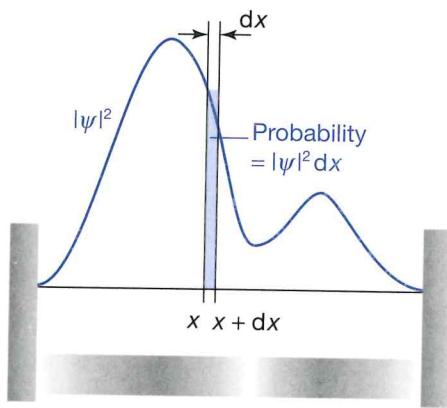


11.4 The Born interpretation of the wavefunction

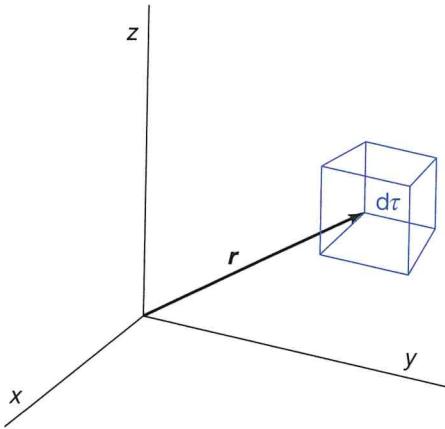
It is a principal tenet of quantum mechanics that the wavefunction contains all the dynamical information about the system it describes. Here we concentrate on the information it carries about the location of the particle.

The interpretation of the wavefunction in terms of the location of the particle is based on a suggestion made by Max Born. He made use of an analogy with the wave theory of light, in which the square of the amplitude of an electromagnetic wave in a region is interpreted as its intensity and therefore (in quantum terms) as a measure of the probability of finding a photon present in the region. The **Born interpretation** of the wavefunction focuses on the square of the wavefunction (or the square modulus, $|\psi|^2 = \psi^* \psi$, if ψ is complex). It states that the value of $|\psi|^2$ at a point is proportional to the probability of finding the particle at that point. Specifically, for a one-dimensional system (Fig. 11.15):

If the wavefunction of a particle has the value ψ at some point x , then the probability of finding the particle between x and $x + dx$ is proportional to $|\psi|^2 dx$.



11.15 The wavefunction ψ is a probability amplitude in the sense that its square modulus ($\psi^* \psi$ or $|\psi|^2$) is a probability density. The probability of finding a particle in the region dx located at x is proportional to $|\psi|^2 dx$.



11.16 The Born interpretation of the wavefunction in three-dimensional space implies that the probability of finding the particle in the volume element $d\tau = dx dy dz$ at some location r is proportional to the product of $d\tau$ and the value of $|\psi|^2$ at that location.

Thus, $|\psi|^2$ is the **probability density**, and to obtain the probability it must be multiplied by the length of the infinitesimal region dx . The wavefunction ψ itself is called the **probability amplitude**. For a particle free to move in three dimensions (for example, an electron near a nucleus in an atom), the wavefunction depends on the point dr with coordinates x , y , and z , and the interpretation of $\psi(r)$ is as follows (Fig. 11.16):

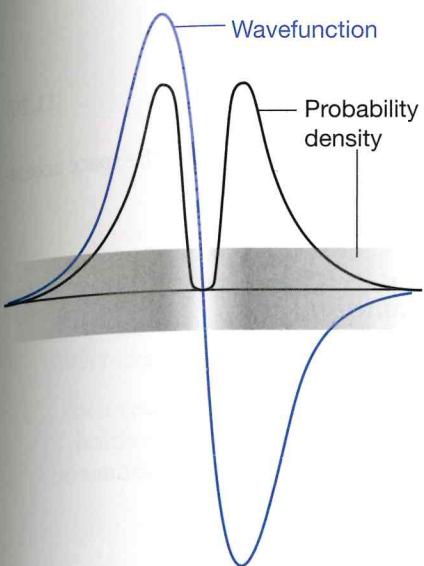
If the wavefunction of a particle has the value ψ at some point r , then the probability of finding the particle in an infinitesimal volume $d\tau = dx dy dz$ at that point is proportional to $|\psi|^2 d\tau$.

The Born interpretation does away with any worry about the significance of a negative (and, in general, complex) value of ψ because $|\psi|^2$ is real and never negative. There is no *direct* significance in the negative (or complex) value of a wavefunction: only the square modulus, a positive quantity, is directly physically significant, and both negative and positive regions of a wavefunction may correspond to a high probability of finding a particle in a region (Fig. 11.17). However, later we shall see that the presence of positive and negative regions of a wavefunction is of great *indirect* significance, because it gives rise to the possibility of constructive and destructive interference between different wavefunctions.

Example 11.3 Interpreting a wavefunction

We shall see in Chapter 13 that the wavefunction of an electron in the lowest energy state of a hydrogen atom is proportional to e^{-r/a_0} , with a_0 a constant and r the distance from the nucleus. (Notice that this wavefunction depends only on this distance, not the angular position relative to the nucleus.) Calculate the relative probabilities of finding the electron inside a region of volume 1.0 pm^3 , which is small even on the scale of the atom, located at (a) the nucleus, (b) a distance a_0 from the nucleus.

Method The region of interest is so small on the scale of the atom that we can ignore the variation of ψ within it and write the probability, P , as proportional to the probability density (ψ^2 ; note that ψ is real) evaluated at the point of interest multiplied by the volume of interest, δV . That is, $P \propto \psi^2 \delta V$, with $\psi^2 \propto e^{-2r/a_0}$.



11.17 The sign of a wavefunction has no direct physical significance: the positive and negative regions of this wavefunction both correspond to the same probability distribution (as given by the square modulus of ψ and depicted by the density of shading).

For systems with spherical symmetry, it is best to work in spherical polar coordinates r, θ, ϕ (Fig. 11.18): $x = r \sin \theta \cos \phi$, $y = r \sin \theta \sin \phi$, $z = r \cos \theta$. The volume element in spherical polar coordinates is $d\tau = r^2 \sin \theta dr d\theta d\phi$. To cover all space, the radius r ranges from 0 to ∞ , the colatitude, θ , ranges from 0 to π , and the azimuth, ϕ , ranges from 0 to 2π (Fig. 11.19).

