale $H(Z,\zeta)/H_0$
Hydrogen	1	$\left(\frac{m_p}{m_p+m_e}\right)$	$\left(\frac{m_p+m_e}{m_p}\right)$	$\left(\frac{m_p}{m_p+m_e}\right)$
He$^+$	2	$\left(\frac{m_\alpha}{m_\alpha+m_e}\right)$	$\frac{1}{2}\left(\frac{m_\alpha+m_e}{m_\alpha}\right)$	$4\left(\frac{m_\alpha}{m_\alpha+m_e}\right)$
Hydrogen-like Z	Z	$\left(\frac{m_N}{m_N+m_e}\right)$	$\frac{1}{Z}\left(\frac{m_N+m_e}{m_N}\right)$	$Z^2\left(\frac{m_N}{m_N+m_e}\right)$
Positronium	1	$\frac{1}{2}$	2	$\frac{1}{2}$
Muonium	1	$\left(\frac{m_\mu}{m_\mu+m_e}\right)$	$\left(\frac{m_\mu+m_e}{m_\mu}\right)$	$\left(\frac{m_\mu}{m_\mu+m_e}\right)$
Muonic Z	Z	$\frac{m_\mu}{m_e}\left(\frac{m_N}{m_N+m_\mu}\right)$	$\frac{m_e}{Zm_\mu}\left(\frac{m_N+m_\mu}{m_N}\right)$	$\frac{Z^2m_\mu}{m_e}\left(\frac{m_N}{m_N+m_\mu}\right)$

The He$^+$ system has a length scale roughly half, and an energy scale roughly four times that of Hydrogen; it is also the $Z = 2$ member of a series of systems described in the table as ‘Hydrogen-like Z.’ These consist of a nucleus with atomic number Z and mass m_N with just one orbiting electron; the length scale is smaller than that of Hydrogen by a factor of roughly Z, and the energy scale larger by a factor of roughly Z^2. Positronium is a system containing an electron and a positron, so that both particles have the same mass m_e. Since the two particles can annihilate each other when they meet, this is a short-lived system, but it is a theoretically very important one because both particles are elementary and genuinely point-like, and we have a good theory of electrons and positrons (Quantum Electrodynamics or QED). High-precision measurements in positronium are therfore very important tests of the theory which avoid complications arising from the structure of protons and other nuclei. We see that positronium has twice the size and half the binding energy of hydrogen. Muonium is a similar system with the positron replaced by a positive muon. The muon is essentially a heavy electron/positron (depending on the charge), with $m_\mu/m_e \sim 207$, which can decay to the lighter particle, so this is another short-lived system, but again a theoretically important one. The size and binding energy are similar to those of hydrogen.

Finally Muonic Z refers to a muonic atom. These are formed when a negative muon beam is directed at an atomic target. Some muons are captured by the attractive potential of the nucleus; these states are $m_\mu/m_e = 207$ times smaller than even the innermst electron states, so the muon is much closer to the nucleus than any of the electrons. It is therefore a good approximation to ignore the electrons altogether, as they hardly modify the potential in which the muon moves, and treat the muons as being in a two-particle system with the nucleus, even though the nucleus may be bound into a solid. The length scale is now so small that the point-nucleus approximation is seriously violated: for a medium-Z atom consider muonic cobalt ($Z = 27$, $A = 100$) for which $a(Z,\zeta) \sim a_0/(27 \times 207) \sim 9.5$ fm while the nuclear radius is of order $1.4 \times (100)^{1/3} \sim 6.5$ fm. Thus the corrections are very significant, and transition energies in muonic atoms are an important source of information on nuclear sizes.

We turn now to the solution of (8.35). It is a particular example of the general central potential problem we considered in the last chapter, so we follow the same approach and solve in spherical polar co-ordinates. ρ, θ, ϕ. We substitute the product eigenfunction

$$\psi(\rho,\theta,\phi) = R_{n\ell}(\rho)Y_{\ell m}(\theta,\phi)$$

where $Y_{\ell m}$ is a spherical harmonic. The ℓ and m quantum numbers have the same significance as before: the total squared angular momentum is $l^2 = \ell(\ell+1)\hbar^2$, and the z-component is $m\hbar$. This substitution yields the radial equation which determines the energy eigenvalues:

$$-\frac{1}{2\rho^2}\frac{d}{d\rho}\rho^2\frac{dR_{n\ell}}{d\rho} + \frac{\ell(\ell+1)}{2\rho^2}R_{n\ell} - \frac{1}{\rho}R_{n\ell} = \epsilon_{n\ell}R_{n\ell}. \tag{8.36}$$

Since this equation does not contain the quantum number m we do not expect the eigenvalues ϵ or eigenfunctions R to depend on it, so we have labelled ϵ and R with ℓ and an additional quantum number n, since we expect to find more than one solution for each ℓ.

Looking at (8.36) it is apparent that a term in $R_{n\ell}$ proportional to ρ^p will give rise to terms in ρ^{p-2} from the first two terms, ρ^{p-1} from the third term and ρ^p from the right-hand side. Thus we cannot solve in series directly, as we will not obtain a two-term recursion relation. We therefore

We make the substitution (8.38); the required derivatives are given by

$$\begin{aligned}\frac{dR}{d\rho} &= \left(\frac{dF}{d\rho} - \alpha F\right) e^{-\alpha\rho}\\ \frac{d^2R}{d\rho^2} &= \left(\frac{d^2F}{d\rho^2} - 2\alpha\frac{dF}{d\rho} + \alpha^2 F\right) e^{-\alpha\rho}.\end{aligned}$$

When we put these into (8.35) the α^2 term cancels the $\epsilon_{n\ell}$ term, leaving

$$-\frac{d^2F}{d\rho^2} - \frac{2}{\rho}\frac{dF}{d\rho} + \frac{\ell(\ell+1)}{\rho^2}F + 2\alpha\frac{dF}{d\rho} + \frac{2\alpha-2}{\rho}F = 0.$$

Using the standard series solution

$$F = \sum_{p=0} a_p \rho^{p+c} \qquad a_0 \neq 0$$

gives

$$\begin{aligned}\sum_{p=0} -\Big((p+c)(p+c+1) - \ell(\ell+1)\Big) a_p \rho^{p+c-2} &+ \\ \sum_{p=0}\Big(2\alpha(p+c+1) - 2\Big) a_p \rho^{p+c-1} &= 0.\end{aligned}$$

We note that $\big((p+c)(p+c+1) - \ell(\ell+1)\big) = (p+c-\ell)(p+c+\ell+1)$. The lowest power of ρ is ρ^{c-2}, and setting the coefficient of this to zero gives the indicial equation: $(c-\ell)(c+\ell+1) = 0$, which gives $c = \ell$ or $c = -\ell - 1$. However the latter root gives a wavefunction which diverges at the origin and is not acceptable, so $c = \ell$. Relabelling the first summation to bring both terms under a single sum we obtain for the remaining powers of ρ:

$$\sum_{p=0}\Big(-(p+1)(p+2\ell+2)a_{p+1} + 2\big(\alpha(p+\ell+1) - 1\big)a_p\Big)\rho^{p+c-1} = 0.$$

Equating these coefficients to zero gives the recursion relation:

$$a_{p+1} = 2\,\frac{\alpha(p+\ell+1) - 1}{(p+1)(p+2\ell+2)}\,a_p.$$

For large p this tends towards $a_{p+1} \sim (2\alpha/(p+1))\,a_p$ which is the series expansion of $e^{2\alpha\rho}$. Hence the series must terminate. If the highest non-zero term is a_q then $\alpha = 1/(q+\ell+1)$. We define the integer $q+\ell+1$ to be n; since $q \geq 0$ we have $n > \ell$. Substituting for α we find

$$\epsilon_{n\ell} = -\frac{1}{2n^2}$$

Box 8.2 Solution of the Hydrogen Radial Equation consider the limit of large ρ. We can always find a ρ so large that the second and third terms are negligibly small compared with the right-hand side (provided $\epsilon_{n\ell} \neq 0$), so in this limit the right-hand side must be balanced by the differential term. If we expand the differential, the first derivative term contains a factor of $2/\rho$ which we also expect to become very small relative to the other terms. Thus in the large-ρ limit (8.36) becomes

$$\frac{d^2 R_{n\ell}}{d\rho^2} = -2\epsilon_{n\ell} R_{n\ell}. \tag{8.37}$$

If $\epsilon > 0$ this gives a sinusoidal function which oscillates with finite amplitude as ρ tends to infinity; such a solution is not normalisable. These are valid solutions, but do not represent bound states of the system, but scattering states where the particles can separate to infinite distance. We shall concentrate on the bound states, for which $\epsilon < 0$. Equation (8.37) then gives

$$R_{n\ell} \sim \exp \pm \left(\sqrt{-2\epsilon_{n\ell}}\,\rho\right)$$

We reject the positive exponent as giving a un-normalisable wavefunction, which we do not expect for a bound state. A sensible substitution into (8.35) is thus

$$R_{n\ell} = F(\rho) e^{-\alpha\rho} \tag{8.38}$$

where $\alpha = \sqrt{-2\epsilon_{n\ell}}$.

This substitution yields an equation for F which does give a two-term recursion relation (for details see Box 8.2). Just as in earlier examples, the function defined by the recursion relation overwhelms the converging exponential factor in R, so ϵ is constrained to take values such that the series terminates, and these are found to be

$$\epsilon_{n\ell} = -\frac{1}{2n^2} \tag{8.39}$$

for integer $n > \ell$. We therefore find that the eigenvalues do *not* depend on ℓ in the sense that different values of ℓ give rise to eigenvalues $\epsilon_{n\ell}$ drawn from the same set, although only for $\ell = 0$ are all values possible. This ℓ-degeneracy is the surprising feature of the quantum-mechanical treatment analogous to the classical surprises referred to at the end of the previous section.

Putting back the energy scaling from (8.34) we find the energy eigenvalues for the bound states of hydrogen-like systems to be

$$E_{n\ell} = -\left(Z^2 \frac{m_r}{m_e} \frac{e^4 m_e}{(4\pi\epsilon_0)^2 \hbar^2}\right)\left(\frac{1}{2n^2}\right) = -\left(Z^2 \zeta H_0\right)\left(\frac{1}{2n^2}\right). \tag{8.40}$$

These energy levels are shown in Figure 8.1, together with a selection of possible radiative transitions beween them. (The possible transitions are restricted by selection rules, which are discussed

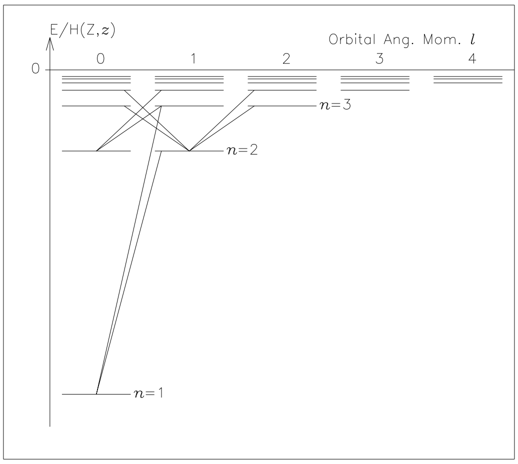


Figure 8.1: *The Energy Levels for a Hydrogen-like system*

in much greater detail in chapter 11; the relevant rule here is $\Delta\ell = \pm 1$.) The wavelengths of these transitions are an important source of data with which to compare the theoretical results. Wavelengths have historically been the directly measured quantity, but it is frequency which is proportional to energy difference. For this reason, comparisons have traditionally been made in terms of reciprocal wavelengths, or wavenumbers $\bar{\nu} = 1/\lambda$:

$$\Delta E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}. \tag{8.41}$$

The wavenumber for a transition from initial state m to final state n is thus

$$\bar{\nu} = (Z^2\zeta)\frac{H_0}{2hc}\left(\frac{1}{n^2} - \frac{1}{m^2}\right). \tag{8.42}$$

All the wavenumbers in the spectrum of a given hydrogenic system are simple multiples of the combination of constants $Z^2\zeta H_0/(2hc)$. The Rydberg constant for this system is conventionally defined without the Z-scaling: $R = \zeta H_0/(2hc)$. A system with infinite nuclear mass has $\zeta = 1$, so the combination $H_0/(2hc)$ is known as R_∞. This is one of the most accurately known physical constants: the CODATA 1998 value of R_∞ has a relative uncertainty of 8×10^{-12}, about four orders of magnitude more accurate than the electron charge or Planck's constant:

$$R_\infty = 10\,973\,731.568\,549(83)\ \mathrm{m}^{-1}. \tag{8.43}$$

The Rydberg constant for hydrogen R_H is smaller by the reduced mass correction ζ:

$$\zeta = \frac{m_r}{m_e} = \frac{1}{1 + m_e/m_p} = 0.999\,4556\,7942\,3 \qquad R_H = 10\,967\,758.340\,650(82)\ \mathrm{m}^{-1}. \tag{8.44}$$

Spectral lines with a common lower state n are said to belong to the same series, and the various series in Hydrogen have traditional names including the Lyman series ($n = 1$) and Balmer series

$(n = 2)$. Series members are denoted by Greek letters beginning with α for the line with $m = n+1$. Thus the lines shown in Figure 8.1 are Lyman α and Lyman β, and Balmer α and Balmer β. Note that whereas each Lyman series line is a single transition, each Balmer series line is a superposition of three transitions, all of which have the same wavenumber at this level of approximation.

8.4 The Hydrogen wavefunctions

In this section we shall try to visualize some of the simpler eigenfunctions which we found in the previous section, and to consider the physical implications of the shapes that we find. Putting together the different parts, the time-dependent eigenfunction is as follows:

$$\Psi(\rho, \theta, \phi, t) = \psi(\rho, \theta, \phi) e^{-i\omega_n t} = R_{n\ell}(\rho) Y_{\ell m}(\theta, \phi) e^{-i\omega_n t} \tag{8.45}$$

where $\hbar\omega_n = E_n$. The radial part is a function of the radial distance in 'natural' units $\rho = r/a(Z, \zeta)$, where a is defined by (8.32). $R_{n\ell}(\rho)$ has the form of an exponential $e^{-\rho/n}$ multiplied by a polynomial in ρ whose first term is ρ^ℓ and whose highest power of ρ is ρ^{n-1}. The normalisation of $R_{n\ell}$ is given by

$$\int_0^\infty |R_{n\ell}|^2 \, \rho^2 \, d\rho = 1.$$

The spherical harmonic $Y_{\ell m}(\theta, \phi)$ has a ϕ-dependence $e^{im\phi}$ and a θ-dependence consisting of $\sin^{|m|}\theta$ multiplied by a polynomial in $\cos\theta$ whose highest power is $\cos^{l-|m|}\theta$, with adjacent terms differing by two powers of $\cos\theta$, so that the lowest power is either 1 or $\cos\theta$ depending on whether $\ell - m$ is even or odd. The spherical harmonic is normalised according to

$$\int |Y_{\ell m}|^2 \; d\Omega = 1$$

where the integral is over solid angle $d\Omega = \sin\theta \, d\theta \, d\phi$. The overall normalisation is thus

$$\int \Psi^\star \Psi \, \rho^2 \, d\rho \, d\Omega = 1.$$

However, it should be remembered that the wavefunction itself has dimensions: $\Psi^\star\Psi$ is probability per unit volume, so Ψ has dimensions of $[\mathrm{L}]^{-3/2}$, giving rise to a factor of $a(Z, \zeta)^{-3/2}$ when the wavefunction is expressed in units other than the 'natural' units, where this factor is 1.

We start with the ground state, $n = 1$ and $\ell = 0$, the $1s$ state. (The letter code for ℓ is defined in **??**.) The radial eigenfunction consists of just the exponential factor, and the angular part is a constant. We thus have a particularly simple eigenfunction (we shall concentrate on the spatial

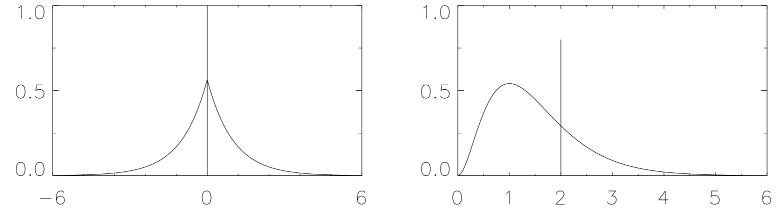


Figure 8.2: *The* $1s$ *wavefunction and radial probability distribution*

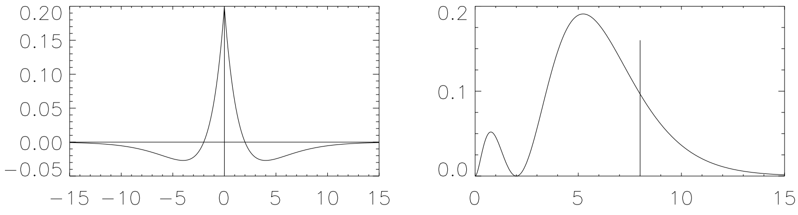


Figure 8.3: *The* $2s$ *wavefunction and radial probability distribution*

part ψ):

$$\psi_{1s}(\rho) = \frac{1}{\sqrt{\pi}} e^{-\rho}. \tag{8.46}$$

We can plot this as a function of ρ, but to a give a better visualization we plot it in Figure 8.2 (left-hand panel) along the z axis. This brings out the surprising feature of the wavefunction: the discontinuity in slope at the origin. The wavefunction is generally required to be continuous and to have a continuous first derivative, but the solution we have arrived at does not, at the origin. The reason is the infinite potential in our model at the origin: the infinity in the potential term in the Schroedinger equation has to balanced by another infinity, and since the eigenvalue is finite, the infinity has to come from the ∇^2 term, which gives rise to the slope discontinuity that we observe. As we mentioned in Section 8.1 the potential we are using is not correct in this region because the nuclear charge distribution has a finite extent. This means that in reality the potential does not go to infinity but to a large negative value, and on a corresponding length scale the curvature of the wavefunction will go to some large but finite value.

It is apparent from Figure 8.2 that the most likely place to find the electron is at the origin, that is, inside the proton. (For the sake of definiteness we shall discuss hydrogen; obviously the features described apply to all the systems discussed above.) It does not follow that the most likely inter-particle distance is zero. The radial probability distribution is given by

$$D_{n\ell}(\rho) = \int |\psi(\rho,\theta,\phi)|^2 \rho^2 \, d\Omega = \rho^2 |R_{n\ell}(\rho)|^2$$

and $D_{1s}(\rho)$ is plotted in the right-hand panel of Figure 8.2. This is actually zero at the origin. The reason for the discrepancy is simply that that $|\psi|^2$ gives the probability per unit volume, whereas D gives probability per unit radial distance, and the volume of the radial shell with zero radius is zero. The most likely radius at which to find the electron is seen to be $\rho = 1$ or $r = a(Z, \zeta)$; this result is sometimes discussed in the context of a comparison with the Bohr model, which uses circular orbits with angular momenta $n\hbar$ and radii $n^2 a(Z, \zeta)$. For the $1s$ state the circular Bohr orbit could not be more dissimilar from the one we have found, since the angular momentum of the quantum mechanical state is zero. Classically this implies a motion that is purely radial, with an outer turning point where the kinetic energy is zero and the potential energy is equal to the binding energy:

$$-\frac{1}{\rho} = -\frac{1}{2n^2}$$

or $\rho = 2n^2$. This turning point is marked on the $D(\rho)$ plot.

We turn next to the $2s$ state. The exponential changes to $e^{-\rho/2}$, and the ρ polynomial now has two terms in it. The ratio of the coefficients in this polynomial is given by the recursion relation in box 8.2: setting $\ell = 0$ and $\alpha = 1/n = 1/2$ it gives $a_1 = -a_0/2$ and $a_2 = 0$. The polynomial is thus $a_0(1 - \rho/2)$, and putting in the normalising factor we find

$$\psi_{2s}(\rho) = \frac{1}{\sqrt{8\pi}}(1 - \rho/2)\, e^{-\rho/2}.$$

This is plotted in Figure 8.3 (left-hand panel), and the corresponding $D_{2s}(\rho)$ in the right-hand panel. The classical turning point ($\rho = 8$) is also shown on the $D(\rho)$ plot. While the origin is still the most likely place to find the electron, the most likely radius is now the outer maximum in $D(\rho)$, just inside the classical turning point.

We see that the zero of the R_{2s} polynomial falls in the positive ρ region, and therefore gives the eigenfunction a spherical nodal surface, which in this case falls at $\rho = 2$. Since the eigrnfunction is required to be orthogonal to the $1s$ eigenfunction, and the $1s$ eigenfunction has the same sign everywhere, the $2s$ eigenfunction must have regions of differing sign in order that the overlap can integrate to zero. In fact all the polynomial zeros of the $R_{n\ell}$ wavefunctions fall at positive ρ, so that the $n\ell$ wavefunction has $n - l - 1$ spherical nodal surfaces.

If we look at an s eigenfunction with much larger n we see that it is simply a spherical standing wave. This is illustrated in Figure 8.4 for the 7s state, showing again the wavefunction along the z axis and the radial probability distribution with the classical turning point marked. Both the features noted for the $2s$ wavefunction appear to be general: the origin is the most likely place, but the outermost maximum just inside the classical turning point is the most likely radius. Note in

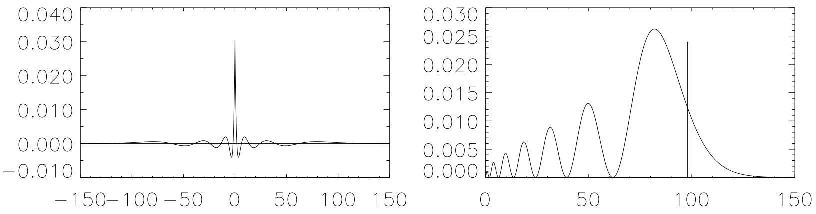


Figure 8.4: *The 7s wavefunction and radial probability distribution*

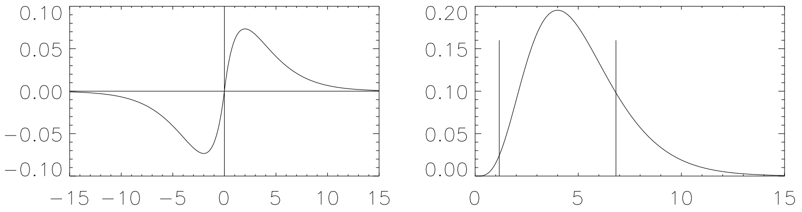


Figure 8.5: *The 2p $m = 0$ wavefunction and radial probability distribution*

addition that the wavelength is shorter near the origin where in the corresponding classical motion the particle is moving more rapidly.

We next look at the $2p$ state. The exponential in R_{2p} is again $e^{-\rho/2}$, while the polynomial has just a single term, ρ. The spherical harmonic has a single cosine or sine, depending on whether $m = 0$ or ± 1, and in the latter case we have a complex exponential $e^{\pm i\phi}$. Putting in normalising factors we find

$$\begin{aligned} \psi_{2p0}(\rho,\theta,\phi) &= \frac{1}{4\sqrt{2\pi}}\rho\cos\theta e^{-\rho/2} \\ \psi_{2p\pm1}(\rho,\theta,\phi) &= \frac{1}{8\sqrt{\pi}}\rho\sin\theta e^{\pm i\phi}e^{-\rho/2}. \end{aligned}$$

The angular part is zero along the z-axis for the $m = \pm 1$ functions, and in the xy-plane for the $m = 0$ function. Figure 8.5 shows the the $m = 0$ eigenfunction along the z axis, together with the radial distribution function $D_{2p}(\rho)$. We see that the wavefunction is zero at the origin, (where the z axis crosses the nodal plane) but its slope is continuous; the slope discontinuity is a feature of the s wavefunctions only. The xy nodal plane divides the wavefunction into two parts of opposite sign. Comparing D_{2p} with D_{2s} we see that the radius of maximum probability is smaller for the $2p$ state. The corresponding classical motion, with the same energy and angular momentum, is an ellipse whose semi-major axis is related to the energy, and whose semi-latus rectum is related to the angular momentum, as discussed in Section 8.2. The radial limits of the classical motion are

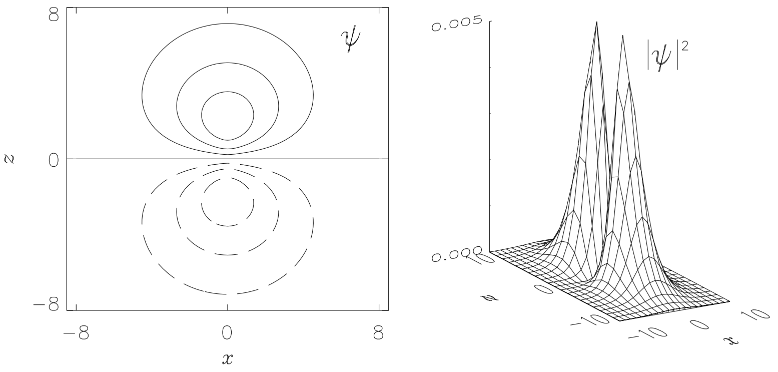


Figure 8.6: *The 2p $m = 0$ wavefunction and probability density in the XZ plane*

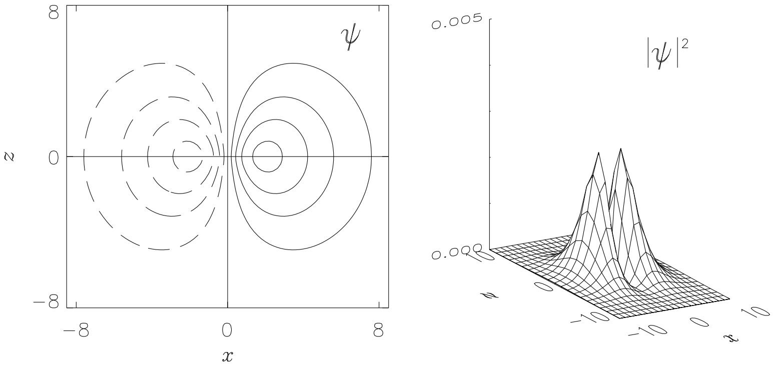


Figure 8.7: *The 2p $m = 1$ wavefunction and probability density in the XZ plane*

$r_\pm = a(1 \pm \varepsilon)$, which corresponds to

$$\rho_\pm = n^2 \left(1 \pm \sqrt{1 - \frac{\ell(\ell+1)}{n^2}} \right) \tag{8.47}$$

(see problem 8.4). These turning points are marked on the D_{2p} plot.

In order to visualize the three-dimensional shape of the eigenfunction we can also represent it as a contour map or surface plot. Using the height dimension to represent ψ or $|\psi|^2$ we can only represent two spatial dimensions, but any eigenfunction with $m = 0$ is independent of the azimuthal angle ϕ, so the plot is identical in any plane containing the z axis. Figure 8.6 shows a contour plot of ψ_{2p0} in the xz plane (dashed contours represent negative values) and a surface plot of the probability density $|\psi_{2p0}|^2$.

