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The foundations of quantum mechanics

The whole of quantum mechanics can be expressed in terms of a small set of postulates. When their consequences are developed, they embrace the behaviour of all known forms of matter, including the molecules, atoms, and electrons that will be at the centre of our attention in this book. This chapter introduces the postulates and illustrates how they are used. The remaining chapters build on them, and show how to apply them to problems of chemical interest, such as atomic and molecular structure and the properties of molecules. We assume that you have already met the concepts of 'hamiltonian' and 'wavefunction' in an elementary introduction, and have seen the Schrödinger equation written in the form

$$H\psi = E\psi$$

This chapter establishes the full significance of this equation, and provides a foundation for its application in the following chapters.

Operators in quantum mechanics

An **observable** is any dynamical variable that can be measured. The principal mathematical difference between classical mechanics and quantum mechanics is that whereas in the former physical observables are represented by functions (such as position as a function of time), in quantum mechanics they are represented by mathematical operators. An **operator** is a symbol for an instruction to carry out some action, an operation, on a function. In most of the examples we shall meet, the action will be nothing more complicated than multiplication or differentiation. Thus, one typical operation might be multiplication by x, which is represented by the operator $x\times$. Another operation might be differentiation with respect to x, represented by the operator $\mathrm{d}/\mathrm{d}x$. We shall represent operators by the symbol Ω (omega) in general, but use $A, B, \ldots$ when we want to refer to a series of operators. We shall not in general distinguish between the observable and the operator that represents that observable; so the position of a particle along the x-axis will be denoted x and the corresponding operator will also be denoted x (with multiplication implied). We shall always make it clear whether we are referring to the observable or the operator.

We shall need a number of concepts related to operators and functions on which they operate, and this first section introduces some of the more important features.

1.1 Linear operators

The operators we shall meet in quantum mechanics are all linear. A **linear operator** is one for which

$$\Omega(af + bg) = a\Omega f + b\Omega g \tag{1.1}$$

where a and b are constants and f and g are functions. Multiplication is a linear operation; so is differentiation and integration. An example of a nonlinear operation is that of taking the logarithm of a function, because it is not true, for example, that $\log 2x = 2\log x$ for all x.

1.2 Eigenfunctions and eigenvalues

In general, when an operator operates on a function, the outcome is another function. Differentiation of $\sin x$, for instance, gives $\cos x$. However, in certain cases, the outcome of an operation is the same function multiplied by a constant. Functions of this kind are called 'eigenfunctions' of the operator. More formally, a function f (which may be complex) is an **eigenfunction** of an operator Ω if it satisfies an equation of the form

$$\Omega f = \omega f \tag{1.2}$$

where ω is a constant. Such an equation is called an **eigenvalue equation**. The function e^{ax} is an eigenfunction of the operator d/dx because $(d/dx)e^{ax} = ae^{ax}$, which is a constant (a) multiplying the original function. In contrast, e^{ax^2} is not an eigenfunction of d/dx, because $(d/dx)e^{ax^2} = 2axe^{ax^2}$, which is a constant ($2a$) times a *different* function of x (the function xe^{ax^2}). The constant ω in an eigenvalue equation is called the **eigenvalue** of the operator Ω.

Example 1.1 Determining if a function is an eigenfunction

Is the function $\cos(3x + 5)$ an eigenfunction of the operator d^2/dx^2 and, if so, what is the corresponding eigenvalue?

Method. Perform the indicated operation on the given function and see if the function satisfies an eigenvalue equation. Use $(d/dx)\sin ax = a\cos ax$ and $(d/dx)\cos ax = -a\sin ax$.

Answer. The operator operating on the function yields

$$\frac{d^2}{dx^2}\cos(3x+5) = \frac{d}{dx}(-3\sin(3x+5)) = -9\cos(3x+5)$$

and we see that the original function reappears multiplied by the eigenvalue -9.

Self-test 1.1. Is the function e^{3x+5} an eigenfunction of the operator d^2/dx^2 and, if so, what is the corresponding eigenvalue?

[Yes; 9]

An important point is that a general function can be expanded in terms of all the eigenfunctions of an operator, a so-called **complete set** of functions.

That is, if f_n is an eigenfunction of an operator Ω with eigenvalue ω_n (so $\Omega f_n = \omega_n f_n$), then[1] a general function g can be expressed as the **linear combination**

$$g = \sum_n c_n f_n \tag{1.3}$$

where the c_n are coefficients and the sum is over a complete set of functions. For instance, the straight line $g = ax$ can be recreated over a certain range by superimposing an infinite number of sine functions, each of which is an eigenfunction of the operator $\mathrm{d}^2/\mathrm{d}x^2$. Alternatively, the same function may be constructed from an infinite number of exponential functions, which are eigenfunctions of $\mathrm{d}/\mathrm{d}x$. The advantage of expressing a general function as a linear combination of a set of eigenfunctions is that it allows us to deduce the effect of an operator on a function that is not one of its own eigenfunctions. Thus, the effect of Ω on g in eqn 1.3, using the property of linearity, is simply

$$\Omega g = \Omega \sum_n c_n f_n = \sum_n c_n \Omega f_n = \sum_n c_n \omega_n f_n$$

A special case of these linear combinations is when we have a set of **degenerate** eigenfunctions, a set of functions with the same eigenvalue. Thus, suppose that $f_1, f_2, \ldots, f_k$ are all eigenfunctions of the operator Ω, and that they all correspond to the same eigenvalue ω:

$$\Omega f_n = \omega f_n \text{ with } n = 1, 2, \ldots, k \tag{1.4}$$

Then it is quite easy to show that *any* linear combination of the functions f_n is also an eigenfunction of Ω with the same eigenvalue ω. The proof is as follows. For an arbitrary linear combination g of the degenerate set of functions, we can write

$$\Omega g = \Omega \sum_{n=1}^{k} c_n f_n = \sum_{n=1}^{k} c_n \Omega f_n = \sum_{n=1}^{k} c_n \omega f_n = \omega \sum_{n=1}^{k} c_n f_n = \omega g$$

This expression has the form of an eigenvalue equation ($\Omega g = \omega g$).

Example 1.2 Demonstrating that a linear combination of degenerate eigenfunctions is also an eigenfunction

Show that any linear combination of the complex functions $\mathrm{e}^{2\mathrm{i}x}$ and $\mathrm{e}^{-2\mathrm{i}x}$ is an eigenfunction of the operator $\mathrm{d}^2/\mathrm{d}x^2$, where $\mathrm{i} = (-1)^{1/2}$.

Method. Consider an arbitrary linear combination $a\mathrm{e}^{2\mathrm{i}x} + b\mathrm{e}^{-2\mathrm{i}x}$ and see if the function satisfies an eigenvalue equation.

Answer. First we demonstrate that $\mathrm{e}^{2\mathrm{i}x}$ and $\mathrm{e}^{-2\mathrm{i}x}$ are degenerate eigenfunctions.

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\mathrm{e}^{\pm 2\mathrm{i}x} = \frac{\mathrm{d}}{\mathrm{d}x}(\pm 2\mathrm{i}\mathrm{e}^{\pm 2\mathrm{i}x}) = -4\mathrm{e}^{\pm 2\mathrm{i}x}$$

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[1] See P.M. Morse and H. Feschbach, *Methods of theoretical physics*, McGraw-Hill, New York (1953).

where we have used $i^2 = -1$. Both functions correspond to the same eigenvalue, -4. Then we operate on a linear combination of the functions.

$$\frac{d^2}{dx^2}(ae^{2ix} + be^{-2ix}) = -4(ae^{2ix} + be^{-2ix})$$

The linear combination satisfies the eigenvalue equation and has the same eigenvalue (-4) as do the two complex functions.

Self-test 1.2. Show that any linear combination of the functions $\sin(3x)$ and $\cos(3x)$ is an eigenfunction of the operator d^2/dx^2.

[Eigenvalue is -9]

A further technical point is that from n basis functions it is possible to construct n linearly independent combinations. A set of functions $g_1, g_2, \ldots, g_n$ is said to be **linearly independent** if we cannot find a set of constants $c_1, c_2, \ldots, c_n$ (other than the trivial set $c_1 = c_2 = \cdots = 0$) for which

$$\sum_i c_i g_i = 0$$

A set of functions that is not linearly independent is said to be **linearly dependent**. From a set of n linearly independent functions, it is possible to construct an infinite number of sets of linearly independent combinations, but each set can have no more than n members. For example, from three 2p-orbitals of an atom it is possible to form any number of sets of linearly independent combinations, but each set has no more than three members.

1.3 Representations

The remaining work of this section is to put forward some explicit forms of the operators we shall meet. Much of quantum mechanics can be developed in terms of an abstract set of operators, as we shall see later. However, it is often fruitful to adopt an explicit form for particular operators and to express them in terms of the mathematical operations of multiplication, differentiation, and so on. Different choices of the operators that correspond to a particular observable give rise to the different **representations** of quantum mechanics, because the explicit forms of the operators represent the abstract structure of the theory in terms of actual manipulations.

One of the most common representations is the **position representation**, in which the position operator is represented by multiplication by x (or whatever coordinate is specified) and the linear momentum parallel to x is represented by differentiation with respect to x. Explicitly:

$$\text{Position representation: } x \rightarrow x \times \qquad p_x \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x} \tag{1.5}$$

where $\hbar = h/2\pi$. Why the linear momentum should be represented in precisely this manner will be explained in the following section. For the time being, it may be taken to be a basic postulate of quantum mechanics. An alternative choice of operators is the **momentum representation**, in which the linear momentum parallel to x is represented by the operation of multiplication by p_x and the position operator is represented by differentiation with respect to p_x. Explicitly:

$$\text{Momentum representation: } x \rightarrow -\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial p_x} \qquad p_x \rightarrow p_x \times \tag{1.6}$$

There are other representations. We shall normally use the position representation when the adoption of a representation is appropriate, but we shall also see that many of the calculations in quantum mechanics can be done independently of a representation.

1.4 Commutation and non-commutation

An important feature of operators is that in general the outcome of successive operations (A followed by B, which is denoted BA, or B followed by A, denoted AB) depends on the order in which the operations are carried out. That is, in general $BA \neq AB$. We say that, in general, operators do not **commute**. For example, consider the operators x and p_x and a specific function x^2. In the position representation, $(xp_x)x^2 = x(2\hbar/\mathrm{i})x = (2\hbar/\mathrm{i})x^2$, whereas $(p_x x)x^2 = p_x x^3 = (3\hbar/\mathrm{i})x^2$. The operators x and p_x do not commute.

The quantity $AB - BA$ is called the commutator of A and B and is denoted $[A, B]$:

$$[A, B] = AB - BA \tag{1.7}$$

It is instructive to evaluate the commutator of the position and linear momentum operators in the two representations shown above; the procedure is illustrated in the following example.

Example 1.3 The evaluation of a commutator

Evaluate the commutator $[x,p_x]$ in the position representation.

Method. To evaluate the commutator $[A,B]$ we need to remember that the operators operate on some function, which we shall write f. So, evaluate $[A,B]f$ for an arbitrary function f, and then cancel f at the end of the calculation.

Answer. Substitution of the explicit expressions for the operators into $[x,p_x]$ proceeds as follows:

$$\begin{aligned}[x, p_x]f &= (xp_x - p_x x)f = x \times \frac{\hbar}{\mathrm{i}}\frac{\partial f}{\partial x} - \frac{\hbar}{\mathrm{i}}\frac{\partial (xf)}{\partial x} \\ &= x \times \frac{\hbar}{\mathrm{i}}\frac{\partial f}{\partial x} - \frac{\hbar}{\mathrm{i}} f - x \times \frac{\hbar}{\mathrm{i}}\frac{\partial f}{\partial x} = \mathrm{i}\hbar f\end{aligned}$$

where we have used $(1/\mathrm{i}) = -\mathrm{i}$. This derivation is true for any function f, so in terms of the operators themselves,

$$[x, p_x] = \mathrm{i}\hbar$$

The right-hand side should be interpreted as the operator 'multiply by the constant $\mathrm{i}\hbar$'.

Self-test 1.3. Evaluate the same commutator in the momentum representation.
[Same]

1.5 The construction of operators

Operators for other observables of interest can be constructed from the operators for position and momentum. For example, the kinetic energy operator T can be constructed by noting that kinetic energy is related to linear momentum by $T = p^2/2m$ where m is the mass of the particle. It follows that in one dimension and in the position representation

$$T = \frac{p_x^2}{2m} = \frac{1}{2m}\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)^2 = -\frac{\hbar}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} \tag{1.8}$$

In three dimensions the operator in the position representation is

$$T = -\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right\} = -\frac{\hbar^2}{2m}\nabla^2 \tag{1.9}$$

Although eqn 1.9 has explicitly used Cartesian coordinates, the relation between the kinetic energy operator and the laplacian is true in *any* coordinate system; for example, spherical polar coordinates.