Answer In each case $\delta V = 1.0 \text{ pm}^3$. (a) At the nucleus, $r = 0$, so

$$P \propto e^0 \times (1.0 \text{ pm}^3) = (1.0) \times (1.0 \text{ pm}^3)$$

(b) At a distance $r = a_0$ in an arbitrary direction,

$$P \propto e^{-2} \times (1.0 \text{ pm}^3) = (0.14) \times (1.0 \text{ pm}^3)$$

Therefore, the ratio of probabilities is $1.0/0.14 = 7.1$.

Comment Note that it is more probable (by a factor of 7) that the electron will be found at the nucleus than in the same volume element located at a distance a_0 from the nucleus. The negatively charged electron is attracted to the positively charged nucleus, and is likely to be found close to it.

Self-test 11.3 The wavefunction for the electron in its lowest energy state in the ion He^+ is proportional to e^{-2r/a_0} . Repeat the calculation for this ion. Any comment? [55; more compact wavefunction]

(a) Normalization

A mathematical feature of the Schrödinger equation is that, if ψ is a solution, then so is $N\psi$, where N is any constant. This feature is confirmed by noting that ψ occurs in every term in eqn 14, so any constant factor can be cancelled. This freedom to vary the wavefunction by a constant factor means that it is always possible to find a **normalization constant**, N , such that the proportionality of the Born interpretation becomes an equality.

We find the normalization constant by noting that, for a normalized wavefunction $N\psi$, the probability that a particle is in the region dx is equal to $(N\psi^*)(N\psi) dx$ (we are taking N to be real). Furthermore, the sum over all space of these individual probabilities must be 1 (the probability of the particle being somewhere is 1). Expressed mathematically, the latter requirement is

$$\int N^2 \psi^* \psi dx = 1 \quad (11.16)$$

where the integral is over all the space accessible to the particle (for instance, from $-\infty$ to $+\infty$ if the particle can be anywhere in an infinite range). It follows that

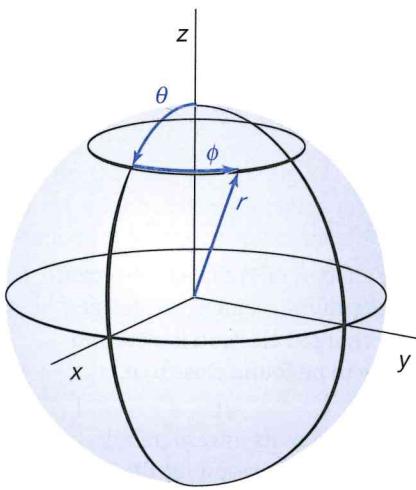
$$N = \frac{1}{\left(\int \psi^* \psi dx \right)^{1/2}} \quad (11.17)$$

Therefore, by evaluating the integral, we can find the value of N and hence ‘normalize’ the wavefunction. From now on, unless we state otherwise, we always use wavefunctions that have been normalized to 1; that is, from now on we assume that ψ already includes a factor that ensures that (in one dimension)

$$\int \psi^* \psi dx = 1 \quad (11.18)$$

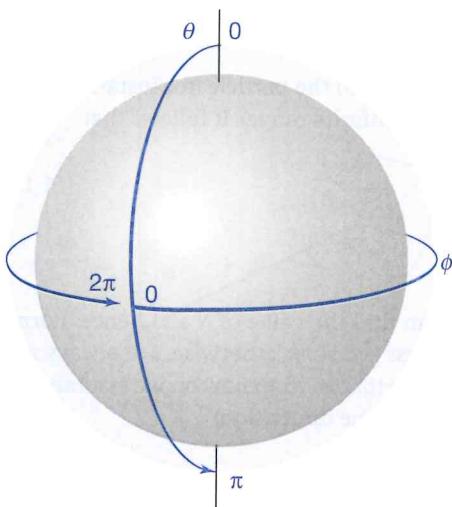
In three dimensions, the wavefunction is normalized if

$$\int \psi^* \psi dx dy dz = 1 \quad (11.19)$$



11.18 The spherical coordinates used for discussing systems with spherical symmetry.

Integrals commonly encountered in physical chemistry are listed inside the front cover.



11.19 The surface of a sphere is covered by allowing θ to range from 0 to π , and then sweeping that arc around a complete circle by allowing ϕ to range from 0 to 2π .

or, more succinctly, if

$$\int \psi^* \psi \, d\tau = 1 \quad (11.20)$$

where $d\tau = dx dy dz$. In all such integrals, the integration is over all the space accessible to the particle.

Example 11.4 Normalizing a wavefunction

Normalize the wavefunction used for the hydrogen atom in Example 11.3.

Method We need to find the factor N that guarantees that the integral in eqn 20 is equal to 1. Because the wavefunction is spherically symmetrical, we work in spherical polar coordinates. A useful integral for calculations on atomic wavefunctions is

$$\int_0^\infty x^n e^{-ax} \, dx = \frac{n!}{a^{n+1}}$$

where $n!$ denotes a factorial: $n! = n(n - 1)(n - 2) \dots 1$.

Answer The integration required is

$$\begin{aligned} \int \psi^* \psi \, d\tau &= N^2 \int_0^\infty r^2 e^{-2r/a_0} \, dr \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} \, d\phi \\ &= N^2 \times \frac{1}{4} a_0^3 \times 2 \times 2\pi = \pi a_0^3 N^2 \end{aligned}$$

Therefore, for this integral to equal 1,

$$N = \left(\frac{1}{\pi a_0^3} \right)^{1/2}$$

and the normalized wavefunction is

$$\psi = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0}$$

Comment If Example 11.3 is now repeated, we can obtain the actual probabilities of finding the electron in the volume element at each location, not just their relative values. Given (from Section 13.1) that $a_0 = 52.9$ pm, the results are (a) 2.2×10^{-6} , corresponding to 1 chance in about 500 000 inspections of finding the electron in the test volume, and (b) 2.9×10^{-7} , corresponding to 1 chance in 3.4 million.

Self-test 11.4 Normalize the wavefunction given in Self-test 11.3.

$$[N = (8/\pi a_0^3)^{1/2}]$$

The quantity $|\psi|^2 d\tau$ is a dimensionless probability and $d\tau$ has the dimensions of volume, $(\text{length})^d$, where d is the number of spatial dimensions. Therefore, the dimensions of a normalized wavefunction are $1/(\text{length})^{d/2}$. Thus, in one spatial dimension, $d = 1$ and a normalized wavefunction has the dimensions of $1/(\text{length})^{1/2}$. For a three-dimensional system, the wavefunction has the dimensions of $1/(\text{length})^{3/2}$, as we saw in Example 11.4.