This technique can also be applied to a wavefunction with $m \neq 0$. In this case there is a ϕ-dependence, and the wavefunction is complex, but the ϕ-dependence is only a phase, and in the xz plane the wavefunction is real. Figure 8.7 shows a contour plot of ψ_{2p1} and a surface plot of $|\psi_{2p1}|^2$. Whereas the probaility density for ψ_{2p0} consists of two lobes of probability (of opposite

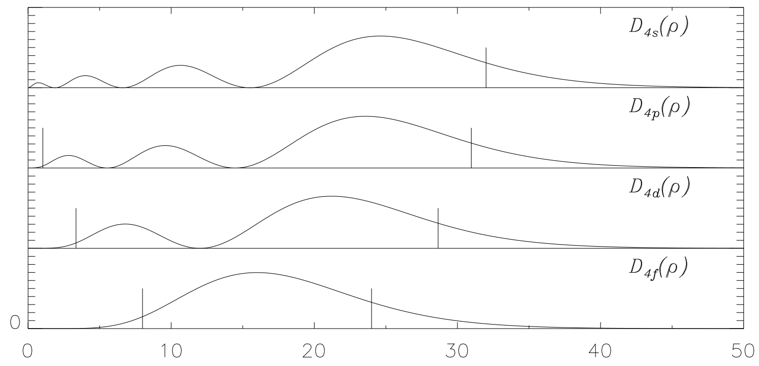


Figure 8.8: *The Radial Probability Distributions for $n = 4$ states*

amplitude) separated by the xy-plane, in the case of ψ_{2p1} it is a ring, or torus, around the z-axis, and the phase of the wavefunction progresses through a full cycle around the ring. All states of maximum $\ell = n - 1$, and maximum $m = \pm\ell$ have this generic shape, becoming at large quantum numbers well-defined circular orbits, almost like those of the Bohr model, with ℓ waves around the ring.

Finally in Figure 8.8 we compare the radial distribution functions for all the n=4 states. The classical turning points given by (8.47) are also marked. These plots illustrate a general feature of the eigenfunctions that we shall refer to in subsequent chapters. Eigenfunctions with low angular momentum (s, p) have significantly more probability in the region around the origin, say $\rho < 5$, than higher angular momentum states. This property is a direct consequence of the angular momentum, which leads to a centrifugal barrier, as discussed in **??**, the approximate location of which is the inner classical turning point. We can therefore reasonably assume that it is a generic feature of the s, p wavefunctions as compared with d and f wavefunctions, not some particular property of the $1/\rho$ potential in hydrogen, and we shall refer to it in subsequent chapters when discussing more complex atoms.

8.5 Problems

8.1 Fill in the missing steps between equations (8.20) and (8.21).

8.2 Draw a diagram showing $\mathbf{r}$ and $\delta\mathbf{r}$ to prove that the area swept out by the radius vector in time δt is $l\,\delta t/2m_r$. Hence derive (8.27). Use the correspondence principle in the form

$$\frac{dE_{nl}}{dn} = 2\pi\hbar\nu(E_{nl}, l)$$

to derive the limiting form of the eigenvalues E_{nl}:

$$E_{nl} = \frac{m_r k^2}{2\hbar^2(n+\delta_l)^2}$$

where we assume that the constant of integration δ_l may be l-dependent. This is, of course, only correct for hydrogen if $\delta_l = 0$, but this more general form is used to fit observed levels in alkali atoms.

8.3 Separate the internal and centre of mass degrees of freedom in the quantum mechanical treatment by changing the variables as follows. The new variables are defined by (8.6) and (8.12). The gradients with respect to the old variables are given in terms of gradients with respect to the new variables by

$$\frac{\partial}{\partial x_1} = \sum_{k=1}^{6} \frac{\partial \xi_k}{\partial x_1}\frac{\partial}{\partial \xi_k}$$

where ξ_k denotes the six new variables, and there are similar equation for the remaining five old variables. Show that these equations simplify to two terms in each sum, and that they can be summarised by

$$\begin{aligned} \nabla_1 &= \nabla + \frac{m_1}{M}\nabla_R \\ \nabla_2 &= -\nabla + \frac{m_2}{M}\nabla_R \end{aligned}$$

Substitute these into (8.28) to give (8.29). This change of variables is algebraically identical with the classical case, because the gradient equations above are equivalent to the classical relations $\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2$ and (8.13).

8.4 The quantum numbers n and ℓ define the energy and squared angular momentum of the quantum mechanical state, and these quantities are sufficient to define the shape of the corresponding classical orbit. Show that this orbit has semi-major axis $a = n^2 a(Z,\zeta)$ and eccentricity

$$\varepsilon = \sqrt{1 - \frac{\ell(\ell+1)}{n^2}}.$$

Hence show that the constraint that n and ℓ are integers implies the quantum condition $n > \ell$. The states with $\ell = n-1$ thus correspond to *nearly circular* orbits; exactly circular orbits do not occur, as these would have a sharply defined value of r, which is not permitted by the uncertainty principle.

8.5 Compare classical time averages of r^p over an orbit with quantum mechanical expectation values for different values of p as follows. The classical average is

$$\overline{r^p} = \frac{1}{T}\int r^p \, dt$$

where the integral is over one orbit. Using the rate of sweeping out area discussed in problem 8.2 we can turn the t integral into a ψ integral

$$\frac{l}{m_r} = \frac{d\text{Area}}{dt} = \frac{1}{2} r^2 \frac{d\psi}{dt}.$$

Show that

$$\overline{r^p} = \frac{\int r^{p+2}\, d\psi}{\int r^2\, d\psi}$$

Evaluate the integral for $p = 1$, -1 and -3. (use the table of definite integrals in Appendix A.3) and use the results of problem 8.4 to compare with the quantum-mechanical expectation values:

$$\begin{aligned} \langle \rho \rangle &= \frac{3n^2 - \ell(\ell+1)}{2} \\ \langle \frac{1}{\rho} \rangle &= \frac{1}{n^2} \\ \langle \frac{1}{\rho^3} \rangle &= \frac{2}{n^3 \ell(\ell+1)(2\ell+1)}. \end{aligned}$$

You should find that the results for $p = 1$ and $p = -1$ are directly comparable, but the results for $p = -3$ are only approximately equivalent.

Chapter 9

Spin-Orbit Interaction

This chapter lacks one section. Possibly add question about spin-orbit interaction in many-electron atoms.

9.1 Spin

In chapter 8 we solved the Schrodinger equation for the hydrogen atom after making a number of simplifications to the Hamiltonian. In this chapter we take account of the most important of these neglected effects, those associated with the electron spin. In this section we discuss electron spin and how to incorporate it into the wavefunction. In section 9.2 we introduce the extra terms in the Hamiltonian, and in section 9.3 we evaluate their effect on the hydrogen energy levels.

The electron spin was introduced in chapter **??** as an example of a system which had half-integral values of the angular momentum quantum number, and it was emphasized that although this property was 'ordinary' angular momentum in the sense that it could be used to convey mechanical angular momentum to another system, it was not *orbital* angular momentum, resulting from the motion of the mass of the electron in three-dimensional space. It is rather an angular momentum possesed by the electron at each point in space, in addition to any orbital angular momentum it may posses. Like any other angular momentum in quantum mechanics the spin has states labelled by two quantum numbers, a 'length' quantum number s, signifying that the square of the angular momentum has eigenvalue $s(s+1)\hbar^2$, and a 'z-component' quantum number m_s, signifying that the z-component of the angular momentum has eigenvalue $m_s\hbar$. As a 'spin-1/2' particle, the electron always has $s = 1/2$, and therefore m_s can take the values $+1/2$ or $-1/2$, which we shall loosely refer to as 'spin-up' and 'spin-down'.

We first need to consider how to represent the spin state in the wavefunction of the electron. The wavefunction for a single particle we have used up to this point has been a function of position in three-dimensional space $\psi(\mathbf{r})$. The reason for this is that the wavefunction gives us the probability amplitude for every possible state of the particle, and we have so far considered one such set of states to be the set of all positions in three-dimensional space. (Similarly, when we considered a wavefunction for the hydrogen atom we used a wavefunction in six-dimensional space, the space of all positions of two particles.) However, if *at each point in space* the electron can be in one of two states, spin-up or spin-down, then the set of all possible states is not three-dimensional space, but a larger set. Obviously the simplest way to give all the required probability amplitudes is to specify separate amplitudes for the electron to be in the spin-up and spin-down states at each point in space. We can then write the wavefunction as a two-component column vector:

$$\boldsymbol{\psi} = \begin{pmatrix} \psi_+(\mathbf{r}) \\ \psi_-(\mathbf{r}) \end{pmatrix} \tag{9.1}$$

where $\psi_+(\mathbf{r})$ is the amplitude for the electron to be at point $\mathbf{r}$ in the spin-up state (or, to be quite precise, $|\psi_+(\mathbf{r})|^2$ is the probability density for the electron to be at $\mathbf{r}$ with spin up) and $\psi_-(\mathbf{r})$ is the probability amplitude for the electron to be at point $\mathbf{r}$ with spin down. The wavefunction can be normalized in the usual way:

$$\int \boldsymbol{\psi}^\dagger \boldsymbol{\psi}\, d^3\mathbf{r} = \int |\psi_+(\mathbf{r})|^2 + |\psi_-(\mathbf{r})|^2\, d^3\mathbf{r} = 1. \tag{9.2}$$

where $\boldsymbol{\psi}^\dagger$ represents the two-component row vector $(\,\psi_+^\star \quad \psi_-^\star\,)$, the adjoint (transposed complex conjugate) of $\boldsymbol{\psi}$.

This wavefunction can represent a completely general state where the amplitudes for spin-up and spin-down vary in an arbitrary way with position. In such a state something must be responsible for the change of spin angular momentum implied by this variation. The hydrogen Hamiltonian used in chapter 8 did not contain the spin at all and, as we shall show shortly, the eigenstates are much simpler — the wave function factorizes

$$\boldsymbol{\psi} = \psi(\mathbf{r}) \begin{pmatrix} a \\ b \end{pmatrix}, \tag{9.3}$$

where a and b are constant relative amplitudes for spin-up and spin-down, multiplied by the position amplitude $\psi(\mathbf{r})$. We give the symbol $\boldsymbol{\chi}$ to the two-component spin part of the wavefunction. This two-component column vector with complex probability amplitudes is referred to as a *spinor,* in this case a constant spinor. (The general wavefunction introduced in (9.1) is also a spinor, but one that varies with position.) We can choose to normalise separately the two parts of the factored wavefunction in (9.3):

$$\int |\psi(\mathbf{r})|^2 \, d^3r = 1 \qquad \text{and} \qquad \boldsymbol{\chi}^\dagger \boldsymbol{\chi} = (\, a^\star \quad b^\star \,) \begin{pmatrix} a \\ b \end{pmatrix} = |a|^2 + |b|^2 = 1. \tag{9.4}$$

The Hamiltonian acts on the space part of this factored wavefunction, and ignores the spin part, so that the effect of including the spin in the Schrodinger equation $H\boldsymbol{\psi} = E\boldsymbol{\psi}$ is just

$$H\psi(\mathbf{r})\boldsymbol{\chi} = E\psi(\mathbf{r})\boldsymbol{\chi} \tag{9.5}$$

which is satisfied by the wavefunctions $\psi_{n\ell m_\ell}$ found in chapter 8 and *arbitrary* spin state $\boldsymbol{\chi}$. We can therefore choose as a basis of eigenstates the spatial states labelled by the quantum numbers n, ℓ and m_ℓ and spin state labelled by m_s, where the spin-up ($m_s = 1/2$) state is $\boldsymbol{\chi}_+$ and the spin-down ($m_s = -1/2$) state is $\boldsymbol{\chi}_-$. Thus if we ignore all effects in the Hamiltonian which relate to the spin, the only effect of its inclusion in the wavefunction is to double the degeneracy of all states. We have used three ways to denote these spin states, their eigenvalues s and m_s, the spinor symbol $\boldsymbol{\chi}$ and the explicit spinors, summarized in the following table.

$$\begin{array}{llll} \text{Spin-up} & |\tfrac{1}{2},\tfrac{1}{2}\rangle & \boldsymbol{\chi}_+ & \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ \text{Spin-down} & |\tfrac{1}{2},-\tfrac{1}{2}\rangle & \boldsymbol{\chi}_- & \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{array} \tag{9.6}$$

The introduction of these spin-up and spin-down states can come as a bit of a shock to the student — it is natural to feel that whereas for the spatial state we have a wavefunction which we can visualize, for the spin state we have just that, a state. The difference is partly that spin has no classical limit, but it is also in part simply a lack of familiarity. The space and spin states are in fact being treated on the same footing, with a probability amplitude for each state, but because there is a continuous space of spatial states we can visualize the resulting function, whereas for the spin state we have just the two amplitudes, and visualization is more difficult. Also we have some experience of what distinguishes a state of being *here* from a state of being *there,* but not what distinguishes a *spin-up* from a *spin-down* state. In other words the spatial part of the wavefunction corresponds to a classical degree of freedom with which we feel comfortable, and the spin part does not. Pauli said of spin that it represented ‘classically non-describable two-valuedness’, which expresses this sense that we have no picture of what distinguishes the states we are talking about.

This is perhaps less true if we view the electron not as a particle but as a wave. The introduction of spin means that the wave is described by two complex numbers at each point rather than one —

in other words, that it is a spinor wave not a scalar wave. In this respect it is not so different from some classical waves with which we are familiar. For example the electric field in an electromagnetic wave is described by three real numbers at each point, the components of a vector. This view of the electron as a spinor wave makes the distinction between spin-up and spin-down rather like the difference between the various polarizations of an electromagnetic wave, and in both cases the angular momentum transported by the wave depends on the polarization.

Whatever our mental picture of the spin states, the important point about them is that we know two of their properties, namely that they are eigenstates of the operators for spin angular momentum squared $\mathbf{s}^2$ and its $z-$component s_z:

$$\mathbf{s}^2\boldsymbol{\chi}_\pm = s(s+1)\hbar^2\boldsymbol{\chi}_\pm \qquad s_z\boldsymbol{\chi}_\pm = m_s\hbar\boldsymbol{\chi}_\pm \tag{9.7}$$

where $s = 1/2$ and $m_s = \pm 1/2$. It turns out that this is all we need to know about these states.

9.2 Spin-Orbit Hamiltonian

There is a fundamental relationship between angular momentum and magnetic moment for a charged system: angular momentum is the result of mass in rotation, and magnetic moment is the result of charge in rotation. They therefore tend to occur together, and the ratio of their sizes, the *gyromagnetic ratio,* is related to the charge-to-mass ratio. For a single charged particle with charge q and mass m orbiting a centre, the gyromagnetic ratio γ has the value $q/2m$ (see **??**):

$$\boldsymbol{\mu}_l = \gamma_l \boldsymbol{l} \qquad \text{where} \qquad \gamma_l = \frac{q}{2m}. \tag{9.8}$$

This would apply, for example, to the magnetic moment resulting from the orbital motion of the electron in hydrogen, with $q = -e$ and m equal to the electron mass.

This makes it entirely likely that the spin angular momentum of the electron will also be associated with a magnetic moment, and this is found to be the case. Since this angular momentum is not the result of the motion of the electron around a centre, we would not expect it to have the same gyromagnetic ratio as above, but perhaps one of the same order-of-magnitude. We therefore write the spin magnetic moment in terms of the spin angular momentum as

$$\boldsymbol{\mu}_s = g_e\frac{-e}{2m}\,\mathbf{s} \tag{9.9}$$

where g_e is known as the g-factor of the elctron and is a numerical scaling factor. (Some authors write this equation without the minus sign, so that their g_e is negative.) Since, as we discussed in the last section, we have no classical picture of why the electron has spin angular momentum, we can have no classical expectation about the value of g_e. It is found that g_e is very close to 2 — in fact in Dirac's theory of the electron it is predicted to be 2 exactly, but this value is subject to corrections. It is one of the most accurately measured and predicted quantities in physics. A recent value (CODATA 1998) for g_e is

$$g_e = 2.002\,319\,304\,3737(82) \tag{9.10}$$

This magnetic moment will interact with a magnetic field, with an interaction Hamiltonian given by $-\boldsymbol{\mu}\cdot\mathbf{B}$, and this is one of the mechanisms producing spin-orbit interaction. However the mechanism is slightly more complicated than this would suggest, as there is a potential discrepancy of reference frame. The magnetic moment of the electron is defined in the electron rest frame, whereas our atomic Hamiltonian is valid in a frame where the nucleus (or the atomic centre of mass — the distinction between these two frames is not very significant) is at rest. We have therefore to transform either the magnetic moment or the magnetic field into the other reference frame. This is done in either case with a Lorentz transformation, although not one as simple as the transformation of, say, energy and momentum, as $\boldsymbol{\mu}$ and $\mathbf{B}$ are both parts of second-rank tensors. This transformation is usually described in terms of transforming the magnetic field into the electron rest frame, probably because the transformation of $\mathbf{E}$ and $\mathbf{B}$ is described in most elementary special relativity texts, which is not true of the transformation of $\boldsymbol{\mu}$. However this leaves both $\mathbf{B}$ and $\boldsymbol{\mu}$ in a different reference frame from the rest of the Hamiltonian, so it seems more logical to refer to the process as transforming the magnetic moment of the moving electron. As long as we keep only terms in $1/c^2$ the result is the same in either case — we can either say that the motion through the electric field $\mathbf{E}$ produces a magnetic field $-\mathbf{v}\wedge\mathbf{E}/c^2$, or that the moving magnetic dipole moment acquires an electric dipole moment $\mathbf{v}\wedge\boldsymbol{\mu}/c^2$. In either case the interaction Hamiltonian is

$$H_M = -\boldsymbol{\mu}\cdot\left(\mathbf{B} - \frac{\mathbf{v}\wedge\mathbf{E}}{c^2}\right). \tag{9.11}$$

This is the general form of the magnetic part of the spin-orbit interaction, where $\mathbf{E}$ and $\mathbf{B}$ are given by the usual expressions in terms of the location of other charges and their motion. In hydrogenic atoms it simplifies: the only other charge is the nucleus, which is not moving (or at least we can ignore its very small motion) so $\mathbf{B} = 0$ and $\mathbf{E}$ is given by the Coulomb field

$$\mathbf{E} = \frac{Ze}{4\pi\epsilon_0 r^3}\mathbf{r}. \tag{9.12}$$

The vector product $\mathbf{v}\wedge\mathbf{E}$ is thus proportional to $\mathbf{v}\wedge\mathbf{r}$, which we can write in terms of the orbital angular momentum as $-\boldsymbol{l}/m$. Putting together (9.9), (9.11) and (9.12) we obtain for the magnetic spin-orbit interaction in one-electron atoms

$$H_M = \frac{g_e}{2}\,\frac{Ze^2}{4\pi\epsilon_0 m^2c^2r^3}\,\boldsymbol{l}\cdot\mathbf{s}. \tag{9.13}$$

There is another effect which couples spin and orbit, which cancels half of H_M. It is a more complicated interaction and we shall not discuss it in the same detail. It arises because of an unexpected property of a Lorentz transformation known as the Thomas precession. For any moving particle we can define a rest frame, a reference frame in which the particle is at rest. An accelerating particle will only be at rest instantaneously in this reference frame, but we can define a succession of instantaneous rest frames, which we can still refer to as a rest frame, although this is not, of course, an inertial frame. If each sucessive instantaneous rest frame is derived from the previous one by a Lorentz transformation without rotation, then the rest frame precesses relative to a fixed frame at the Thomas precession rate

$$\boldsymbol{\omega}_T = \frac{\gamma^2}{\gamma+1}\frac{\mathbf{a}\wedge\mathbf{v}}{c^2} \approx \frac{\mathbf{a}\wedge\mathbf{v}}{2c^2}. \tag{9.14}$$

where $\mathbf{v}$, $\mathbf{a}$ and γ are the velocity, acceleration and relativistic factor $1\sqrt{1-v^2/c^2}$ in the fixed frame. (A short derivation of (9.14) is given in the box.) Since this expression involves the cross-product of acceleration and velocity it is zero in simple situations such as a linear motion.

We can apply this result to the motion of an accelerated system with internal angular momentum, for example the Earth around the Sun. If there are no external torques on the Earth then in an instantaneous rest frame there is no precession of its spin axis, because in this frame the motion is non-relativistic. In the fixed frame (which we can identify with the solar rest frame) there will be a precession of the spin axis given by $\boldsymbol{\omega}_T$, because this is the precession rate between the two frames. In the fixed frame, therefore, the calculation of the rotational kinetic energy of the Earth is modified; it becomes $\frac{1}{2}\mathbf{I}_E(\boldsymbol{\omega}_E+\boldsymbol{\omega}_T)^2$ where $\boldsymbol{\omega}_E$ is the angular velocity of the Earth in its rest frame. Expanding this we get $\frac{1}{2}\mathbf{I}_E\boldsymbol{\omega}_E^2+\mathbf{s}_E\cdot\boldsymbol{\omega}_T+\frac{1}{2}\mathbf{I}_E\boldsymbol{\omega}_T^2$, where $\mathbf{s}_E=\mathbf{I}_E\boldsymbol{\omega}_E$ is the spin angular momentum of the Earth. The last term is of order c^{-4} and must be neglected, because we have already neglected other terms of this order in our earlier approximation. The first term is the rotational kinetic energy in the rest frame, so the additional term is just $\mathbf{s}_E\cdot\boldsymbol{\omega}_T$. (It should be pointed out that this effect is irrelevant to the actual precession of the Earth's spin axis, as there are torques, and the resulting precession is several orders of magnitude larger than $\boldsymbol{\omega}_T$.)

This analogy suggests that the additional term in the atomic Hamiltonion due to the Thomas precesion of the electron spin angular momentum is just

$$H_T = \mathbf{s}\cdot\boldsymbol{\omega}_T = \frac{\mathbf{s}\cdot\mathbf{a}\wedge\mathbf{v}}{2c^2} \tag{9.15}$$

Four-vectors, such as $\mathsf{x} = \begin{pmatrix} ct \\ \mathbf{r} \end{pmatrix}$ can be transformed from the ‘fixed’ frame S_0 to an instantaneous rest frame S_1 by a Lorentz transformation without rotation: $\mathsf{x} = \mathsf{L}(\boldsymbol{\beta})\mathsf{x}_0$ where the Lorentz transformation matrix is given by

$$\mathsf{L}(\boldsymbol{\beta}) = \begin{pmatrix} \gamma & -\gamma\boldsymbol{\beta}^T \\ -\gamma\boldsymbol{\beta} & \mathbf{I} + \frac{\gamma-1}{\beta^2}\boldsymbol{\beta}\boldsymbol{\beta}^T \end{pmatrix}.$$

Here $\boldsymbol{\beta} = \mathbf{v}/c$, $\gamma = 1/\sqrt{1-\beta^2}$ and the 4×4 matrix L has been written in blocks of 1×1, 1×3, 3×1 and 3×3. ($\mathbf{I}$ is the 3×3 unit matrix amd $\boldsymbol{\beta}^T$ denotes the transposed (row) matrix, so that $\boldsymbol{\beta}\boldsymbol{\beta}^T$ is a 3×3 matrix.) A Lorentz transformation between successive instantaneous rest frames S_1 and S_2 is effected by $\mathsf{L}(\delta\boldsymbol{\beta}_1) = \begin{pmatrix} 1 & -\delta\boldsymbol{\beta}_1^T \\ -\delta\boldsymbol{\beta}_1 & \mathbf{I} \end{pmatrix}$ to first order in the velocity increment $\delta\boldsymbol{\beta}_1$ (as seen in S_1). The combined transformation can be written $\mathsf{x}_2 = \mathsf{L}(\delta\boldsymbol{\beta}_1)\mathsf{x}_1 = \mathsf{L}(\delta\boldsymbol{\beta}_1)\mathsf{L}(\boldsymbol{\beta})\mathsf{x}_0$. The matrix product $\mathsf{L}(\delta\boldsymbol{\beta}_1)\mathsf{L}(\boldsymbol{\beta})$ is *not* in the form $\mathsf{L}(\boldsymbol{\beta}')$ for any $\boldsymbol{\beta}'$, but is combined with a small rotation, with 3×3 rotation matrix $\mathbf{R} = \mathbf{I} + \delta\mathbf{R}$. Thus

$$\begin{pmatrix} 1 & 0 \\ 0 & \mathbf{I} + \delta\mathbf{R} \end{pmatrix} \begin{pmatrix} \gamma' & -\gamma'\boldsymbol{\beta}'^T \\ -\gamma'\boldsymbol{\beta}' & \mathbf{I} + \frac{\gamma'-1}{\beta'^2}\boldsymbol{\beta}'\boldsymbol{\beta}'^T \end{pmatrix} = \begin{pmatrix} 1 & -\delta\boldsymbol{\beta}_1^T \\ -\delta\boldsymbol{\beta}_1 & \mathbf{I} \end{pmatrix} \begin{pmatrix} \gamma & -\gamma\boldsymbol{\beta}^T \\ -\gamma\boldsymbol{\beta} & \mathbf{I} + \frac{\gamma-1}{\beta^2}\boldsymbol{\beta}\boldsymbol{\beta}^T \end{pmatrix}.$$

If we evaluate the upper right and lower left elements of this matrix we obtain

$$\gamma'\boldsymbol{\beta}' = \gamma\boldsymbol{\beta} + \delta\boldsymbol{\beta}_1 + \frac{\gamma-1}{\beta^2}\delta\boldsymbol{\beta}_1 \cdot \boldsymbol{\beta}\,\boldsymbol{\beta} \qquad \text{and} \qquad \gamma'\boldsymbol{\beta}' + \delta\mathbf{R}\gamma'\boldsymbol{\beta}' = \gamma\boldsymbol{\beta} + \gamma\,\delta\boldsymbol{\beta}_1.$$

Substituting for $\gamma'\boldsymbol{\beta}'$ in the second of these equations, and neglecting second-order terms, we obtain

$$\delta\mathbf{R}\boldsymbol{\beta} = \frac{\gamma-1}{\gamma\beta^2}(\delta\boldsymbol{\beta}_1\boldsymbol{\beta}^T - \boldsymbol{\beta}\delta\boldsymbol{\beta}_1^T) = -\frac{\gamma-1}{\gamma\beta^2}(\delta\boldsymbol{\beta}_1 \wedge \boldsymbol{\beta}) \wedge \boldsymbol{\beta}.$$

Since an infinitesimal rotation of axes by $\delta\boldsymbol{\phi}$ changes the components of a vector $\mathbf{A}$ according to $\mathbf{A}' = \mathbf{A} - \delta\boldsymbol{\phi} \wedge \mathbf{A}$) this implies that the rotation generated by $\mathbf{I} + \delta\mathbf{R}$ is $\delta\boldsymbol{\phi} = ((\gamma-1)/\gamma\beta^2)\delta\boldsymbol{\beta}_1 \wedge \boldsymbol{\beta}$. If we express this rotation in terms of the velocity increment $\delta\boldsymbol{\beta}$ seen in S_0 we obtain (see problem 9.1) $\delta\boldsymbol{\phi} = ((\gamma-1)/\beta^2)\delta\boldsymbol{\beta}_1 \wedge \boldsymbol{\beta}$. Finally we divide by the time taken for the velocity increment to develop δt, giving us the precession rate $\boldsymbol{\omega}_T = \delta\boldsymbol{\phi}/\delta t$ of the rest frame as seen from S_0, in terms of the acceleration $\mathbf{a} = \delta\mathbf{v}/\delta t$ in the same frame:

$$\boldsymbol{\omega}_T = \frac{\gamma-1}{\beta^2}\frac{\mathbf{a} \wedge \mathbf{v}}{c^2} = \frac{\gamma^2}{\gamma+1}\frac{\mathbf{a} \wedge \mathbf{v}}{c^2}$$

where we have used $\gamma^2 - 1 = (\gamma+1)(\gamma-1) = \beta^2\gamma^2$. In the limit of small velocities $\gamma \approx 1$, giving the approximate form for $\boldsymbol{\omega}_T$ given in the text.