The operator ∇^2, which is read 'del squared' and called the **laplacian**, is the sum of the three second derivatives.

The operator for potential energy of a particle in one dimension, $V(x)$, is multiplication by the function $V(x)$ in the position representation. The same is true of the potential energy operator in three dimensions. For example, in the position representation the operator for the Coulomb potential energy of an electron (charge $-e$) in the field of a nucleus of atomic number Z is the multiplicative operator

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r}\times \tag{1.10}$$

where r is the distance from the nucleus to the electron. It is usual to omit the multiplication sign from multiplicative operators, but it should not be forgotten that such expressions are multiplications.

The operator for the total energy of a system is called the **hamiltonian operator** and is denoted H:

$$H = T + V \tag{1.11}$$

The name commemorates W.R. Hamilton's contribution to the formulation of classical mechanics in terms of what became known as a hamiltonian *function*. To write the explicit form of this operator we simply substitute the appropriate expressions for the kinetic and potential energy operators in the chosen representation. For example, the hamiltonian for a particle of mass m moving in one dimension is

$$H = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) \tag{1.12}$$

where $V(x)$ is the operator for the potential energy. Similarly, the hamiltonian operator for an electron of mass m_e in a hydrogen atom is

$$H = -\frac{\hbar^2}{2m_\mathrm{e}}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \tag{1.13}$$

The general prescription for constructing operators in the position representation should be clear from these examples. In short:

1. Write the classical expression for the observable in terms of position coordinates and the linear momentum.
2. Replace x by multiplication by x, and replace p_x by $(\hbar/\mathrm{i})\partial/\partial x$ (and likewise for the other coordinates).

1.6 Integrals over operators

When we want to make contact between a calculation done using operators and the actual outcome of an experiment, we need to evaluate certain integrals. These integrals all have the form

$$I = \int f_m^* \Omega f_n \, \mathrm{d}\tau \tag{1.14}$$

where f_m^* is the complex conjugate of f_m. In this integral $\mathrm{d}\tau$ is the **volume element**. In one dimension, $\mathrm{d}\tau$ can be identified as $\mathrm{d}x$; in three dimensions it is $\mathrm{d}x\mathrm{d}y\mathrm{d}z$. The integral is taken over the entire space available to the system, which is typically from $x = -\infty$ to $x = +\infty$ (and similarly for the other coordinates). A glance at the later pages of this book will show that many molecular properties are expressed as combinations of integrals of this form (often in a notation which will be explained later). Certain special cases of this type of integral have special names, and we shall introduce them here.

The complex conjugate of a complex number $z = a + ib$ is $z^* = a - ib$. Complex conjugation amounts to everywhere replacing i by $-$i. The square modulus $|z|^2$ is given by $zz^* = a^2 + b^2$ since $|\mathrm{i}|^2 = 1$.

When the operator Ω in eqn 1.14 is simply multiplication by 1, the integral is called an **overlap integral** and commonly denoted S:

$$S = \int f_m^* f_n \, \mathrm{d}\tau \tag{1.15}$$

It is helpful to regard S as a measure of the similarity of two functions: when $S = 0$, the functions are classified as **orthogonal**, rather like two perpendicular vectors. When S is close to 1, the two functions are almost identical. The recognition of mutually orthogonal functions often helps to reduce the amount of calculation considerably, and rules will emerge in later sections and chapters.

The **normalization integral** is the special case of eqn 1.15 for $m = n$. A function f_m is said to be **normalized** (strictly, normalized to 1) if

$$\int f_m^* f_m \, \mathrm{d}\tau = 1 \tag{1.16}$$

It is almost always easy to ensure that a function is normalized by multiplying it by an appropriate numerical factor, which is called a **normalization factor**, typically denoted N and taken to be real so that $N^* = N$. The procedure is illustrated in the following example.

Example 1.4 How to normalize a function

A certain function f is $\sin(\pi x/L)$ between $x = 0$ and $x = L$ and is zero elsewhere. Find the normalized form of the function.

Method. We need to find the (real) factor N such that $N\sin(\pi x/L)$ is normalized to 1. To find N we substitute this expression into eqn 1.16, evaluate the integral, and select N to ensure normalization. Note that 'all space' extends from $x = 0$ to $x = L$.

Answer. The necessary integration is

$$\int f^* f \,\mathrm{d}\tau = \int_0^L N^2 \sin^2(\pi x/L)\mathrm{d}x = \tfrac{1}{2}LN^2$$

where we have used $\int \sin^2 ax\,\mathrm{d}x = (x/2)(\sin 2ax)/4a + \text{constant}$. For this integral to be equal to 1, we require $N = (2/L)^{1/2}$. The normalized function is therefore

$$f = \left(\frac{2}{L}\right)^{1/2} \sin(\pi x/L)$$

Comment. We shall see later that this function describes the distribution of a particle in a square well, and we shall need its normalized form there.

Self-test 1.4. Normalize the function $f = \mathrm{e}^{\mathrm{i}\phi}$, where ϕ ranges from 0 to 2π.

$[N = 1/(2\pi)^{1/2}]$

A set of functions f_n that are (a) normalized and (b) mutually orthogonal are said to satisfy the **orthonormality condition:**

$$\int f_m^* f_n \,\mathrm{d}\tau = \delta_{mn} \tag{1.17}$$

In this expression, δ_{mn} denotes the **Kronecker delta**, which is 1 when $m = n$ and 0 otherwise.

1.7 Dirac bracket notation

With eqn 1.14 we are on the edge of getting lost in a complicated notation. The appearance of many quantum mechanical expressions is greatly simplified by adopting the **Dirac bracket notation** in which integrals are written as follows:

$$\langle m|\Omega|n\rangle = \int f_m^* \Omega f_n \,\mathrm{d}\tau \tag{1.18}$$

The symbol $|n\rangle$ is called a **ket**, and denotes the state described by the function f_n. Similarly, the symbol $\langle n|$ is called a **bra**, and denotes the complex conjugate of the function, f_n^*. When a bra and ket are strung together with an operator between them, as in the **bracket** $\langle m|\Omega|n\rangle$, the integral in eqn 1.18 is to be understood. When the operator is simply multiplication by 1, the 1 is omitted and we use the convention

$$\langle m|n\rangle = \int f_m^* f_n \,\mathrm{d}\tau \tag{1.19}$$

This notation is very elegant. For example, the normalization integral becomes $\langle n|n\rangle = 1$ and the orthogonality condition becomes $\langle m|n\rangle = 0$ for $m \neq n$. The combined orthonormality condition (eqn 1.17) is then

$$\langle m|n\rangle = \delta_{mn} \tag{1.20}$$

A final point is that, as can readily be deduced from the definition of a Dirac bracket,

$$\langle m|n\rangle = \langle n|m\rangle^*$$

1.8 Hermitian operators

An operator is **hermitian** if it satisfies the following relation:

$$\int f_m^* \Omega f_n \, \mathrm{d}\tau = \left\{ \int f_n^* \Omega f_m \mathrm{d}\tau \right\}^* \tag{1.21a}$$

for any two functions f_m and f_n. An alternative version of this definition is

$$\int f_m^* \Omega f_n \, \mathrm{d}\tau = \int (\Omega f_m)^* f_n \, \mathrm{d}\tau \tag{1.21b}$$

This expression is obtained by taking the complex conjugate of each term on the right-hand side of eqn 1.21a. In terms of the Dirac notation, the definition of hermiticity is

$$\langle m|\Omega|n\rangle = \langle n|\Omega|m\rangle^* \tag{1.22}$$

Example 1.5 How to confirm the hermiticity of operators

Show that the position and momentum operators in the position representation are hermitian.

Method. We need to show that the operators satisfy eqn 1.21a. In some cases (the position operator, for instance), the hermiticity is obvious as soon as the integral is written down. When a differential operator is used, it may be necessary to use integration by parts at some stage in the argument to transfer the differentiation from one function to another:

$$\int u \, \mathrm{d}v = uv - \int v \, \mathrm{d}u$$

Answer. That the position operator is hermitian is obvious from inspection:

$$\int f_m^* x f_n \, \mathrm{d}\tau = \int f_n x f_m^* \, \mathrm{d}\tau = \left\{ \int f_n^* x f_m \, \mathrm{d}\tau \right\}^*$$

We have used the facts that $(f^*)^* = f$ and x is real. The demonstration of the hermiticity of p_x, a differential operator in the position representation, involves an integration by parts:

$$\begin{aligned}\int f_m^* p_x f_n \, \mathrm{d}x &= \int f_m^* \frac{\hbar}{\mathrm{i}} \frac{\mathrm{d}}{\mathrm{d}x} f_n \, \mathrm{d}x = \frac{\hbar}{\mathrm{i}} \int f_m^* \, \mathrm{d}f_n \\ &= \frac{\hbar}{\mathrm{i}} \left\{ f_m^* f_n - \int f_n \mathrm{d}f_m^* \right\} \Bigg|_{x=-\infty}^{x=\infty} \\ &= \frac{\hbar}{\mathrm{i}} \left\{ f_m^* f_n \big|_{x=-\infty}^{x=\infty} - \int_{-\infty}^{\infty} f_n \frac{\mathrm{d}}{\mathrm{d}x} f_m^* \, \mathrm{d}x \right\}\end{aligned}$$

The first term on the right is zero (because when $|x|$ is infinite, a normalizable function must be vanishingly small; see Section 1.12). Therefore,

$$\int f_m^* p_x f_n \, \mathrm{d}x = -\frac{\hbar}{\mathrm{i}} \int f_n \frac{\mathrm{d}}{\mathrm{d}x} f_m^* \, \mathrm{d}x$$
$$= \left\{ \int f_n^* \frac{\hbar}{\mathrm{i}} \frac{\mathrm{d}}{\mathrm{d}x} f_m \, \mathrm{d}x \right\}^* = \left\{ \int f_n^* p_x f_m \, \mathrm{d}x \right\}^*$$

Hence, the operator is hermitian.

Self-test 1.5. Show that the two operators are hermitian in the momentum representation.

As we shall now see, the property of hermiticity has far-reaching implications. First, we shall establish the following property:

Property 1. The eigenvalues of hermitian operators are real.

Proof 1.1 The reality of eigenvalues

Consider the eigenvalue equation

$$\Omega|\omega\rangle = \omega|\omega\rangle$$

The ket $|\omega\rangle$ denotes an **eigenstate** of the operator Ω in the sense that the corresponding function f_ω is an eigenfunction of the operator Ω and we are labelling the eigenstates with the eigenvalue ω of the operator Ω. It is often convenient to use the eigenvalues as labels in this way. Multiplication from the left by $\langle\omega|$ results in the equation

$$\langle\omega|\Omega|\omega\rangle = \omega\langle\omega|\omega\rangle = \omega$$

taking $|\omega\rangle$ to be normalized. Now take the complex conjugate of both sides:

$$\langle\omega|\Omega|\omega\rangle^* = \omega^*$$

However, by hermiticity, $\langle\omega|\Omega|\omega\rangle^* = \langle\omega|\Omega|\omega\rangle$. Therefore, it follows that $\omega = \omega^*$, which implies that the eigenvalue ω is real.

The second property we shall prove is as follows:

Property 2. Eigenfunctions corresponding to different eigenvalues of an hermitian operator are orthogonal.

That is, if we have two eigenfunctions of an hermitian operator Ω with eigenvalues ω and ω', with $\omega \neq \omega'$, then $\langle\omega|\omega'\rangle = 0$. For example, it follows at once that all the eigenfunctions of a harmonic oscillator (Section 2.16) are mutually orthogonal, for as we shall see each one corresponds to a different energy (the eigenvalue of the hamiltonian, an hermitian operator).