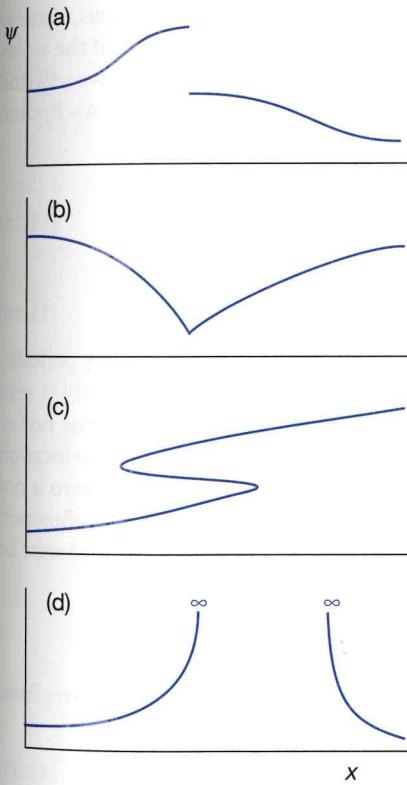
(b) Quantization

The Born interpretation puts severe restrictions on the acceptability of wavefunctions. The principal constraint is that ψ must not be infinite anywhere.⁷ If it were, the integral in eqn 20 would be infinite and the normalization constant would be zero. The normalized function would then be zero everywhere, except where it is infinite, which would be unacceptable. The requirement that ψ is finite everywhere rules out many possible solutions of the Schrödinger equation, because many mathematically acceptable solutions rise to infinity and are therefore physically unacceptable. We shall meet several examples shortly.

The requirement that ψ is finite everywhere is not the only restriction implied by the Born interpretation. We could imagine (and in Section 12.6a will meet) a solution of the Schrödinger equation that gives rise to more than one value of $|\psi|^2$ at a single point. The Born interpretation implies that such solutions are unacceptable, because it would be absurd to have more than one probability that a particle is at the same point. This restriction is expressed by saying that the wavefunction must be *single-valued*; that is, have only one value at each point of space.

The Schrödinger equation itself also implies some mathematical restrictions on the type of functions that will occur. Because it is a second-order differential equation, the second derivative of ψ must be well-defined if the equation is to be applicable everywhere. We can take the second derivative of a function only if it is continuous (so there are no sharp steps in it, Fig. 11.20) and if its first derivative, its slope, is continuous (so there are no kinks).⁸

At this stage we see that ψ must be continuous, have a continuous slope, be single-valued, and be finite everywhere. An acceptable wavefunction cannot be zero everywhere, because the particle it describes must be somewhere. These are such severe restrictions that acceptable solutions of the Schrödinger equation do not in general exist for arbitrary values of the energy E . In other words, a particle may possess only certain energies, for otherwise its wavefunction would be physically unacceptable. That is, *the energy of a particle is quantized*. We can find the acceptable energies by solving the Schrödinger equation for motion of various kinds, and selecting the solutions that conform to the restrictions listed above. That is the task of the next chapter.



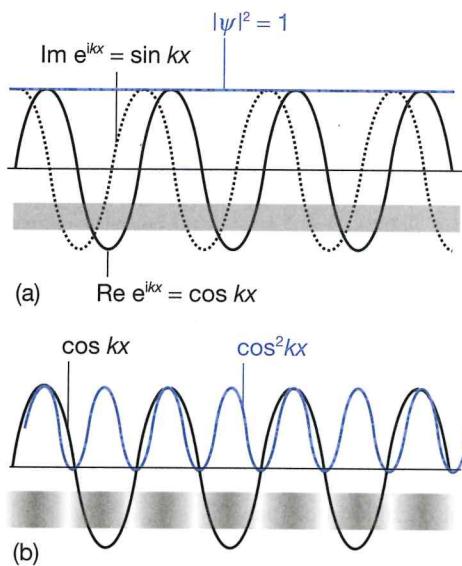
11.20 The wavefunction must satisfy stringent conditions for it to be acceptable. (a) Unacceptable because it is not continuous, (b) unacceptable because its slope is discontinuous, (c) unacceptable because it is not single-valued, (d) unacceptable because it is infinite over a finite region.

Quantum mechanical principles

We have claimed that a wavefunction contains all the information it is possible to obtain about the dynamical properties (for example, its location and momentum) of the particle. We have seen that the Born interpretation tells us as much as we can know about location, but how do we find any additional information?

7. Infinitely sharp spikes are acceptable provided they have zero width. A more complete formulation of the constraint is that the wavefunction must not be infinite over any finite region and, specifically, that the integral of ψ^2 is finite. In elementary quantum mechanics the simpler restriction, to finite ψ , is sufficient.

8. There are cases, and we shall meet them, where acceptable wavefunctions have kinks. These cases arise when the potential energy has peculiar properties, such as rising abruptly to infinity. When the potential energy is smoothly well-behaved and finite, the slope of the wavefunction must be continuous; if the potential energy becomes infinite, then the slope of the wavefunction need not be continuous. There are only two cases of this behaviour in elementary quantum mechanics, and the peculiarity will be mentioned when we meet them.



11.21 (a) The square modulus of a wavefunction corresponding to a definite state of linear momentum is a constant; so it corresponds to a uniform probability of finding the particle anywhere. (b) The probability distribution corresponding to the superposition of states of equal magnitude of linear momentum but opposite direction of travel.

We use the relation $\cos \theta = \frac{1}{2}(e^{i\theta} + e^{-i\theta})$.

11.5 The information in a wavefunction

The Schrödinger equation for a particle of mass m free to move parallel to the x -axis with zero potential energy is obtained from eqn 14 by setting $V = 0$, and is

$$\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (11.21)$$

The solutions of this equation have the form

$$\psi = Ae^{ikx} + Be^{-ikx} \quad E = \frac{k^2\hbar^2}{2m} \quad (11.22)$$

where A and B are constants. To verify that ψ is a solution of eqn 21, we simply substitute it into the left-hand side of the equation and confirm that we obtain $E\psi$.