Box 9.1 The Thomas Precession

and this is the correct result. However if the reader feels less than convinced by this mixture of relativistic and non-relativistic ideas this is probably the correct reaction. Historically this line of argument slightly pre-dated Dirac's relativistic theory of the electron, but the fact we can derive this Hamiltonian from the Dirac theory in the appropriate limit is probably a more compelling reason for thinking it incorporates the right physics. There does not seem to be a straightforward derivation starting from the non-relativistic end.

We can now compare the relative sizes of the two spin-orbit interactions H_M and H_T. They involve different properties of the electron. In the one-electron case, where we can put $\mathbf{B} = 0$, the magnetic term is given by $H_M = \boldsymbol{\mu} \cdot (\mathbf{v} \wedge \mathbf{E})/c^2$, whereas if the acceleration is due to the electric field the Thomas term is given by $H_T = (e/2m)\, \mathbf{s} \cdot (\mathbf{v} \wedge \mathbf{E})/c^2$. However, since $\boldsymbol{\mu} = (-ge/2m)\mathbf{s}$, the two terms only differ by a factor of $-g$, so that the Thomas term cancels roughly half the magnetic term. The combined result for one-electron atoms is thus

$$H_{\text{so}} = \frac{g_e - 1}{2} \frac{Ze^2}{4\pi\epsilon_0 m^2 c^2 r^3} \boldsymbol{l} \cdot \mathbf{s}. \tag{9.16}$$

(This relationship between the two terms does not hold in general: for example in nuclei the nucleons are subject to a much larger acceleration due to non-electromagnetic forces — the strong nuclear force — and the dominant spin-orbit interaction is the Thomas term.)

9.3 Effect on energy levels

9.4 Problems

9.1 Evaluate γ' in terms of γ, $\boldsymbol{\beta}$ and $\delta\boldsymbol{\beta}_1$ from the top left element of the matrix equation in box 9.1, and combine this with the expression given there for $\gamma'\boldsymbol{\beta}'$ to find $\boldsymbol{\beta}'$ to first order:

$$\boldsymbol{\beta}' = \boldsymbol{\beta} + \frac{1}{\gamma}\delta\boldsymbol{\beta}_1 - \frac{\gamma - 1}{\gamma^2\beta^2}\boldsymbol{\beta} \cdot \delta\boldsymbol{\beta}_1\, \boldsymbol{\beta}.$$

The velocity increment in the S_0 reference frame corresponding to $\delta\boldsymbol{\beta}_1$ in S_1 is thus $\delta\boldsymbol{\beta} = \delta\boldsymbol{\beta}_1/\gamma - ((\gamma - 1)/\gamma^2\beta^2)\boldsymbol{\beta} \cdot \delta\boldsymbol{\beta}_1\, \boldsymbol{\beta}$. Hence show that $\boldsymbol{\beta} \wedge \delta\boldsymbol{\beta}_1 = \gamma\boldsymbol{\beta} \wedge \delta\boldsymbol{\beta}$. This substitution is used in the expression for $\boldsymbol{\omega}_T$ in box 9.1

Chapter 10

The Virial Theorem

10.1 Introduction

In this chapter we shall derive an interesting theorem for a non-relativistic system of particles interacting by means of radial forces varying as the inverse square of the inter-particle separation R_{ij}, comparing the classical (section 10.2) and quantum (section 10.3) derivations. The particular system we have in mind is a simple atomic model in which all the charged particles (nucleus, electrons) are bound together by electrostatic forces varying as $1/R_{ij}^2$, derived from a potential varying as $1/R_{ij}$. However the theorem applies equally to stars bound in a galaxy by gravitational forces, and by re-working the derivation a modified form of the theorem can be applied to a system of particles interacting by forces varying as a different power of the separation. This atomic model is the starting point for many realistic atomic calculations, even if relativistic corrections are added at a later stage, so that because within these approximations (non-relativistic, Coulomb forces) it is an exact result, the virial theorem is of some practical significance. However the reasons for studying it also include the insight given by the derivation into the similarities and differences between classical mechanics and quantum mechanics. We shall find that the two derivations exhibit considerable algebraic similarities, but also significant interpretational differences.

We start with the Hamiltonian. We label the $N+1$ particles with an index i running from 0 to N, with 0 labelling the nucleus, and 1 to N being electrons. The position vectors are $\mathbf{R}_i$ and charges q_i, so that $q_0 = +Ze$ and $q_1 = -e$. Thus the potential energy V is given by

$$V = \sum_{i>j=0}^{N} \frac{q_i q_j}{4\pi\epsilon_0 R_{ij}} \tag{10.1}$$

where the label on the summation indicates that we are summing over *pairs* of particles. For example with three particles ($N = 2$) the summation would run over the pairs {1,0}, {2,0} and {2,1}, which are all the pairs of labels with $2 \geq i > j \geq 0$. The kinetic energy is given by the usual non-relativistic form in terms of the momentum $\mathbf{P}_i$ and mass m_i:

$$T = \sum_{i=0}^{N} \frac{\mathbf{P}_i^2}{2m_i}. \tag{10.2}$$

The model Hamiltonian is therefore

$$H = T + V = \sum_{i=0}^{N} \frac{\mathbf{P}_i^2}{2m_i} + \sum_{i>j=0}^{N} \frac{q_i q_j}{4\pi\epsilon_0 R_{ij}}. \tag{10.3}$$

10.2 Classical Derivation

The classical derivation starts by defining a function of all the positions and momenta:

$$\mathcal{V} = \sum_{i=0}^{N} \mathbf{R}_i \cdot \mathbf{P}_i \tag{10.4}$$

where the sum runs over all the $N + 1$ particles. We then consider the rate of change of $\mathcal{V}$:

$$\frac{d\mathcal{V}}{dt} = \sum_i \frac{d\mathbf{R}_i}{dt} \cdot \mathbf{P}_i + \sum_i \mathbf{R}_i \cdot \frac{d\mathbf{P}_i}{dt}. \tag{10.5}$$

The first term on the right-hand side is simply twice the kinetic energy, summed over all the particles:

$$\sum_i \frac{d\mathbf{R}_i}{dt} \cdot \mathbf{P}_i = \sum_i \frac{\mathbf{P}_i^2}{m_i} = 2T, \tag{10.6}$$

whereas the second term can be simplified using the equations of motion as follows. The rate of change of momentum for each particle i is given by the net force $\mathbf{F}_i$ on the particle. $\mathbf{F}_i$ is given by the sum of the Coulomb forces from all the other particles:

$$\frac{d\mathbf{P}_i}{dt} = \mathbf{F}_i = \sum_{j \neq i} \frac{q_i q_j \mathbf{R}_{ij}}{4\pi\epsilon_0 R_{ij}^3} \tag{10.7}$$

where the label on the summation implies that we are summing over j from 0 to N, but excluding $j = i$. The vector $\mathbf{R}_{ij}$ is directed from particle j to i: $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$. We form the scalar product of each equation with the corresponding position vector $\mathbf{R}_i$ and sum over i:

$$\sum_{i=0}^{N} \mathbf{R}_i \cdot \frac{d\mathbf{P}_i}{dt} = \sum_{i=0}^{N} \sum_{j \neq i} \frac{q_i q_j}{4\pi\epsilon_0 R_{ij}^3} \mathbf{R}_i \cdot \mathbf{R}_{ij}. \tag{10.8}$$

On the right-hand side of (10.8) every pair of particles occurs twice, with the Coulomb force between them dotted with each of the two position vectors. For example, for the pair of particles 1 and 2 these terms are

$$\frac{q_1 q_2}{4\pi\epsilon_0 R_{12}^3}\Big(\mathbf{R}_1\cdot\mathbf{R}_{12}+\mathbf{R}_2\cdot\mathbf{R}_{21}\Big).$$

Since $\mathbf{R}_{21} = -\mathbf{R}_{12}$ we can combine the two terms in the bracket:

$$(\mathbf{R}_1\cdot\mathbf{R}_{12}+\mathbf{R}_2\cdot\mathbf{R}_{21}) = (\mathbf{R}_1-\mathbf{R}_2)\cdot\mathbf{R}_{12} = R_{12}^2$$

Thus the two terms combine to give $q_1q_2/(4\pi\epsilon_0 R_{12})$, the potential energy between these two particles. A similar reduction occurs for the two terms corresponding to every pair of particles, so that the right-hand side of (10.8) reduces to the potential energy V. It should be apparent that this combining of terms simply follows from the fact that the forces act along the line joining the particles and are equal and opposite; these conditions are sufficient to make the two terms for each pair of particles combine. For example if $\mathbf{F}_{12}$ is the force on particle 1 due to particle 2, and if Newton's third law of motion applies so that $\mathbf{F}_{21} = -\mathbf{F}_{12}$ then these terms combine as

$$\mathbf{R}_1\cdot\mathbf{F}_{12}+\mathbf{R}_2\cdot\mathbf{F}_{21} = \mathbf{R}_{12}\cdot\mathbf{F}_{12} = R_{12}F_{12} \propto V_{12}$$

where the first step uses Newton's third law, the second step uses the action along the line joining the particles, and the last step is only valid for forces varying as a power of the separation, with the coefficient of proportionality depending on the power.

The virial theorem follows from the equation we have derived for $d\mathcal{V}/dt$:

$$\frac{d\mathcal{V}}{dt} = 2T + V. \tag{10.9}$$

If we integrate this equation over a time τ and divide by τ then the right-hand side becomes the average value of $2T + V$ over this time interval, while the left-hand side, being a time derivative, can be expressed in terms of initial and final conditions:

$$\frac{\mathcal{V}(\tau)-\mathcal{V}(0)}{\tau} = 2\overline{T} + \overline{V} \tag{10.10}$$

If the motion is periodic we can choose τ to be a multiple of the period; all the particles have then returned to their initial positions and momenta, and the left-hand side vanishes. If the motion is not periodic but bounded (that is, the magnitudes of all positions and momenta remain less than some upper bound) then by waiting long enough we can make the left-hand side as small as we please. Thus it appears in general that

$$\overline{V} = -2\overline{T} \tag{10.11}$$

and this is the usual statement of the virial theorem for forces varying as $1/R^2$.

However, for the model we have defined neither of the conditions defined in the last paragraph is valid. This is because the 'atom' we have defined can move as a unit, and in the absence of an external force it will continue to do so indefinitely. Thus, even if the internal motion is periodic, the motion of the system as a whole is not, so that while the momenta may be periodic in time, the position co-ordinates are not. Thus the motion as a whole is not periodic, and neither is it bounded, since the position co-ordinates can become arbitrarily large after long times.

There are two ways of recovering a useful result from this difficulty. The first is to make the approximation that the mass of the nucleus is infinite. This prevents the motion of the system as a whole, and the nucleus becomes a fixed point which we can take as an origin for describing the motion of the system. The variables $\mathbf{R}_i$ and $\mathbf{P}_i$ are defined in an arbitrary reference frame; we now introduce variables defined in a specific reference frame. We define

$$\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_0 \tag{10.12}$$

as the position vector *relative to the nucleus,* and $\mathbf{p}_i$ as the momentum *relative to the centre of mass.* In this case, with infinite nuclear mass, the centre of mass is coincident with the nucleus, but the distinction will become significant in the subsequent discussion.

In the reference frame in which the nucleus is fixed, and in terms of these variables, the kinetic energy (10.2) becomes

$$T_\infty = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i}, \tag{10.13}$$

where the summation now runs only over the electrons. The potential energy becomes

$$V_\infty = \sum_{i=1}^{N} \frac{q_0 q_i}{4\pi\epsilon_0 r_i} + \sum_{i>j=1}^{N} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \tag{10.14}$$

where the first sum gives the potential energy between nucleus and electrons, and the second sum gives the potential energy of electron-electron interactions, with every pair of electrons occurring once. (We are here using $\mathbf{r}_{ij}$ for the inter-particle separation: $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. This is simply for notational consistency: since $\mathbf{r}_{ij} = \mathbf{R}_{ij}$, we could have continued to use $\mathbf{R}_{ij}$.)

We modify the definition of $\mathcal{V}$:

$$\mathcal{V}_\infty = \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{p}_i. \tag{10.15}$$

We can re-work the derivation above: we differentiate $\mathcal{V}_\infty$ to give obtain instead of (10.5)

$$\frac{d\mathcal{V}_\infty}{dt} = \sum_i \frac{d\mathbf{r}_i}{dt} \cdot \mathbf{p}_i + \sum_i \mathbf{r}_i \cdot \frac{d\mathbf{p}_i}{dt}. \tag{10.16}$$

and as before the first term is simply $2T_\infty$. In the second term the rate of change of momentum is again given by the sum of Coulomb forces:

$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i = \frac{q_0 q_i \mathbf{r}_i}{4\pi\epsilon_0 r_i^3} + \sum_{j\neq i} \frac{q_i q_j \mathbf{r}_{ij}}{4\pi\epsilon_0 r_{ij}^3} \tag{10.17}$$

where the leading term is the force due to the nucleus, and the summation represents the forces due to the other electrons. We take the scalar product with $\mathbf{r}_i$ and sum over i:

$$\sum_{i=1}^{N} \mathbf{r}_i \cdot \frac{d\mathbf{p}_i}{dt} = \sum_{i=1}^{N} \frac{q_0 q_i}{4\pi\epsilon_0 r_i} + \sum_{i=1}^{N} \sum_{j\neq i} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}^3} \mathbf{r}_i \cdot \mathbf{r}_{ij}. \tag{10.18}$$

The first summation here is the sum of electron-nucleus potential energies, and the second term can be re-arranged to give the sum of electron-electron potential energies, exactly as above following (10.8). Thus we deduce

$$\frac{d\mathcal{V}_\infty}{dt} = 2T_\infty + V_\infty \tag{10.19}$$

in direct analogy with (10.9). The difference is that the discussion following (10.9) is now applicable: as long as the atom is in a bound state, so that no particles escape to infinity, then over a long interval τ this rate of change is either exactly or essentially zero, so that the virial theorem becomes

$$\overline{V}_\infty = -2\overline{T}_\infty \tag{10.20}$$

for an atom with an infinitely heavy nucleus.

A rather more satisfactory approach to the problem, instead of artificially fixing the atom by using an infinite value for its nuclear mass, is to work in a reference frame in which the centre of mass is at rest. This is known as the centre-of-mass or centre-of-momentum frame. We start by deriving the relationship of this reference frame to the arbitrary reference frame with which we started. We define the total mass of the atom to be $M_c = \sum_{i=0}^{N} m_i$, and the position of the centre of mass in the arbitrary reference frame is then

$$\mathbf{R}_c = \frac{\sum_i m_i \mathbf{R}_i}{M_c}. \tag{10.21}$$

Differentiating we find

$$\mathbf{V}_c = \frac{\sum_i m_i \mathbf{V}_i}{M_c} = \frac{\sum_i \mathbf{P}_i}{M_c} = \frac{\mathbf{P}_c}{M_c} \tag{10.22}$$

where we have defined the total momentum to be $\mathbf{P}_c$. If we change to a reference frame moving with velocity $\mathbf{V}_c$ then the centre of mass will be at rest, and the momentum of particle i in this frame will be related to the momentum in the arbitrary frame by

$$\mathbf{p}_i = m_i(\mathbf{V}_i - \mathbf{V}_c) = \mathbf{P}_i - m_i \mathbf{V}_i = \mathbf{P}_i - \frac{m_i}{M_c}\mathbf{P}_c. \tag{10.23}$$

The total momentum in this frame is then $\sum_i \mathbf{p}_i = \mathbf{P}_c - (\sum_i m_i/M_c)\mathbf{P}_c = 0$, which is why this reference frame is also called the centre-of-momentum frame. This means that the momenta in this frame are not all independent; we can express one of them in terms of the other N, for example $\mathbf{p}_0 = -\sum_{i=1}^{N} \mathbf{p}_i$.

The kinetic energy in this frame is given by

$$T_c = \sum_{i=0}^{N} \frac{\mathbf{p}_i^2}{2m_i}. \tag{10.24}$$

We can relate this to the kinetic energy in the arbitrary frame T by substituting from (10.23):

$$T_c = \sum_{i=0}^{N} \frac{(\mathbf{P}_i - m_i\mathbf{P}_c/M_c)^2}{2m_i} = \sum_{i=0}^{N} \frac{\mathbf{P}_i^2}{2m_i} - \frac{\mathbf{P}_c^2}{2M_c} = T - \frac{\mathbf{P}_c^2}{2M_c}. \tag{10.25}$$

This is a physically reasonable result: it states that the difference between T and T_c is simply the kinetic energy of translation of the system as a whole, with mass M_c and momentum $\mathbf{P}_c$. The potential energy still consists just of the sum of electrostatic interactions, so is given by V in (10.1). Alternatively we can express it in terms of the vectors relative to the nucleus in the same form as V_∞ in (10.14):

$$V_c = \sum_{i=1}^{N} \frac{q_0 q_i}{4\pi\epsilon_0 r_i} + \sum_{i>j=1}^{N} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}. \tag{10.26}$$

With these forms for the kinetic and potential energies we can re-work the derivation of the virial theorem again. We start from

$$\mathcal{V}_c = \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{p}_i. \tag{10.27}$$

This is the same definition as $\mathcal{V}_\infty$, but the equations of motion are different. We differentiate:

$$\frac{d\mathcal{V}_c}{dt} = \sum_i \frac{d\mathbf{r}_i}{dt} \cdot \mathbf{p}_i + \sum_i \mathbf{r}_i \cdot \frac{d\mathbf{p}_i}{dt}. \tag{10.28}$$

In the first term $d\mathbf{r}_i/dt$ is not now $\mathbf{p}_i/m_i$. This is the point at which the distinction between $\mathbf{r}_i$ as a position relative to the nucleus, and $\mathbf{p}_i$ as a momentum relative to the centre of mass becomes significant: the rate of change of $\mathbf{r}_i$ is given by the difference velocity between electron i and the nucleus:

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i - \mathbf{v}_0 = \frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_0}{m_0}. \tag{10.29}$$

Putting this into the summation we find

$$\sum_{i=1}^{N} \frac{d\mathbf{r}_i}{dt} \cdot \mathbf{p}_i = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - \frac{\mathbf{p}_0}{m_0} \cdot \sum_{i=1}^{N} \mathbf{p}_i = \sum_{i=0}^{N} \frac{\mathbf{p}_i^2}{m_i}$$

where in the final step we have used the relationship between the momenta $\mathbf{p}_0 = -\sum_{i=1}^{N} \mathbf{p}_i$. Thus the whole summation is once again twice the total kinetic energy. In the second term of (10.28) the rate of change of momentum $\mathbf{p}_i$ is given by the force on particle i, and this expression is identical to (10.17). The following working is also unchanged, and the second term is thus the potential energy V_c. Thus, as in the previous derivations we find

$$\frac{d\mathcal{V}_c}{dt} = 2T_c + V_c. \tag{10.30}$$

Because $\mathcal{V}_c$ is defined in terms of positions relative to the nucleus it is again true that the coordinates are either periodic or bounded, so that either a over multiple of a period the average rate of change of $\mathcal{V}_c$ is exactly zero, or over a long averaging time it tends to zero, so that

$$\overline{V}_c = -2\overline{T}_c. \tag{10.31}$$

Within these conditions this is an exact result for the classical motion in the centre-of-mass frame.

Since at any time the total energy of the system is given by $E = T + V$, alternative statements of the theorem are $-\overline{E}_c = \overline{T}_c$ or $2\overline{E}_c = \overline{V}_c$. We can compare this result with the classical results for hydrogenic atoms in chapter 8. The classical model used there corresponds directly to the centre-of-mass case just considered. Equation (8.26) gives $E_c = -k/2a$, V_c is given by $-k/r$ and problem 8.5 gives

$$\overline{\frac{1}{r}} = \frac{1}{a} \tag{10.32}$$

where the average is taken over one period of the motion. Hence this very simple atomic model gives an example of the much more general theorem $2\overline{E}_c = \overline{V}_c$.

10.3 Quantum Derivation

We now turn to the quantum-mechanical derivation. The main classical results are (10.19) and (10.30), which both involve time differentials. Our general work on commutators in **??** suggests that the corresponding quantum-mechanical results will involve the commutator with the Hamiltonian, divided by $(i\hbar)$. For each case we will therefore need an expression for the corresponding Hamiltonian. For the infinitely heavy nucleus, the Hamiltonian is just the sum of the kinetic energy T_∞ given by (10.13) and the potential energy V_∞ given by (10.14):

$$H_\infty = T_\infty + V_\infty = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \sum_{i=1}^{N} \frac{q_0 q_i}{4\pi\epsilon_0 r_i} + \sum_{i>j=1}^{N} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}. \tag{10.33}$$

We shall start by deriving a result analogous to (10.19), by calculating the commutator of $\mathcal{V}_\infty$ with H_∞. We shall compare the derivation step-by-step with the classical derivation above, equations (10.15) – (10.19). Using the elementary properties of commutators **??** we find

$$\frac{1}{i\hbar}\left[\mathcal{V}_\infty, H_\infty\right] = \frac{1}{i\hbar}\sum_{i=1}^{N}\Big([\mathbf{r}_i, H_\infty]\cdot\mathbf{p}_i + \mathbf{r}_i\cdot[\mathbf{p}_i, H_\infty]\Big) \qquad \frac{d\mathcal{V}_\infty}{dt} = \sum_{i=1}^{N}\Big(\frac{d\mathbf{r}_i}{dt}\cdot\mathbf{p}_i + \mathbf{r}_i\cdot\frac{d\mathbf{p}_i}{dt}\Big). \quad (10.34)$$

The commutators are not difficult to evaluate, though we shall leave the details to a problem (10.2). In the first commutator, V_∞ commutes with $\mathbf{r}_i$, as do all the terms in T_∞ except $\mathbf{p}_i^2/2m_i$. The commutator is given by

$$\frac{1}{i\hbar}[\mathbf{r}_i, H_\infty] = \frac{\mathbf{p}_i}{m_i} \qquad \frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i}. \quad (10.35)$$

In the second commutator, $\mathbf{p}_i$ commutes with all the momentum operators in T_∞, but not with V_∞:

$$\frac{1}{i\hbar}[\mathbf{p}_i, H_\infty] = -\nabla_i V_\infty \qquad \frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i. \quad (10.36)$$

Each of the commutators is directly equivalent to the corresponding classical equation involving a time differential. The algebra combining these terms is now identical with the classical case, so that (10.34) reduces to

$$\frac{1}{i\hbar}[\mathcal{V}_\infty, H_\infty] = 2T_\infty + V_\infty \qquad \frac{dV_\infty}{dt} = 2T_\infty + V_\infty. \quad (10.37)$$

Up to this point the classical and quantum derivations are essentially identical, deriving equivalent results (10.37) by an equivalent set of steps. However the use that is made of this result is different in the two cases.

The classical result relates the rate of change of an observable property of the system $\mathcal{V}_\infty$ to other observables T_∞ and V_∞, and by following the trajectory of the system with time in configfuration space we can integrate this equation, as in the previous section, to derive a relationship between *time averages* of T_∞ and V_∞, taken over either a time period of the system, or an unspecified 'long' time interval. The quantum-mechanical result cannot necessarily be treated in this way. As it stands (10.37) is a result involving operators, and to apply it to a specific situation we need to evaluate its expectation value. If the system being considered were essentially classical (as for example the gravitational case mentioned in the introduction) then a classical wave-packet superposition state could presumably be constructed, which would follow a classical trajectory in configuration space and yield a result directly analogous to the classical one, in terms of time-averages.

However the atomic system we are considering is far from classical, and the wavefunction we shall use is for a single energy eigenstate ψ_n with energy E_n. In such a state the expectation value of a commutator with the Hamiltonian H_∞ vanishes:

$$\int \psi_n^\star [\mathcal{V}_\infty, H_\infty] \psi_n \, d\tau = \int \psi_n^\star \mathcal{V}_\infty H_\infty - H_\infty \mathcal{V}_\infty \psi_n \, d\tau = E_n \left(\int \psi_n^\star \mathcal{V}_\infty \psi_n \, d\tau - \int \psi_n^\star \mathcal{V}_\infty \psi_n \, d\tau \right) = 0. \tag{10.38}$$

Thus the expectation value of the left-hand side of (10.37) vanishes. The expectation value of the right-hand side thuerefore also vanishes, and this gives us the quantum-mechanical version of the virial theorem for an atom with an infinitely heavy nucleus:

$$\langle V_\infty \rangle = -2 \langle T_\infty \rangle \tag{10.39}$$

involving expectation values rather than time averages.

In order to derive the analogous result for the centre-of-mass system we again need the Hamiltonian. This is in fact given by the sum of T_c from (10.24) and V_c from (10.22), but strictly speaking there is a technical difficulty at this point. In the original arbitrary reference frame the positions $\mathbf{R}_i$ and momenta $\mathbf{P}_i$ are *conjugate* variables, which means that $\mathbf{P}_i$ has the operator representation $-i\hbar\nabla_i$, and corresponding components have the standard commutator $[X_i, -i\hbar\frac{\partial}{\partial X_i}] = i\hbar$. We cannot carry out arbitrary *independent* changes of variable $\mathbf{r}_i(\mathbf{R}_0 \ldots \mathbf{R}_N)$ and $\mathbf{p}_i(\mathbf{P}_0 \ldots \mathbf{P}_N)$ and simply assume that these new variables are still conjugate. In fact the $\mathbf{p}_i$ are indeed conjugate to the $\mathbf{r}_i$, which is why they were introduced in the previous section; the proof of this is left to problem 10.3. Thus the Hamiltonian in the centre-of-mass frame is

$$H_c = T_c + V_c = \sum_{i=0}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \sum_{i=1}^{N} \frac{q_0 q_i}{4\pi\epsilon_0 r_i} + \sum_{i>j=1}^{N} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \tag{10.40}$$

where $\mathbf{p}_0$ is not independent but is defined by $\mathbf{p}_0 = -\sum_{i=1}^{N} \mathbf{p}_i$. This differs from H_∞ only in the the extra term representing the kinetic energy of the nucleus. In consequence, our final derivation of the virial theorem only differs marginally from the infinite nuclear mass case.

The function $\mathcal{V}_c$ is the same as $\mathcal{V}_\infty$, so the first step is the same as (10.34):

$$\frac{1}{i\hbar}[\mathcal{V}_c, H_c] = \frac{1}{i\hbar}\sum_{i=1}^{N}\Big([\mathbf{r}_i, H_c]\cdot\mathbf{p}_i + \mathbf{r}_i\cdot[\mathbf{p}_i, H_c]\Big) \qquad \frac{d\mathcal{V}_c}{dt} = \sum_{i=1}^{N}\Big(\frac{d\mathbf{r}_i}{dt}\cdot\mathbf{p}_i + \mathbf{r}_i\cdot\frac{d\mathbf{p}_i}{dt}\Big). \tag{10.41}$$

The $\mathbf{p}_i$ commutator is unchanged, since the extra term in H_c commutes with $\mathbf{p}_i$. However the $\mathbf{r}_i$ commutator picks up an extra term (see problem 10.2):

$$\frac{1}{i\hbar}[\mathbf{r}_i, H_c] = \frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_0}{m_0} \qquad \frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i} - \frac{\mathbf{p}_0}{m_0} \tag{10.42}$$

as discussed in the previous section in conjunction with (10.29). The quantum commutators are again exactly equivalent to the classical equations, and they combine in the same way to give

$$\frac{1}{i\hbar}[\mathcal{V}_c, H_c] = 2T_c + V_c \qquad \frac{dV_c}{dt} = 2T_c + V_c. \tag{10.43}$$

Taking the expectation value of this in an energy eigenstate we again find

$$\langle V_c \rangle = -2\langle T_c \rangle \tag{10.44}$$

for the virial theorem in the centre of mass frame.