Proof 1.2 The orthogonality of eigenstates

Suppose we have two eigenstates $|\omega\rangle$ and $|\omega'\rangle$ that satisfy the following relations:

$$\Omega|\omega\rangle = \omega|\omega\rangle \quad \text{and} \quad \Omega|\omega'\rangle = \omega'|\omega'\rangle$$

Then multiplication of the first relation by $\langle\omega'|$ and the second by $\langle\omega|$ gives

$$\langle\omega'|\Omega|\omega\rangle = \omega\langle\omega'|\omega\rangle \quad \text{and} \quad \langle\omega|\Omega|\omega'\rangle = \omega'\langle\omega|\omega'\rangle$$

Now take the complex conjugate of the second relation and subtract it from the first while using Property 1 ($\omega'^* = \omega'$):

$$\langle\omega'|\Omega|\omega\rangle - \langle\omega|\Omega|\omega'\rangle^* = \omega\langle\omega'|\omega\rangle - \omega'\langle\omega|\omega'\rangle^*$$

Because Ω is hermitian, the left-hand side of this expression is zero; so (noting that ω' is real and using $\langle\omega|\omega'\rangle^* = \langle\omega'|\omega\rangle$ as explained earlier) we arrive at

$$(\omega - \omega')\langle\omega'|\omega\rangle = 0$$

However, because the two eigenvalues are different, the only way of satisfying this relation is for $\langle\omega'|\omega\rangle = 0$, as was to be proved.

The postulates of quantum mechanics

Now we turn to an application of the preceding material, and move into the foundations of quantum mechanics. The postulates we use as a basis for quantum mechanics are by no means the most subtle that have been devised, but they are strong enough for what we have to do.

1.9 States and wavefunctions

The first postulate concerns the information we can know about a state:

Postulate 1. The state of a system is fully described by a function $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, t)$.

In this statement, $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots$ are the spatial coordinates of particles 1, 2, ... that constitute the system and t is the time. The function Ψ (uppercase psi) plays a central role in quantum mechanics, and is called the **wavefunction** of the system (more specifically, the time-dependent wavefunction). When we are not interested in how the system changes in time we shall denote the wavefunction by a lowercase psi as $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)$ and refer to it as the time-independent wavefunction. The state of the system may also depend on some internal variable of the particles (their spin states); we ignore that for now and return to it later. By 'describe' we mean that the wavefunction contains information about all the properties of the system that are open to experimental determination.

We shall see that the wavefunction of a system will be specified by a set of labels called **quantum numbers**, and may then be written $\psi_{a,b,\ldots}$, where $a, b, \ldots$ are the quantum numbers. The values of these quantum numbers specify the wavefunction and thus allow the values of various physical observables to be calculated. It is often convenient to refer to the **state** of the system without referring to the corresponding wavefunction; the state is specified by listing the values of the quantum numbers that define it.

1.10 The fundamental prescription

The next postulate concerns the selection of operators:

Postulate 2. Observables are represented by hermitian operators chosen to satisfy the commutation relations

$$[q, p_{q'}] = \mathrm{i}\hbar\delta_{qq'} \qquad [q, q'] = 0 \quad [p_q, p_{q'}] = 0$$

where q and q' each denote one of the coordinates x, y, z and p_q and $p_{q'}$ the corresponding linear momenta.

The requirement that the operators are hermitian ensures that the observables have real values (see below). Each commutation relation is a basic, unprovable, and underivable postulate. Postulate 2 is the basis of the selection of the form of the operators in the position and momentum representations for all observables that depend on the position and the momentum.[2] Thus, if we define the position representation as the representation in which the position operator is multiplication by the position coordinate, then as we saw in Example 1.3, it follows that the momentum operator must involve differentiation with respect to x, as specified earlier. Similarly, if the momentum representation is defined as the representation in which the linear momentum is represented by multiplication, then the form of the position operator is fixed as a derivative with respect to the linear momentum. The coordinates x, y, and z commute with each other as do the linear momenta p_x, p_y, and p_z.

1.11 The outcome of measurements

The next postulate brings together the wavefunction and the operators and establishes the link between formal calculations and experimental observations:

Postulate 3. When a system is described by a wavefunction ψ, the mean value of the observable Ω in a series of measurements is equal to the expectation value of the corresponding operator.

The **expectation value** of an operator Ω for an arbitrary state ψ is denoted $\langle\Omega\rangle$ and defined as

$$\langle\Omega\rangle = \frac{\int \psi^*\Omega\psi \, \mathrm{d}\tau}{\int \psi^*\psi \mathrm{d}\tau} = \frac{\langle\psi|\Omega|\psi\rangle}{\langle\psi|\psi\rangle} \tag{1.23}$$

If the wavefunction is chosen to be normalized to 1, then the expectation value is simply

$$\langle\Omega\rangle = \int \psi^*\Omega\psi \, \mathrm{d}\tau = \langle\psi|\Omega|\psi\rangle \tag{1.24}$$

Unless we state otherwise, from now on we shall assume that the wavefunction is normalized to 1.

---

[2] This prescription excludes intrinsic observables, such as spin (Section 4.8).

The meaning of Postulate 3 can be unravelled as follows. First, suppose that ψ is an eigenfunction of Ω with eigenvalue ω; then

$$\langle\Omega\rangle = \int \psi^* \Omega \psi \, \mathrm{d}\tau = \int \psi^* \omega \psi \, \mathrm{d}\tau = \omega \int \psi^* \psi \, \mathrm{d}\tau = \omega \qquad (1.25)$$

That is, a series of experiments on identical systems to determine Ω will give the average value ω (a real quantity, because Ω is hermitian). Now suppose that although the system is in an eigenstate of the hamiltonian it is not in an eigenstate of Ω. In this case the wavefunction can be expressed as a linear combination of eigenfunctions of Ω:

$$\psi = \sum_n c_n \psi_n \quad \text{where} \quad \Omega\psi_n = \omega_n \psi_n$$

In this case, the expectation value is

$$\begin{aligned}\langle\Omega\rangle &= \int \left(\sum_m c_m \psi_m\right)^* \Omega \left(\sum_n c_n \psi_n\right) \mathrm{d}\tau = \sum_{m,n} c_m^* c_n \int \psi_m^* \Omega \psi_n \, \mathrm{d}\tau \\ &= \sum_{m,n} c_m^* c_n \omega_n \int \psi_m^* \psi_n \, \mathrm{d}\tau\end{aligned}$$

Because the eigenfunctions form an orthonormal set, the integral in the last expression is zero if $n \neq m$, is 1 if $n = m$, and the double sum reduces to a single sum:

$$\langle\Omega\rangle = \sum_n c_n^* c_n \omega_n \int \psi_n^* \psi_n \, \mathrm{d}\tau = \sum_n c_n^* c_n \omega_n = \sum_n |c_n|^2 \omega_n \qquad (1.26)$$

That is, the expectation value is a weighted sum of the eigenvalues of Ω, the contribution of a particular eigenvalue to the sum being determined by the square modulus of the corresponding coefficient in the expansion of the wavefunction.

We can now interpret the difference between eqns 1.25 and 1.26 in the form of a subsidiary postulate:

Postulate 3′. When ψ is an eigenfunction of the operator Ω, the determination of the property Ω always yields one result, namely the corresponding eigenvalue ω. The expectation value will simply be the eigenvalue ω. When ψ is not an eigenfunction of Ω, a single measurement of the property yields a single outcome which is one of the eigenvalues of Ω, and the probability that a particular eigenvalue ω_n is measured is equal to $|c_n|^2$, where c_n is the coefficient of the eigenfunction ψ_n in the expansion of the wavefunction.

One measurement can give only one result: a pointer can indicate only one value on a dial at any instant. A series of determinations can lead to a series of results with some mean value. The subsidiary postulate asserts that a measurement of the observable Ω always results in the pointer indicating one of the eigenvalues of the corresponding operator. If the function that describes the state of the system is an eigenfunction of Ω, then every pointer reading is precisely ω and the mean value is also ω. If the system has been prepared in a state that is not an eigenfunction of Ω, then different measurements give different values, but every individual measurement is one of the eigenvalues of

Ω, and the probability that a particular outcome ω_n is obtained is determined by the value of $|c_n|^2$. In this case, the mean value of all the observations is the weighted average of the eigenvalues. Note that in either case, the hermiticity of the operator guarantees that the observables will be real.

Example 1.6 How to use Postulate 3′.

An operator A has eigenfunctions $f_1, f_2, \ldots, f_n$ with corresponding eigenvalues $a_1, a_2, \ldots, a_n$. The state of a system is described by a normalized wavefunction ψ given by

$$\psi = \tfrac{1}{2}f_1 - \left(\tfrac{3}{8}\right)^{1/2} f_2 + \left(\tfrac{3}{8}\mathrm{i}\right)^{1/2} f_3$$

What will be the outcome of measuring the observable A?

Method. First, we need to determine if ψ is an eigenfunction of the operator A. If it is, then we shall obtain the same eigenvalue of A in every measurement. If it is not, we shall obtain different values in a series of different measurements. In the latter case, if we have an expression for ψ in terms of the eigenfunctions of A, then we can determine what different values are possible, the probabilities of obtaining them, and the average value from a large series of measurements.

Answer. To test whether ψ is an eigenfunction of the operator A we proceed as follows:

$$\begin{aligned} A\psi &= A\left[\tfrac{1}{2}f_1 - \left(\tfrac{3}{8}\right)^{1/2} f_2 + \left(\tfrac{3}{8}\,\mathrm{i}\right)^{1/2} f_3\right] \\ &= \tfrac{1}{2}a_1 f_1 - \left(\tfrac{3}{8}\right)^{1/2} a_2 f_2 + \left(\tfrac{3}{8}\,\mathrm{i}\right)^{1/2} a_3 f_3 \neq \text{constant} \times \psi \end{aligned}$$

Therefore, ψ is not an eigenfunction of A. However, because ψ is a linear combination of f_1, f_2, and f_3 we will obtain, in different measurements, the values a_1, a_2, and a_3 (the eigenvalues of the eigenfunctions of A that contribute to ψ). The probabilities of obtaining a_1, a_2, and a_3 are, respectively, $\tfrac{1}{4}$, $\tfrac{3}{8}$, and $\tfrac{3}{8}$. The average value, given by eqn 1.26, is

$$\langle A \rangle = \tfrac{1}{4}a_1 + \tfrac{3}{8}a_2 + \tfrac{3}{8}a_3$$

Comment. The normalization of ψ is reflected in the fact that the probabilities sum to 1. Because the eigenfunctions $f_4, f_5, \ldots$ do not contribute here to ψ, there is zero probability of finding $a_4, a_5, \ldots$.

Self-test 1.6. Repeat the problem using $\psi = \tfrac{1}{3}f_2 + \left(\tfrac{7}{9}\right)^{1/2} f_4 - \tfrac{1}{3}\mathrm{i}f_5$.

$[\langle A \rangle = \tfrac{1}{9}a_2 + \tfrac{7}{9}a_4 + \tfrac{1}{9}a_5]$

1.12 The interpretation of the wavefunction

The next postulate concerns the interpretation of the wavefunction itself, and is commonly called the **Born interpretation**:

Postulate 4. The probability that a particle will be found in the volume element $\mathrm{d}\tau$ at the point $\boldsymbol{r}$ is proportional to $|\psi(\boldsymbol{r})|^2\mathrm{d}\tau$.

As we have already remarked, in one dimension the volume element is dx. In three dimensions the volume element is dxdydz. It follows from this interpretation that $|\psi(\boldsymbol{r})|^2$ is a **probability density**, in the sense that it yields a probability when multiplied by the volume dτ of an infinitesimal region. The wavefunction itself is a **probability amplitude**, and has no direct physical meaning. Note that whereas the probability density is real and non-negative, the wavefunction may be complex and negative. It is usually convenient to use a normalized wavefunction; then the Born interpretation becomes an equality rather than a proportionality. The implication of the Born interpretation is that the wavefunction should be square-integrable; that is

$$\int |\psi|^2 \, \mathrm{d}\tau < \infty$$

because there must be a finite probability of finding the particle somewhere in the whole of space (and that probability is 1 for a normalized wavefunction). This postulate in turn implies that $\psi \to 0$ as $x \to \pm\infty$, for otherwise the integral of $|\psi|^2$ would be infinite. We shall make frequent use of this implication throughout the text.

1.13 The equation for the wavefunction

The final postulate concerns the dynamical evolution of the wavefunction with time:

Postulate 5. The wavefunction $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, t)$ evolves in time according to the equation

$$\mathrm{i}\hbar \frac{\partial \Psi}{\partial t} = H\Psi \tag{1.27}$$

This partial differential equation is the celebrated **Schrödinger equation** introduced by Erwin Schrödinger in 1926. At this stage, we are treating the equation as an unmotivated postulate. However, in Section 1.24 we shall advance arguments in support of its plausibility. The operator H in the Schrödinger equation is the hamiltonian operator for the system, the operator corresponding to the total energy. For example, by using the expression in eqn 1.12, we obtain the time-dependent Schrödinger equation in one dimension (x) with a time-independent potential energy for a single particle:

$$\mathrm{i}\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi \tag{1.28}$$

We shall have a great deal to say about the Schrödinger equation and its solutions in the rest of the text.