(a) The probability density

Suppose that $B = 0$ in eqn 22,⁹ then the wavefunction is simply

$$\psi = Ae^{ikx} \quad (11.23)$$

Where is the particle? We form the square modulus to find the probability density:

$$|\psi|^2 = (Ae^{ikx})^*(Ae^{ikx}) = (A^*e^{-ikx})(Ae^{ikx}) = |A|^2 \quad (11.24)$$

This probability is independent of x ; so, wherever we look along the x -axis, there is an equal probability of finding the particle (Fig. 11.21a). In other words, if the wavefunction of the particle is given by eqn 23, then we cannot predict where we will find the particle. The same would be true if the wavefunction in eqn 22 had $A = 0$; then the probability density would be $|B|^2$, a constant.¹⁰

Now suppose that in the wavefunction $A = B$. Then eqn 22 becomes

$$\psi = A(e^{ikx} + e^{-ikx}) = 2A \cos kx \quad (11.25)$$

The probability density now has the form

$$|\psi|^2 = (2A \cos kx)^*(2A \cos kx) = 4|A|^2 \cos^2 kx \quad (11.26)$$

This function is illustrated in Fig. 11.21b. As we see, the probability density periodically varies between 0 and $4|A|^2$. The locations where the probability density is zero correspond to *nodes* in the wavefunction: particles will never be found at the nodes. Specifically, a **node** is a point where a wavefunction passes through zero. The location where a wavefunction approaches zero without actually passing through zero is not a node. Nodes are defined in terms of the probability amplitude, the wavefunction itself. The probability density, of course, never passes through zero as it cannot be negative.

(b) Eigenvalues and eigenfunctions

Because the total energy of the particle is its kinetic energy, $p^2/2m$, it follows from eqn 22 that

$$p = k\hbar \quad (11.27)$$

This value is independent of the values of A and B .

9. We shall see later what determines the values of A and B ; for the time being we can treat them as arbitrary constants.

10. It follows that if x is allowed to range from $-\infty$ to $+\infty$, the normalization constants, A or B , are 0. To avoid this embarrassing problem, x is allowed to range from $-L$ to $+L$, and L is allowed to go to infinity at the end of all calculations. We ignore this complication here.

To find a systematic way of extracting information from the wavefunction, we first note that any Schrödinger equation (such as those in eqns 14 and 21) may be written in the succinct form

$$H\psi = E\psi \quad (11.28)$$

with (in one dimension)

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \quad (11.29)$$

The quantity H is an **operator**, something that carries out a mathematical operation on the function ψ . In this case, the operation is to take the second derivative of ψ and (after multiplication by $-\hbar^2/2m$) to add the result to the outcome of multiplying ψ by V . The operator H plays a special role in quantum mechanics, and is called the **hamiltonian operator** after the nineteenth century mathematician William Hamilton.¹¹ The hamiltonian operator is the operator corresponding to the total energy of the system, the sum of the kinetic and potential energies. Consequently, we can infer that the first term in eqn 29 (the term proportional to the second derivative) must be the operator for the kinetic energy. When the Schrödinger equation is written as in eqn 28, it is seen to be an **eigenvalue equation**, an equation of the form

$$(\text{Operator})(\text{function}) = (\text{constant factor}) \times (\text{same function})$$

If we denote a general operator by $\hat{\Omega}$ (where Ω is upper-case omega) and a constant factor by ω (lower-case omega), an eigenvalue equation has the form

$$\hat{\Omega}\psi = \omega\psi \quad (11.30)$$

The factor ω is called the **eigenvalue** of the operator $\hat{\Omega}$. The eigenvalue in eqn 28 is the energy. The function ψ is called an **eigenfunction** and is different for each eigenvalue. The eigenfunction in eqn 28 is the wavefunction corresponding to the energy E . It follows that another way of saying 'solve the Schrödinger equation' is 'find the eigenvalues and eigenfunctions of the hamiltonian operator for the system'. The wavefunctions are the eigenfunctions of the hamiltonian operator, and the corresponding eigenvalues are the allowed energies.

Example 11.5 Identifying an eigenfunction

Show that e^{ax} is an eigenfunction of the operator d/dx , and find the corresponding eigenvalue. Show that e^{ax^2} is not an eigenfunction of d/dx .

Method We need to operate on the function with the operator and check whether the result is a constant factor times the original function.

Answer For $\hat{\Omega} = d/dx$ and $\psi = e^{ax}$:

$$\hat{\Omega}\psi = \frac{d}{dx} e^{ax} = ae^{ax} = a\psi$$

11. Hamilton developed a form of classical mechanics that, it subsequently turned out, is well suited to the formulation of quantum mechanics and which shows very clearly the relation between the two theories.

Therefore e^{ax} is indeed an eigenfunction of d/dx , and its eigenvalue is a . For $\psi = e^{ax^2}$,

$$\hat{\Omega}\psi = \frac{d}{dx}e^{ax^2} = 2axe^{ax^2} = 2ax \times \psi$$

which is not an eigenvalue equation even though the same function ψ occurs on the right, because ψ is now multiplied by a variable factor ($2ax$), not a constant factor. Alternatively, if the right-hand side is written $2a(xe^{ax^2})$, we see that it is a constant times a *different* function.

Comment Much of quantum mechanics involves looking for functions that are eigenfunctions of a given operator, especially of the hamiltonian operator for the energy.

Self-test 11.5 Is the function $\cos ax$ an eigenfunction of (a) d/dx , (b) d^2/dx^2 ?
[(a) No, (b) yes]

The importance of eigenvalue equations is that the pattern

$$(\text{Energy operator})\psi = (\text{energy}) \times \psi$$

exemplified by the Schrödinger equation is repeated for other **observables**, or measurable properties of a system, such as the momentum or the electric dipole moment. Thus, it is often the case that we can write

$$(\text{Operator corresponding to an observable})\psi = (\text{value of observable}) \times \psi$$

The symbol $\hat{\Omega}$ in eqn 30 is then interpreted as an operator (for example, the hamiltonian, H) corresponding to an observable (for example, the energy), and the eigenvalue ω is the value of that observable (for example, the value of the energy, E). Therefore, if we know both the wavefunction ψ and the operator corresponding to the observable Ω of interest, and the wavefunction is an eigenfunction of the operator $\hat{\Omega}$, we can predict the outcome of an observation of the property Ω (for example, an atom's energy) by picking out the factor ω in the eigenvalue equation, eqn 30.