I hope this box can filled with the hydrogen stuff from the end of the previous section, and some non-trivial numerical results

Box 10.1 Examples of the Virial Theorem

This completes our discussion of the virial theorem except for one loose end. In section 10.2 we started by deriveng the theorem in an arbitrary reference fame, and then deduced that the theorem failed to work because of the motion of the system as a whole. Essentially the same happens with the quantum mechanical derivation, but the detail is subtly different. In the arbitrary reference frame we can compute the commutator of $\mathcal{V}$ from (10.4) and H from (10.3) and deduce

$$\frac{1}{i\hbar}[\mathcal{V}, H] = 2T + V \qquad \frac{dV}{dt} = 2T + V. \tag{10.45}$$

It thus appears that we can can take the expectation value of this equation and derive the virial theorem for this case too. However the centre-of-mass motion prevents this. The Hamiltonian includes the centre mass motion of the system as a free particle (see problem 10.3). As we saw in **??**, the eigenvalues of this part of the Hamiltonian are not quantized, but lie in a continuous range, and the energy eigenstates are not normalisable, and thus not physically realizable. A physically realizable free-particle state is a wave-packet, and this is not an energy eigenstate. We cannot use energy eigenstates to evaluate the expectation value of (10.45), as we need a normalised wavefunction to do this, and if we use a wave-packet then the expectation value of the commutator does not vanish. The quantum-mechanical version of the virial theorem in an arbitrary reference frame thus fails, just as the classical version did.

10.4 Problems

10.1 The virial theorem as we have derived it can be written $\langle T \rangle = -\frac{1}{2}\langle V \rangle$ for $V \propto r^{-1}$. Using the discussion on page 152 prove that for a potential $V \propto r^n$ the theorem takes the form $\langle T \rangle = \frac{n}{2}\langle V \rangle$. Thus for the harmonic oscillator $\langle T \rangle = \langle V \rangle$ as we noted in chapter 4.

10.2 Fill in the missing steps in the evaluation of the commutators in section 10.3 as follows.

(i) Using the fundamental commutator $[x_i, (\mathbf{p}_i)_x] = i\hbar$ show that $[x_i, T_\infty] = (\mathbf{p}_i)_x/m_i$, and hence derive (10.35).

(ii) Show that for any potential energy function $V(\mathbf{r}_1, \mathbf{r}_2 \ldots)$ the commutator with the momentum of the i'th particle is $[\mathbf{p}_i, V] = -i\hbar\nabla_i V$. Hence derive (10.36).

(iii) Using the fundamental commutator $[x_i, (\mathbf{p}_i)_x] = i\hbar$ and the definition of $\mathbf{p}_0$ in terms of $\mathbf{p}_i$ show that $[x_i, (\mathbf{p}_0)_x] = -i\hbar$. Hence show that the commutator of the extra term in T_c with $\mathbf{r}_i$ is $[\mathbf{r}_i, \mathbf{p}_0^2/2m_i] = -\mathbf{p}_0/m_i$. Hence derive (10.42).

10.3 Consider a linear change of variables in a Hamiltonian $H(X_i, P_i)$ where i runs from 1 to M — in other words an M-dimensional configuration space. (For the Hamiltonians considered in this chapter M is equal to either $3N$ or $3N+3$.) Define new variables by $x_i = \sum_j A_{ij} X_j$ with constant coefficients A_{ij}. We can also write this using an M-vector and an $M \times M$ matrix as $\mathbf{x} = \mathbf{A}\mathbf{X}$. The inverse transformation is required to exist: $\mathbf{X} = \mathbf{A}^{-1}\mathbf{x}$. Using the chain rule show that

$$\frac{\partial}{\partial X_i} = \sum_j A_{ji} \frac{\partial}{\partial x_j} \tag{10.46}$$

or in vector notation $\mathbf{P} = \mathbf{A}^T\mathbf{p}$ and conversely $\mathbf{p} = (\mathbf{A}^{-1})^T\mathbf{P}$. (This is the general case of which problem 8.3 is a particular example.) Thus a linear change of position co-ordinates induces a specific, but different, linear change of momentum co-ordinates.

(i) In the case of a rotation of co-ordinates for a single particle show that the $\mathbf{p}$ transforms with the *same* linear transformation as $\mathbf{x}$.

(ii) The case considered in section 10.3 involves $3N+3$ co-ordinates, of which $3N$ of the new co-ordinates are defined by $\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_0$. We take the remaining co-ordinates to be the centre of mass $\mathbf{R}_c = \sum_{i=0}^N \mathbf{R}_i/M$. Show that the inverse transformation is

$$\begin{aligned} \mathbf{R}_0 &= \mathbf{R}_c - \sum_{i=1}^N \frac{m_i\mathbf{r}_i}{M} \\ \mathbf{R}_i &= \mathbf{R}_c + \mathbf{r}_i - \sum_{i=1}^N \frac{m_i\mathbf{r}_i}{M} \qquad \{i = 1\ldots N\}. \end{aligned}$$

Hence show that the momenta transform according to

$$\begin{aligned} \mathbf{P}_c &= \sum_{i=0}^N \mathbf{P}_i \\ \mathbf{p}_i &= \mathbf{P}_i - \frac{m_i}{M}\sum_{i=0}^N \mathbf{P}_i \qquad \{i = 1\ldots N\} \end{aligned}$$

or conversely

$$\begin{aligned}
\mathbf{P}_0 &= \frac{m_0}{M}\mathbf{P}_c - \sum_{i=1}^{N} \mathbf{p}_i \\
\mathbf{P}_i &= \frac{m_i}{M}\mathbf{P}_c + \mathbf{p}_i \qquad \{i = 1 \ldots N\}
\end{aligned}$$

in agreement with (10.23). Hence show that the Hamiltonian in the arbitrary reference frame (10.3) splits up as $H = H_c + \mathbf{P}_c^2/2M$.

Chapter 11

Radiative Transitions

11.1 Electromagnetic Waves

There is a certain inconsistency in our treatment of quantum-mechanical systems up to this point. We have assumed, following Schrodinger, that the allowed states of the system are given by the solutions of the time-independent wave equation. We have also assumed, following Bohr, that transitions between these states can occur by the emission and absorption of photons, with energy given by the difference in the energies of the states involved. Thus if an atom has two energy levels E_1 and E_2, transitions between them involve the emission or absorption of photons with frequency ν_{12} or angular frequency ω_{12}:

$$h\nu_{12} = \hbar\omega_{12} = E_2 - E_1. \tag{11.1}$$

The inconsistency is that the solutions of the time-independent wave equation are also eigenfunctions of the time-dependent wave equation and thus stationary states: no transitions in fact occur according to the theory as we have developed it.

The same limitation is present in the classical theory we have developed for hydrogen-like atoms, where the electrostatic force between the particles is the only force we include, and the resulting motion is stable and periodic. We have not included any additional forces due to incident electromagnetic waves, nor have we included the effect of radiation by the accelerating charged particles. If we had, then the motion would no longer be periodic, but one orbit would evolve into another under the influence of these additional forces; it is therefore reasonable to suppose if we can include these effects in our quantum theory we will obtain predictions for the rates at which transitions between states occur. This is indeed the case, and is the subject of the present chapter.

However these two types of interaction with radiation — the induced response of the atom to a prescribed incident radiation field, and the atom as a spontaneous source of radiation — differ greatly in how easily they can be handled in quantum theory, and our approach will be somewhat indirect. In the next section we present a very powerful argument due to Einstein that relates the spontaneous and induced processes to each other, and in section 11.3 we calculate the rate of the induced process using time-dependent perturbation theory. This allows us to circumvent the much more difficult problem of a direct calculation of the spontaneous rate. The final section contains a discussion of selection rules governing all radiative processes. In the remainder of this section the fields of an electromagnetic wave are briefly described.

An electromagnetic wave is a solution to Maxwell's equations in a region where there are no sources — that is, no charges or currents. Of course the atom itself contains lots of charges and currents, but the radiation due to these is not what we are currently interested in, since we are considering an incident wave due to distant sources. Thus in Maxwell's equations

$$\nabla \cdot \mathbf{E} = \rho/\epsilon_0 \tag{11.2}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{11.3}$$

$$\nabla \wedge \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0 \tag{11.4}$$

$$\nabla \wedge \mathbf{B} - \mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} = \mu_0 \mathbf{J} \tag{11.5}$$

we can set the charge density ρ and current density $\mathbf{J}$ to zero. (The reader may be familiar with other forms of Maxwell's equations containing the fields $\mathbf{D}$ and $\mathbf{H}$. These include the effects of sources bound into matter; if *all* sources are represented explicitly by ρ and $\mathbf{J}$ the equations take the above form.) These equations possess wave-like solutions of many different types, describing everything from the electromagnetic field around a power line to the light emitted by a galaxy. We shall just consider the simplest solutions, plane waves. By this we mean that at every point all components of the fields have harmonic time-dependence, with different points in general having oscillations with different phase, and that surfaces of constant phase are planes:

$$\text{each component of } \mathbf{E}, \mathbf{B} \propto \cos(\mathbf{k} \cdot \mathbf{r} - \omega t + \phi). \tag{11.6}$$

The structure of the equations is much simplified if we adopt a complex notation. If we re-write (11.6) in terms of complex exponentials we obtain, for example for E_x with amplitude $|E_x|$:

$$\begin{aligned} E_x &= \frac{|E_x|}{2}\left(e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t+\phi)} + e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t+\phi)}\right) \\ &= \frac{|E_x| e^{i\phi}}{2} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \text{ c.c.} \end{aligned}$$

where we have denoted the complex conjugate by c.c. These two terms, the positive frequency and negative frequency terms, are separately solutions of Maxwell's equations, and we need only write down one of them explicitly. Denoting the complex amplitude $|E_x|e^{i\phi}/2$ as the x-component of a vector $\boldsymbol{\mathcal{E}}$ we can write the whole solution for $\mathbf{E}$ and $\mathbf{B}$ as

$$\begin{aligned} \mathbf{E} &= \boldsymbol{\mathcal{E}} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \text{ c.c.} \qquad (11.7) \\ \mathbf{B} &= \boldsymbol{\mathcal{B}} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \text{ c.c.} \qquad (11.8) \end{aligned}$$

These we could substitute into Maxwell's equations to find the relationships between the various constants we have introduced, $\mathbf{k}$, ω, $\boldsymbol{\mathcal{E}}$ and $\boldsymbol{\mathcal{B}}$.

However we shall not do this, but first introduce the potentials. We have already noted that while in classical mechanics force $\mathbf{F}$ is a central concept, in quantum mechanics it is the potentials V which appear in Schrodinger's equation as part of the Hamiltonian, from which the forces are derived by differentiation: $\mathbf{F} = -\nabla V$. In the same way, while it is the fields $\mathbf{E}$ and $\mathbf{B}$ that exert forces on charges and currents, it is the electromagnetic scalar and vector potentials Φ and $\mathbf{A}$ which appear in the Hamiltonian, from which the fields are found by differentiation:

$$\begin{aligned} \mathbf{E} &= -\nabla\Phi - \frac{\partial \mathbf{A}}{\partial t} \qquad (11.9) \\ \mathbf{B} &= \nabla \wedge \mathbf{A}. \qquad (11.10) \end{aligned}$$

These forms ensure that the second and third Maxwell equations are always satisfied, so that we only need to satisfy the first and fourth.

However, the actual fields $\mathbf{A}$ and Φ are not fully determined by (11.9) and (11.10), but are to some degree arbitrary. In the case of Φ this degree of freedom is well-known — we can add an arbitrary constant to Φ without changing $\nabla\Phi$. (This is usually resolved with electrostatic potentials by setting $\Phi = 0$ at infinity.) Similarly with $\mathbf{A}$, adding a time-independent gradient $\nabla\chi(\mathbf{r})$ to $\mathbf{A}$ does not change either $\frac{\partial \mathbf{A}}{\partial t}$ or $\nabla \wedge \mathbf{A}$. (In the magnetostatic case this is usually resolved by setting $\nabla \cdot \mathbf{A} = 0$.) However in the general case more interesting changes to Φ and $\mathbf{A}$ are possible without changing the fields — gauge transformations. Using any continuous function $\chi(\mathbf{r}, t)$ we can change $\mathbf{A}$ and Φ to

$$\mathbf{A}' = \mathbf{A} + \nabla\chi \qquad \Phi' = \Phi - \frac{\partial \chi}{\partial t} \qquad (11.11)$$

without changing the fields $\mathbf{E}$ and $\mathbf{B}$. (This includes the electrostatic and magnetostatic transformations as special cases.) This freedom to represent the same physical situation with different potentials is one we shall employ below.

Thus the fields we substitute into Maxwell's equations are those derived from

$$\Phi = \varphi e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \text{ c.c.} \tag{11.12}$$

$$\mathbf{A} = \boldsymbol{\mathcal{A}} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \text{ c.c.} \tag{11.13}$$

This is a solution to Maxwell's equations provided the phase velocity of the waves is $\omega/k = 1/\sqrt{\mu_0\epsilon_0} = c$ and φ is related to $\boldsymbol{\mathcal{A}}$ by $\varphi = \hat{\mathbf{k}} \cdot \mathbf{A}/c$. We can, if we wish, use the gauge degree of freedom to set φ, and hence $\hat{\mathbf{k}} \cdot \mathbf{A}$ to zero. The simplest form for the potential is then

$$\mathbf{A} = \boldsymbol{\mathcal{A}} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \text{ c.c.} \tag{11.14}$$

where $\boldsymbol{\mathcal{A}}$ is a (possibly complex) vector in the plane perpendicular to $\mathbf{k}$.

Finally then we can relate the amplitudes of the various fields together: (11.9) and (11.10) give

$$\boldsymbol{\mathcal{E}} = i\omega\boldsymbol{\mathcal{A}} \qquad \text{and} \qquad \boldsymbol{\mathcal{B}} = i\mathbf{k}\wedge\boldsymbol{\mathcal{A}}. \tag{11.15}$$

Alternatively we can relate the field amplitudes to each other by eliminating $\boldsymbol{\mathcal{A}}$: $c\boldsymbol{\mathcal{B}} = \hat{\mathbf{k}} \wedge \boldsymbol{\mathcal{E}}$ or $\boldsymbol{\mathcal{E}} = -c\hat{\mathbf{k}}\wedge\boldsymbol{\mathcal{B}}$ where $\hat{\mathbf{k}}$ denotes the unit vector in the $\mathbf{k}$ direction. These amplitudes define the energy flow in the field: the energy density in the field is given by $u = \frac{\epsilon_0}{2}\left(E^2 + c^2B^2\right)$, while Poynting's vector $\mathbf{S} = \mathbf{E} \wedge \mathbf{B}/\mu_0$ tells us the power per unit area carried by the wave. If we substitute for the fields from (11.7) and (11.8), and the amplitudes from (11.15) we can find these quantities in terms of $\boldsymbol{\mathcal{A}}$, and so relate the optical field strengths at a given point to observable quantities like energy flow in the radiation field. A fact we shall use in section 11.3 is that the time-averages of the two terms in u are of equal value — see problem 11.1.

11.2 Einstein's Treatment of Radiative Processes

In 1905 Einstein, then an unknown clerk in the Swiss Patent Office, published three papers in *Annalen der Physik:* one on the statistical explanation of Brownian motion, one on the photon interpretation of photoelectric effect observations, and finally the defining account of the special theory of relativity. These three areas of theoretical physics — statistical mechanics, quantum theory and relativity — remained central to his work, and in 1917 he published a remarkable paper combining all three disciplines, in which he calculated the necessary relationship between spontaneous radiative processes — an isolated atom in an excited state E_2 making a transition to a lower state E_1 and emitting a photon $h\nu_{12}$ — and stimulated processes, in which both the emission process and the reverse process of photon absorption occur in the presence of radiation. In this section we shall discuss part of the argument of this paper.

The essentials of the approach are as follows. Firstly the atoms must be in one of a discrete set of quantum states $\{E_i\}$. (By atoms we simply mean weakly interacting identical quantum systems; the same arguments apply to molecules in a gas.) Of course the analysis pre-dates quantum mechanics in its present form, so the idea of superposition states is not allowed for. We consider a fixed number of atoms N, with N_i in state i, where $\sum N_i = N$, and discuss the rate at which atoms make the transition $i \to j$. (We could equivalently discuss a number density n, partial number densities n_i and transition rates per unit volume, or occupation probabilities p_i and probabilities of transition per atom per unit time.) Secondly, specific assumptions about the dependence of the rates for the processes are required. Since the atoms are assumed to be independent, every rate is proportional to the number of atoms in the initial state. We shall discuss the spontaneous and stimulated rates separately.

The spontaneous emission process is one in which the atom makes a transition from state j to a lower state i while emitting a photon of frequency ν_{ij}. The rate for this process, apart from the proportionality to N_i, cannot depend on anything else except the initial and final states j and i, since the process is considered to be spontaneous. Thus the rate can be written in terms of its contribution to the time derivative of N_j and N_i

$$-\left.\frac{\partial N_j}{\partial t}\right|_{\text{spon}} = \left.\frac{\partial N_i}{\partial t}\right|_{\text{spon}} = N_j A_{ji} \tag{11.16}$$

where A_{ji} is a constant for any given transition $j \to i$.

The stimulated rates are also proportional to the number of atoms in the initial state, but they must in addition depend on some quantity pertaining to the radiation field. The resonance condition (11.1) further suggests that the quantity ought to depend on the radiation at the resonance frequency. (The spectral lines do in fact have a finite spectral width, but for the purposes of this discussion they are assumed to be infinitely narrow.) On the basis of a classical model Einstein suggested that the appropriate quantity should be the spectral energy density $\rho_\nu(\nu)$ at the exact resonance frequency ν_{ij}, that is, $\rho_\nu(\nu_{ij})$:

$$\left.\frac{\partial N_j}{\partial t}\right|_{\text{stim}} = -\left.\frac{\partial N_i}{\partial t}\right|_{\text{stim}} = N_j B_{ji} \rho_\nu(\nu_{ij}) \tag{11.17}$$

$$\left.\frac{\partial N_i}{\partial t}\right|_{\text{abs}} = -\left.\frac{\partial N_j}{\partial t}\right|_{\text{abs}} = N_i B_{ij} \rho_\nu(\nu_{ij}). \tag{11.18}$$

The first equation (11.17) defines the rate for stimulated emission, where the radiation field stimulates the atom to emit a photon while making a transition to a lower state, and (11.18) defines

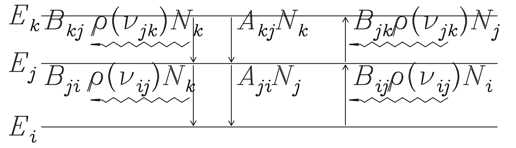


Figure 11.1: *The basic radiative processes*

the rate for absorption of radiation while making an upward transition. Putting together the spontaneous and stimulated rates we obtain the total rate of change for N_j:

$$\frac{dN_j}{dt} = \sum_k \Big(N_k A_{kj} + (N_k B_{kj} - N_j B_{jk})\rho_\nu(\nu_{jk})\Big) - \sum_i \Big(N_j A_{ji} + (N_j B_{ji} - N_i B_{ij})\rho_\nu(\nu_{ij})\Big). \quad (11.19)$$

Here the first sum represents spontaneous and stimulated decays from higher states, and absorption up to higher states, and the second sum represents spontaneous and stimulated decays to lower states, and absorption from lower states. These processes are all illustrated in Figure 11.1

The concept of spectral energy density ρ_ν deserves a few words. It should not be confused with the energy density u, defined above in terms of $\mathbf{E}$ and $\mathbf{B}$ at a given point. The definition of ρ_ν assumes that it is possible to decompose u into contributions associated with radiation of different frequencies, so that the energy density associated with radiation with frequencies between ν and $\nu + \Delta\nu$ is $\rho_\nu(\nu)\Delta\nu$:

$$u = \int_0^\infty \rho_\nu(\nu)\, d\nu. \quad (11.20)$$

The spectral energy density is thus a density in two senses, the energy per unit volume per unit frequency range. It can also be written as a function of the angular frequency ω:

$$u = \int_0^\infty \rho_\omega(\omega)\, d\omega. \quad (11.21)$$

Since $d\omega = 2\pi\, d\nu$ it follows from (11.20) and (11.21) that $\rho_\omega = \rho_\nu/(2\pi)$; if we then use ρ_ω to define the stimulated rates the B coefficients will change to $B^{(\omega)} = 2\pi B$. We shall only use ρ_ν and the B coefficients defined above, but see problem 11.2 for results using the other convention.

This standard account of the spectral energy density begs the question of whether such a quantity exists. It seems a natural consequence of the fact that solutions A and B of Maxwell's equations can be superposed to give $A+B$ that the energy density of such superpositions $u(A+B)$

is just $u(A)+u(B)$, and this idea, together with the idea of Fourier decomposition of the fields, leads directly to (11.20). However this is much too simple an argument, which does not take account of the fact that the energy is quadratic in the fields, and the phenomenon of interference is precisely the fact that $u(A+B)$ is *not* $u(A)+u(B)$. Thus for ρ_ν to exist we need to assume that the radiation at different frequencies is incoherent. In fact at a point in an *arbitrary* radiation field ρ_ν does not necessarily exist, and if it does, it is a statistical property of the field, the result of some sort of averaging — either over space or time, or an ensemble of physically equivalent realizations of the same field. There are some quite difficult issues involved here, that have only been fully understood in recent decades; for the present purposes we simply follow Einstein in assuming that after whatever averaging is necessary (11.17) and (11.18) define the stimulated transition rates.

We have now introduced the required definitions, and can present Einstein's argument for two necessary relationships between the A and B coefficients. These relationships depend on the *possibility* of thermal equilibrium — that is, thermal equilibrium as normally understood is impossible unless these relations are valid. This is a very striking result, obtaining constraints on model coefficients simply from supposing that it is possible for thermal equilibrium to exist. Indeed it is a very suggestive result — it suggests that the processes are not really independent but different aspects of the same atom-field interaction. This is indeed the case, but it only appears when we have a quantum theory of the field, whereas we are treating the radiation classically.

We therefore consider a radiation field in equilibrium with some atoms a a definite temperature T. The first property of thermal equilibrium that we use is that it is a completely steady state: all rates of change must on average be zero. In particular, $\frac{dN_j}{dt}$ in (11.19) must be zero for every state j. However we can go further than this: this zero must not be the result of cancelling contributions from the sums over energy levels on the right-hand side, but every group of terms relating to the same pair of energy levels in (11.19) must be zero. This is because in addition to the atom distribution being in steady state, the photon distribution must also be in steady state, which requires that there is no net absorption or emission at any frequency. Since in general there is no reason for different spectral lines to occur at the same frequency, there must be no net absorption or emission associated with each spectral line, so the three terms representing spontaneous and stimulated emission and absorption must add up to zero for each spectral line. (This result is sometimes referred to as the principle of detailed balance.) Thus from this property of thermal equilibrium we derive the result

$$\left(N_j^{(\mathrm{eq})}A_{ji}+(N_j^{(\mathrm{eq})}B_{ji}-N_i^{(\mathrm{eq})}B_{ij})\rho_\nu^{(\mathrm{eq})}(\nu_{ij})\right)=0 \tag{11.22}$$

where $N^{(\mathrm{eq})}$ and $\rho_\nu^{(\mathrm{eq})}$ are the equilibrium values of the state populations and spectral energy density. (It is worth pointing out in passing that (11.19) is still valid in non-equilibrium situations.)

The second property of the thermal equilibrium which we can use is the dependence of the state populations and radiation spectral energy density on the temperature T. The state populations follow a Maxwell-Boltzmann distribution. If the degeneracies of the states are g_i, g_j, then

$$\frac{N_i^{(\mathrm{eq})}}{N_j^{(\mathrm{eq})}} = \frac{g_i}{g_j} \exp\left(\frac{E_j - E_i}{kT}\right) = \frac{g_i}{g_j} e^{h\nu_{ij}/kT} \tag{11.23}$$

while the spectral energy density is given by the Planck distribution:

$$\rho_\nu^{(\mathrm{eq})}(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}. \tag{11.24}$$

Substituting these results into (11.22) and re-arranging to isolate ρ_ν we find

$$\frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} = \frac{A_{ji}/B_{ji}}{(N_i^{(\mathrm{eq})} B_{ij}/N_j^{(\mathrm{eq})} B_{ji}) - 1} = \frac{A_{ji}/B_{ji}}{(g_i B_{ij}/g_j B_{ji}) e^{h\nu_{ij}/kT} - 1} \tag{11.25}$$

Comparing the two sides we find the required relationships between the coefficients:

$$A_{ji} = \frac{8\pi h\nu^3}{c^3} B_{ji} \tag{11.26}$$

$$g_i B_{ij} = g_j B_{ji}. \tag{11.27}$$

Equations (11.26) and (11.27) are Einstein's relations between the A and B coefficients for radiative transitions between levels i and j.

In the 1917 paper Einstein went on to introduce relativistic ideas: if the atom and the radiation field are exchanging energy, then they must necessarily be exchanging momentum also. He showed that a condition for thermal equilibrium of the momentum distribution was that this momentum was a directed quantity in each spontaneous emission, and only zero on average, just as though the atom was firing a bullet in a random direction. This he cited as a reason for attributing some degree of physical reality to the photon concept.

11.3 Quantum-mechanical calculation of the B Coefficient

In this section we shall compute the transition rate between two states induced by a radiation field. The result is (11.33) below, but this is not in the Einstein form $B\rho$. The reason for this is that the Einstein form is not the final word on the response of the atom to radiation, and it is only valid under certain conditions, which are briefly discussed.

In the long-wavelength approximation the interaction Hamiltonian (11.28), with $\Phi = 0$, becomes

$$H_{E1}(t) = \frac{-e}{m}\mathbf{A}(t) \cdot \sum_i \mathbf{p}_i$$

where we have dropped the $\mathbf{r}$ argument, as the potential is assumed to be uniform over the atom. The fields derived derived from $\mathbf{A}(t)$ are a spatially uniform electric field $\mathbf{E}(t) = -\frac{d\mathbf{A}(t)}{dt}$ and zero magnetic field, $\mathbf{B} = 0$. We can now reconsider our choice of potentials, and do a gauge transformation to represent these fields in a different way. We use a gauge transformation function $\chi = -\mathbf{r} \cdot \mathbf{A}(t)$, so that $\nabla\chi = -\mathbf{A}(t)$. Using (11.11) this transforms the potentials to $\Phi' = -\frac{d\chi}{dt} = -\mathbf{r} \cdot \mathbf{E}(t)$ and $\mathbf{A}' = 0$. Putting these potentials into (11.28) we get

$$H_{E1}(t) = e\sum_i \mathbf{r}_i \cdot \mathbf{E}(t).$$

These two forms for H_{E1}, because they are related by a gauge transformation, are exactly equivalent. In the last equation we can identify $\mathbf{D} = -\sum_i e\mathbf{r}_i$ as the electric dipole moment of the atom, giving us $H_{E1}(t) = -\mathbf{E}(t) \cdot \mathbf{D}$.