1.14 The separation of the Schrödinger equation

The Schrödinger equation can often be separated into equations for the time and space variation of the wavefunction. The separation is possible when the potential energy is independent of time.

In one dimension the equation has the form

$$H\Psi = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi = \mathrm{i}\hbar\frac{\partial\Psi}{\partial t}$$

Equations of this form can be solved by the technique of **separation of variables**, in which a trial solution takes the form

$$\Psi(x,t) = \psi(x)\theta(t)$$

When this substitution is made, we obtain

$$-\frac{\hbar^2}{2m}\theta\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi\theta = \mathrm{i}\hbar\psi\frac{\mathrm{d}\theta}{\mathrm{d}t}$$

Division of both sides of this equation by $\psi\theta$ gives

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x) = \mathrm{i}\hbar\frac{1}{\theta}\frac{\mathrm{d}\theta}{\mathrm{d}t}$$

Only the left-hand side of this equation is a function of x, so when x changes, only the left-hand side can change. But as the left-hand side is equal to the right-hand side, and the latter does not change, the left-hand side must be equal to a constant. Because the dimensions of the constant are those of an energy (the same as those of V), we shall write it E. It follows that the time-dependent equation separates into the following two differential equations:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi \tag{1.29a}$$

$$\mathrm{i}\hbar\frac{\mathrm{d}\theta}{\mathrm{d}t} = E\theta \tag{1.29b}$$

The second of these equations has the solution

$$\theta \propto \mathrm{e}^{-\mathrm{i}Et/\hbar} \tag{1.30}$$

Therefore, the complete wavefunction ($\Psi = \psi\theta$) has the form

$$\Psi(x,t) = \psi(x)\mathrm{e}^{-\mathrm{i}Et/\hbar} \tag{1.31}$$

The constant of proportionality in eqn 1.30 has been absorbed into the normalization constant for ψ. The time-independent wavefunction satisfies eqn 1.29a, which may be written in the form

$$H\psi = E\psi$$

This expression is the **time-independent Schrödinger equation**, on which much of the following development will be based.

This analysis stimulates several remarks. First, eqn 1.29a has the form of a standing-wave equation. Therefore, so long as we are interested only in the spatial dependence of the wavefunction, it is legitimate to regard the time-independent Schrödinger equation as a wave equation. Second, when the potential energy of the system does not depend on the time, and the system is in a state of energy E, it is a very simple matter to construct the time-dependent wavefunction from the time-independent wavefunction simply by multiplying the latter by $e^{-iEt/\hbar}$. The time dependence of such a wavefunction is simply a modulation of its phase, because we can write

$$e^{-iEt/\hbar} = \cos(Et/\hbar) - i\sin(Et/\hbar)$$

It follows that the time-dependent factor oscillates periodically from 1 to $-i$ to -1 to i and back to 1 with a frequency E/h and period h/E. This behaviour is depicted in Fig. 1.1. Therefore, to imagine the time-variation of a wavefunction of a definite energy, think of it as flickering from positive through imaginary to negative amplitudes with a frequency proportional to the energy.

We have used Euler's relation,

$$e^{ix} = \cos x + i\sin x$$

as well as $\sin(-x) = -\sin(x)$ and $\cos(-x) = \cos(x)$.

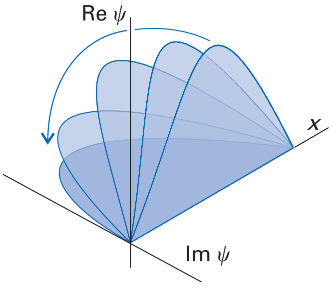

Fig. 1.1 A wavefunction corresponding to an energy E rotates in the complex plane from real to imaginary and back to real at a circular frequency $E/\hbar$.

Although the phase of a wavefunction Ψ with definite energy E oscillates in time, the product $\Psi^*\Psi$ (or $|\Psi|^2$) remains constant:

$$\Psi^*\Psi = (\psi^* e^{iEt/\hbar})(\psi e^{-iEt/\hbar}) = \psi^*\psi$$

States of this kind are called **stationary states**. From what we have seen so far, it follows that systems with a specific, precise energy and in which the potential energy does not vary with time are in stationary states. Although their wavefunctions flicker from one phase to another in repetitive manner, the value of $\Psi^*\Psi$ remains constant in time.

The specification and evolution of states

Let us suppose for the moment that the state of a system can be specified as $|a,b,\ldots\rangle$, where each of the eigenvalues $a, b, \ldots$ corresponds to the operators representing different observables $A, B, \ldots$ of the system. If the system is in the state $|a,b,\ldots\rangle$, then when we measure the property A we shall get exactly a as an outcome, and likewise for the other properties. But can a state be specified *arbitrarily* fully? That is, can it be *simultaneously* an eigenstate of all possible observables $A, B, \ldots$ without restriction? With this question we are moving into the domain of the uncertainty principle.

1.15 Simultaneous observables

As a first step, we establish the conditions under which two observables may be specified simultaneously with arbitrary precision. That is, we establish the conditions for a state $|\psi\rangle$ corresponding to the wavefunction ψ to be simultaneously an eigenstate of two operators A and B. In fact, we shall prove the following:

Property 3. If two observables are to have simultaneously precisely defined values, then their corresponding operators must commute.

That is, AB must equal BA, or equivalently, $[A,B] = 0$.

Proof 1.3 Simultaneous eigenstates

Assume that $|\psi\rangle$ *is* an eigenstate of both operators: $A|\psi\rangle = a|\psi\rangle$ and $B|\psi\rangle = b|\psi\rangle$. That being so, we can write the following chain of relations:

$$AB|\psi\rangle = Ab|\psi\rangle = bA|\psi\rangle = ba|\psi\rangle = ab|\psi\rangle = aB|\psi\rangle = Ba|\psi\rangle = BA|\psi\rangle$$

Therefore, if $|\psi\rangle$ is an eigenstate of both A and B, and if the same is true for all functions ψ of a complete set, then it is certainly necessary that $[A,B]=0$. However, does the condition $[A,B]=0$ actually guarantee that A and B have simultaneous eigenvalues? In other words, if $A|\psi\rangle=a|\psi\rangle$ and $[A,B]=0$, can we be confident that $|\psi\rangle$ is also an eigenstate of B? We confirm this as follows. Because $A|\psi\rangle=a|\psi\rangle$, we can write

$$BA|\psi\rangle = Ba|\psi\rangle = aB|\psi\rangle$$

Because A and B commute, the first term on the left is equal to $AB|\psi\rangle$. Therefore, this relation has the form

$$A(B|\psi\rangle) = a(B|\psi\rangle)$$

However, on comparison of this eigenvalue equation with $A|\psi\rangle=a|\psi\rangle$, we can conclude that $B|\psi\rangle \propto |\psi\rangle$, or $B|\psi\rangle=b|\psi\rangle$, where b is a coefficient of proportionality. That is, $|\psi\rangle$ is an eigenstate of B, as was to be proved.

It follows from this discussion that we are now in a position to determine which observables may be specified simultaneously. All we need do is to inspect the commutator $[A,B]$: if it is zero, then A and B may be specified simultaneously.

Example 1.7 How to decide whether observables may be specified simultaneously

What restrictions are there on the simultaneous specification of the position and the linear momentum of a particle?

Method. To answer this question we have to determine whether the position coordinates can be specified simultaneously, whether the momentum components can be specified simultaneously, and whether the position and momentum can be specified simultaneously. The answer is found by examining the commutators (Section 1.10; Postulate 2) of the corresponding operators.

Answer. All three position operators x, y, and z commute with one another, so there is no constraint on the complete specification of position. The same is true of the three operators for the components of linear momentum. So all three components can be determined simultaneously. However, x and p_x do not commute, so these two observables cannot be specified simultaneously, and likewise for (y,p_y) and (z,p_z). The consequent pattern of permitted simultaneous specifications is illustrated in Fig. 1.2.

Self-test 1.7. Can the kinetic energy and the linear momentum be specified simultaneously?

[Yes]

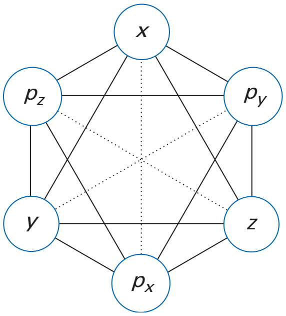

Fig. 1.2 A summary of the position and momentum observables that can be specified simultaneously with arbitrary precision (joined by solid lines) and those that cannot (joined by dotted lines).

Pairs of observables that *cannot* be determined simultaneously are said to be **complementary**. Thus, position along the x-axis and linear momentum parallel to that axis are complementary observables. Classical physics made the mistake of presuming that there was no restriction on the simultaneous determination of observables, that there was no complementarity. Quantum mechanics forces us to choose a selection of all possible observables if we seek to specify a state fully.

1.16 The uncertainty principle

Although we cannot specify the eigenvalues of two non-commuting operators simultaneously, it is possible to give up precision in the specification of one property in order to acquire greater precision in the specification of a complementary property. For example, if we know the location of a particle to within a range Δx, then we can specify the linear momentum parallel to x to within a range Δp_x subject to the constraint

$$\Delta x \Delta p_x \geq \tfrac{1}{2}\hbar \tag{1.32}$$

Thus, as Δx increases (an increased uncertainty in x), the uncertainty in p_x can decrease, and vice versa. This relation between the uncertainties in the specification of two complementary observables is a special case of the **uncertainty principle** proposed by Werner Heisenberg in 1927. A very general form of the uncertainty principle was developed by H.P. Robertson in 1929 for two observables A and B:

$$\Delta A \Delta B \geq \tfrac{1}{2}|\langle [A, B]\rangle| \tag{1.33}$$

where the **root mean square deviation** of A is defined as

$$\Delta A = \left\{\langle A^2\rangle - \langle A\rangle^2\right\}^{1/2} \tag{1.34}$$

This is an exact and precise form of the uncertainty principle: the precise form of the 'uncertainties' ΔA and ΔB are given (they are root mean square deviations) and the right-hand side of eqn 1.33 gives a precise lower bound on the value of the product of uncertainties.

Proof 1.4 The uncertainty principle

Suppose that the observables A and B obey the commutation relation $[A,B] = \mathrm{i}C$. (The imaginary i is included for future convenience. For $A = x$ and $B = p_x$ it follows from the fundamental commutation relation that $C = \hbar$.) We shall suppose that the system is prepared in a normalized but otherwise arbitrary state $|\psi\rangle$, which is not necessarily an eigenstate of either operator A or B. The mean values of the observables A and B are expressed by the expectation values

$$\langle A\rangle = \langle\psi|A|\psi\rangle \text{ and } \langle B\rangle = \langle\psi|B|\psi\rangle$$

The operators for the spread of individual determinations of A and B around their mean values are

$$\delta A = A - \langle A\rangle \quad \text{and} \quad \delta B = B - \langle B\rangle$$

It is easy to verify that the commutation relation for these deviation operators is

$$[\delta A, \delta B] = [A - \langle A \rangle, B - \langle B \rangle] = [A, B] = \mathrm{i}C$$

because the expectation values $\langle A \rangle$ and $\langle B \rangle$ are simple numbers and commute with operators.