Quantum mechanical calculations are often simplified by using a property of wavefunctions called 'orthogonality'. To say that two functions are **orthogonal** means that

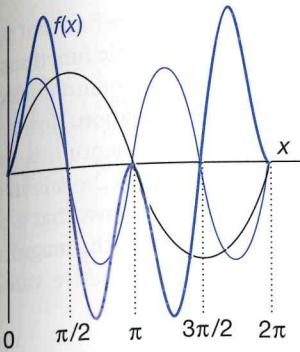
$$\int \psi_i^* \psi_j d\tau = 0 \quad (11.31)$$

Strictly speaking, this rule applies only to *Hermitian operators*, which are operators for which $\int \psi_i^* \hat{\Omega} \psi_j d\tau = (\int \psi_j^* \hat{\Omega} \psi_i d\tau)^*$. We shall be dealing only with Hermitian operators.

A very general rule in quantum mechanics is that *eigenfunctions corresponding to different eigenvalues of the same operator are orthogonal*. For example, if ψ_1 corresponds to one energy, and ψ_2 corresponds to a different energy, then we know at once that the two functions are orthogonal and that the integral of their product is zero.

Illustration 11.1

The wavefunctions $\sin x$ and $\sin 2x$ are eigenfunctions of the operator d^2/dx^2 , with eigenvalues -1 and -4 , respectively. To verify that the two wavefunctions are mutually orthogonal, we integrate the product $(\sin x)(\sin 2x)$ over all space, which we may take to span from $x = 0$ to $x = 2\pi$. A useful integral for this calculation is



11.22 The integral of the function $f(x) = (\sin x)(\sin 2x)$ is equal to the area below the dark blue curve, and is zero, as can be inferred by symmetry.

$$\int \sin ax \sin bx \, dx = \frac{\sin(a-b)x}{2(a-b)} - \frac{\sin(a+b)x}{2(a+b)} + \text{constant}, \quad \text{if } a^2 \neq b^2$$

It follows that, for $a = 1$ and $b = 2$,

$$\int_0^{2\pi} (\sin x)(\sin 2x) \, dx = 0$$

Self-test 11.6 Plot the function $f(x) = (\sin x)(\sin 2x)$ and verify graphically that its integral from $x = 0$ to $x = 2\pi$ is equal to zero.

[The plot (Fig. 11.22) shows that

$$\begin{aligned} \int_0^{\pi/2} f(x) \, dx &= \int_{3\pi/2}^{2\pi} f(x) \, dx = - \int_{\pi/2}^{\pi} f(x) \, dx = - \int_{\pi}^{3\pi/2} f(x) \, dx, \\ \text{so } \int_0^{2\pi} f(x) \, dx &= 0. \end{aligned}$$

(c) Operators

To make these abstract procedures concrete, we need to set up and use the operator corresponding to a given observable. The procedure is summarized by the following rule:¹²

Observables, Ω , are represented by operators, $\hat{\Omega}$, built from the following position and momentum operators:

$$\hat{x} = x \times \quad \hat{p}_x = \frac{\hbar}{i} \frac{d}{dx} \quad [11.32]$$

That is, the operator for location along the x -axis is multiplication (of the wavefunction) by x and the operator for linear momentum parallel to the x -axis is proportional to taking the derivative (of the wavefunction) with respect to x .

Justification 11.2

To confirm that the operator for linear momentum in eqn 32 is plausible, we show here that it is consistent with the de Broglie relation. First, we set up the eigenvalue equation

$$\hat{p}_x \psi = p_x \psi \quad [11.33]$$

in the form

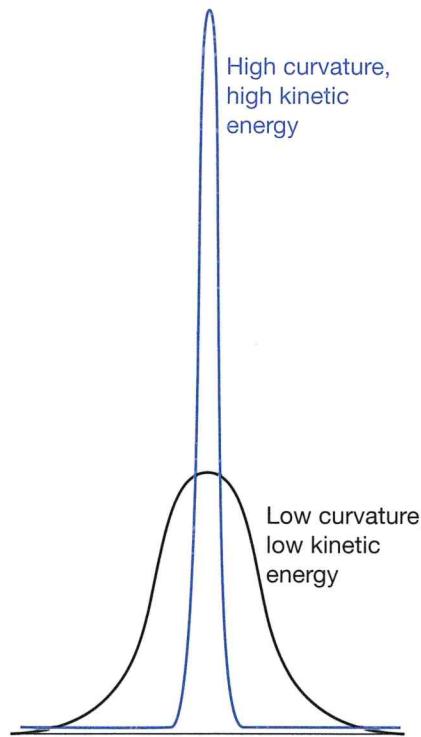
$$\frac{\hbar}{i} \frac{d\psi}{dx} = p_x \psi$$

If the wavefunction is the one given in eqn 22 with $B = 0$,

$$\frac{\hbar}{i} \frac{d\psi}{dx} = \frac{\hbar}{i} A \frac{de^{ikx}}{dx} = \frac{\hbar}{i} A \times ike^{ikx} = k\hbar A e^{ikx} = k\hbar \psi$$

12. This rule applies to observables that depend on spatial variables; intrinsic properties, such as spin (see Section 12.8) are treated differently.

This is an eigenvalue equation, and by comparing it with eqn 30 we find that $p_x = \pm k\hbar$. Because $e^{ikx} = \cos kx + i \sin kx$, and we have seen that the harmonic functions $\cos kx$ and $\sin kx$ describe waves of wavelength $\lambda = 2\pi/k$, this linear momentum is equal to $p_x = \pm(2\pi/\lambda)(\hbar/2\pi) = \hbar/\lambda$, which is in accord with the de Broglie relation. However, the result is richer: the positive value implies that the linear momentum is directed towards positive x . Now suppose instead that the wavefunction is the one in eqn 22 with $A = 0$; then the same kind of calculation gives $p_x = -k\hbar$. It follows that a particle described by the second wavefunction has the same wavelength, magnitude of momentum, and the same kinetic energy as before, but the negative value of p_x implies that the motion is towards $-x$.



11.23 Even if a wavefunction does not have the form of a periodic wave, it is still possible to infer from it the average kinetic energy of a particle by noting its average curvature. This illustration shows two wavefunctions: the sharply curved function corresponds to a higher kinetic energy than the less sharply curved function.