Box 11.1 The Electric Dipole Hamiltonian

In order to calculate the transition rate betwen two states of an atom induced by an electromagnetic field we need first the interaction Hamiltonian, and then we can apply the time-dependent perturbation theory described in **??**. As suggested above, the interaction Hamiltonian involves the potentials $\mathbf{A}$ and Φ rather than the fields $\mathbf{E}$ and $\mathbf{B}$. The part involving Φ is fairly obvious — every charge q_i at $\mathbf{r}_i$ contributes a term $q_i\Phi(\mathbf{r}_i)$. (Indeed, in a sense we have used this already in our electrostatic Hamiltonians (**??**), where the infinitely heavy nucleus appears simply as an external source of electrostatic potential $\Phi = Ze/4\pi\epsilon_0 r$ which gives the electron a potential energy of $-e\Phi(\mathbf{r}_i) = -Ze^2/4\pi\epsilon_0 r_i$.) In the part involving $\mathbf{A}$, every moving charge q_i with mass m_i contributes a term $(q_i/m_i)\mathbf{A}(\mathbf{r}_i) \cdot \mathbf{p}_i$. This is in fact exactly the same as the classical interaction Hamiltonian, but it is not simply related to ideas of potential energy in the same way as the Φ term, and we shall not discuss its derivation. There is also an additional term due to spins which is discussed in problem 11.3. Thus the interaction Hamiltonian for the atomic electrons ($q = -e$) is

$$H_{\mathrm{EM}}(t) = \frac{-e}{m}\sum_i \Big(\mathbf{A}(\mathbf{r}_i, t) \cdot \mathbf{p}_i + \Phi(\mathbf{r}_i, t)\Big). \tag{11.28}$$

In this form the interaction Hamiltonian is rather difficult to use, but there are several simplifications possible. Firstly, as mentioned in section 11.1, we can choose to represent the radiation by a vector potential with no scalar potential, and thus set $\Phi = 0$ in (11.28). Secondly, we can make use of a long-wavelength approximation: for atoms interacting with radiation in the ultra-violet, visible or any longer wavelength we can make the approximation that the wavelength of the radiation ($\gtrsim 100$ nm) is much greater than the size of the atom (~ 0.1 nm). Thus the vector potential $\mathbf{A}$ is very nearly uniform over the atom, and we can replace $\mathbf{A}(\mathbf{r}_i, t)$ with $\mathbf{A}(\mathbf{0}, t)$ where the origin is the centre of the nucleus. In the box we show that the interaction Hamiltonian is equivalent to

$$H_{\mathrm{E1}}(t) = -\mathbf{E}(t) \cdot \mathbf{D}, \tag{11.29}$$

where the electric dipole moment $\mathbf{D}$ is given by $\mathbf{D} = -e \sum \mathbf{r}_i$. The interaction is between the electric field of the radiation and the electric dipole of the atom and the long-wavelength approximation is therefore known as the *electric dipole approximation.* If, for reasons of symmetry discussed in the next section, this approximation gives zero transition probabilities we can consider the second term in the series $\mathbf{A}(\mathbf{r}, t) = \mathbf{A}(\mathbf{0}, t) + (\mathbf{r} \cdot \nabla)\mathbf{A}(\mathbf{0}, t) \ldots$; this term is discussed in problem 11.3.

With the interaction Hamiltonian given by (11.29), which is a function of time through the time-dependence of $\mathbf{E}(t)$, we can now use time-dependent perturbation theory. However the case we are considering does not fall simply into the standard cases considered in **??**. In the case of a harmonic time-dependence for $\mathbf{E}(t)$ we have only considered transitions between a discrete state and a continuum. The reason for this is that the combination of discrete states and harmonic time-dependence is bound to lead to a discontinuous result — if the frequency of the perturbation is equivalent to an energy difference between two states (in the sense $h\nu = \Delta E$) then we expect the perturbation to drive the corresponding transition, but if it is not, even by a minute amount, then we do not expect any transitions to take place. We can avoid this problem, which is in any case mathematical rather than physical, since real light sources do not have a pure sinusoidal time-dependence, by keeping the time-dependence of $\mathbf{E}(t)$ arbitrary, and using the analysis to tell us what property of the field is important in driving the transitions. However, we have not previously considered the case of a more general time-dependence.

The problem we consider is the atom in state i at time $t = 0$, at which time a radiation field with electric field $\mathbf{E}(t)$ is switched on. We wish to use perturbation theory to find out the probability that the atom is in a different state j at time $t = T$. We therefore turn off the perturbation at time T, so that $\mathbf{E}$ is only non-zero between $t = 0$ and $t = T$. Standard time-dependent perturbation theory (**??**) gives us the equation of motion for the probability amplitude to be in state j:

$$\frac{ih}{2\pi}\frac{dc_j}{dt} = -e^{2\pi i \nu_{ij} t} \langle j | \mathbf{E}(t) \cdot \mathbf{D} | i \rangle \tag{11.30}$$

where the frequency ν_{ij} in the exponent is defined by $h\nu_{ij} = E_j - E_i$, the resonance frequency for the transition $i \to j$. (ν_{ij} is negative if $E_j < E_i$.) The use of ν rather than ω here makes the use of h rather than $\hbar$ more natural in (11.30). The first-order approximation has already been made in (11.30) with the replacement of c_i by 1 and all the other amplitudes c_j by zero on the right-hand side. The three components of the matrix element of $\mathbf{D}$ form a vector, which we call $\boldsymbol{\mathcal{D}}_{ij}$. The dot product $\mathbf{E} \cdot \boldsymbol{\mathcal{D}}_{ij}$ projects out a specific component of the electric field which interacts with the atom to drive the $i \to j$ transition. As far as this transition is concerned, this is the only component of the field that matters. We can then integrate (11.30) to find the amplitude to be in state j at $t = T$:

$$c_j(T) = \frac{2\pi i}{h} \int_0^T \mathbf{E}(t) \cdot \boldsymbol{\mathcal{D}}_{ij} e^{2\pi i \nu_{ij} t}\, dt. \tag{11.31}$$

Since $\mathbf{E}(t)$ is zero outside this interval we can formally extend the range of integration to $[-\infty, \infty]$. This allows us to express the integral in terms of the Fourier Transform of $\mathbf{E}(t)$. We define

$$\tilde{\mathbf{E}}_T(\nu) = \int_{-\infty}^{\infty} \mathbf{E}(t) e^{2\pi i \nu t}\, dt \tag{11.32}$$

where the subscript T is to remind us that the electric field is turned off at T; the integral in our expression for $c_j(T)$ is then $\tilde{\mathbf{E}}_T(\nu_{ij}) \cdot \boldsymbol{\mathcal{D}}_{ij}$.

We have therefore found that the amplitude to be in state j at time T depends on the matrix element between initial and final state of the dipole moment, and on the Fourier Transform of the corresponding component of the electric field evaluated at the resonance frequency, with only that part of the electric field for $t \le T$ contributing, an obvious causal requirement. Squaring to find the probability, and dividing by T to find the rate $R_{i \to j}(T)$ averaged over this period we find

$$R_{i \to j}(T) = \frac{4\pi^2}{h^2 T} |\tilde{\mathbf{E}}_T(\nu_{ij}) \cdot \langle j|\mathbf{D}|i\rangle|^2. \tag{11.33}$$

This is the general perturbation theory result for the transition rate, per atom in state i (because we assumed $c_i = 1$ at $t = 0$). The use of first-order perturbation theory (setting $c_i(t) = 1$ and $c_j(t) = 0$ in (11.30)) restricts the validity of this result to $T < T_{\max}$, where $T_{\max}$ is such that the total probability of transition to all other states is much less than 1. There is also the neglected process of spontaneous emission, which we cannot include in our Schrodinger equation. The effect of spontaneous emission is that atoms in level i or j make transitions to other states. We can therefore define a spontaneous emission lifetime for level i, given by $1/\tau_i = \sum A_{ik}$, where the sum runs over all lower levels k to which the state i can radiate. The validity of (11.33) is then clearly also restricted to $T \ll \tau_i, \tau_j$. Note that there is no lower time limit to the validity of (11.33), only upper limits; which upper limit is the most stringent depends on the states and radiation field strength in a particular case.

There is an obvious problem involved in expressing this result for the transition rate in the Einstein form $B_{ij}\rho_\nu(\nu_{ij})$ — eqation (11.33) only involves a specific component of the electric field, defined by $\boldsymbol{\mathcal{D}}_{ij}$, and this clearly cannot be expressed in terms of the spectral energy density. If, for example, the radiation has electric field perpendicular to $\boldsymbol{\mathcal{D}}_{ij}$ then the rate given by (11.33) is in fact zero regardless of the spectral energy density. It appears that the Einstein result is simply wrong. This prompts us to consider why Einstein proposed that the rate should depend on the spectral energy density. He probably had in mind a specific classical model for the response of the atom to radiation, the isotropic oscillator. In this model the atom develops a dipole moment proportional to the applied electric field, independent of the direction of $\mathbf{E}$. We have found, by contrast, that for the transition $i \to j$ the atom is highly anisotropic: only the component of $\mathbf{E}$ parallel to $\boldsymbol{\mathcal{D}}_{ij}$ has any effect on it. Einstein's assumption seems rather more plausible than what quantum mechanics is telling us! What is it in the atom that defines this preferred axis direction?

The answer lies in the ubiquitous degeneracy of atomic energy levels with respect to the quantum number M_J. Unless there is something to define an axis — for example a magnetic field — the $(2J+1)$ states with M_J running from $-J$ to J are all degenerate. There are thus two possibilities. Either there is something to define an axis, in which case we cannot assume that the states will be isotropic, and the anisotropy we have found is not unreasonable, or else we are dealing with several different transitions occurring at the same frequency, not $i \to j$ but $J_i, M_i \to J_j, M_j$. We shall discuss the first case in chapter **??** when we discuss the Zeeman effect. In the second case the observable quantity is the total transition rate between these two groups of states. The rate we have found applies to one specific possible transition:

$$R_{J_i,M_i\to J_j,M_j}(T) = \frac{4\pi^2}{h^2T}\,|\tilde{\mathbf{E}}_T(\nu_{ij})\cdot\langle J_jM_j|\mathbf{D}|J_iM_i\rangle|^2 \quad \text{per atom in } J_iM_i. \tag{11.34}$$

The rate we want is this rate summed over M_i and M_j, and then divided by $2J_i+1$ to convert it from a rate per atom in J_iM_i to a rate per atom in level J_i:

$$R_{J_i\to J_j}(T) = \frac{4\pi^2}{h^2T}\,\frac{1}{2J_i+1}\sum_{M_i,M_j}|\tilde{\mathbf{E}}_T(\nu_{ij})\cdot\langle J_jM_j|\mathbf{D}|J_iM_i\rangle|^2 \quad \text{per atom in } J_i. \tag{11.35}$$

This summation has the effect that all components of the electric field now contribute equally — the atom when summed over final M_j states and averaged over initial M_i states is indeed an isotropic oscillator. The proof involves some slightly more advanced ideas, and is given in Box ??. A simple argument to make it appear reasonable is that the squared matrix element $|\langle J_jM_j|D_k|J_iM_i\rangle|^2$ has three orientation-defining quantities in it: the orientation of the two wavefunctions in space, defined by M_i and M_j, and the component k of the vector $\mathbf{D}$; if we sum over two of these it is plausible

The expression we need to simplify is the sum in (11.35):

$$\sum_{M_i,M_j,k,l} \tilde{E}_{T,k}\langle J_jM_j|D_k|J_iM_i\rangle\langle J_iM_i|D_l|J_jM_j\rangle\tilde{E}^\star_{T,l}.$$

where we have written out the complex conjugate explicitly, using the Hermitian property of $\mathbf{D}$, and also written out the scalar product as a sum over components. ($\tilde{E}_{T,k}$ is the k'th component of $\tilde{\mathbf{E}}_T$.) We write this as a sum over the components of two tensors, one depending on $\tilde{\mathbf{E}}_T$ and the the other on the matrix elements of $\mathbf{D}$: $\sum_{k,l}\mathcal{F}_{kl}\mathcal{S}_{kl}$ where

$$\mathcal{F}_{kl} = \tilde{E}_{T,k}\tilde{E}^\star_{T,l} \qquad \text{and} \qquad \mathcal{S}_{kl} = \sum_{M_i,M_j}\langle J_jM_j|D_k|J_iM_i\rangle\langle J_iM_i|D_l|J_jM_j\rangle.$$

$\mathcal{S}_{kl}$ is the quantity which we can simplify. We comsider rotating the wavefunctions through an arbitrary angle, as in **??**. The rotated $|JM\rangle$ state (indicated with a round bracket) can be expressed as a linear combination of the unrotated states: $|JM) = \sum_{M'} D_{JMM'}|JM'\rangle$ where the matrix D_J is unitary: $\sum_M D_{JMM'}D^\star_{JMM''} = \delta_{M'M''}$. Thus the combination of states which occurs in the middle of $\mathcal{S}_{kl}$ after rotation can be written

$$\sum_M |J_iM)(J_iM| = \sum_{M,M',M''} D_{J_iMM'}|J_iM'\rangle\langle J_iM''|D^\star_{J_iMM''} = \sum_{M'}|J_iM'\rangle\langle J_iM'|$$

where we have used the unitary property of D_{J_i}. Thus this combination of the J_i, M_i wavefunctions is unchanged by rotation; a similar argument applies also to the sum over J_j, M_j wavefunctions. The components of the $\mathbf{D}$ operator are unaffected by rotating the wavefunction, and so $\mathcal{S}_{kl}$ is unchanged by rotation, $\mathcal{S}'_{kl} = \mathcal{S}_{kl}$. However from **??** we know how $\mathcal{S}_{kl}$ is changed by a rotation, since it is constructed from matrix elements of vector components whose behaviour under rotations we know: $\mathcal{S}'_{kl} = R_{kk'}R_{ll'}\mathcal{S}_{k'l'}$ where R is the 3×3 rotation matrix for vectors. These two facts about the behaviour of $\mathcal{S}$ under rotations are only compatible if $\mathcal{S}_{kl}$ is a multiple of the unit tensor $\mathcal{S}_{kl} = (1/3)\left(\sum_n \mathcal{S}_{nn}\right)\delta_{kl}$, where we have written the constant as a third of the trace. This converts the sum above into

$$\frac{1}{3}\sum_k |\tilde{E}_{T,k}|^2 \sum_{M_i,M_j,k} |\langle J_jM_j|D_k|J_iM_i\rangle|^2 = \frac{1}{3}|\tilde{\mathbf{E}}_T|^2 \sum_{M_i,M_j}|\langle J_jM_j|\mathbf{D}|J_iM_i\rangle|^2.$$

and substituting this into (11.35) gives (11.36).

Box 11.2 Summing rates over M_J quantum numbers that the result is independent of the third. This converts (11.35) into

$$R_{J_i \to J_j}(T) = \frac{4\pi^2}{3(2J_i+1)} \frac{1}{h^2 T} |\tilde{\mathbf{E}}_T(\nu_{ij})|^2 \sum_{M_i, M_j} |\langle J_j M_j | \mathbf{D} | J_i M_i \rangle|^2. \tag{11.36}$$

In order to express this result in terms of the spectral energy density we need to introduce the energy density in the electromagnetic field. As mentioned in section 11.1 this is given by $u = \frac{1}{2}\epsilon_0 \mathbf{E}^2 + \frac{1}{2}\mathbf{B}^2/\mu_0$. Furthermore the average energy densities in the electric and magnetic fields are equal in radiation fields. (This is generally true in travelling waves, although not necessarily in standing or guided wave fields.) Thus we can write $u = \epsilon_0 \mathbf{E}^2$. We can introduce a spectral decomposition of u using Parseval's theorem, which relates the square-integral of a function and its Fourier transform:

$$\int_{-\infty}^{\infty} |\mathbf{E}(t)|^2 \, dt = \int_{-\infty}^{\infty} |\tilde{\mathbf{E}}_T(\nu)|^2 \, d\nu. \tag{11.37}$$

Since $\mathbf{E}(t)$ is only non-zero between 0 and T, the left-hand side of (11.37) is simply the square of the electric field integrated over this interval, and if we divide by T it gives the average value $\langle \mathbf{E}^2 \rangle$ over this interval. Multiplying by ϵ_0 turns the left-hand side into the average energy density $\langle u \rangle = \epsilon_0 \langle \mathbf{E}^2 \rangle$:

$$\langle u \rangle = \frac{\epsilon_0}{T} \int_{-\infty}^{\infty} |\tilde{\mathbf{E}}_T(\nu)|^2 \, d\nu. \tag{11.38}$$

On the right-hand side we can use the fact that $\mathbf{E}$ is real, so that $\tilde{\mathbf{E}}(-\nu) = \tilde{\mathbf{E}}(\nu)^\star$, to re-write the integral over positive frequencies only:

$$\langle u \rangle = \int_0^{\infty} \frac{2\epsilon_0}{T} |\tilde{\mathbf{E}}_T(\nu)|^2 \, d\nu. \tag{11.39}$$

This expresses the energy density $\langle u \rangle$ as an integral over frequency, analogous to (11.20), so we identify the integrand as the spectral energy density of the radiation between $t = 0$ and T:

$$\rho_\nu(\nu, T) = \frac{2\epsilon_0}{T} |\tilde{\mathbf{E}}_T(\nu)|^2. \tag{11.40}$$

$|\tilde{\mathbf{E}}_T(\nu_{ij}|^2/T$ appears in out expression (11.35) for the transition rate averaged over time T, so provided we can identify $\rho_\nu(\nu, T)$ with $\rho_\nu(\nu)$ (that is, provided $\rho_\nu(\nu, T)$ does not depend on T) we can write our result in the Einstein form $R_{J_i \to J_j}(T) = B_{ij}\rho_\nu(\nu_{ij})$ where

$$B_{ij} = \frac{8\pi^3}{3(2J_i+1)} \frac{1}{4\pi\epsilon_0 h^2} \sum_{M_i, M_j} |\langle J_j M_j | \mathbf{D} | J_i M_i \rangle|^2. \tag{11.41}$$

However this identification is not completely straightforward — there is a question of timescale. There are two relevant timescales associated with the radiation. The first is the time period of the optical cycle — about 10^{-15} s in the visible. For times T much greater than this we can safely assume that $\langle u \rangle$ as defined above is an accurate time-average over the rapid oscillations in u. Thus in this limit we can safely assume that the left-hand side of (11.39) is independent of T, and hence so is the integral of $\rho_\nu(\nu, T)$ on the right-hand side. The second timescale is the coherence time of the radiation, t_c. This is time over which we can predict, given the amplitude and phase of the electric field at time t, the amplitude and phase at time $t + t_c$. (This is obviously not a precise time — there is a period over which our predictive power falls from near-perfect to near-zero.) For $T \ll t_c$ the dependence of $\rho_\nu(\nu, T)$ on ν becomes seriously affected by the truncation of the field at $t = 0$ and $t = T$ — roughly speaking, the width of the distribution over ν varies as T^{-1}, and the height as T. In this region $\rho_\nu(\nu, T)$ is not a property of the source of radiation but also of the time for which it has been observed. However for $T \gg t_c$, $\rho_\nu(\nu, T)$ becomes independent of T, and thus only a property of the source; in this limit it can indeed be identified with $\rho_\nu(\nu)$.

Given the caveats expressed in section 11.2 about the existence of $\rho_\nu(\nu)$ it is not surprising that there should be some complication before we can derive an equation in which $\rho_\nu(\nu)$ actually appears, nor that the same sort of complications are involved — time-averaging and coherence. However for $T \gg t_c$ we do now have an expression for $\rho_\nu(\nu)$. The conditions for a transition rate averaged over time T which depends only on the populations and $\rho_\nu(\nu_{ij})$, as assumed by Einstein, are thus $T \gg t_c$, and $T \ll \tau_i$, τ_j, $T_{\max}$ as discussed above. This raises the possibility of the situation $t_c > \tau_i$, in which case the conditions for a T-independent transtion rate can never be met for any field strength. Whether this can happen in practice is a question of actual values. Many atomic levels have lifetimes on the order of 10^{-10}–10^{-9} s; values longer than this are not uncommon, but values shorter than this are generally associated only with much more energetic decays, in the far ultra-violet region. Thermal radiation, which is the specific case considered by Einstein, is an incoherent superposition of a broad spectrum, and thus has a coherence time of only a few optical cycles, much less than τ_i. The coherence time of other sources, say a spectral lamp with a filter to isolate just one spectral line, is longer, but still less than τ_i. There are thus many cases for which the Einstein B coefficients express the transition rates between states. However, in the opposite limit of a perfectly coherent source — a perfect sine wave — the coherence time is infinite and the conditions for a T-independent rate are not met. This case is discussed in problem **??**. In practice, with a sufficiently coherent source (a laser with sufficiently narrow bandwidth) the observed transitions between states are not described by a Einstein's rate equations.

Finally we consider our result (11.41) for the Einstin B coefficient. It is symmetrical in i and j, apart from the $(2J_i + 1)$ factor, the degeneracy of the initial state, which was called g_i in section 11.2. Interchanging i and j we thus obtain one of Einstein's results, $(2J_i + 1)B_{ij} = (2J_j + 1)B_{ji}$.

Identifying level i with the upper state we can use the other result (11.26) to obtain

$$A_{ij} = \frac{64\pi^4}{3(2J_i+1)}\,\frac{\nu^3}{4\pi\epsilon_0 hc^3}\sum_{M_i,M_j}|\langle jM_j|\mathbf{D}|iM_i\rangle|^2 \tag{11.42}$$

for the spontaneous radiation coefficient.

This is one of the longest and most difficult sections in the whole book; looking back, it is striking that the difficulties are not associated with deriving the result (11.33) but in re-casting it in the Einstien form $B\rho$, because of the slightly subtle conditions under which it is valid.

11.4 Selection Rules

Of all the possible radiative transitions between different atomic levels, only a small subset are actually observed to happen, or at least, to happen at any appreciable rate. There are clearly many pairs of levels for which the matrix element of $\mathbf{D}$ is either zero, or unusually small. This is the result of the action of a selection rule, either exact or approximate — the selection rule defines a set of valid transitions, and other transitions either do not occur, or else occur very slowly, in which case they are known as forbidden transitions. In this section we shall derive the selection rules for electric dipole transitions.

Mathematically, selection rules usually follow from commutation relations of operators. Physically they usually represent conservation laws — transitions violating the selection rule represent processes in which the 'conserved' quantity is in fact *not* conserved. We shall look at selection rules in both of these ways.

Thinking first of conservation laws, we consider the obvious classically conserved quantities of energy, linear momentum and angular momentum. All of these are conserved in radiative transitions. Energy conservation is expressed by the resonance condition $h\nu = h\nu_{ij} = E_i - E_j$, which is a sort of selection rule, but not one giving us any information about the possible pairs of states i amd j. Linear momentum is also conserved: the emitted or absorbed photon causes the atom to recoil, but again this does not lead to a useful selection rule. Angular momentum conservation, on the other hand, does lead to a very important set of selection rules which we will discuss shortly. However we start by considering a non-classical conserved quantity, parity. The parity operator P has been introduced in **??** as the operator which inverts the system through the origin, and if the Hamiltonian commutes with P, $[H,P]=0$, then all eigenstates of H are also eigenstates of P. This is the case with atoms in the absence of radiation. All electromagnetic terms in the atomic Hamiltonian commute with P, including small terms which we have not discussed. There are physical interactions which do *not* commute with P, but these are due to the weak interaction, and these terms are many orders of magnitude smaller than the electromagnetic terms in the atomic Hamiltonian . In some very nearly exact sense then, $[P, H_{\text{atom}}] = 0$, and all atomic levels can be assigned a parity.

The atomic operator which occurs in the electric dipole Hamiltonian is the electric dipole moment $\mathbf{D}$. This does not commute with P, it antcommutes: $\mathbf{D}$ is given by $-e\sum \mathbf{r}_i$, and if P acts on this all the $\mathbf{r}_i$ become $-\mathbf{r}_i$, so $P\mathbf{D} = -\mathbf{D}P$ or $P\mathbf{D} + \mathbf{D}P = 0$. We take the matrix element of this anti-commutator between two states i and j and use the fact that these states are eigenstates of P:

$$\langle j|P\mathbf{D} + \mathbf{D}P|i\rangle = (p_j + p_i)\langle j|\mathbf{D}|i\rangle = 0 \tag{11.43}$$

where p_i and p_j are the two parity quantum numbers, either $+1$ or -1. Now suppose that the two states have opposite parity: then $p_i + p_j = 0$, and (11.43) gives $0 = 0$, which is correct, but tells us nothing. However, if the two states have the same parity, then $p_i + p_j$ is either $+2$ or -2, which we can cancel to leave $\langle j|\mathbf{D}|i\rangle = 0$. The anti-commutator therefore gives us the selection rule

Parity must change.

In fact this is usually expressed in the form of an answer to the question 'Does the parity change?', so that the selection rule is YES. We have not made any approximations in this derivation, so this is known as an exact selection rule.

How does this selection rule tally with the idea of conservation of parity, since it involves transitions between states of different parity? The answer lies in the parity of the fields either created or absorbed in the transition: for an electric dipole transition these have negative parity, so that, for example, in the emission process $i \rightarrow j + h\nu$ the overall parity of the final state is the same as the initial state. The interaction Hamiltonian, in addition to the atomic dipole moment $\mathbf{D}$, also contains the electric field $\mathbf{E}$, and this also anti-commutes with P, so that overall the interaction Hamiltonian commutes with P, and the parity of the whole system of (atom + radiation) is conserved.

We now come on to the the rather more difficult case of angular momentum, and we will treat this in the reverse order, first looking at it from the conservation law viewpoint. The angular momentum quantum number of the emitted or absorbed electric dipole field is 1. Thus if we consider an absorption process, we have an initial atomic state with angular momentum quantum number J_i absorbing radiation with angular momentum quantum number 1 to give a final state with angular momentum quantum number J_f. This is now a question of addition of angular momenta: J_f has to be a possible resultant of the addition of J_i and 1. If $J_i \geq 1$ the the possible resultants are $J_i + 1$, J_i and $J_i - 1$. Thus in general the angular momentum selection rule is $\Delta J = 0,\ \pm 1$. However if $J_i = \frac{1}{2}$ or 0 then some of these are not allowed. If $J_i = \frac{1}{2}$ then the only possible values for J_f are $\frac{1}{2}$ or $\frac{3}{2}$, while if $J_i = 0$ then the only possible value of J_f is 1. Thus the cases we have to exclude from the general rule are $\frac{1}{2} \to -\frac{1}{2}$, $0 \to -1$ and $0 \to 0$. In fact only the last of these needs to be stated, since J is a non-negative quantum number, so states with negative J simply do not exist. Thus the J selection rule is

$$\Delta J = 0,\ \pm 1, \quad 0 \not\to 0. \tag{11.44}$$

If the angular momentum quantum number of the emitted or absorbed radiation is 1 then the z-component quantum number must be 0 or ± 1, so that the selection rule for the z-component of angular momentum is

$$\Delta M_J = 0,\ \pm 1. \tag{11.45}$$

These rules can be also derived from commutators; this is covered in detail in Appendix C. This more rigorous approach arrives at the same selection rules, and with no approximations, so these are also exact rules, provided the angular momentum **J** is the total angular momentum of the system. If there is no nuclear angular momentum then this is indeed the angular momentum we normally refer to as **J**: the sum of electron orbital and spin angular momenta. If the nucleus has angular momentum, then the total angular momentum of the atom includes this also , and this angular momentum is usually called **F**. In this case our argument strictly applies to **F** not **J**; however the effect of the coupling of the nuclear to the electronic angular momentum (hyperfine interaction; see chapter **??**) is usually so weak that we can consider the J selection rule to be exact.

We now come on to approximate rules. The approximation, in these cases, lies not in the derivation of the rule, but in the assignment of the relevant quantum number to the atom in the first place. All free atoms have a well-defined total angular momentum and parity, as discussed above. Except in special cases, like one-electron atoms, *all* other quantum numbers are, to a greater or lesser extent, approximate. It must therefore follow that a selection rule based on the assumption that the state has the property implied by the quantum number must be approximate. We shall consider only the two major approximations in atomic structure, the LS coupling approximation and the independent-particle central-field approximation.