Now consider the properties of the following integral, where α is a real but otherwise arbitrary number:

$$I = \int |(\alpha \delta A - \mathrm{i}\delta B)\psi|^2 \,\mathrm{d}\tau$$

The integral I is clearly non-negative as the integrand is positive everywhere. This integral can be developed as follows:

$$\begin{aligned} I &= \int \{(\alpha\,\delta A - \mathrm{i}\delta B)\psi\}^* \{(\alpha\,\delta A - \mathrm{i}\delta B)\psi\}\,\mathrm{d}\tau \\ &= \int \psi^*(\alpha\delta A + \mathrm{i}\delta B)(\alpha\delta A - \mathrm{i}\delta B)\psi\,\mathrm{d}\tau \end{aligned}$$

In the second step we have used the hermitian character of the two operators (as expressed in eqn 1.21b). At this point it is convenient to recognize that the final expression is an expectation value, and to write it in the form

$$I = \langle(\alpha\delta A + \mathrm{i}\delta B)(\alpha\delta A - \mathrm{i}\delta B)\rangle$$

This expression expands to

$$I = \alpha^2\langle(\delta A)^2\rangle + \langle(\delta B)^2\rangle - \mathrm{i}\alpha\langle\delta A\delta B - \delta B\delta A\rangle = \alpha^2\langle(\delta A)^2\rangle + \langle(\delta B)^2\rangle + \alpha\langle C\rangle$$

In the second step we have recognized the presence of the commutator. The integral is still non-negative, even though that is no longer obvious. At this point we recognize that I has the general form of a quadratic expression in α, and so express it as a square:

$$I = \langle(\delta A)^2\rangle\left(\alpha + \frac{\langle C\rangle}{2\langle(\delta A)^2\rangle}\right)^2 + \langle(\delta B)^2\rangle - \frac{\langle C\rangle^2}{4\langle(\delta A)^2\rangle}$$

(We have 'completed the square' for the first term.) This expression is still non-negative whatever the value of α, and remains non-negative even if we choose a value for α that corresponds to the minimum value of I. That value of α is the value that ensures that the first term on the right is zero (because that term always supplies a positive contribution to I). Therefore, with that choice of α, we obtain

$$I = \langle(\delta B)^2\rangle - \frac{\langle C\rangle^2}{4\langle(\delta A)^2\rangle} \geq 0$$

The inequality rearranges to

$$\langle(\delta A)^2\rangle\langle(\delta B)^2\rangle \geq \tfrac{1}{4}\langle C\rangle^2$$

The expectation values on the left can be put into a simpler form by writing them as follows:

$$\begin{aligned} \langle(\delta A)^2\rangle &= \langle(A - \langle A\rangle)^2\rangle \\ &= \langle A^2 - 2A\langle A\rangle + \langle A\rangle^2\rangle = \langle A^2\rangle - 2\langle A\rangle\langle A\rangle + \langle A\rangle^2 \\ &= \langle A^2\rangle - \langle A\rangle^2 \end{aligned}$$

We see that $\langle(\delta A)^2\rangle$ is the mean square deviation of A from its mean value (and likewise for B).

Then the inequality becomes

$$\Delta A \Delta B \geq \tfrac{1}{2}|\langle C\rangle|$$

Then, because $[A, B] = \mathrm{i}C$, we obtain the final form of the uncertainty principle in eqn 1.33.

1.17 Consequences of the uncertainty principle

The first point to note is that the uncertainty principle is consistent with Property 3, for if A and B commute, then C is zero and there is no constraint on the uncertainties: there is no inconsistency in having both $\Delta A = 0$ and $\Delta B = 0$. On the other hand, when A and B do not commute, the values of ΔA and ΔB are related. For instance, while it may be possible to prepare a system in a state in which $\Delta A = 0$, the uncertainty then implies that ΔB must be infinite in order to ensure that $\Delta A\Delta B$ is not less than $\tfrac{1}{2}|\langle[\mathrm{A,B}]\rangle|$. In the particular case of the simultaneous specification of x and p_x, as we have seen, $[x, p_x] = \mathrm{i}\hbar$, so the lower bound on the simultaneous specification of these two complementary observables is $\tfrac{1}{2}\hbar$.

Example 1.8 How to calculate the joint uncertainty in two observables

A particle was prepared in a state with wavefunction $\psi = N\exp(-x^2/2\Gamma)$, where $N = (1/\pi\Gamma)^{1/4}$. Evaluate Δx and Δp_x, and confirm that the uncertainty principle is satisfied.

Method. We must evaluate the expectation values $\langle x\rangle$, $\langle x^2\rangle$, $\langle p_x\rangle$, and $\langle p_x^2\rangle$ by integration and then combine their values to obtain Δx and Δp_x. There are two short cuts. For $\langle x\rangle$, we note that ψ is symmetrical around $x = 0$, and so $\langle x\rangle = 0$. The value of $\langle p_x\rangle$ can be obtained by noting that p_x is an imaginary hermitian operator and ψ is real. Because hermiticity implies that $\langle p_x\rangle^* = \langle p_x\rangle$ whereas the imaginary character of p_x implies that $\langle p_x\rangle^* = -\langle p_x\rangle$, we can conclude that $\langle p_x\rangle = 0$. For the remaining integrals we use

$$\int_{-\infty}^{\infty} \mathrm{e}^{-ax^2}\,\mathrm{d}x = \left(\frac{\pi}{a}\right)^{1/2} \text{ and } \int_{-\infty}^{\infty} x^2\mathrm{e}^{-ax^2}\,\mathrm{d}x = \frac{1}{2a}\left(\frac{\pi}{a}\right)^{1/2}$$

Answer. The following integrals are obtained:

$$\langle x^2\rangle = N^2\int_{-\infty}^{\infty} x^2\mathrm{e}^{-x^2/\Gamma}\,\mathrm{d}x = \frac{1}{2}\Gamma$$

$$\begin{aligned}\langle p_x^2\rangle &= N^2\int_{-\infty}^{\infty} \mathrm{e}^{-x^2/2\Gamma}\left(-\hbar^2\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right)\mathrm{e}^{-x^2/2\Gamma}\,\mathrm{d}x \\ &= \hbar^2N^2\left\{\frac{1}{\Gamma}\int_{-\infty}^{\infty}\mathrm{e}^{-x^2/\Gamma}\,\mathrm{d}x - \frac{1}{\Gamma^2}\int_{-\infty}^{\infty}x^2\mathrm{e}^{-x^2/\Gamma}\,\mathrm{d}x\right\} = \frac{\hbar^2}{2\Gamma}\end{aligned}$$

It follows that (because $\langle x\rangle = 0$ and $\langle p_x\rangle = 0$)

$$\Delta x\Delta p_x = \langle x^2\rangle^{1/2}\langle p_x^2\rangle^{1/2} = \tfrac{1}{2}\hbar$$

Comment. In this example, $\Delta x\Delta p_x$ has its minimum permitted value. This is a special feature of 'gaussian' wavefunctions, wavefunctions of the form $\exp(-ax^2)$. A gaussian wavefunction is encountered in the ground state of a harmonic oscillator (see Section 2.16).

Self-test 1.8. Calculate the value of $\Delta x\Delta p_x$ for a wavefunction that is zero everywhere except in a region of space of length L, where it has the form $(2/L)^{1/2}\sin(\pi x/L)$.

$[(\hbar/2(3)^{1/2})(\pi^2-6)^{1/2}]$

The uncertainty principle in the form given in eqn 1.33 can be applied to all pairs of complementary observables. We shall see additional examples in later chapters.

1.18 The uncertainty in energy and time

Finally, it is appropriate at this point to make a few remarks about the so-called **energy–time uncertainty relation**, which is often expressed in the form $\Delta E\Delta t \geq \hbar$ and interpreted as implying a complementarity between energy and time. As we have seen, for this relation to be a true uncertainty relation, it would be necessary for there to be a non-zero commutator for energy and time. However, although the energy operator is well defined (it is the hamiltonian for the system), *there is no operator for time in quantum mechanics*. Time is a *parameter*, not an observable. Therefore, strictly speaking, there is no uncertainty relation between energy and time. In Section 6.18 we shall see the true significance of the energy–time 'uncertainty principle' is that it is a relation between the uncertainty in the energy of a system that has a finite lifetime τ (tau), and is of the form $\delta E \approx \hbar/2\tau$.

1.19 Time-evolution and conservation laws

As well as determining which operators are complementary, the commutator of two operators also plays a role in determining the time-evolution of systems and in particular the time-evolution of the expectation values of observables. The precise relation for operators that do not have an intrinsic dependence on the time (in the sense that $\partial\Omega/\partial t = 0$) is

$$\frac{\mathrm{d}\langle\Omega\rangle}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}\langle[H,\Omega]\rangle \tag{1.35}$$

We see that if the operator for the observable commutes with the hamiltonian, then the expectation value of the operator does not change with time. An observable that commutes with the hamiltonian for the system, and which therefore has an expectation value that does not change with time, is called a **constant of the motion**, and its expectation value is said to be **conserved**.

Proof 1.5 Time evolution

Differentiation of $\langle\Omega\rangle$ with respect to time gives

$$\frac{\mathrm{d}\langle\Omega\rangle}{\mathrm{d}t}=\frac{\mathrm{d}}{\mathrm{d}t}\langle\Psi|\Omega|\Psi\rangle=\int\left(\frac{\partial\Psi^*}{\partial t}\right)\Omega\Psi\,\mathrm{d}\tau+\int\Psi^*\Omega\left(\frac{\partial\Psi}{\partial t}\right)\mathrm{d}\tau$$

because only the state Ψ (not the operator Ω) depends on the time. The Schrödinger equation lets us write

$$\int\Psi^*\Omega\left(\frac{\partial\Psi}{\partial t}\right)\mathrm{d}\tau=\int\Psi^*\Omega\left(\frac{1}{\mathrm{i}\hbar}\right)H\Psi\,\mathrm{d}\tau=\frac{1}{\mathrm{i}\hbar}\int\Psi^*\Omega H\Psi\,\mathrm{d}\tau$$

$$\int\left(\frac{\partial\Psi^*}{\partial t}\right)\Omega\Psi\,\mathrm{d}\tau=-\int\left(\frac{1}{\mathrm{i}\hbar}\right)(H\Psi)^*\Omega\Psi\,\mathrm{d}\tau=-\left(\frac{1}{\mathrm{i}\hbar}\right)\int\Psi^*H\Omega\Psi\,\mathrm{d}\tau$$

In the second line we have used the hermiticity of the hamiltonian (in the form of eqn 1.21b). It then follows, by combining these two expressions, that

$$\frac{\mathrm{d}\langle\Omega\rangle}{\mathrm{d}t}=-\left(\frac{1}{\mathrm{i}\hbar}\right)(\langle H\Omega\rangle-\langle\Omega H\rangle)=\frac{\mathrm{i}}{\hbar}\langle[H,\Omega]\rangle$$

as was to be proved.

As an important example, consider the rate of change of the expectation value of the linear momentum of a particle in a one-dimensional system. The commutator of H and p_x is

$$[H,p_x]=\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+V,\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right]=\frac{\hbar}{\mathrm{i}}\left[V,\frac{\mathrm{d}}{\mathrm{d}x}\right]$$

because the derivatives commute. The remaining commutator can be evaluated by remembering that there is an unwritten function on the right on which the operators operate, and writing

$$\begin{aligned}[H,p_x]\psi&=\frac{\hbar}{\mathrm{i}}\left\{V\frac{\mathrm{d}\psi}{\mathrm{d}x}-\frac{\mathrm{d}(V\psi)}{\mathrm{d}x}\right\}=\frac{\hbar}{\mathrm{i}}\left\{V\frac{\mathrm{d}\psi}{\mathrm{d}x}-V\frac{\mathrm{d}\psi}{\mathrm{d}x}-\frac{\mathrm{d}V}{\mathrm{d}x}\psi\right\}\\&=-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}V}{\mathrm{d}x}\psi\end{aligned}$$

This relation is true for all functions ψ; therefore the commutator itself is

$$[H,p_x]=-\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}V}{\mathrm{d}x}\tag{1.36}$$

It follows that the linear momentum is a constant of the motion if the potential energy does not vary with position, that is when $\mathrm{d}V/\mathrm{d}x=0$. Specifically, we can conclude that the rate of change of the expectation value of linear momentum is

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle p_x\rangle=\frac{\mathrm{i}}{\hbar}\langle[H,p_x]\rangle=-\left\langle\frac{\mathrm{d}V}{\mathrm{d}x}\right\rangle\tag{1.37}$$

Then, because the negative slope of the potential energy is by definition the **force** that is acting ($F = -\mathrm{d}V/\mathrm{d}x$), the rate of change of the expectation value of linear momentum is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle p_x\rangle = \langle F\rangle \tag{1.38}$$

That is, *the rate of change of the expectation value of the linear momentum is equal to the expectation value of the force*. It is also quite easy to prove in the same way that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle = \frac{\langle p_x\rangle}{m} \tag{1.39}$$

which shows that the rate of change of the mean position can be identified with the mean velocity along the x-axis. These two relations jointly constitute **Ehrenfest's theorem**. Ehrenfest's theorem clarifies the relation between classical and quantum mechanics: classical mechanics deals with average values (expectation values); quantum mechanics deals with the underlying details.

Matrices in quantum mechanics

As we have seen, the fundamental commutation relation of quantum mechanics, $[x,p_x] = i\hbar$, implies that x and p_x are to be treated as operators. However, there is an alternative interpretation: that x and p_x should be represented by matrices, for matrix multiplication is also non-commutative. We shall introduce this approach here as it introduces a language that is widely used throughout quantum mechanics even though matrices are not being used explicitly.