We use the definitions in eqn 32 to construct operators for other spatial observables. For example, suppose we wanted the operator for a potential energy of the form

$$V = \frac{1}{2}kx^2 \quad (11.34a)$$

with k a constant (later, we shall see that this potential describes the vibrations of atoms in molecules). Then it follows from eqn 32 that the operator corresponding to V is multiplication by x^2 :

$$\hat{V} = \frac{1}{2}kx^2 \times \quad (11.34b)$$

In normal practice, the multiplication sign is omitted. To construct the operator for kinetic energy, we make use of the classical relation between kinetic energy and linear momentum, which in one dimension is

$$E_K = \frac{p_x^2}{2m} \quad (11.35a)$$

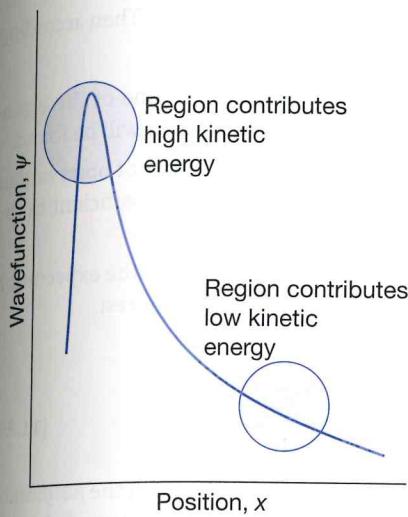
Then, using the operator for p_x in eqn 32 we find:

$$\hat{E}_K = \frac{1}{2m} \left(\frac{\hbar}{i} \frac{d}{dx} \right) \left(\frac{\hbar}{i} \frac{d}{dx} \right) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad (11.35b)$$

It follows that the operator for the total energy, the hamiltonian operator, is

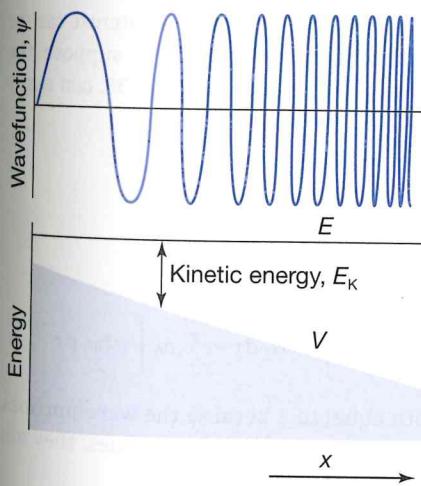
$$\hat{H} = \hat{E}_K + \hat{V} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \hat{V} \quad (11.36)$$

The expression for the kinetic energy operator, eqn 35b, gives another clue to the qualitative interpretation of a wavefunction and the structure of the Schrödinger equation. In mathematics, the second derivative of a function is a measure of its curvature: a large second derivative indicates a sharply curved function (Fig. 11.23). It follows that a sharply curved wavefunction is associated with a high kinetic energy, and one with a low curvature is associated with a low kinetic energy. This interpretation is consistent with the de Broglie relation, which predicts a short wavelength (a sharply curved wavefunction) when the linear momentum (and hence the kinetic energy) is high. However, it extends the interpretation to wavefunctions that do not spread through space and resemble those shown in Fig. 11.23. The curvature of a wavefunction in general varies from place to place. Wherever a wavefunction is sharply curved, its contribution to the total kinetic energy is large (Fig. 11.24). Wherever the wavefunction is not sharply curved, its contribution to the overall kinetic energy is low. As we shall shortly see, the observed kinetic energy of the particle is an integral of all the contributions of the kinetic energy from each region.



11.24 The observed kinetic energy of a particle is an average of contributions from the entire space covered by the wavefunction. Sharply curved regions contribute a high kinetic energy to the average; slightly curved regions contribute only a small kinetic energy.

In general, a linear combination of two functions f and g is $c_1f + c_2g$, where c_1 and c_2 are numerical coefficients, so a linear combination is a more general term than 'sum'. In a sum, $c_1 = c_2 = 1$.



11.25 The wavefunction of a particle in a potential decreasing towards the right and hence subjected to a constant force to the right. Only the real part of the wavefunction is shown, the imaginary part is similar, but displaced to the right.

Hence, we can expect a particle to have a high kinetic energy if the average curvature of its wavefunction is high.

The association of high curvature with high kinetic energy will turn out to be a valuable guide to the interpretation of wavefunctions and the prediction of their shapes. For example, suppose we need to know the wavefunction of a particle with a given total energy and a potential energy that decreases with increasing x (Fig. 11.25). Because the difference $E - V = E_K$ increases from left to right, the wavefunction must become more sharply curved as x increases: its wavelength decreases as the local contributions to its kinetic energy increase. We can therefore guess that the wavefunction will look like the function sketched in the illustration, and more detailed calculation confirms this to be so.

(d) Superpositions and expectation values

Suppose now that the wavefunction is the one given in eqn 25 (with $A = B$). What is the linear momentum of the particle it describes? We quickly run into trouble if we use the operator technique. When we operate with \hat{p}_x , we find

$$\frac{\hbar}{i} \frac{d\psi}{dx} = \frac{2\hbar}{i} A \frac{d \cos kx}{dx} = -\frac{2k\hbar}{i} A \sin kx \quad (11.37)$$

This expression is not an eigenvalue equation, because the function on the right ($\sin kx$) is different from that on the left ($\cos kx$).

When the wavefunction of a particle is not an eigenfunction of an operator, the property to which the operator corresponds does not have a definite value. However, in the current example the momentum is not completely indefinite because the cosine wavefunction is a **linear combination**, or sum, of e^{ikx} and e^{-ikx} , and these two functions, as we have seen, individually correspond to definite momentum states. We say that the total wavefunction is a **superposition** of more than one wavefunction. Symbolically we can write the superposition as

$$\begin{aligned} \psi = & \psi_{\rightarrow} + \psi_{\leftarrow} \\ \text{Particle} & \quad \text{Particle} \\ \text{with linear} & \quad \text{with linear} \\ \text{momentum} & \quad \text{momentum} \\ + k\hbar & \quad -k\hbar \end{aligned}$$

The interpretation of this composite wavefunction is that, if the momentum of the particle is repeatedly measured in a long series of observations, then its magnitude will be found to be $k\hbar$ in all the measurements (because that is the value for each component of the wavefunction). However, because the two component wavefunctions occur equally in the superposition, half the measurements will show that the particle is moving to the right ($p_x = +k\hbar$), and half the measurements will show that it is moving to the left ($p_x = -k\hbar$). According to quantum mechanics, we cannot predict in which direction the particle will in fact be found to be travelling; all we can say is that, in a long series of observations, there are equal probabilities of finding the particle travelling to the right and to the left.