In the LS coupling approximation the total electronic angular momentum $\mathbf{J}$ is assumed to be made up from a spin angular momentum $\mathbf{S}$ with quantum number S and an orbital angular momentum $\mathbf{L}$ with quantum number L. To be specific, the atomic state is assumed to be an eigenstate of $\mathbf{S}^2$ with eigenvalue $S(S+1)\hbar^2$ and $\mathbf{L}^2$ with eigenvalue $L(L+1)\hbar^2$. We can therefore look for selection rules on these quantum numbers. The selection rule on S is very straightforward. The dipole moment operator $\mathbf{D}$ only involves the positions of the electrons, not their spins, so $[\mathbf{S},\mathbf{D}] = 0$, and hence $[\mathbf{S}^2,\mathbf{D}] = 0$. Taking a matrix element of this commutator between two LS-coupled states we find

$$\langle L'S'J'M_J'|\mathbf{S}^2\mathbf{D}-\mathbf{D}\mathbf{S}^2|LSJM_J\rangle = \hbar^2\Big(S'(S'+1)-S(S+1)\Big)\langle L'S'J'M_J'|\mathbf{D}|LSJM_J\rangle = 0. \quad (11.46)$$

As with the discussion of the parity case, (11.43), one factor must vanish, so the matrix element is zero unless ΔS satisfies the selection rule

$$\Delta S = 0.$$

The L selection rule follows very simply from this. Since $\mathbf{L} = \mathbf{J}-\mathbf{S}$, and $\mathbf{D}$ commutes with $\mathbf{S}$, $\mathbf{D}$ has the same commutator with $\mathbf{L}$ as with $\mathbf{J}$. Thus the argument from the commutator follows in exactly the same way, giving the L selection rule as

$$\Delta L = 0\ \pm 1, \quad 0 \not\to 0.$$

(In fact the argument does *not* follow in quite the same way, as the atomic state is *not* assumed to be an eigenstate of L_z. However, it can be checked that although eigenstates of J_z were used in the derivation of the J selection rule, this property of the states was not essential to this part of the argument in Appendix C.)

In the independent-particle central-field approximation the atomic wavefunction is built from individual electron orbitals with quantum numbers n_i and ℓ_i. The selection rule on these quantum numbers is unusual in that it does not follow from a commutator, but from the form of the electric dipole operator $\mathbf{D}$ and the wavefunction. The relevant fact about the operator is that it is a single-particle operator $\mathbf{D} = \sum_i \mathbf{d}_i$ where the contribution to $\mathbf{D}$ from the i'th electron is $\mathbf{d}_i = -e\mathbf{r}_i$. The relevant fact about the wavefunction is that it is a product of single-electron wavefunctions $|i\rangle = |\alpha_1\rangle|\beta_2\rangle$ for a two-electron state, where α and β are a set of quantum numbers for electrons 1 and 2. (The generalization to an antisymmetrized N-electron state is straightforward but tedious, and we shall only only consider this simple case.) A general matrix element between the state $|i\rangle$ and a state $|j\rangle$ where the single-electron quantum numbers are α' and β' thus takes the form

$$\langle j|\mathbf{D}|i\rangle = \langle\alpha_1'|\mathbf{d}_1|\alpha_1\rangle\langle\beta_2'|\beta_2\rangle + \langle\alpha_1'|\alpha_1\rangle\langle\beta_2'|\mathbf{d}_2\beta_2\rangle. \quad (11.47)$$

	E1	M1
	Exact	
J:	$\Delta J = 0, \pm 1, \quad 0 \not\to 0$	$\Delta J = 0, \pm 1, \quad 0 \not\to 0$
Parity:	YES	NO
	LS Coupling	
L:	$\Delta L = 0, \pm 1, \quad 0 \not\to 0$	$\Delta L = 0$
S:	$\Delta S = 0$	$\Delta S = 0$
	Central field	
$\{n_i \ell_i\}$:	Single electron jump	No electron jump
ℓ:	$\Delta \ell = \pm 1$	$\Delta \ell = 0$

Table 11.1: Selection Rules for Electric Dipole (E1) and Magnetic Dipole (M1) Transitions

The presence of the overlap integrals $\langle \alpha_1' | \alpha_1 \rangle$ and $\langle \beta_2' | \beta_2 \rangle$ means that these terms are zero unless $\alpha' = \alpha$ or $\beta' = \beta$ respectively. Thus not more than one electron can change its quantum numbers. However, at least one electron must change its quantum numbers, because the parity of the state is the product of the parities of the single-electron states, each of which is $(-1)^\ell$, and if there is no change in single-electron quantum numbers there can be no change in parity, which is required by the exact selection rule. The selection rule is thus

Single electron jump.

In other words, the set of $\{n_i \ell_i\}$ for the two states can only differ for one electron. The selection rule for the jumping electron we would expect to be $\Delta \ell = \pm 1, 0, \quad 0 \not\to 0$, but, as we have seen, $\Delta \ell = 0$ is ruled out by parity considerations so that in this case the rule is simply

$$\Delta \ell = \pm 1.$$

The electric dipole selection rules are summarised in Table 11.1. The rules for magnetic dipole radiation are also given for reference. Magnetic dipole radiation is briefly discussed in problem 11.3.

11.5 Problems

11.1 Show that the fields derived from the potentials (11.12) and (11.13) are solutions of Maxwell's equations provided $\mathbf{k}^2 = \omega^2 \mu_0 \epsilon_0$ and $\varphi = \hat{\mathbf{k}} \cdot \mathbf{A}/c$. Show that a gauge transformation with

$$\chi = \frac{i\varphi}{\omega} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \text{ c.c.}$$

gives $\Phi' = 0$ and $\mathbf{A}'$ in the form of (11.14). Show that the electric and magnetic contributions to the energy density u are equal.

11.2 Several results in this chapter take different forms if transition frequencies are expressed in terms of ω rather than ν, and correspondingly $\hbar$ is used inperference to h. Show that (11.26) and (11.41) become

$$\begin{aligned} A_{ji} &= \frac{\hbar\omega^3}{\pi^2 c^3} B_{ji}^{(\omega)} \\ B_{ij}^{(\omega)} &= \frac{1}{3(2J_i+1)} \frac{1}{4\pi\epsilon_0\hbar^2} \sum_{M_i,M_j} |\langle J_j M_j|\mathbf{D}|J_i M_i\rangle|^2. \end{aligned} \tag{11.48}$$

and hence (11.42) becomes

$$A_{ij} = \frac{4}{3(2J_i+1)} \frac{\omega^3}{4\pi\epsilon_0\hbar c^3}. \sum_{M_i,M_j} |\langle J_j M_j|\mathbf{D}|J_i M_i\rangle|^2.$$

11.3 Consider the effect of the second term in the Taylor expansion of the vector potential $(\mathbf{r}\cdot\nabla)\mathbf{A}(\mathbf{0},t)$. Show that the effect of a gauge transformation with $\chi = -\frac{1}{2} r_i r_j \frac{\partial A_i}{\partial r_j}$ is $\Phi' = -\frac{1}{2} r_i r_j \left.\frac{\partial E_i}{\partial r_j}\right|_{\mathbf{r}=0}$ and $A_i' = \frac{r_j}{2}\left(\left.\frac{\partial A_i}{\partial r_j}\right|_{\mathbf{r}=0} - \left.\frac{\partial A_j}{\partial r_i}\right|_{\mathbf{r}=0}\right)$. This transformation splits the term into two parts, and these are associated with electric and magnetic field respectively. The Φ term describes an electric field gradient across the atom; this couples to the electric quadrupole moment of the atom, but we shall not discuss this term further. Show that the $\mathbf{A}$ term can be written in terms of the magnetic field at the origin as $\mathbf{A}' = -\frac{1}{2}\mathbf{r} \wedge \mathbf{B}(t)$, which is the vector potential of a uniform magnetic field over the atom. This term gives rise to magnetic dipole radiation. Show that the interaction Hamiltonian becomes

$$H_{M1}(t) = \frac{e}{2m} \sum_i \boldsymbol{l}_i \cdot \mathbf{B}(t) = -\boldsymbol{\mu}_l \cdot \mathbf{B}(t)$$

where $\boldsymbol{\mu}_l$ is the orbital contribution to the magnetic dipole moment of the atom. (See chapter **??** for a discussion of magnetic moments.) The spin magnetic dipole moments also contribute; there is an extra term in the interaction Hamiltonian of $-\boldsymbol{\mu}_s \cdot \mathbf{B}(\mathbf{r}_i, t)$ for each spin at $\mathbf{r}_i$, where $\boldsymbol{\mu}_s$ is the spin magnetic dipole moment. In the long-wavelength approximation this term becomes $-\boldsymbol{\mu}_s \cdot \mathbf{B}(\mathbf{0}, t)$, so the whole magnetic dipole Hamiltonian becomes

$$H_{M1}(t) = -\boldsymbol{\mu} \cdot \mathbf{B}(t)$$

in exact analogy with the electric dipole case.

Chapter 12

Helium

Chapter 13

Central Field Approximation

Chapter 14

Alkali Spectra

Chapter 15

Coupling Schemes

Chapter 16

Hyperfine Structure

Chapter 17

Zeeman Effect

Chapter 18

X-Rays

18.1 Introduction

[Figures 1 (?and 2) do not exist. Add NI to Bohr-Coster diag, add signal labels to 12.5. Change font for labels. Add Dirac sigma as problem]

In this final chapter we discuss atomic energy levels involving excitation of electrons from filled shells. Transitions between levels of this sort are one mechanism responsible for the emission of X-rays. In fact, to describe these energy levels as atomic is almost unnecessary — the excitation energies involved are so large that the chemical state of the atom (free, bound into a molecule, bound in a crystal lattice) is almost irrelevant, leading to changes of only a few electron volts in an energy of, typically, many keV. Although we shall discuss these levels as though we were dealing with free atoms, in practice they are observed in whatever state the element is available in, so that the observations are usually only made on free atoms in the case of the noble gases.

X-rays were discovered at the very end of the nineteenth century, and much experimental work was done in the early years of the twentieth century, so that the nomenclature developed independently of the spectroscopic notation we have been using to discuss other atomic levels. Also the processes involved in X-ray production and absorption are sufficiently different from those we have been considering that it is necessary to discuss them in rather more detail. The next section describes the X-ray production and absorption, and the systematics of the atomic energy levels responsible for X-ray transitions are described in section 18.3.

18.2 X-Ray Production and Absorption Processes

X-rays were discovered by Roentgen in 1895 as an emission of very penetrating radiation from a target when struck by cathode rays, that is, electrons that have been accelerated by a large voltage. They are now known to be electromagnetic radiation with wavelengths in the region of 1Å (10^{-10}m), and any radiation in this region of the electromagnetic spectrum, however produced, is quite likely to be called X-radiation. However, there is an ambiguity in common usage as to whether X-ray refers to a spectral region or a production process. In this chapter we are specifically concerned with atomic processes, and other sources of radiation in this region, such as low-energy nuclear radiations, are outside our scope, whereas some of the X-ray transitions we shall mention are in what would normally be called the ultra-violet part of the spectrum.

The process we are considering, then, is the passage of a beam of high energy (several keV) electrons through a target material. The apparatus is illustrated in Figure **??**: electrons emitted by a heated cathode are accelerated through a large potential difference V before striking the anode. X-rays are emitted by the anode, and can be observed from outside the vacuum envelope surrounding the X-ray tube. Because X-ray wavelengths are in the region of 1Å, the same order of magnitude as atomic sizes, they can be diffracted by a crystal acting as a diffraction grating. The output from an X-ray tube can thus be spectrally analysed with a crystal spectrometer, and a typical spectrum from an X-ray tube is shown in **??**. Because the spectrometer analyses the spectrum by wavelength, it is customary to present spectra of this sort on a wavelength scale, although for interpretational purposes a frequency (i.e. energy) scale would be more convenient.

The spectrum consists of two components: a *line spectrum* superimposed on a *continuous spectrum* which result from different atomic processes inside the anode material. The continuous spectrum is emitted by electrons being scattered by the electrostatic field of the atomic nuclei. This field is, of course, substantially screened by the surrounding atomic electrons, but some of the incident electrons penetrate to a region of strong electrostatic field, and experience a sharp burst of acceleration. The accelerated charge generates electromagnetic radiation, and so loses kinetic energy. Since the initial and final states of the electron are not discrete energy states but lie in the continuum, the emitted spectrum is also continuous. It is known as ‘braking radiation’, or in German ‘Bremsstrahlung’. There is an obvious lower wavelength limit to the spectrum given by energy conservation: a photon carrying off all the initial kinetic energy of the electron eV would have wavelength λ_0 given by

$$\frac{hc}{\lambda_0} = eV \tag{18.1}$$

and this cut-off is a significant feature of the spectrum in figure ??

Superimposed on the Bremsstrahlung spectrum is a line spectrum that is characteristic of the elements present in the anode material, emitted by atoms making transitions between discrete excited electronic states. The nature of these 'X-ray states' can be understood in quite simple terms, by considering possible re-arrangements of the atomic electrons. The atomic ground state consists of a number of filled shells, and one or more partly-filled valence shells. Excitation of an electron from the valence shells gives rise to the excited configurations we have discussed in earlier chapters, but there is an upper limit to the energy of such configurations given by the ionisation energy of, perhaps, ten or twenty eV. (In solid materials we should discuss this in terms of the work function, the least energy needed to remove an electron, but this is also of the same typical size.) X-ray transitions obviously cannot involve low-energy excited electron configurations of this sort. Instead they have to involve the excitation of an electron from a filled shell, creating a vacancy in that shell. The electron cannot simply move up to the next shell if that is already full, but must move to one of the vacant states, or be removed completely. For excitation energies in the keV range these two options are virtually equivalent, since as we have just seen they cannot differ by more than 20 eV or so. Thus the 'X-ray states' consist of atoms which have had an inner electron removed, leaving a vacancy in an inner shell. The X-ray states of a medium-Z element, silver ($Z = 47$) are shown in Figure 18.1. The details of these states will be discussed in the next section, but for the moment we simply note that the levels fall into three groups corresponding to a vacancy in each of the three filled shells in the silver atom, $n = 1$, 2 and 3. Obviously the order of the levels is such that the highest-energy level involves a vacancy in the n =1 shell. Also shown are the possible transitions following the excitation to this highest-energy level.

To understand whether or not a given line is observable in a given tube spectrum we shall introduce the important concept of absorption edges. These are features of the absorption spectrum of X-rays by a given element. The absorption spectrum of the anode material is shown in the lower part of Figure **??**, plotted as the absorption cross-section per atom. The absorption process involved here is essentially the photoelectric effect — the absorption of a photon of energy $h\nu$ resulting in the ejection of a single electron with kinetic energy T given by

$$h\nu = E_n + T \tag{18.2}$$

where E_n is the energy required to create a vacancy in the n'th energy level, the quantity shown on

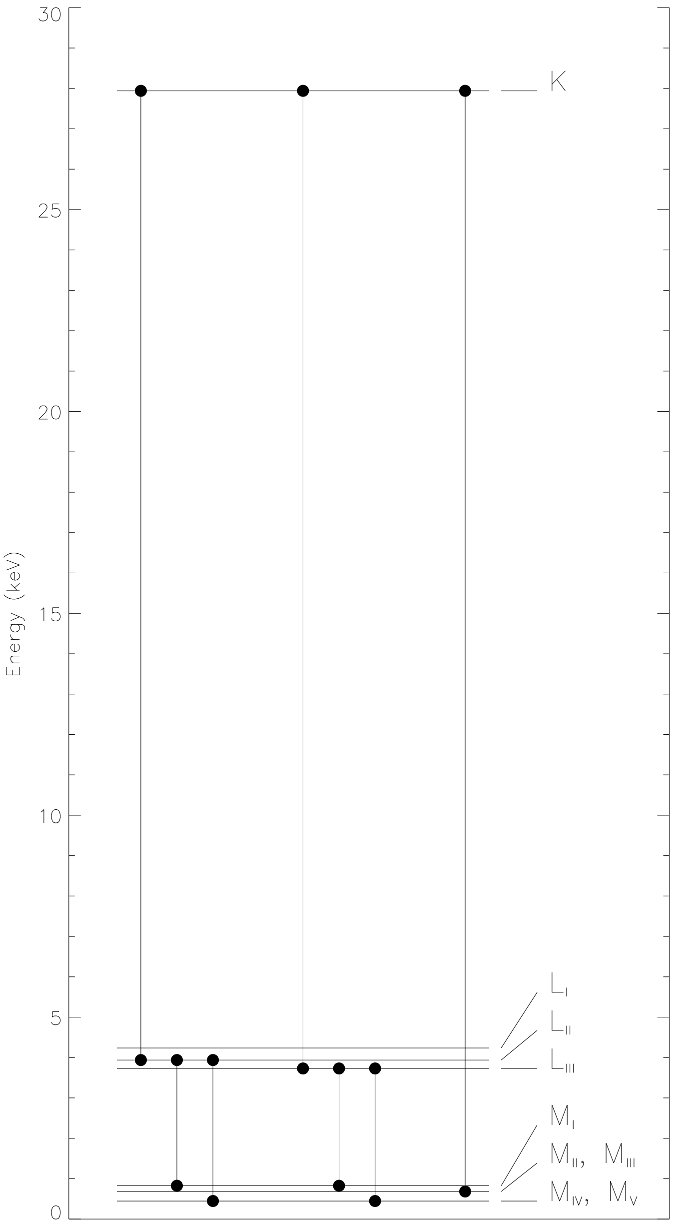


Figure 18.1: The X-ray levels of Silver ($Z = 48$) and some allowed transitions

the vertical axis of Figure 18.1. However there is a slight difference between this process and the photoelectric effect with ultraviolet light, as normally discussed in elementary treatments. With the lower energies of a UV photon (a few eV) the E_n for a metal surface form a continuous distribution, but with a least value — the least energy needed to liberate an electron, or work function W. Consequently the photoelectron kinetic energy has a *continuous range* of values with a *maximum* T_0 given by $h\nu = W + T_0$. In the X-ray case the energy needed to liberate a given inner-shell electron is essentially sharply-defined, being uncertain by the ten or twenty eV between the lowest-energy vacant state and completely-free states. Thus in the X-ray case the photoelectron energies are discrete, and correspond to the different X-ray states of the absorber. As the incident X-ray energy increases past one of the X-ray state energies E_n of the absorber it becomes energetically possible for this absorption process to occur — this is known as the threshold for this absorption process. It is apparent from the form of the absorption spectrum that the cross-section is finite at threshold — there is an abrupt jump in cross-section at the threshold energy. These jumps are the absorption edges, and they occur at photon energies equal to the X-ray state energies E_n. It is also apparent that the cross-section decreases above threshold. The reason for this is discussed below??

We can now understand the criterion for the appearance in the emission spectrum of an X-ray tube of a given spectral line between upper state E_n and lower state E_m. For this line to appear the initial state has to be created, which requires an incident electron energy of at least E_n. But, as we have seen, the incident electron energy is equal to the energy of photons at the cut-off wavelength of the continuous component of the spectrum λ_0. Thus the condition for the observation of a given transition $E_n \rightarrow E_m$ (in addition to selection rules) is $\lambda_0 < \lambda_n$ where λ_n is the wavelength of the absorption edge corresponding to E_n. If the tube voltage is decreased, λ_0 increases, and eventually this condition is no longer fulfilled. At this point all the X-ray lines starting from the state E_n vanish from the spectrum. The striking aspect of this phenomenon is that the critical energy E_n or wavelength λ_n for the disappearance has no obvious significance in terms of the emission spectrum — the disappearing lines all lie at longer wavelength than the cut-off — and can only be understood with reference to the absorption spectrum.

Once a vacancy is created in a given inner shell the atom can decay back towards the ground state by radiative decays, that is by emission of X-rays, as illustrated in Figure 18.1. However this is not the only possible process, and in some cases not the most likely. A competing decay process is autoionisation, which in this context is referred to as the Auger process after its discoverer. The initial state is, as we have discussed, a singly-ionised atom, with the vacancy in an inner shell; the final state of the Auger process is a doubly-ionised atom, and an ejected electron, where the two vacancies are in less-tightly bound states. As an example we shall consider a very light atom, magnesium ($Z = 12$), for which the Auger process is significantly more likely. (As a rule the fraction of decays that occur radiatively increases with Z.) The Mg ground state is $1s^2 2s^2 2p^6 3s^2$, so that there are three possible 'X-ray levels', with vacancies in $1s$, $2s$, and $2p$. The energies of these three states relative to neutral Mg (i.e., the energies of the absorption edges) are 1305, 89 and 51 eV. The selection rules (discussed in the next section) permit the radiative transition from the first to the third of these, with energy 1254 eV, but a significantly more likely decay is an Auger process to a doubly ionised atom. We can write this process as

$$\begin{array}{ccccc} \mathrm{Mg}_n^+ & \rightarrow & \mathrm{Mg}_{mm'}^{++} & + & e^- \\ E_n & = & E_{mm'} & + & T \end{array}$$

where the initial state with a vacancy in n and energy E_n decays to the doubly-ionised state $E_{mm'}$ with vacancies in both m and m', and an electron with kinetic energy T.

These energy needed to create these final states cannot be calculated from the absorption edges, but a very crude estimate can be made as follows. The energy needed to create each of these vacancies singly is given by the absorption edge data above, so we can guess that the double vacancy has an energy of roughly the sum of the two single vacancies: $E_{mm'} \approx E_m + E_{m'}$. In fact this will certainly be an underestimate, because removing any electron makes the remaining electrons more tightly bound, so we can write $E_{mm'} = E_m + E_{m'} + \delta$, where this simple calculation gives us no guide as to the magnitude of the error δ. The Auger electron energy is thus given by $T = E_n - E_m - E_{m'} - \delta$. There are three possible final states, with either two vacancies in $2s$, two in $2p$ or one in each of $2s$ and $2p$. (Final states involving vacancies in $1s$ obviously have higher energy than the initial state, and can be disregarded.) Thus the Auger electron energies for each decay route are predicted to be

$$\begin{array}{lllcl} 1s^1 2s^2 2p^6 3s^2 \rightarrow 1s^2 \quad\ \ 2p^6 3s^2 : & & 1305 - 89 - 89 - \delta & = & 1127 - \delta \\ 1s^1 2s^2 2p^6 3s^2 \rightarrow 1s^2 2s^1 2p^5 3s^2 : & & 1305 - 89 - 54 - \delta' & = & 1162 - \delta' \\ 1s^1 2s^2 2p^6 3s^2 \rightarrow 1s^2 2s^2 2p^4 3s^2 : & & 1305 - 54 - 54 - \delta'' & = & 1197 - \delta''. \end{array}$$

The actual energies are 1102, 1145 and 1180, so that δ is in the region of 20 eV in these cases. (In the second and third cases the final configuration has several terms extending over several eV, and the Auger electron energies given are configuration averages.)

This completes our discussion of the atomic processes involved in X-ray production; in the next section we discuss the systematic Z-dependence of the energy levels.

18.3 Systematics of X-ray Energy Levels

X-ray spectra vary in a very smooth and predictable way with atomic number Z, for single vacancies in filled shells. The number of different single vacancies obviously increases with Z as more shells are filled, although we shall concentrate on vacancies in the first three shells. The traditional nomenclature used is different from that used in other branches of atomic physics, with a capital letter used to indicate the principal quantum number n, ($1 \equiv K$, $2 \equiv L$, $3 \equiv M$ etc.) and the angular momentum subshells indicated by Roman numerals. The angular momentum of a subshell which is full except for a single vacancy is equal to the angular momentum of the removed electron, so that the possible states are the same as in a single-electron spectrum, with $j = \frac{1}{2}$ for an s-electron, and $j = \ell \pm \frac{1}{2}$ for an electron with angular momentum ℓ. The correspondence between the two systems of nomenclature for the first three shells is given below; the extension to higher shells is obvious.

n	1	2	3
$s_{1/2}$	K	L_{I}	M_{I}
$p_{1/2}$		L_{II}	M_{II}
$p_{3/2}$		L_{III}	M_{III}
$d_{3/2}$			M_{IV}
$d_{5/2}$			M_{V}

In fact there is some logic to keeping the two systems of nomenclature: $2p_{1/2}$ denotes an electron, whereas L_{II} denotes a vacancy in an otherwise filled $2p$ shell. All of these X-ray levels for Silver are shown in Figure 18.1, except that the splittings between the M_{II} and M_{III}, and between M_{IV} and M_{V} are too small to be indicated on this scale.

The selection rules for radiative transistions are the same as in the optical region: $\Delta J = 0, \pm 1$, Parity changes, and $\Delta \ell = \pm 1$ for the jumping electron. If we ignore any angular momenta in valence shells then we can identify J with the total angular momentum of the vacancy j introduced above. We then have the typical single-electron selection rules $\Delta j = 0, \pm 1$ and $\Delta \ell = \pm 1$. There is a standard nomenclature for transitions as well: transitions originating in the K level are referred to as the K series, with series members indicated by Greek suffixes starting at the long-wavelength end, so $K \rightarrow L$ is indicated as K_α, $K \rightarrow M$ as K_β etc. The two fine-structure components are labelled numerically. Similarly, transitions originating in the L-shell are referred to as the L-series, but the nomenclature for individual transitions is not systematic, and will not be described. All the allowed transitions between K, L and M shells are shown in the following table, either by the standard name in the case of the K series, or for the L series with a tick indicating that the transition is allowed. All of these transitions are shown in Figure 18.1, again subject to the constraints of the scale in the case of the $M_{\mathrm{II}} - M_{\mathrm{V}}$ levels.

	K	L_{I}	L_{II}	L_{III}
$\to L_{\mathrm{I}}$				
$\to L_{\mathrm{II}}$	$K_{\alpha 2}$			
$\to L_{\mathrm{III}}$	$K_{\alpha 1}$			
$\to M_{\mathrm{I}}$			$\surd$	$\surd$
$\to M_{\mathrm{II}}$	$K_{\beta 2}$	$\surd$		
$\to M_{\mathrm{III}}$	$K_{\beta 1}$	$\surd$		
$\to M_{\mathrm{IV}}$			$\surd$	$\surd$
$\to M_{\mathrm{V}}$				$\surd$

We now turn to the energy of the X-ray levels. The model we shall use, like most of the simple models in atomic physics, is a single-electron model. The starting assumption is that the energy needed to create a vacancy in a given state is simply the binding energy the electron had in that state. If the electron were the only electron in the atom, in a state with principal quantum number n, then its binding energy would be (in the non-relativistic approximation)

$$E_n(Z) = \frac{Z^2 E_H}{n^2} \tag{18.3}$$

where E_H is the binding energy of the electron in hydrogen, 13.6 eV. If we assume that the effect of the other electrons is simply to screen some of the nuclear charge, then we can model that by introducing an effective nuclear charge $Z^{\star}$, modifying the above formula to

$$E_n(Z) = \frac{(Z^{\star})^2 E_H}{n^2} \qquad \text{where} \qquad Z^{\star} = Z - \sigma_n \tag{18.4}$$

and σ_n is known as the screening constant. This model suggests a plot of $\sqrt{E_n/E_H}$ against Z; if σ_n is constant we will get a straight line with x-intercept of σ_n and a slope of $1/n$. This plot is variously referred to as a Bohr-Coster diagram or a Mosely plot, and is shown in Figure 18.2. Only data for X-ray levels in full shells are shown, so that the K-shell data start at $Z = 3$, L-shell at $Z = 11$, M_{I}–M_{III} at $Z = 19$ and M_{IV}, M_{V} at $Z = 31$. (There are gaps in the database for some M levels). The dashed lines are the 'unscreened' values $\sqrt{E_n/E_H} = Z/n$.