1.20 Matrix elements

A **matrix**, $\boldsymbol{M}$, is an array of numbers (which may be complex), called **matrix elements**. Each element is specified by quoting the row (r) and column (c) that it occupies, and denoting the matrix element as M_{rc}. The rules of matrix algebra are set out in *Further information* 23. For our present purposes it is sufficient to emphasize the rule of **matrix multiplication**: the product of two matrices $\boldsymbol{M}$ and $\boldsymbol{N}$ is another matrix $\boldsymbol{P} = \boldsymbol{MN}$ with elements given by the rule

$$P_{rc} = \sum_s M_{rs}N_{sc} \tag{1.40}$$

The order of matrix multiplication is important, and it is essential to note that $\boldsymbol{MN}$ is not necessarily equal to $\boldsymbol{NM}$. Hence, $\boldsymbol{MN} - \boldsymbol{NM}$ is not in general zero. Heisenberg formulated his version of quantum mechanics, which is called **matrix mechanics**, by representing position and linear momentum by the matrices $\boldsymbol{x}$ and $\boldsymbol{p}_x$, and requiring that $\boldsymbol{x}\boldsymbol{p}_x - \boldsymbol{p}_x\boldsymbol{x} = i\hbar\boldsymbol{1}$ where $\boldsymbol{1}$ is the **unit matrix**, a square matrix with all diagonal elements (those for which $r = c$) equal to 1 and all others 0.

Throughout this chapter we have encountered quantities of the form $\langle m|\Omega|n\rangle$. These quantities are commonly abbreviated as Ω_{mn}, which immediately suggests that they are elements of a matrix. For this reason, the Dirac bracket $\langle m|\Omega|n\rangle$ is often called a **matrix element** of the operator Ω. A **diagonal matrix element** Ω_{nn} is then a bracket of the form $\langle n|\Omega|n\rangle$ with the bra and the ket referring to the same state. We shall often encounter sums over products of Dirac brackets that have the form

$$\sum_s \langle r|A|s\rangle\langle s|B|c\rangle$$

If the brackets that appear in this expression are interpreted as matrix elements, then we see that it has the form of a matrix multiplication, and we may write

$$\sum_s \langle r|A|s\rangle\langle s|B|c\rangle = \sum_s A_{rs}B_{sc} = (AB)_{rc} = \langle r|AB|c\rangle \tag{1.41}$$

That is, the sum is equal to the single matrix element (bracket) of the product of operators AB. Comparison of the first and last terms in this line of equations also allows us to write the symbolic relation

$$\sum_s |s\rangle\langle s| = 1 \tag{1.42}$$

This **completeness relation** is exceptionally useful for developing quantum mechanical equations. It is often used in reverse: the matrix element $\langle r|AB|c\rangle$ can always be split into a sum of two factors by regarding it as $\langle r|A1B|c\rangle$ and then replacing the 1 by a sum over a complete set of states of the form in eqn 1.42.

Example 1.9 How to make use of the completeness relation

Use the completeness relation to prove that the eigenvalues of the square of an hermitian operator are non-negative.

Method. We have to prove, for $\Omega^2|\omega\rangle = \omega|\omega\rangle$, that $\omega \geq 0$ if Ω is hermitian. If both sides of the eigenvalue equation are multiplied by $\langle\omega|$, converting it to $\langle\omega|\Omega^2|\omega\rangle = \omega$, we see that the proof requires us to show that the expectation value on the left is non-negative. As it has the form $\langle\omega|\Omega\Omega|\omega\rangle$, it suggests that the completeness relation might provide a way forward. The hermiticity of Ω implies that it will be appropriate to use the property $\langle m|\Omega|n\rangle = \langle n|\Omega|m\rangle^*$ at some stage in the argument.

Answer. The diagonal matrix element $\langle\omega|\Omega^2|\omega\rangle$ can be developed as follows:

$$\begin{aligned}\langle\omega|\Omega^2|\omega\rangle &= \langle\omega|\Omega\Omega|\omega\rangle = \sum_s \langle\omega|\Omega|s\rangle\langle s|\Omega|\omega\rangle \\ &= \sum_s \langle\omega|\Omega|s\rangle\langle\omega|\Omega|s\rangle^* = \sum_s |\langle\omega|\Omega|s\rangle|^2 \geq 0\end{aligned}$$

The final inequality follows from the fact that all the terms in the sum are non-negative.

Self-test 1.9. Show that if $(\Omega f)^* = -\Omega f^*$, then $\langle\Omega\rangle = 0$ for any real function f.

The origin of the completeness relation, which is also known as the **closure relation**, can be demonstrated by the following argument. Suppose we have a complete set of orthonormal states $|s_i\rangle$. Then, by definition of complete, we can expand an arbitrary state $|\psi\rangle$ as a linear combination:

$$|\psi\rangle = \sum_i c_i|s_i\rangle$$

Multiplication from the left by the bra $\langle s_j|$ and use of the orthonormality of the complete basis set gives $c_j = \langle s_j|\psi\rangle$. Thus

$$|\psi\rangle = \sum_i \langle s_i|\psi\rangle|s_i\rangle = \sum_i |s_i\rangle\langle s_i|\psi\rangle$$

which immediately implies the completeness relation.

1.21 The diagonalization of the hamiltonian

The time-independent form of the Schrödinger equation, $H\psi = E\psi$, can be given a matrix interpretation. First, we express $|\psi\rangle$ as a linear combination of a complete set of states $|n\rangle$:

$$H|\psi\rangle = H\sum_n c_n|n\rangle = \sum_n c_n H|n\rangle$$

$$E|\psi\rangle = E\sum_n c_n|n\rangle$$

These two lines are equal to one another. Next, multiply the right-hand sides of the above two equations from the left by an arbitrary bra $\langle m|$ and use the orthonormality of the states to obtain

$$\sum_n c_n\langle m|H|n\rangle = E\sum_n c_n\langle m|n\rangle = Ec_m$$

In matrix notation this equation is

$$\sum_n H_{mn}c_n = Ec_m \tag{1.43}$$

Now suppose that we can find the set of states such that $H_{mn} = 0$ unless $m = n$; that is, when using this set, the hamiltonian has a diagonal matrix. Then this expression becomes

$$H_{mm}c_m = Ec_m \tag{1.44}$$

and the energy E is seen to be the diagonal element of the hamiltonian matrix. In other words, *solving the Schrödinger equation is equivalent to diagonalizing the hamiltonian matrix* (see *Further information* 23). This is yet another link between the Schrödinger and Heisenberg formulations of quantum mechanics. Indeed, it was reported that when Heisenberg was looking for ways of diagonalizing his matrices, the mathematician David Hilbert suggested to him that he should look for the corresponding differential equation instead. Had he done so, Schrödinger's wave mechanics would have been Heisenberg's too.

Example 1.10 How to diagonalize a simple hamiltonian

In a system that consists of only two orthonormal states $|1\rangle$ and $|2\rangle$ (such as electron spin in a magnetic field, when the electron spin can be in one of two orientations), the hamiltonian has the following matrix elements: $H_{11}=\langle 1|H|1\rangle=a$, $H_{22}=\langle 2|H|2\rangle=b$, $H_{12}=d$, $H_{21}=d^*$. For notational simplicity, we shall suppose that d is real, so $d^*=d$. Find the energy levels and the eigenstates of the system.

Method. The energy levels are the eigenvalues of the hamiltonian matrix. We use the procedure explained in *Further information* 23 to find the eigenvalues and eigenstates. We describe the procedure here briefly, specifically for the two-state system. One eigenstate is $|j\rangle=c_1|1\rangle+c_2|2\rangle$ and the other is $|k\rangle=d_1|1\rangle+d_2|2\rangle$. Beginning twice with $H|j\rangle=E|j\rangle$ and multiplying one on the left by $\langle 1|$ and the second on the left by $\langle 2|$, we obtain two equations which in matrix form are

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

There is a (non-trivial, c_1 and c_2 non-zero) solution to this matrix equation only if the determinant of the matrix on the left-hand side vanishes. A similar argument develops if we begin with $H|k\rangle=E|k\rangle$. The two energy eigenvalues are determined from the secular determinant $|\boldsymbol{H}-E\boldsymbol{1}|=0$ and the two energy eigenvalues, denoted $E_\pm$, are the diagonal elements of the matrix $\boldsymbol{E}$. To find the eigenstates, we form the matrix $\boldsymbol{T}$ composed of the two column vectors of the eigenstates:

$$\boldsymbol{T}=\begin{pmatrix} c_1 & d_1 \\ c_2 & d_2 \end{pmatrix}$$

The matrix $\boldsymbol{T}$ satisfies the equation $\boldsymbol{HT}=\boldsymbol{TE}$. The best procedure is to choose the coefficients c_1, c_2, d_1, and d_2 so that the eigenstates are given by $|j\rangle=|1\rangle\cos\zeta+|2\rangle\sin\zeta$ and $|k\rangle=-|1\rangle\sin\zeta+|2\rangle\cos\zeta$, where ζ is a parameter, for this parametrization ensures that the two eigenstates are orthonormal for all values of ζ. After solving the secular determinant equation for the eigenvalues, we form $\boldsymbol{T}^{-1}\boldsymbol{HT}$, equate it to the matrix $\boldsymbol{E}$, and then solve for ζ.

Answer. Because the states $|1\rangle$ and $|2\rangle$ are orthonormal, the secular determinant is

$$\det|\boldsymbol{H}-E\boldsymbol{1}|=\begin{vmatrix} a-E & d \\ d & b-E \end{vmatrix}=(a-E)(b-E)-d^2=0$$

This quadratic equation for E has the roots

$$E_\pm=\tfrac{1}{2}(a+b)\pm\tfrac{1}{2}\{(a-b)^2+4d^2\}^{1/2}=\tfrac{1}{2}(a+b)\pm\Delta$$

where $\Delta=\tfrac{1}{2}\{(a-b)^2+4d^2\}^{1/2}$. These are the eigenvalues, and hence they are the energy levels. We next form the transformation matrix and its reciprocal:

$$\boldsymbol{T}=\begin{pmatrix} \cos\zeta & -\sin\zeta \\ \sin\zeta & \cos\zeta \end{pmatrix}\quad \boldsymbol{T}^{-1}=\begin{pmatrix} \cos\zeta & \sin\zeta \\ -\sin\zeta & \cos\zeta \end{pmatrix}$$

Then construct the following matrix equation:

$$\begin{pmatrix} E_+ & 0 \\ 0 & E_- \end{pmatrix} = \boldsymbol{T}^{-1}\boldsymbol{HT} = \begin{pmatrix} \cos\zeta & \sin\zeta \\ -\sin\zeta & \cos\zeta \end{pmatrix} \begin{pmatrix} a & d \\ d & b \end{pmatrix} \begin{pmatrix} \cos\zeta & -\sin\zeta \\ \sin\zeta & \cos\zeta \end{pmatrix}$$

$$= \begin{pmatrix} a\cos^2\zeta + b\sin^2\zeta + 2d\cos\zeta\sin\zeta & d(\cos^2\zeta - \sin^2\zeta) + (b-a)\cos\zeta\sin\zeta \\ d(\cos^2\zeta - \sin^2\zeta) + (b-a)\cos\zeta\sin\zeta & b\cos^2\zeta + a\sin^2\zeta - 2d\cos\zeta\sin\zeta \end{pmatrix}$$

Consequently, by equating matching off-diagonal elements, we obtain

$$d(\cos^2\zeta - \sin^2\zeta) + (b-a)\ \cos\ \zeta\ \sin\zeta = 0$$

which solves to

$$\zeta = -\tfrac{1}{2}\arctan\left(\frac{2d}{b-a}\right)$$

Comment. The two-level system occurs widely in quantum mechanics, and we shall return to it in Chapter 6. The parametrization of the states in terms of the angle ζ is a very useful device, and we shall encounter it again.

The plausibility of the Schrödinger equation

The Schrödinger equation is properly regarded as a postulate of quantum mechanics, and hence we should not ask for a deeper justification. However, it is often more satisfying to set postulates in the framework of the familiar. In this section we shall see that the Schrödinger equation is a plausible description of the behaviour of matter by going back to the formulation of classical mechanics devised by W.R. Hamilton in the nineteenth century. We shall concentrate on the qualitative aspects of the approach: the calculations supporting these remarks will be found in *Further information* 1.

1.22 The propagation of light

In geometrical optics, light travels in straight lines in a uniform medium, and we know that the physical nature of light is a wave motion. In classical mechanics particles travel in straight lines unless a force is present. Moreover, we know from the experiments performed at the end of the nineteenth century and the start of the twentieth century that particles have a wave character. There are clearly deep analogies here. We shall therefore first establish how, in optics, wave motion can result in straight-line motion, and then argue by analogy about the wave nature of particles.