The same interpretation applies to any wavefunction written as a linear combination of eigenfunctions of an operator. Thus, suppose the wavefunction is known to be a superposition of many different linear momentum eigenfunctions and written as the linear combination

$$\psi = c_1\psi_1 + c_2\psi_2 + \dots = \sum_k c_k\psi_k \quad (11.38)$$

where the c_k are numerical coefficients and the ψ_k correspond to different momentum states. The functions ψ_k are said to form a **complete set** in the sense that any

arbitrary function can be expressed as a linear combination of them. Then according to quantum mechanics:

1 When the momentum is measured, in a single observation one of the eigenvalues corresponding to the ψ_k that contribute to the superposition will be found.

2 The probability of measuring a particular eigenvalue in a series of observations is proportional to the square modulus ($|c_k|^2$) of the corresponding coefficient in the linear combination.

3 The average value of a large number of observations is given by the expectation value, $\langle \Omega \rangle$, of the operator $\hat{\Omega}$ corresponding to the observable of interest.

The **expectation value** of an operator $\hat{\Omega}$ is defined as

$$\langle \Omega \rangle = \int \psi^* \hat{\Omega} \psi \, d\tau \quad [11.39]$$

This formula is valid only for normalized wavefunctions. As we see in the *Justification* below, an expectation value is the weighted average of a large number of observations of a property.

Justification 11.3

If ψ is an eigenfunction of $\hat{\Omega}$ with eigenvalue ω , the expectation value of Ω is

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

because ω is a constant and may be taken outside the integral, and the resulting integral is equal to 1 for a normalized wavefunction. The interpretation of this expression is that, because every observation of the property Ω results in the value ω (because the wavefunction is an eigenfunction of $\hat{\Omega}$), the mean value of all the observations is also ω .

A wavefunction that is not an eigenfunction of the operator of interest can be written as a linear combination of eigenfunctions. For simplicity, suppose the wavefunction is the sum of two eigenfunctions (the general case, eqn 38, can easily be developed). Then

$$\begin{aligned} \langle \Omega \rangle &= \int (c_1 \psi_1 + c_2 \psi_2)^* \hat{\Omega} (c_1 \psi_1 + c_2 \psi_2) \, d\tau \\ &= \int (c_1 \psi_1 + c_2 \psi_2)^* (c_1 \omega_1 \psi_1 + c_2 \omega_2 \psi_2) \, d\tau \\ &= c_1^* c_1 \omega_1 \int \psi_1^* \psi_1 \, d\tau + c_2^* c_2 \omega_2 \int \psi_2^* \psi_2 \, d\tau + c_1^* c_2 \omega_2 \int \psi_1^* \psi_2 \, d\tau + c_2^* c_1 \omega_1 \int \psi_2^* \psi_1 \, d\tau \end{aligned}$$

The first two integrals on the right are both equal to 1 because the wavefunctions are normalized. Because ψ_1 and ψ_2 correspond to different eigenvalues, they are orthogonal, so we can conclude that

$$\langle \Omega \rangle = |c_1|^2 \omega_1 + |c_2|^2 \omega_2$$

This expression shows that the expectation value is the sum of the two eigenvalues weighted by the probabilities that each one will be found in a series of measurements. Hence, the expectation value is the weighted mean of a series of observations.

Example 11.6 Calculating an expectation value

Calculate the average value of the distance of an electron from the nucleus in the hydrogen atom in its state of lowest energy.

Method The average radius is the expectation value of the operator corresponding to the distance from the nucleus, which is multiplication by r . To evaluate $\langle r \rangle$, we need to know the normalized wavefunction (from Example 11.4) and then evaluate the integral in eqn 39.

Answer The average value is given by the expectation value

$$\langle r \rangle = \int \psi^* r \psi \, d\tau$$

which we evaluate by using spherical polar coordinates. Using the normalized function in Example 11.4 gives

$$\begin{aligned} \langle r \rangle &= \frac{1}{\pi a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} d\phi \\ &= \frac{1}{\pi a_0^3} \times \frac{3! a_0^4}{2^4} \times 2 \times 2\pi = \frac{3}{2} a_0 \end{aligned}$$

Because $a_0 = 52.9 \text{ pm}$ (see Section 13.1), $\langle r \rangle = 79.4 \text{ pm}$.

Comment The result means that, if a very large number of measurements of the distance of the electron from the nucleus are made, their mean value will be 79.4 pm. However, each different observation will give a different and unpredictable individual result because the wavefunction is not an eigenfunction of the operator corresponding to r .

Self-test 11.7 Evaluate the root mean square distance, $\langle r^2 \rangle^{1/2}$, of the electron from the nucleus in the hydrogen atom. $[3^{1/2} a_0 = 91.6 \text{ pm}]$

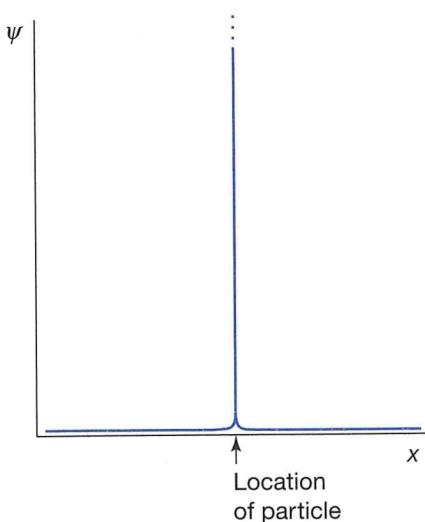
The mean kinetic energy of a particle in one dimension is the expectation value of the operator given in eqn 35b. Therefore, we can write

$$\langle E_K \rangle = \int \psi^* \hat{E}_K \psi \, d\tau = -\frac{\hbar^2}{2m} \int \psi^* \frac{d^2 \psi}{dx^2} \, d\tau \quad (11.40)$$

This conclusion confirms the previous assertion that the kinetic energy is a kind of average over the curvature of the wavefunction: we get a large contribution to the observed value from regions where the wavefunction is sharply curved (so $d^2 \psi / dx^2$ is large) and the wavefunction itself is large (so that ψ^* is large too).