It is apparent from Figure 18.2 that this simple model correctly predicts the overall trend of the data, with the solid lines roughly parallel to but displaced from the unscreened dashed lines. Our expectation would be that σ_K would be quite small, and σ_L somewhat larger, because there are more electrons screening the nuclear charge in the latter case, and this expectation is also broadly consistent with Figure 18.2.

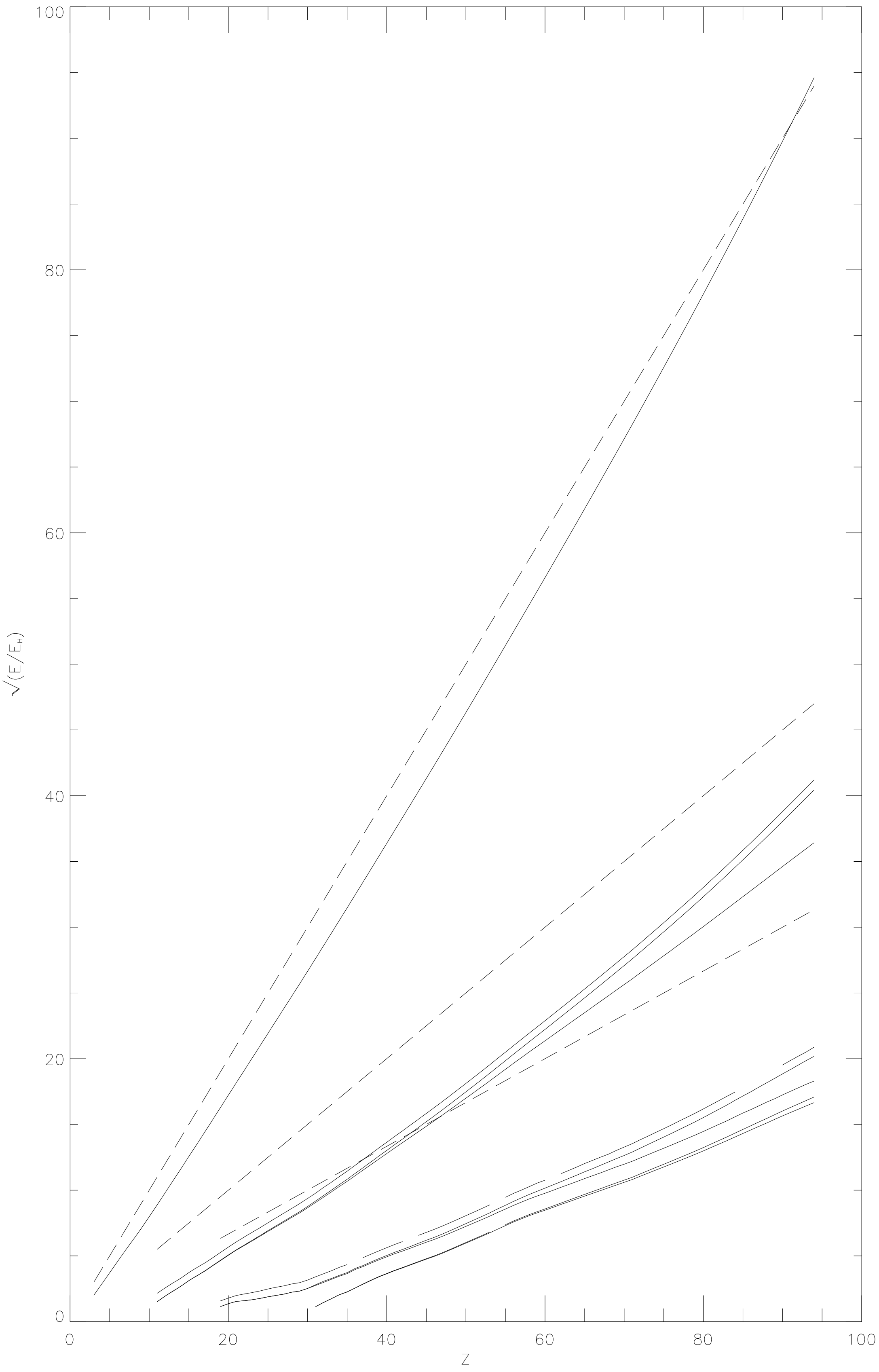


Figure 18.2: Bohr-Coster Diagram. (Data from Rev. Mod. Phys etc.)

However in detail the situation is not so straightforward. Figure 18.3 presents the same data in a different way, plotting the K and L-shell screening constants against Z. The solid lines are the screening constants calculated according to equation (18.4) above. Since this is a one-parameter model, with the parameter σ adjusted to fit the observed X-ray energies, all deficiencies in the model are reflected in the values of the screening constant, and some of these problems are apparent in Figure 18.3, as we shall now discuss.

We first consider the K-shell screening constant σ_K, shown in the left-hand panel of figure 18.3. The most obvious features of the data are that σ_K rises to a maximum of about 3.5 at medium Z, and then decreases again at large Z. Two different physical effects are at work here, one responsible for the increase and one for the decrease. The decrease in σ_K at large Z is a relativistic effect: the model we are using, defined by (18.4) is non-relativistic, whereas relativistic corrections for K-shell electrons at large Z are by no means small. The simplest way to correct our model for this defect is to use the Dirac eigenvalue for the point-charge model, and adjust the magnitude of the nuclear charge Z^* to fit the absorption edge energy E_K, just as we did above with the Schrodinger eigenvalue. The algebra is more involved, and is left to problem **??**; the result of the calculation, a relativistic screening constant σ_K is shown as a dashed line in figure 18.3. For a given Z the Dirac equation leads to more tightly bound levels than the Schrodinger equation, so that a smaller Z^* is needed to fit a given absorption edge energy, giving a larger σ_K. Thus the relativistic σ_K is equivalent to the non-relativistic one at low Z, but is significantly larger at medium and large Z.

Having improved our model slightly we now have a screening constant that increases monotonically with Z, reaching values in excess of 5. This makes it very clear that a simplistic charge screening model cannot explain these values — it is simply not credible to suppose that a $1s$ electron sees a nuclear charge screened to this extent. One way of looking at this is to recognize that the larger part of what we are calling screening represents not the reduction of binding energy of the electron in the initial state prior to its removal, but the increase in binding energy of all the other electrons in the final state consequent upon its removal. To take a very simple example we consider helium, which, as we saw in chapter **??**, we can consider to a reasonable approximation to consist of two electrons each with a screening constant of 5/16: $77 \text{ eV} \approx 2 \times (2 - \frac{5}{16})^2 \times 13.6 \text{ eV}$. However, the energy needed to (*check numbers*) remove one of the electrons is much less — the first ionization energy of 22 eV — because of the removal of screening in the final state, which increases the binding energy of the remaining electron to the hydrogen-like value of $2^2 \times 13.6 \text{ eV} = 54 \text{ eV}$. More fundamentally, the very concept of the binding energy of a single electron in a multi-electron system is not defined. The only quantity we can define for a system of several interacting particles

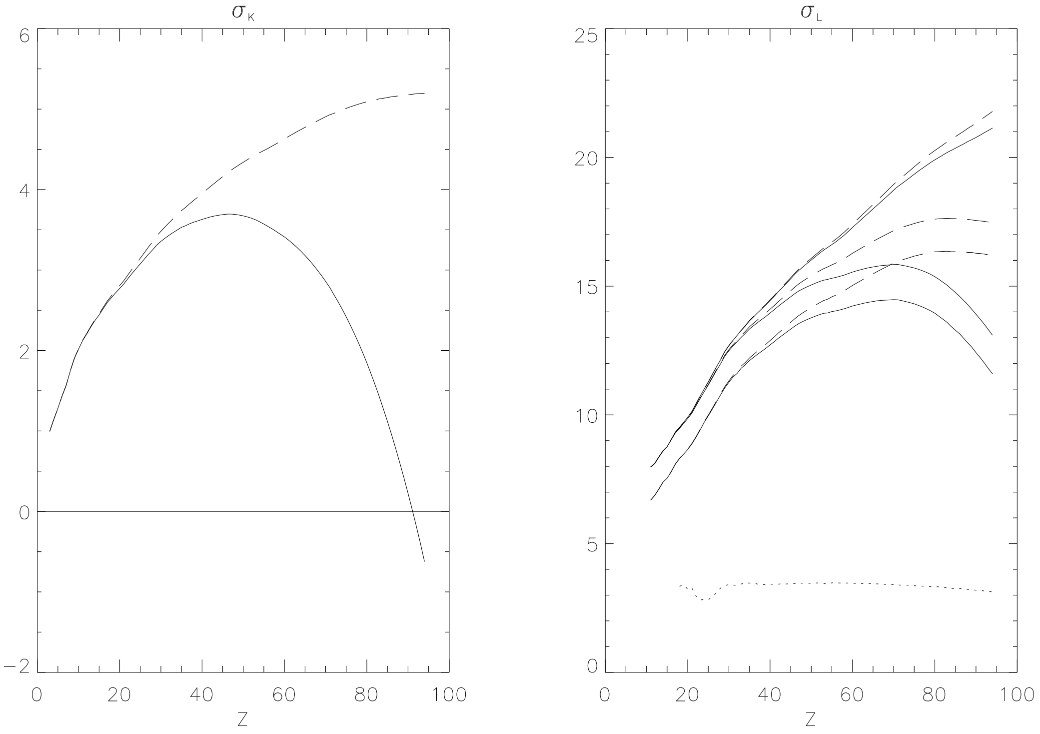


Figure 18.3: K and L-shell screening constants

is a total binding energy, the energy needed to separate *all* the particles. The absorption edge energy is not a binding energy, it is a separation energy, a difference between the binding energies of the neutral atom and the atom with vacancy. There is thus a fundamental limitation to our single-particle model.

Secondly, we consider the L-shell screening constants. The most significant feature in the right-hand panel of figure 18.3 is the large difference between the $\sigma_{L\mathrm{II}}$ and $\sigma_{L\mathrm{III}}$ values, which grows very rapidly with Z. This is due to the spin-orbit interaction, which grows as Z^4, and is nothing to do with screening at all; it is appearing as a difference in screening simply because the spin-orbit interaction is not present in our non-relativistic one-parameter model. (By contrast, the difference $\sigma_{L\mathrm{II}} - \sigma_{L\mathrm{I}}$ genuinely does represent a difference in screening, and remains fairly constant with Z.)

That this spltting is due to the spin-orbit interaction is demonstrated by figure 18.4, which shows (solid line) the actual spin-orbit energy difference $\Delta E_L = E_{L\mathrm{III}} - E_{L\mathrm{II}}$ as a function of Z on a log-log plot, together with (dashed line) the corresponding difference between the Dirac eigenvalues. (The log-log plot is chosen because the non-relativistic formula $\Delta E_L/E_H = \alpha^2 Z^4/16$ gives a straight line. The slight curvature of the dashed line represents higher-order relativistic corrections.) It's clear that the simple hydrogenic model reproduces the observed energy difference

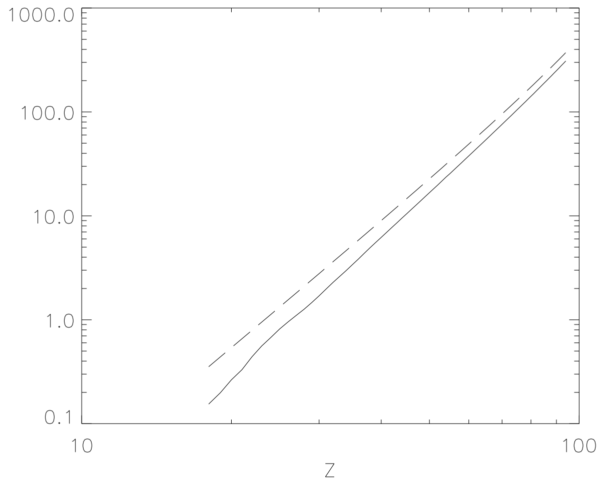


Figure 18.4: L-shell spin-orbit interaction

well over several orders of magnitude; the actual spin-orbit interaction is slightly smaller than the hydrogenic formula because of screening effects, as we shall see shortly. The simplest way to incorporate the spin-orbit interaction into the one-parameter model is to use the Dirac formulae for the level energies. These relativistic screening constants are shown as dashed lines in figure 18.3, and as before the relativistic correction leads to larger screening constants. It is apparent that the effect of including the spin-orbit interaction in the one-parameter model is to reduce but by no means to eliminate the screening constant difference between the L_{II} and L_{III} levels. This is because the spin-orbit interation has a *different* screening constant: we can use the offset in Z between the data and the formula in figure 18.4 to define yet another screening constant and effective Z, this time the Z which reproduces the spin-orbit splitting. This screening constant is shown as a dotted line in figure 18.3: the size of the spin-orbit interaction corresponds to an effective Z of about $Z - 3$. This finally makes it clear that our one-parameter model has broken down - we need a smaller screening constant to describe the spin-orbt enteraction than to describe the gross energy, and this is because we are using a hydrogenic model to describe a non-hydrogenic system.

This completes our discussion of screening constants except for one small point. There is a fairly widespread belief that that σ_K is 'of order one' which, as we have seen, is incorrect except at very low Z, or, due to a fortuitous cancellation of two effects, at very high Z. There are probably two reasons for this belief. One is that there is a prior expectation that σ_K 'ought' to be of order one, because the K-shell electron is only screened to a significant extent by the other K-shell electron; this, as we have also seen, is using too narrow a view of screening, focussing on the screening in the state prior to the removal of the electron and neglecting the change in screening in the state subsequent to the electron removal. The other reason is that there is a related screening constant, Moseley's screening constant, which *is* of order one. Moseley measured the wavelength of the K_α X-ray lines of a wide range of medium-Z elements and interpreted them in accordance with the latest atomic theory, Bohr's atomic model of the planetary atom. According to Bohr's model, or the Schrodinger hydrogenic model since they have the same state energies, the transition energy from $n = 2$ to $n = 1$ is

$$\Delta E = Z^2 E_H \left(1 - \frac{1}{2^2}\right) = \frac{3}{4} Z^2 E_H.$$

Mosely modified this formula (*quote?*) to take account of the other electrons (thereby introducing the concept of screening constants), and applied it to the X-ray energy difference between the K and L shells:

$$E_K - E_L = \frac{3}{4}(Z - \Sigma)^2 E_H. \tag{18.5}$$

and found that Σ was of order one (*quote?*). For example, using the same data as in figures 18.2 – 18.4 we can compute Σ, and this is shown in figure **??** (solid line) for both components of the K_α transition (in other words, using both $E_{L\text{II}}$ and $E_{L\text{III}}$ for E_L). We can relate Σ to the screening constants introduced earlier, by substituting in equation (18.5) for E_K and E_L from equation (18.4):

$$\frac{(Z - \sigma_K)^2 E_H}{1} - \frac{(Z - \sigma_L)^2 E_H}{4} = \frac{3}{4}(Z - \Sigma)^2 E_H.$$

After a little algebra we can deduce

$$(Z - \Sigma)^2 = \left(Z - \frac{4\sigma_K - \sigma_L}{3}\right)^2 - \left(\frac{2\sigma_L - 2\sigma_K}{3}\right)^2 \tag{18.6}$$

in which, at least at medium to high Z, we can neglect the second term in comparison with the first. Thus in this approximation $\Sigma \approx (4\sigma_K - \sigma_L)/3$, and this clearly leads to cancellation since for a wide range of elements $\sigma_L \approx 4\sigma_K$. (The dotted line in figure **??** shows this approximation for Σ.) Thus, as with σ_K at large Z, we have a screening constant turning out to be of order one due to a fortuitous cancellation. We can also use the relativistic formula for the energy difference, and this gives the screening constants shown by the dotted line.

Appendix A

Definite Integrals

A.1 Integrals involving Exponentials

Integrals over harmonic oscillator or hydrogen radial wavefunctions frequently reduce to forms such as

$$F_1(n,a) = \int_0^\infty x^n e^{-x/a}\,dx \tag{A.1}$$

$$F_2(n,a) = \int_0^\infty x^n e^{-x^2/a^2}\,dx \tag{A.2}$$

These integrals are closely related, and both can be expressed in terms of the gamma function, which is a natural generalization of the factorial function to non-integer arguments.

The gamma function $\Gamma(s)$ is defined for $s > 0$ by

$$\Gamma(s) = \int_0^\infty \xi^{s-1} e^{-\xi}\,d\xi. \tag{A.3}$$

For $s > 1$ we can derive a reduction formula, to relate $\Gamma(s)$ in this region to $\Gamma(s)$ with $0 \le s < 1$. We integrate (A.3) by parts, integrating $e^{-\xi}$ to $-e^{-\xi}$ and differentiating ξ^{s-1} to $(s-1)\xi^{s-2}$. The integrated part vanishes at both limits to leave

$$\Gamma(s) = \int_0^\infty (s-1)\xi^{s-2} e^{-\xi}\,d\xi = (s-1)\Gamma(s-1). \tag{A.4}$$

$\Gamma(1)$ is straightforward:

$$\Gamma(1) = \int_0^\infty e^{-\xi}\,d\xi = 1 \tag{A.5}$$

so that for integer values of s the gamma function reduces to the factorial function

$$\Gamma(n) = (n-1)! \tag{A.6}$$

The gamma function for half-integer values of s can be derived from $\Gamma(\frac{1}{2})$:

$$\Gamma(\tfrac{1}{2}) = \int_0^\infty e^{-\xi} \frac{d\xi}{\sqrt{\xi}}. \tag{A.7}$$

We make the substitution $\xi = x^2$, $d\xi = 2x\,dx$:

$$\Gamma(\tfrac{1}{2}) = 2\int_0^\infty e^{-x^2}\,dx = \int_{-\infty}^\infty e^{-x^2}\,dx = \sqrt{\pi}. \tag{A.8}$$

Iterating the reduction formula we find the gamma function for half-integer values of s:

$$\Gamma\left(\frac{2m+1}{2}\right) = \frac{(1)(3)\dots(2m-1)}{2^m}\sqrt{\pi} \tag{A.9}$$

The integrals (A.1) and (A.2) can easily be written in terms of the gamma function. In (A.1) we make the substitution $\xi = x/a$, $dx = a\,d\xi$:

$$F_1(n,a) = a^{n+1}\Gamma(n+1) = a^{n+1}n! \tag{A.10}$$

In (A.2) we make the substitution $\xi = x^2/a^2$, $dx = a\,d\xi/(2\sqrt{\xi})$:

$$F_2(n,a) = \frac{1}{2}a^{n+1}\Gamma(\frac{n+1}{2}). \tag{A.11}$$

For odd $n = 2m+1$ this can be written in terms of factorials:

$$F_2(2m+1,a) = \frac{1}{2}a^{2m+2}m! \tag{A.12}$$

and for even $n = 2m$ in terms of the gamma function for half-integers:

$$F_2(2m,a) = \frac{1}{2}a^{2m+1}\frac{(1)(3)\dots(m-1)}{2^m}\sqrt{\pi}. \tag{A.13}$$

If the F_2 integral is over the range $-\infty$ to ∞ then the result is zero if n is odd, and twice the value in (A.13) if n is even.

A.2 Trignometric Integrals

Integrals over the θ factor of spherical harmonics frequently involve forms such as

$$\int_0^\pi \mathcal{P}\sin\theta\,d\theta \tag{A.14}$$

where $\mathcal{P}$ is a polynomial involving $\sin\theta$ and $\cos\theta$. We can distinguish several cases.

If $\mathcal{P}$ involves only $\cos\theta$ the substitution $z = \cos\theta$ reduces the integral to a polynomial in z over the range -1 to 1, which is straightforward.

If $\mathcal{P}$ involves only $\sin\theta$ then the integral can be written as a sum of integrals of the form

$$G(m) = \int_0^\pi \sin^m\theta\,d\theta. \tag{A.15}$$

For $m = 0$ this gives π and for $m = 1$ it gives 2. Higher values of m can be handled with a reduction formula. We write the integrand as

$$\sin^m\theta = sin^{m-2}\theta(1-\cos^2\theta) \tag{A.16}$$

which gives

$$G(m) = G(m-2) - \int_0^\pi \sin^{m-2}\theta\cos^2\theta\,d\theta. \tag{A.17}$$

In the remaining integral we integrate by parts: $\cos\theta$ differentiates to $-\sin\theta$, while $\sin^{m-2}\theta\cos\theta$ integrates to $(\sin^{m-1}\theta)/(m-1)$. The integrated part vanishes at both limits to leave

$$G(m) = G(m-2) - \frac{G(m)}{m-1} \tag{A.18}$$

which we can re-arrange to give

$$G(m) = \frac{m-1}{m}\,G(m-2). \tag{A.19}$$

Thus for odd m we obtain

$$G(m) = \frac{(2)(4)\ldots(m-1)}{(1)(3)\ldots(m)}\,2 \tag{A.20}$$

and for even m

$$G(m) = \frac{(1)(3)\ldots(m-1)}{(2)(4)\ldots(m)}\,\pi. \tag{A.21}$$

If $\mathcal{P}$ involves both $\sin\theta$ and $\cos\theta$ analogous methods can be employed; we shall not go into details here. For integrals over spherical harmonics much more powerful techniques are available using their functional properties: see, for example, ???????

The square well overlap and normalisation inegrals are of the form (after a substitution $y = \pi x/a$)

$$N(n,m) = \int_0^\pi \sin ny \sin my\,dy. \tag{A.22}$$

Using the difference relation we can re-write the integrand

$$\sin ny \sin my = \frac{1}{2}\left(\cos(n-m)y - \cos(n+m)y\right) \tag{A.23}$$

and if $n \neq m$ both terms vanish on integrating. If $n = m$ the first term in (A.23) is $\frac{1}{2}$ so this integrates to $N(n,n) = \pi/2$.

Matrix elements of x with square well eigenfunctions involve (with the same substitution) integrals of the form

$$\int_0^\pi y \sin ny \sin my \, dy = \int_0^\pi \frac{y}{2}\Big(\cos(n-m)y - \cos(n+m)y\Big)\, dy \tag{A.24}$$

where we have used the same difference relation. Agaian we treat the cases $n \neq m$ and $n = m$ separately. In the case $n \neq m$ we integrate each term by parts to give (the integrated part vanishes at both limits)

$$\frac{1}{2}\int_0^\pi \frac{\sin(n-m)y}{n-m} - \frac{\sin(n+m)y}{n+m}\, dy = -\frac{1}{2}\left[\frac{\cos(n-m)y}{(n-m)^2} - \frac{\cos(n+m)y}{(n+m)^2}\right]_0^\pi. \tag{A.25}$$

Putting in the limits, we obtain zero if n and m differ by an even number, and otherwise

$$\int_0^\pi y \sin ny \sin my \, dy = \frac{1}{(n-m)^2} - \frac{1}{(n+m)^2} \qquad n - m = \text{odd}. \tag{A.26}$$

In the case $n = m$ the second term in (A.24) integrates to zero as $n + m$ is an even number, but the first term is just y and integrates to

$$\int_0^\pi y \sin^2 ny \, dy = \left[\frac{y^2}{4}\right]_0^\pi = \frac{\pi^2}{4}. \tag{A.27}$$

A.3 Trignometric forms involving $(1 + e\cos\theta)$

Radial averages over classical elliptic motion give rise to integrals of the form

$$E(n, e) = \int_{-\pi}^\pi \frac{d\theta}{(1 + e\cos\theta)^n}. \tag{A.28}$$

For $n \leq 0$ this is simply a polynomial in $\cos\theta$, which is relatively straightforward, so we shall concentrate on $n > 0$. The substitution $\tan\frac{1}{2}\theta = t$, $d\theta = 2\,dt/(1+t^2)$ yields

$$E(n, e) = \int_{-\infty}^\infty \frac{2(1+t^2)^{n-1}}{\Big((1+e) + (1-e)t^2\Big)^n} dt. \tag{A.29}$$

A second substitution $s = \sqrt{\frac{(1-e)}{(1+e)}}\,t$ gives

$$E(n, e) = \frac{2}{\sqrt{1-e^2}(1-e)^{n-1}} \int_{-\infty}^\infty \left(\frac{\frac{1-e}{1+e} + s^2}{1+s^2}\right)^{n-1} \frac{ds}{1+s^2}. \tag{A.30}$$

The factor in the large bracket can be simplified:

$$\frac{\frac{1-e}{1+e} + s^2}{1+s^2} = 1 - \frac{\frac{2e}{1+e}}{1+s^2}. \tag{A.31}$$

We can expand using the binomial coefficients $\binom{n}{m}$:

$$\left(1-\frac{\frac{2e}{1+e}}{1+s^2}\right)^{n-1} = \sum_{m=0}^{n-1}\binom{n-1}{m}\left(\frac{-2e}{1+e}\right)^m \frac{1}{(1+s^2)^m}. \tag{A.32}$$

The integral $E(n,e)$ can thus be expanded in terms of the simpler integrals

$$H(m) = \int_{-\infty}^{\infty}\frac{ds}{(1+s^2)^m}. \tag{A.33}$$

The explicit expansion is

$$E(n,e) = \frac{2}{\sqrt{1-e^2}(1-e)^{n-1}}\sum_{m=0}^{n-1}\binom{n-1}{m}\left(\frac{-2e}{1+e}\right)^m H(m). \tag{A.34}$$

For $H(m)$ we can derive a reduction formula: we write

$$\frac{1}{(1+s^2)^{m-1}} = \frac{1+s^2}{(1+s^2)^m} = \frac{1}{(1+s^2)^m} + \frac{s^2}{(1+s^2)^m}. \tag{A.35}$$

Hence

$$H(m-1) = H(m) + \int_{-\infty}^{\infty}\frac{s^2\,ds}{(1+s^2)^m}. \tag{A.36}$$

The final term we can integrate by parts, differentiating s to 1 and integrating $s/(1+s^2)^m$ to $-1/(2(m-1)(1+s^2)^{m-1})$. The integrated term vanishes at both limits to leave

$$H(m-1) = H(m) + \frac{1}{2(m-1)}H(m-1) \tag{A.37}$$

which can be rearranged to give

$$H(m) = \frac{(2m-3)}{(2m-2)}H(m-1). \tag{A.38}$$

This result enables us to express all the H integrals in terms of H(1) which is given by

$$H(1) = \int_{-\infty}^{\infty}\frac{ds}{1+s^2} = \pi. \tag{A.39}$$

Equations (A.34) and (A.38) enable us to evaluate $E(n,e)$; for example

$$E(1,e) = \frac{2}{\sqrt{1-e^2}}H(1) = \frac{2\pi}{\sqrt{1-e^2}} \tag{A.40}$$

$$E(2,e) = \frac{2}{\sqrt{1-e^2}(1-e)}\Big(H(1) - \frac{2e}{1+e}H(2)\Big) = \frac{2\pi}{(1-e^2)^{3/2}}. \tag{A.41}$$

Appendix B

Solution of Linear Differential Equations

Appendix C

Matrix Elements of Vector Operators

C.1 Introduction

In this appendix we draw together a number of general results relating to matrix elements of vector operators between angular momentum eigenstates. We shall make extensive use of index notation for vectors, so we first explain this.

A vector $\mathbf{A}$ has three components A_i where the index i takes the values x, y and z, or 1, 2 and 3. We can write an equality between two vectors either as $\mathbf{A} = \mathbf{B}$ in vector notation, or $A_i = B_i$ in index notation , where the index i on each side of the equation can take any of the three allowed values. Two important vector constructions are the scalar and vector product, and we need to be able to write these in index notation as well.