The basic rule governing light propagation in geometrical optics is **Fermat's principle of least time**. A simple form of the principle is that the path taken by a ray of light through a medium is such that its time of passage is a minimum. As an illustration, consider the relation between the angles of incidence and reflection for light falling on a mirror (Fig. 1.3). The briefest path between source, mirror, and observer is clearly the one corresponding to equal angles of incidence and reflection. In the case of refraction, it is necessary to take into

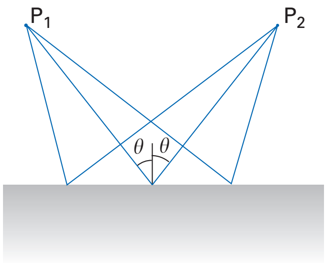

Fig. 1.3 When light reflects from a surface, the angle of reflection is equal to the angle of incidence.

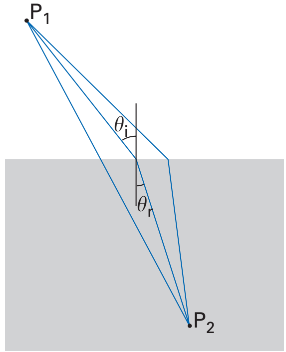

Fig. 1.4 When light is refracted at the interface of two transparent media, the angle of refraction, θ_r, and the angle of incidence, θ_i, are related by Snell's law.

account the different speeds of propagation in the two media. In Fig. 1.4, the geometrically straight path is not necessarily the briefest, because the light travels relatively slowly through the denser medium. The briefest path is in fact easily shown to be the one in which the angles of incidence θ_i and refraction θ_r are related by Snell's law, that $\sin\theta_r/\sin\theta_i = n_1/n_2$. (The refractive indexes n_1 and n_2 enter because the speed of light in a medium of refractive index n is c/n, where c is the speed of light in a vacuum.)

How can the wave nature of light account for this behaviour? Consider the case illustrated in Fig. 1.5, where we are interested in the propagation of light between two fixed points P_1 and P_2. A wave of electromagnetic radiation travelling along some general path A arrives at P_2 with a particular phase that depends on its path length. A wave travelling along a neighbouring path A′ travels a different distance and arrives with a different phase. Path A has very many neighbouring paths, and there is destructive interference between the waves. Hence, an observer concludes that the light does not travel along a path like A. The same argument applies to every path between the two points, with one exception: the straight line path B. The neighbours of B do not interfere destructively with B itself, and it survives. The mathematical reason for this exceptional behaviour can be seen as follows.

The amplitude of a wave at some point x can be written $a\mathrm{e}^{2\pi\mathrm{i}x/\lambda}$, where λ is the wavelength. It follows that the amplitude at P_1 is $a\mathrm{e}^{2\pi\mathrm{i}x_1/\lambda}$ and that at P_2 it is $a\mathrm{e}^{2\pi\mathrm{i}x_2/\lambda}$. The two amplitudes are therefore related as follows:

$$\Psi(P_2) = a\mathrm{e}^{2\pi\mathrm{i}x_2/\lambda} = \mathrm{e}^{2\pi\mathrm{i}(x_2-x_1)/\lambda}\mathrm{e}^{2\pi\mathrm{i}x_1/\lambda} = \mathrm{e}^{2\pi\mathrm{i}(x_2-x_1)/\lambda}\Psi(P_1)$$

This relation between the two amplitudes can be written more simply as

$$\Psi(P_2) = \mathrm{e}^{\mathrm{i}\phi}\Psi(P_1) \quad \text{with } \phi = 2\pi(x_2 - x_1)/\lambda \tag{1.45}$$

The function ϕ is the **phase length** of the straight-line path. The relative phases at P_2 and P_1 for waves that travel by curved paths are related by an expression of the same kind, but with the phase length determined by the length, L, of the path:

$$\phi = \frac{2\pi L}{\lambda} \tag{1.46}$$

Now we consider how the path length varies with the distortion of the path from a straight line. If we distort the path from B to A in Fig. 1.5, ϕ changes as depicted in Fig. 1.6. Obviously, ϕ goes through a minimum at B. Now we arrive at the crux of the argument. Consider the phase length of the paths in the vicinity of A. The phase length of A′ is related to the phase length at A by the following Taylor expansion:

$$\phi(A') = \phi(A) + \left(\frac{\mathrm{d}\phi}{\mathrm{d}s}\right)_A \delta s + \tfrac{1}{2}\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}s^2}\right)_A \delta s^2 + \cdots \tag{1.47}$$

where δs is a measure of the distortion of the path. This expression should be compared with the similar expression for the path lengths of B and its neighbours:

$$\begin{aligned}\phi(B') &= \phi(B) + \left(\frac{\mathrm{d}\phi}{\mathrm{d}s}\right)_B \delta s + \tfrac{1}{2}\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}s^2}\right)_B \delta s^2 + \cdots \\ &= \phi(B) + \tfrac{1}{2}\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}s^2}\right)_B \delta s^2 + \cdots\end{aligned} \tag{1.48}$$

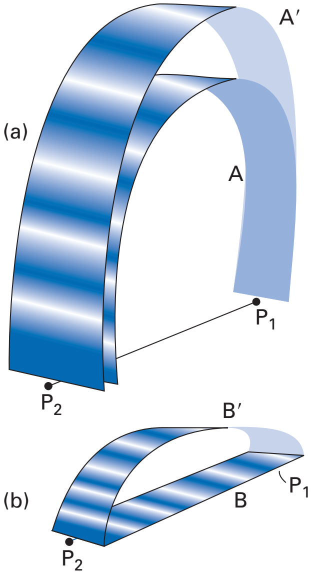

Fig. 1.5 (a) A curved path through a uniform medium has neighbours with significantly different phases at the destination point, and there is destructive interference between them. (b) A straight path between two points has neighbours with almost the same phase, and these paths do not interfere destructively.

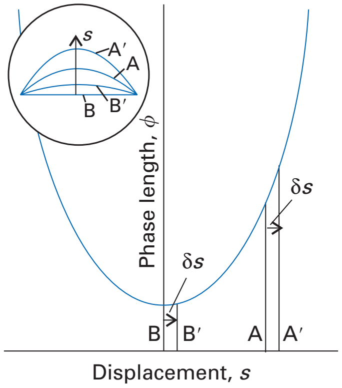

Fig. 1.6 The variation of phase length with displacement from a straight line path. The phase length at A′ differs from that at A by a first-order term; the phase lengths at B and B′ differ only to second order in the displacement.

The term in δs is zero because the first derivative is zero at the minimum of the curve. In other words, to first order in the displacement, *straight line paths have neighbours with the same phase length*. On the other hand, *curved paths have neighbours with different phase lengths*. This difference is the reason why straight line propagation survives whereas curved paths do not: the latter have annihilating neighbours.

Two further points now need to be made. When the medium is not uniform, the wavelength of a wave varies with position. Because $\lambda = v/\nu$, and v, the speed of propagation, is equal to c/n, where the refractive index n varies with position, a more general form of the phase length is

$$\phi = 2\pi \int_{P_1}^{P_2} \frac{dx}{\lambda(x)} = \frac{2\pi\nu}{c} \int_{P_1}^{P_2} n(x)\, dx \qquad (1.49)$$

The same argument applies, but because of the dependence of the refractive index on position, *a curved or kinked path may turn out to correspond to the minimum phase length*, and therefore have, to first order at least, no destructive neighbours. Hence, the path adopted by the light will be curved or kinked. The focusing caused by a lens is a manifestation of this effect.

The second point concerns the stringency of the conclusion that the minimum-phase-length paths have non-destructive neighbours. Because the wavelength of the radiation occurs in the denominator of the expression defining the phase length, waves of short wavelength will have larger phase lengths for a given path than radiation of long wavelength. The variation of phase length with wavelength is indicated in Fig. 1.7. It should be clear that neighbours annihilate themselves much more strongly when the light has a short wavelength than when it is long. Therefore, the rule that light (or any other form of wave motion) propagates itself in straight lines becomes more stringent as its wavelength shortens. Sound waves travel only in approximately straight lines; light waves travel in almost exactly straight lines. Geometrical optics is the limit of infinitely short wavelengths, where the annihilation by neighbours is so effective that the light appears to travel in perfectly straight lines.

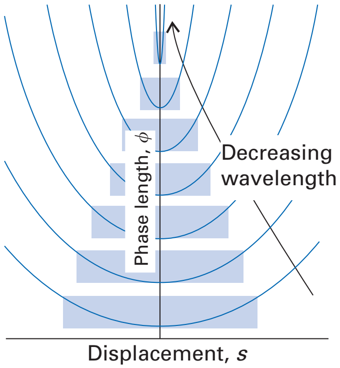

Fig. 1.7 The variation of phase length with wavelength. Interference between neighbours is most acute for short wavelengths. The geometrical limit corresponds to zero wavelength, where even infinitesimal neighbours interfere destructively and completely.

1.23 The propagation of particles

The path taken by a particle in classical mechanics is determined by Newton's laws. However, it turns out that these laws are equivalent to **Hamilton's principle**, which states that particles adopt paths between two given points such that the **action** S associated with the path is a minimum. There is clearly a striking analogy between Fermat's principle of least time and Hamilton's principle of least action.

The formal definition of action is given in *Further information* 1, where it is seen to be an integral taken along the path of the particle, just like the phase length in optics. When we turn to the question of why particles adopt the path of least action, we can hardly avoid the conclusion that the reason must be the same as why light adopts the path of least phase length. But to apply that argument to particles, we have to suppose that particles have an associated wave character. You can see that this attempt to 'explain' classical mechanics leads almost unavoidably to the heart of quantum mechanics and the duality of matter. We have the experimental evidence to encourage us to pursue the analogy; Hamilton did not.

1.24 The transition to quantum mechanics

The hypothesis we now make is that a particle is described by some kind of amplitude Ψ, and that amplitudes at different points are related by an expression of the form $\Psi(\mathrm{P}_2) = \mathrm{e}^{\mathrm{i}\phi}\Psi(\mathrm{P}_1)$. By analogy with optics, we say that the wave is propagated along the path that makes ϕ a minimum. But we also know that in the classical limit, the particle propagates along a path that corresponds to least action. As ϕ is dimensionless (because it appears as an exponent), the constant of proportionality between ϕ and S must have the dimensions of 1/action. Furthermore, we have seen that geometrical optics, the classical form of optics, corresponds to the limit of short wavelengths and very large phase lengths. In classical mechanics, particles travel along 'geometrical' trajectories, corresponding to large ϕ. Hence, the constant with the dimensions of action must be very small. The natural quantity to introduce is Planck's constant, or some small multiple of it. It turns out that agreement with experiment (that is, the correct form of the Schrödinger equation) is obtained if we use $\hbar$; we therefore conclude that we should write $\phi = S/\hbar$.

You should notice the relation between this approach and Heisenberg's. In his, a 0 was replaced by $\hbar$ (in the commutator $[x,p_x]$), and classical mechanics 'evolved' into quantum mechanics. In the approach we are presenting here, a 0 has also been replaced by $\hbar$, for had we wanted *precise* geometrical trajectories, then we would have divided S by 0.

We have arrived at the stage where the amplitude associated with a particle is described by a relation of the form

$$\Psi(\mathrm{P}_2) = \mathrm{e}^{\mathrm{i}S/\hbar}\Psi(\mathrm{P}_1) \tag{1.50}$$

where S is the action associated with the path from P_1 (at x_1, t_1) to P_2 (at x_2, t_2). This expression lets us develop an equation of motion, because we can differentiate Ψ with respect to the time t_2:

$$\left(\frac{\partial\Psi(\mathrm{P}_2)}{\partial t_2}\right) = \frac{\mathrm{i}}{\hbar}\left(\frac{\partial S}{\partial t_2}\right)\mathrm{e}^{\mathrm{i}S/\hbar}\Psi(\mathrm{P}_1) = \frac{\mathrm{i}}{\hbar}\left(\frac{\partial S}{\partial t_2}\right)\Psi(\mathrm{P}_2)$$

One of the results derived in *Further information* 1 is that the rate of change of the action is equal to $-E$, where E is the total energy, $T + V$:

$$\left(\frac{\partial S}{\partial t}\right) = -E \tag{1.51}$$

Therefore, the equation of motion at all points of a trajectory is

$$\left(\frac{\partial\Psi}{\partial t}\right) = -\frac{\mathrm{i}}{\hbar}E\Psi$$

The final step involves replacing E by its corresponding operator H, which then results in the time-dependent Schrödinger equation, eqn 1.27.