The scalar product is given by

$$\mathbf{A} \cdot \mathbf{B} = A_x B_x + A_y B_y + A_z B_z = \sum_i A_i B_i = A_i B_i. \tag{C.1}$$

The second form gives the scalar product as an explicit sum over components; the third form gives it as a sum in index notation, summing over the index i. Note that i here is a *dummy index* — because we are summing over it we could equally well call it j or k. The final form uses Einstein's summation convention: expressions involving a repeated index nearly always involve summing over the index, so that the repeated index is also a dummy index. The convention is that all such repeated indices are summed over unless the contrary is explicitly indicated. Thus, for example, we can write the squared length of the vector as $\mathbf{A}^2 = A_i A_i$.

The vector product is slightly more difficult. The vector equation $\mathbf{A} = \mathbf{B} \wedge \mathbf{C}$ is equivalent to $A_x = B_y C_z - B_z C_y$ and cyclically. To write this in index notation we need to define the alternating tensor ϵ_{ijk} which is $+1$ if ijk is a cyclic permutation of 123, -1 if an anticyclic permutation and 0 if any index is repeated:

$$\epsilon_{123} = \epsilon_{231} = \epsilon_{312} = +1 \qquad \epsilon_{321} = \epsilon_{213} = \epsilon_{132} = -1.$$

Using ϵ_{ijk} and the summation convention we can write the vector product definition as

$$A_i = \epsilon_{ijk} B_j C_k. \tag{C.2}$$

Combining (C.1) and (C.2) we can write an expression for a scalar triple product

$$\mathbf{A} \cdot \mathbf{B} \wedge \mathbf{C} = \epsilon_{ijk} A_i B_j C_k$$

which makes the symmetry $\mathbf{A} \cdot \mathbf{B} \wedge \mathbf{C} = \mathbf{A} \wedge \mathbf{B} \cdot \mathbf{C}$ immediately apparent, as the two expressions become identical in index notation.

For simple expressions vector notation is far preferable to index notation, but in more complicated expressions, particularly with non-commuting operators, index notation enables us to write expressions which cannot be written in vector notation. As an example of this, we consider a vector triple product. If $\mathbf{A}$, $\mathbf{B}$ and $\mathbf{C}$ commute then the usual rule for expanding a vector triple product is

$$\mathbf{A} \wedge (\mathbf{B} \wedge \mathbf{C}) = (\mathbf{A} \cdot \mathbf{C})\mathbf{B} - (\mathbf{A} \cdot \mathbf{B})\mathbf{C}. \tag{C.3}$$

This is equivalent to the following rule for expanding products of ϵ_{ijk} with one index in common:

$$\epsilon_{ijk}\epsilon_{klm} = \delta_{il}\delta_{jm} - \delta_{im}\delta_{jl}. \tag{C.4}$$

This rule allows us to expand triple products of non-commuting vector operators:

$$\Big(\mathbf{A} \wedge (\mathbf{B} \wedge \mathbf{C})\Big)_i = \epsilon_{ijk} A_j \epsilon_{klm} B_l C_m = A_j B_i C_j - A_j B_j C_i$$

where the last term is equivalent to the last term of (C.3), but the first terms are only equivalent if $\mathbf{B}$ and $\mathbf{C}$ commute, and as it stands this term cannot be written in vector notation.

C.2 The Fundamental Commutators

The commutator of total angular momentum $\mathbf{J}$ and any vector $\mathbf{A}$ has been derived in **??** from the very general premise that vectors have to transform in a known way under rotations:

$$[J_i, A_j] = i\hbar\epsilon_{ijk} A_k. \tag{C.5}$$

(In this expression $i\hbar$ denotes $\hbar$ multiplied by the square root of minus one; there should not be any confusion between this i and the index i!) The same argument for a scalar operator S, using the fact that it has to be invariant under rotation, gives

$$[J_i, S] = 0. \tag{C.6}$$

These are the fundamental commutators which we can use to derive many properties of the matrix elements of these operators.

We should first check these results for consistency. There are three simple ways of combining scalars and vectors to produce scalars and vectors, and the fundamental commutators should be consistent with these processes. The three are as follows: the product $\mathbf{B} = S\mathbf{A}$ of a scalar and a vector is a vector, the scalar product $S = \mathbf{A}\cdot\mathbf{B}$ of two vectors is a scalar, and the vector product $\mathbf{C} = \mathbf{A}\wedge\mathbf{B}$ of two vectors is a vector. We shall use repeatedly the rule for a commutator of a product of operators

$$[P, QR] = [P, Q]R + Q[P, R]. \tag{C.7}$$

The first case is straightforward:

$$[J_i, B_j] = [J_i, SA_j] = [J_i, S]A_j + S[J_i, A_j] = Si\hbar\epsilon_{ijk}A_k = i\hbar\epsilon_{ijk}B_k$$

where we have used the definition of $\mathbf{B}$, then (C.7), then the scalar and vector fundamental commutators (C.6) and (C.5) and finally the definition of $\mathbf{B}$ again. The result is that $\mathbf{B}$ has a vector commutator with $\mathbf{J}$ as required.

The second case is relatively simple:

$$[J_i, A_jB_j] = [J_i, A_j]B_j + A_j[J_i, B_j] = i\hbar(\epsilon_{ijk}A_kB_j + \epsilon_{ijk}A_jB_k)$$

where again we have used (C.7) and (C.5). Since both j and k are dummy indices, we can interchange j and k in the first term. This gives

$$[J_i, A_jB_j] = i\hbar(\epsilon_{ikj} + \epsilon_{ijk})A_jB_k = 0$$

since interchanging two indices on the alternating tensor causes it to change sign. Thus the scalar product of any two vectors which obey (C.5) obeys (C.6) as required.

The third case is a little bit lengthier:

$$[J_i, C_j] = [J_i, \epsilon_{jkl}A_kB_l] = \epsilon_{jkl}\Big([J_i, A_k]B_l + A_k[J_i, B_l]\Big)$$

Using the vector commutator (C.5) this becomes

$$[J_i, C_j] = i\hbar\epsilon_{jkl}(\epsilon_{ikm}A_m B_l + \epsilon_{ilm}A_k B_m).$$

Expanding each product of alternating tensors we find

$$[J_i, C_j] = i\hbar(\delta_{ij}A_m B_m - A_j B_i + A_i B_j - \delta_{ij}A_m B_m) = i\hbar(A_i B_j - A_j B_i)$$

and this is readily shown to be equivalent to the correct result:

$$i\hbar\epsilon_{ijk}C_k = i\hbar\epsilon_{ijk}\epsilon_{klm}A_l B_m = i\hbar(A_i B_j - A_j B_i).$$

Note that we have made no assumption in any of proofs about the commutation of S, $\mathbf{A}$ and $\mathbf{B}$ with each other; in each expression they always occur in the same order.

We shall also make much use of the following properties of angular momentum eigenstates $|qJM\rangle$ found in **??** (where q denotes other quantum numbers). They are eigenstates of $\mathbf{J}^2$ and J_z:

$$\mathbf{J}^2|qJM\rangle = J(J+1)\hbar^2|qJM\rangle \qquad J_z|JM\rangle = M\hbar|JM\rangle$$

and $J_\pm = J_x \pm iJ_y$ are shift or ladder operators:

$$J_\pm|qJM\rangle = \sqrt{J(J+1) - M(M\pm 1)}\hbar|qJ(M\pm 1)\rangle.$$

J_+ and J_- are Hermitian conjugates of each other, so when operating 'backwards' we have, for example, $\langle qJM|J_+ = \sqrt{J(J+1) - M(M-1)}\hbar\langle qJ(M-1)|$. We shall also use these combinations of components for other vector operators, defining $A_\pm = A_x \pm iA_y$. The commutators of these operators with $\mathbf{J}$ follow directly from (C.5):

$$[J_z, A_\pm] = \pm\hbar A_\pm \qquad [J_\pm, A_z] = \mp\hbar A_\pm \tag{C.8}$$

for commutators involving one z and one shift operator, and

$$[J_+, A_+] = [J_-, A_-] = 0 \qquad [J_+, A_-] = 2\hbar A_z \qquad [J_-, A_+] = -2\hbar A_z \tag{C.9}$$

for commutators involving two shift operators.

C.3 Matrix Elements of Scalar Operators

Using these results we shall first discuss matrix elements of scalar operators S. We can readily prove the following results.

1. $\mathbf{J}^2$ *commutes with* S. This follows directly from the commutator (C.6): $[J_iJ_i, S] = J_i[J_i, S] + [J_i, S]J_i = 0$.

2. *The only non-zero matrix elements of* S *are diagonal in* J *and* M. Take a general matrix element of the above commutator:

   $$\langle q'J'M'|\mathbf{J}^2S - S\mathbf{J}^2|qJM\rangle = \Big(J'(J'+1) - J(J+1)\Big)\hbar^2\langle q'J'M'|S|qJM\rangle = 0$$

   Hence one of these factors must vanish. The first is equal to $(J'-J)(J'+J+1)$, and $(J+J'+1)$ is positive definite, so the matrix element is zero unless $J' = J$. The proof for $M' = M$ is very similar, using the commutator $[J_z, S] = 0$:

   $$\langle q'J'M'|J_zS - SJ_z|qJM\rangle = (M'-M)\hbar\langle q'J'M'|S|qJM\rangle = 0$$

   so that the matrix element is zero unless $M' = M$.

3. *All the matrix elements* $\langle q'JM|S|qJM\rangle$ *for different* M *are equal.* This follows from the commutator $[J_+, S] = 0$. Take the matrix element diagonal in J and with $M' = M+1$:

   $$\langle q'J(M+1)|J_+S - SJ_+|qJM\rangle = 0.$$

   Using the ladder property of J_+ on the left-hand side this becomes

   $$\sqrt{J(J+1) - M(M+1)}\hbar\Big(\langle q'J'M|S|qJM\rangle - \langle q'J'(M+1)|S|qJ(M+1)\rangle\Big) = 0$$

   The square root is non-zero (except when $J = M$, in which case the $|qJ(M+1)\rangle$ state does not exist) so the bracketed factor must vanish. Thus the (M, M) matrix element is equal to the $(M+1, M+1)$ matrix element. By repeating the argument we can establish the required result. We shall denote such matrix elements $\langle q'J'|S|qJ\rangle$, since they are independent of M.

The matrix elements of scalars are thus very simple: between any two levels qJ and $q'J$ the $(2J+1) \times (2J+1)$ matrix is a multiple of the unit matrix.

C.4 Matrix Elements of Vector Operators

We now apply a similar approach to a discussion of matrix elements of vector operators.

1. *The only non-zero matrix elements of* A_z *are diagonal in* M. This follows from the commutator $[J_z, A_z] = 0$ exactly as for the commutator $[J_z, S] = 0$ above.

2. *The only non-zero matrix elements of* $A_\pm$ *have* $M' = M \pm 1$. This follows from the commutator (C.8): $[J_z A_\pm - A_\pm J_z] = \pm\hbar A_+$. Taking a general matrix element we find

   $$\langle q'J'M'|J_z A_\pm - A_\pm J_z|qJM\rangle = (M' - M)\hbar\langle q'J'M'|A_\pm|JM\rangle = \pm\hbar\langle q'J'M'|A_\pm|JM\rangle$$

   which re-arranges to

   $$(M' - M \mp 1)\langle q'J'M'|A_\pm|JM\rangle = 0.$$

   One factor must vanish, so the matrix element of $A_\pm$ is zero unless $M' = M \pm 1$ as stated.

3. *The selection rule on* M *for vector operators is* $\Delta M = 0, \pm 1$. This follows from the previous two results: any component of $\mathbf{A}$ can be written in terms of A_z and $A_\pm$, so the only values of $M' - M$ giving non-zero matrix elements are 0, ± 1.

4. *Matrix elements of* $\mathbf{A}$ *with* $J' = J = 0$ *are zero.* Recalling that a state $|q00\rangle$ with $J = M = 0$ satisfies $J_i|q00\rangle = 0$ for all components of $\mathbf{J}$, we can simply take the matrix element of the fundamental commutator (C.5) between two such states:

   $$\langle q'00|J_i A_j - A_j J_i|q00\rangle = 0 = i\hbar\epsilon_{ijk}\langle q'00|A_k|q00\rangle.$$

   This shows that all such matrix elements are zero.

Before deriving the general selection rule on J we first derive an important relationship involving $\mathbf{A}$ and $\mathbf{J}^2$. We start by finding the commutator with $\mathbf{J}^2$:

$$[\mathbf{J}^2, A_j] = [J_i J_i, A_j] = J_i[J_i, A_j] + [J_i, A_j]J_i = i\hbar\epsilon_{ijk}(J_i A_k + A_k J_i).$$

If we now take the commutator of this whole expression with $\mathbf{J}^2$ (remembering that $[\mathbf{J}^2, J_i] = 0$ so we have only to commute $\mathbf{J}^2$ with the components of $\mathbf{A}$ on the right-hand side) we obtain

$$\left[\mathbf{J}^2, [\mathbf{J}^2, \mathbf{A}]\right] = -\hbar^2\epsilon_{ijk}\epsilon_{lkm}\Big(J_i J_l A_m + J_i A_m J_l + J_l A_m J_i + A_m J_l J_i\Big).$$

Expanding the product of ϵ_{ijk} gives eight terms, four of which can be written in vector notation directly:

$$-\hbar^2\Big(J_i J_j A_i + \mathbf{J}\cdot\mathbf{A}\,J_j + J_j\,\mathbf{A}\cdot\mathbf{J} + A_i J_j J_i - \mathbf{J}^2 A_j - J_i A_j J_i - J_i A_j J_i - A_j\mathbf{J}^2\Big)$$

This simplifies a lot. The order of the factors in terms involving $\mathbf{J}$ and $\mathbf{J}\cdot\mathbf{A}$ is immaterial, since $\mathbf{J}\cdot\mathbf{A} = \mathbf{A}\cdot\mathbf{J}$, and both commute with $\mathbf{J}$. The four terms in index notation can be grouped in pairs

$$J_i(J_j A_i - A_j J_i) - (J_i A_j - A_i J_j)J_i$$

which we can simplify using the following trick. The fundamental commutator (C.5) is antisymmetric in i and j, so $[J_i, A_j] + [J_j, A_i] = 0$ which re-arranges to $(J_iA_j - A_iJ_j) = (A_jJ_i - J_jA_i)$. With this substitution all terms can now be written in vector notation:

$$\big[\mathbf{J}^2, [\mathbf{J}^2, \mathbf{A}]\big] = 2\hbar^2(\mathbf{A}\mathbf{J}^2 + \mathbf{J}^2\mathbf{A}) - 4\hbar^2\mathbf{A}\cdot\mathbf{J}\,\mathbf{J}.$$

The derivation of this result is simply lengthy algebra, but the result itself, a necessary consequence of the fundamental commutator (C.5), is of remarkable significance. Re-arranging the order of the factors, and expanding the double commutator, we obtain

$$2\hbar^2(\mathbf{J}^2\mathbf{A} + \mathbf{A}\mathbf{J}^2) = \Big((\mathbf{J}^2)^2\mathbf{A} - 2\mathbf{J}^2\mathbf{A}\mathbf{J}^2 + \mathbf{A}(\mathbf{J}^2)^2\Big) + 4\hbar^2\mathbf{A}\cdot\mathbf{J}\,\mathbf{J}. \tag{C.10}$$

This expresses the operator on the left as the sum of two terms on the right. The first of these has no matrix elements diagonal in J, by an argument that is now familiar: the eigenvalues of $\mathbf{J}^2$ cancel and the term is zero. The second term has only matrix elements diagonal in J, since both $\mathbf{J}$ and the scalar operator $\mathbf{A}\cdot\mathbf{J}$ commute with $\mathbf{J}^2$. Thus in discussing the consequences of this result we can take the cases $J' = J$ and $J' \neq J$ separately.

5. *Matrix elements of* $\mathbf{A}$ *off-diagonal in* J *are zero unless* $J' = J \pm 1$. This follows from a general matrix element of (C.10) with $J' \neq J$. We can then ignore the second term on the right-hand side, as it has zero matrix element:

   $$2\Big(J'(J'+1) + J(J+1)\Big)\langle q'J'M'|\mathbf{A}|qJM\rangle = \Big(J'(J'+1) - J(J+1)\Big)^2\langle q'J'M'|\mathbf{A}|qJM\rangle.$$

   This re-arranges to

   $$(J'+J)(J'+J+1)(J'-J-1)(J'-J+1)\langle q'J'M'|\mathbf{A}|qJM\rangle = 0.$$

   One of the factors must be zero, and the first two are positive definite, so the matrix element is zero unless $J' - J = \pm 1$.

6. *Matrix elements of* $\mathbf{A}$ *diagonal in* J *are proportional to the corresponding matrix element of* $\mathbf{J}$. This follows from a general matrix element of (C.10) with $J' = J$. We can then ignore the first term on the right-hand side:

   $$J(J+1)\langle q'JM'|\mathbf{A}|qJM\rangle = \langle q'JM'|\mathbf{A}\cdot\mathbf{J}\,\mathbf{A}|qJM\rangle.$$

   If we insert a complete set of states between these two operators, the only non-zero matrix element has quantum numbers M', because $\mathbf{A}\cdot\mathbf{J}$ is diagonal in M, and q, J because $\mathbf{J}$ is diagonal in these quantum numbers. Hence

$$\langle q'JM'|\mathbf{A}|qJM\rangle = \frac{\langle q'J|\mathbf{A}\cdot\mathbf{J}|qJ\rangle}{J(J+1)}\langle qJM'|\mathbf{J}|qJM\rangle.$$

7. *The selection rule on J for vector operators is* $\Delta J = 0, \pm 1,\ 0 \not\to 0$. This follows from results 1, 2 and 3 above. Note that $\Delta J = 0$ is only possible if $\mathbf{A}\cdot\mathbf{J}$ has a non-zero matrix element between the two states. Whether or not this is so cannot be determined from the fundamental commutators.

It is worth pausing for a moment to reflect on the remarkable result 2 above. If we just concentrate on matrix elements diagonal in q and J — expectation values — then it states that on average all vectors are either zero or parallel to $\langle\mathbf{J}\rangle$. This is a very important result, and it is used in the text in several places: the derivation of the atomic g_J factor and the derivation of both the $\mathbf{L}\cdot\mathbf{S}$ form of the spin-orbit interaction in LS coupling, and the $\mathbf{I}\cdot\mathbf{J}$ form of the magnetic dipole hyperfine interaction.

However we have not yet exhausted the conclusions to be drawn from the fundamental commutators. We can also derive the complete M-dependence of the matrix elements.

We start from the commutator (C.9) $[J_+, A_+] = 0$, and take a general matrix element, except that since both A_+ and J_+ act as shift operators, we must take $M' = M + 2$:

$$\langle q'J'(M+2)|J_+A_+ - A_+J_+|qJM\rangle = 0.$$

Using the shift property of J_+ we can expand this as

$$\sqrt{J'(J'+1)-(M+1)(M+2)}\langle q'J'(M+1)|A_+|qJM\rangle =$$
$$\sqrt{J(J+1)-M(M+1)}\langle q'J'(M+2)|A_+|qJ(M+1)\rangle$$

which we can re-arrange as

$$\frac{\langle q'J'(M+1)|A_+|qJM\rangle}{\sqrt{J(J+1)-M(M+1)}} = \frac{\langle q'J'(M+2)|A_+|qJ(M+1)\rangle}{\sqrt{J'(J'+1)-(M+1)(M+2)}}. \tag{C.11}$$

This result will enable us to calculate the M-dependence of matrix elements of A_+.

The commutator (C.9) $[J_-, A_+] = -2\hbar A_z$ then enables us to relate these matrix elements to those of A_z. This time the M quantum numbers have to be equal:

$$\langle q'J'M|J_-A_+ - A_+J_-|qJM\rangle = -2\hbar\langle q'J'M|A_z|qJM\rangle.$$

Using the shift property we find

$$\begin{aligned}\sqrt{J'(J'+1)-M(M+1)}\langle q'J'(M+1)|A_+|qJM\rangle &\quad - \\ \sqrt{J(J+1)-(M-1)M}\langle q'J'M|A_+|qJ(M-1)\rangle &= -2\langle q'J'M|A_z|qJM\rangle. \qquad \text{(C.12)}\end{aligned}$$

Finally the commutator (C.8) $[J_-, A_z] = \hbar A_-$ enables us to relate these matrix elements to those of A_-. We require $M' = M - 1$, and proceed as in the previous two cases:

$$\begin{aligned}\sqrt{J'(J'+1)-(M-1)M}\langle q'J'M|A_z|qJM\rangle &\quad - \\ \sqrt{J(J+1)-(M-1)M}\langle q'J'(M-1)|A_z|qJ(M-1)\rangle &= \langle q'J'(M-1)|A_-|qJM\rangle. \quad \text{(C.13)}\end{aligned}$$

We first consider the case $J' = J$.

4. *Matrix elements of A_+ diagonal in J are proportional to $\sqrt{J(J+1)-M(M+1)}$.* This follows from (C.11) with $J' = J$:
$$\frac{\langle q'J(M+1)|A_+|qJM\rangle}{\sqrt{J(J+1)-M(M+1)}} = \frac{\langle q'J(M+2)|A_+|qJ(M+1)\rangle}{\sqrt{J(J+1)-(M+1)(M+2)}}.$$
The right-hand side is equivalent to the left-hand side with M replaced everywhere by $M+1$. Repeating the argument for different values of M shows that this ratio is independent of M. If we therefore call the ratio K we can write
$$\langle q'J(M+1)|A_+|qJM\rangle = K\sqrt{J(J+1)-M(M+1)}$$
as required.

5. *Matrix elements of A_z diagonal in J are proportional to M.* This follows from (C.12) with $J' = J$, using the result from 1 to evaluate the matrix elements of A_+:
$$K\Big(J(J+1)-M(M+1)-J(J+1)+(M-1)M\Big) = -2\langle q'JM|A_z|qJM\rangle$$
which reduces to
$$\langle q'JM|A_z|qJM\rangle = MK$$
as required.

6. *Matrix elements of A_- diagonal in J are proportional to $\sqrt{J(J+1)-(M-1)M}$.* This follows from (C.13) with $J' = J$, using the result from 2 to evaluate the matrix elements of A_z:
$$K\sqrt{J(J+1)-(M-1)M} = \langle q'J(M-1)|A_-|qJM\rangle$$
as required.

Results 1–3 for matrix elements diagonal in J also follow directly from result 2 above. Furthermore, result 2 also provides an explicit expression for K:

$$K = \frac{\langle q'JM|\mathbf{A}\cdot\mathbf{J}|qJM\rangle}{J(J+1)}.$$

However, having evaluated them from equations (C.11)–(C.13) we can now follow exactly the same approach for the case $J' \neq J$.

4. *Matrix elements of A_+ with $J' = J+1$ are proportional to $\sqrt{(J+M+1)(J+M+2)}$.* This follows from (C.11) with $J' = J+1$:

   $$\frac{\langle q'(J+1)(M+1)|A_+|qJM\rangle}{\sqrt{J(J+1)-M(M+1)}} = \frac{\langle q'(J+1)(M+2)|A_+|qJ(M+1)\rangle}{\sqrt{(J+1)(J+2)-(M+1)(M+2)}}.$$

   Factorizing the denominators we have

   $$\frac{\langle q'(J+1)(M+1)|A_+|qJM\rangle}{\sqrt{(J-M)(J+M+1)}} = \frac{\langle q'(J+1)(M+2)|A_+|qJ(M+1)\rangle}{\sqrt{(J-M)(J+M+3)}}.$$

   We can cancel the $(J-M)$ factor to leave

   $$\frac{\langle q'(J+1)(M+1)|A_+|qJM\rangle}{\sqrt{J+M+1}} = \frac{\langle q'(J+1)(M+2)|A_+|qJ(M+1)\rangle}{\sqrt{J+M+3}}.$$

   This time the right-hand side is *not* equal to the left-hand side with M replaced by $M+1$, but it becomes so if we divide by $\sqrt{(J+M+2)}$:

   $$\frac{\langle q'(J+1)(M+1)|A_+|qJM\rangle}{\sqrt{(J+M+1)(J+M+2)}} = \frac{\langle q'(J+1)(M+2)|A_+|qJ(M+1)\rangle}{\sqrt{(J+M+2)(J+M+3)}}.$$

   Thus the ratio is independent of M. Calling it K' we can write

   $$\langle q'(J+1)(M+1)|A_+|qJM\rangle = K'\sqrt{(J+M+1)(J+M+2)}$$

   as required.

5. *Matrix elements of A_z with $J' = J+1$ are proportional to $-\sqrt{(J+1)^2-M^2}$.* This follows from (C.12) with $J' = J+1$, using the result from 1 to evaluate the matrix elements of A_+:

   $$K'\left(\sqrt{(J-M+1)(J+M+2)(J+M+1)(J+M+2)} - \sqrt{(J-M+1)(J+M)(J+M)(J+M+1)}\right) = -2\langle q'(J+1)M|A_z|qJM\rangle$$

   which reduces to

   $$\langle q'(J+1)M|A_z|qJM\rangle = -\sqrt{(J+1-M)(J+1+M)}K'$$

   as required.

M' :	$M-1$	M	$M+1$
J' :	$\frac{1}{2}(\hat{\mathbf{x}}+i\hat{\mathbf{y}})\times$	$\hat{\mathbf{z}}\times$	$\frac{1}{2}(\hat{\mathbf{x}}-i\hat{\mathbf{y}})\times$
$J-1$	$\sqrt{(J+M-1)(J+M)}\,K''$	$-\sqrt{J^2-M^2}\,K''$	$\sqrt{(J-M-1)(J-M)}\,K''$
J	$\sqrt{(J-M+1)(J+M)}\,K$	$M\,K$	$\sqrt{(J-M)(J+M+1)}\,K$
$J+1$	$\sqrt{(J-M+1)(J-M+2)}\,K'$	$-\sqrt{(J+1)^2-M^2}\,K'$	$\sqrt{(J+M+1)(J+M+2)}\,K'$

Table C.1: Matrix elements $\langle q'J'M'|\mathbf{A}|qJM\rangle$

6. *Matrix elements of A_- with $J' = J+1$ are proportional to $\sqrt{(J-M+1)(J-M+2)}$.* This follows from (C.13) with $J' = J+1$, using the result from 2 to evaluate the matrix elements of A_z:

$$\begin{aligned} K'\Big(\sqrt{(J-M+2)(J+M+1)(J+M+1)(J-M+1)} \quad - \\ \sqrt{(J-M+1)(J+M)(J+M)(J-M+2)}\Big) \quad &= \quad \langle q'(J+1)M|A_-|qJM\rangle \end{aligned}$$

which reduces to

$$\langle q'(J+1)(M-1)|A_-|qJM\rangle = \sqrt{(J-M+1)(J-M+2)}K'$$

as required.

Exactly the same method gives the results for $J' = J-1$. The results are presented in a slightly different way in the table, as matrix elements of the vector $\mathbf{A}$, instead of its components. We write

$$\mathbf{A} = A_x\hat{\mathbf{x}} + A_y\hat{\mathbf{y}} + A_z\hat{\mathbf{z}}.$$

Noting that $A_x = \frac{1}{2}(A_+ + A_-)$ and $A_y = \frac{i}{2}(A_-A_+)$ we can re-write $\mathbf{A}$ as

$$\mathbf{A} = A_z\hat{\mathbf{z}} + \frac{1}{2}A_+(\hat{\mathbf{x}} - i\hat{\mathbf{y}}) + \frac{1}{2}A_-(\hat{\mathbf{x}} + i\hat{\mathbf{y}}).$$

Each of the possible values of ΔM picks out one term in the operator to give the results in the table. The table is read by multiplying the entry in the J', M' cell by the vector at the head of the column to give the matrix element $\langle q'J'M'|\mathbf{A}|qJM\rangle$.