There are a few points that are worth noting about this justification. First, we have argued by analogy with classical optics, and have sought to formulate equations that are consistent with classical mechanics. It should therefore not be surprising that the approach might not generate some purely quantum mechanical properties. Indeed, we shall see later that the property of electron spin has been missed, for despite its evocative name, spin has no classical counterpart. A related point is that the derivation has been entirely non-relativistic: at no point have we tried to ensure that space and time are treated on an equal footing. The alignment of relativity and quantum mechanics was achieved by P.A.M. Dirac, who found a way of treating space and time symmetrically, and in the process accounted for the existence of electron spin. Finally, it should be noted that the time-dependent Schrödinger equation is not a wave equation. A wave equation has a second derivative with respect to time, whereas the Schrödinger equation has a first derivative. We have to conclude that the time-dependent Schrödinger equation is therefore a kind of diffusion equation, an equation of the form

$$\frac{\partial f}{\partial t} = D\nabla^2 f \tag{1.52}$$

where f is a probability density and D is a diffusion coefficient. There is perhaps an intuitive satisfaction in the notion that the solutions of the basic equation of quantum mechanics evolve by some kind of diffusion.

PROBLEMS

1.1 Which of the following operations are linear and which are non-linear: (a) integration, (b) extraction of a square root, (c) translation (replacement of x by $x+a$, where a is a constant), (d) inversion (replacement of x by $-x$)?

1.2 Find the operator for position x if the operator for momentum p is taken to be $(\hbar/2m)^{1/2}(A+B)$, with $[A,B]=1$ and all other commutators zero.

1.3 Which of the following functions are eigenfunctions of (a) $\mathrm{d}/\mathrm{d}x$, (b) $\mathrm{d}^2/\mathrm{d}x^2$: (i) e^{ax}, (ii) e^{ax^2}, (iii) x, (iv) x^2, (v) $ax+b$, (vi) $\sin x$?

1.4 Construct quantum mechanical operators in the position representation for the following observables: (a) kinetic energy in one and in three dimensions, (b) the inverse separation, $1/x$, (c) electric dipole moment, (d) z-component of angular momentum, (e) the mean square deviations of the position and momentum of a particle from the mean values.

1.5 Repeat Problem 1.4, but find operators in the momentum representation. *Hint*. The observable $1/x$ should be regarded as x^{-1}; hence the operator required is the inverse of the operator for x.

1.6 In relativistic mechanics, energy and momentum are related by the expression $E^2=p^2c^2+m^2c^4$. Show that when $p^2c^2 \ll m^2c^4$ this expression reduces to $E=p^2/2m+mc^2$. Construct the relativistic analogue of the Schrödinger equation from the relativistic expression. What can be said about the conservation of probability? *Hint:* For the latter part, see Problem 1.36.

1.7 Confirm that the operators (a) $T=-(\hbar^2/2m)(\mathrm{d}^2/\mathrm{d}x^2)$ and (b) $l_z=(\hbar/\mathrm{i})(\mathrm{d}/\mathrm{d}\phi)$ are hermitian. *Hint*. Consider the integrals $\int_0^L \psi_a^* T\psi_b\,\mathrm{d}x$ and $\int_0^{2\pi} \psi_a^* l_z\psi_b\,\mathrm{d}\phi$ and integrate by parts.

1.8 Demonstrate that the linear combinations $A+\mathrm{i}B$ and $A-\mathrm{i}B$ are not hermitian if A and B are hermitian operators.

1.9 Evaluate the expectation values of the operators p_x and p_x^2 for a particle with wavefunction $(2/L)^{1/2}\sin(\pi x/L)$ in the range 0 to L.

1.10 Are the linear combinations $2x-y-z$, $2y-x-z$, $2z-x-y$ linearly independent or not?

1.11 Evaluate the commutators (a) $[x,y]$, (b) $[p_x,p_y]$, (c) $[x,p_x]$, (d) $[x^2,p_x]$, (e) $[x^n,p_x]$.

1.12 Evaluate the commutators (a) $[(1/x),p_x]$, (b) $[(1/x), p_x^2]$, (c) $[xp_y - yp_x, yp_z - zp_y]$, (d) $[x^2(\partial^2/\partial y^2), y(\partial/\partial x)]$.

1.13 Show that (a) $[A,B] = -[B,A]$, (b) $[A^m,A^n] = 0$ for all m, n, (c) $[A^2,B] = A[A,B] + [A,B]A$, (d) $[A,[B,C]] + [B,[C,A]] + [C,[A,B]] = 0$.

1.14 Evaluate the commutator $[l_y,[l_y,l_z]]$ given that $[l_x,l_y] = i\hbar l_z$, $[l_y,l_z] = i\hbar l_x$, and $[l_z,l_x] = i\hbar l_y$.

1.15 The operator e^A has a meaning if it is expanded as a power series: $e^A = \Sigma_n(1/n!)A^n$. Show that if $|a\rangle$ is an eigenstate of A with eigenvalue a, then it is also an eigenstate of e^A. Find the latter's eigenvalue.

1.16 (a) Show that $e^A e^B = e^{A+B}$ only if $[A,B] = 0$. (b) If $[A,B] \neq 0$ but $[A,[A,B]] = [B,[A,B]] = 0$, show that $e^A e^B = e^{A+B} e^f$, where f is a simple function of $[A,B]$. *Hint*. This is another example of the differences between operators (q-numbers) and ordinary numbers (c-numbers). The simplest approach is to expand the exponentials and to collect and compare terms on both sides of the equality. Note that $e^A e^B$ will give terms like $2AB$ while e^{A+B} will give $AB + BA$. Be careful with order.

1.17 Evaluate the commutators (a) $[H,p_x]$ and (b) $[H,x]$, where $H = p_x^2/2m + V(x)$. Choose (i) $V(x) = V$, a constant, (ii) $V(x) = \frac{1}{2}kx^2$, (iii) $V(x) \to V(r) = e^2/4\pi\varepsilon_0 r$.

1.18 Evaluate (by considering eqn 1.33) the limitation on the simultaneous specification of the following observables: (a) the position and momentum of a particle, (b) the three components of linear momentum of a particle, (c) the kinetic energy and potential energy of a particle, (d) the electric dipole moment and the total energy of a one-dimensional system, (e) the kinetic energy and the position of a particle in one dimension.

1.19 An electron is confined to a linear box of length 0.10 nm. What are the minimum uncertainties in (a) its velocity and (b) its kinetic energy?

1.20 Use the uncertainty principle to estimate the order of magnitude of the diameter of an atom. Compare the result with the radius of the first Bohr orbit of hydrogen, $a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$. *Hint*. Suppose the electron is confined to a region of extent Δx; this confinement implies a non-zero kinetic energy. There is also a potential energy of order of magnitude $-e^2/4\pi\varepsilon_0\Delta x$. Find Δx such that the total energy is a minimum, and evaluate the expression.

1.21 Use eqn 1.35 to find expressions for the rate of change of the expectation values of position and momentum of a harmonic oscillator; solve the pair of differential equations, and show that the expectation values change in time in the same way as for a classical oscillator.

1.22 Confirm that the z-component of angular momentum, $l_z = (\hbar/i)\, d/d\phi$, is a constant of the motion for a particle on a ring with uniform potential energy $V(\phi) = V$.

1.23 The only non-zero matrix elements of x and p_x for a harmonic oscillator are

$$\langle v+1|x|v\rangle = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(v+1)^{1/2}$$

$$\langle v-1|x|v\rangle = \left(\frac{\hbar}{2m\omega}\right)^{1/2}v^{1/2}$$

$$\langle v+1|p_x|v\rangle = i\left(\frac{\hbar m\omega}{2}\right)^{1/2}(v+1)^{1/2}$$

$$\langle v-1|p_x|v\rangle = i\left(\frac{\hbar m\omega}{2}\right)^{1/2}v^{1/2}$$

(and their hermitian conjugates); see Section 2.17. Write out the matrices of x and p_x explicitly (label the rows and columns $v = 0, 1, 2, \ldots$) up to about $v = 4$, and confirm by matrix multiplication that they satisfy the commutation rule. Construct the hamiltonian matrix by forming $p_x^2/2m + \frac{1}{2}kx^2$ by matrix multiplication and addition, and infer the eigenvalues.

1.24 Use the completeness relation, eqn 1.42, and the information in Problem 1.23 to deduce the value of the matrix element $\langle v|xp_x{}^2x|v\rangle$.

1.25 Write the time-independent Schrödinger equations for (a) the hydrogen atom, (b) the helium atom, (c) the hydrogen molecule, (d) a free particle, (e) a particle subjected to a constant, uniform force.

1.26 The time-dependent Schrödinger equation is separable when V is independent of time. (a) Show that it is also separable when V is a function only of time and uniform in space. (b) Solve the pair of equations. Let $V(t) = V\cos\omega t$; find an expression for $\Psi(x, t)$ in terms of $\Psi(x, 0)$. (c) Is $\Psi(x, t)$ stationary in the sense specified in Section 1.12?

1.27 The ground-state wavefunction of a hydrogen atom has the form $\psi(\boldsymbol{r}) = Ne^{-br}$, b being a collection of fundamental constants with the magnitude 1/(53 pm). Normalize this spherically symmetrical function. *Hint*. The volume element is $d\tau = \sin\theta\, d\theta\, d\phi\, r^2\, dr$, with $0 \le \theta \le \pi$, $0 \le \phi \le 2\pi$, and $0 \le r < \infty$. 'Normalize' always means 'normalize to 1' in this text.

1.28 A particle in an infinite one-dimensional system was described by the wavefunction $\psi(x) = Ne^{-x^2/2\Gamma^2}$. Normalize this function. Calculate the probability of finding the particle in the range $-\Gamma \le x \le \Gamma$. *Hint*.
The integral encountered in the second part is the error function. It is defined and tabulated in M. Abramowitz and I.A. Stegun, *Handbook of mathematical functions*, Dover (1965).

1.29 An excited state of the system in the previous problem is described by the wavefunction

$\psi(x) = Nxe^{-x^2/2\Gamma^2}$. Where is the most probable location of the particle?

1.30 On the basis of the information in Problem 1.27, calculate the probability density of finding the electron (a) at the nucleus, (b) at a point in space 53 pm from the nucleus. Calculate the probabilities of finding the electron inside a region of volume 1.0 pm^3 located at these points assuming that the probability density is constant inside the small volume region.

1.31 (a) Calculate the probability of the electron being found anywhere within a sphere of radius 53 pm for the atom defined in Problem 1.27. (b) If the radius of the atom is defined as the radius of the sphere inside which there is a 90 per cent probability of finding the electron, what is the atom's radius?

1.32 A particle is confined to the region $0 \leq x \leq \infty$ and its state is described by the unnormalized wavefunction $\psi(x) = e^{-2x}$. What is the probability of finding the particle at a distance $x \geq 1$?

1.33 A particle is moving in a circle in the xy plane. The only coordinate of importance is the angle ϕ which can vary from 0 to 2π as the particle goes around the circle. We are interested in measurements of the angular momentum L of the particle. The angular momentum operator for such a system is given by $(\hbar/i)\,d/d\phi$. (a) Suppose that the state of the particle is described by the wavefunction $\psi(\phi) = Ne^{-i\phi}$ where N is the normalization constant. What values will we find when we measure the angular momentum of the particle? If more than one value is possible, what is the probability of obtaining each result? What is the expectation value of the angular momentum? (b) Now suppose that the state of the particle is described by the normalized wavefunction $\psi(\phi) = N\{(3/4)^{1/2}e^{-i\phi} - (i/2)e^{2i\phi}\}$. When we measure the angular momentum of the particle, what value(s) will we find? If more than one value is possible, what is the probability of obtaining each result? What is the expectation value of the angular momentum?

1.34 Explore the concept of phase length as follows. First, consider two points P_1 and P_2 separated by a distance l, and let the paths taken by waves of wavelength λ be a straight line from P_1 to a point a distance d above the midpoint of the line P_1P_2, and then on to P_2. Find an expression for the phase length and sketch it as a function of d for various values of λ. Confirm explicitly that $\phi' = 0$ at $d = 0$.

1.35 Confirm that the path of minimum phase length for light passing from one medium to another corresponds to light being refracted at their interface in accord with Snell's law (Section 1.21).

1.36 Show that if the Schrödinger equation had the form of a true wave equation, then the integrated probability would be time-dependent. *Hint*. A wave equation has $\kappa\partial^2/\partial t^2$ in place of $\partial/\partial t$, where κ is a constant with the appropriate dimensions (what are they?). Solve the time component of the separable equation and investigate the behaviour of $\int \Psi^*\Psi \, d\tau$.