11.6 The uncertainty principle

We have seen that, if the wavefunction is Ae^{ikx} , then the particle it describes has a definite state of linear momentum, namely travelling to the right with momentum $p_x = +k\hbar$. However, we have also seen that the position of the particle described by this wavefunction is completely unpredictable. In other words, if the momentum is specified precisely, it is impossible to predict the location of the particle. This statement is one-half of a special case of the **Heisenberg uncertainty principle**, one of the most celebrated results of quantum mechanics:



11.26 The wavefunction for a particle at a well-defined location is a sharply spiked function that has zero amplitude everywhere except at the particle's position.

It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.

Before discussing the principle further, we must establish its other half: that, if we know the position of a particle exactly, then we can say nothing about its momentum. The argument draws on the idea of regarding a wavefunction as a superposition of eigenfunctions, and runs as follows.

If we know that the particle is at a definite location, its wavefunction must be large there and zero everywhere else (Fig. 11.26). Such a wavefunction can be created by superimposing a large number of harmonic (sine and cosine) functions, or, equivalently, a number of e^{ikx} functions. In other words, we can create a sharply localized wavefunction, called a **wave packet**, by forming a linear combination of wavefunctions that correspond to many different linear momenta. The superposition of few harmonic functions gives a wavefunction that spreads over a range of location (Fig. 11.27). However, as the number of wavefunctions in the superposition increases, the wave packet becomes sharper on account of the more complete interference between the positive and negative regions of the individual waves. When an infinite number of components is used, the wave packet is a sharp, infinitely narrow spike, which corresponds to perfect localization of the particle. Now the particle is perfectly localized. However, we have lost all information about its momentum because, as we saw above, a measurement of the momentum will give a result corresponding to any one of the infinite number of waves in the superposition, and which one it will give is unpredictable. Hence, if we know the location of the particle precisely (implying that its wavefunction is a superposition of an infinite number of momentum eigenfunctions), then its momentum is completely unpredictable.

A quantitative version of this result is

$$\Delta p \Delta q \geq \frac{1}{2} \hbar \quad (11.4)$$

In this expression Δp is the ‘uncertainty’ in the linear momentum parallel to the axis q , and Δq is the uncertainty in position along that axis. These ‘uncertainties’ are precisely defined, for they are the root mean square deviations of the properties from their mean values:

$$\Delta p = \{\langle p^2 \rangle - \langle p \rangle^2\}^{1/2} \quad \Delta q = \{\langle q^2 \rangle - \langle q \rangle^2\}^{1/2} \quad (11.4)$$

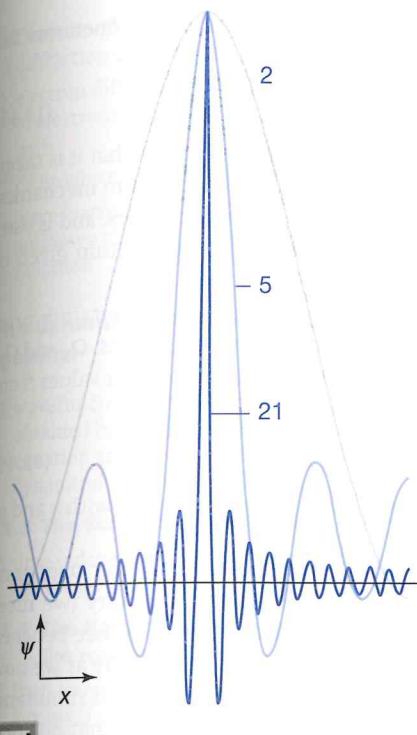
If there is complete certainty about the position of the particle ($\Delta q = 0$), the only way that eqn 41 can be satisfied is for $\Delta p = \infty$, which implies complete uncertainty about the momentum. Conversely, if the momentum is known exactly ($\Delta p = 0$), then the position must be completely uncertain ($\Delta q = \infty$).

The p and q that appear in eqn 41 refer to the same direction in space. Therefore, whereas position on the x -axis and momentum parallel to the x -axis are restricted by the uncertainty relation, simultaneous location of position on x and motion parallel to y or z are not restricted.

Example 11.7 Using the uncertainty principle

The speed of a projectile of mass 1.0 g is known to within $1 \mu\text{m s}^{-1}$. Calculate the minimum uncertainty in its position.

Method Estimate Δp from $m\Delta v$, where Δv is the uncertainty in the speed; then use eqn 41 to estimate the minimum uncertainty in position, Δq .



11.27 The wavefunction for a particle with an ill-defined location can be regarded as the superposition of several wavefunctions of definite wavelength that interfere constructively in one place but destructively elsewhere. As more waves are used in the superposition (as given by the numbers attached to the curves), the location becomes more precise at the expense of uncertainty in the particle's momentum. An infinite number of waves is needed to construct the wavefunction of a perfectly localized particle.

Answer The minimum uncertainty in position is

$$\Delta q = \frac{\hbar}{2m\Delta v} = \frac{1.055 \times 10^{-34} \text{ Js}}{2 \times (1.0 \times 10^{-3} \text{ kg}) \times (1 \times 10^{-6} \text{ m s}^{-1})} = 5 \times 10^{-26} \text{ m}$$

where we have used $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$.

Comment The uncertainty is completely negligible for all practical purposes concerning macroscopic objects. However, if the mass is that of an electron, the same uncertainty in speed implies an uncertainty in position far larger than the diameter of an atom; so the concept of a trajectory, the simultaneous possession of a precise position and momentum, is untenable.

Self-test 11.8 Estimate the minimum uncertainty in the speed of an electron in a one-dimensional region of length $2a_0$. [500 km s $^{-1}$]

The Heisenberg uncertainty principle is more general than eqn 41 suggests. It applies to any pair of observables called **complementary observables**, which are defined in terms of the properties of their operators. Specifically, two observables Ω_1 and Ω_2 are complementary if

$$\hat{\Omega}_1(\hat{\Omega}_2\psi) \neq \hat{\Omega}_2(\hat{\Omega}_1\psi) \quad (11.43)$$

When the effect of two operators depends on their order (as this equation implies), we say that they do not **commute**.

Illustration 11.2

To show that the operators for position and momentum do not commute (and hence are complementary observables) we consider the effect of $\hat{x}\hat{p}_x$ (that is, the effect of \hat{p}_x followed by the effect on the outcome of multiplication by x) on a wavefunction ψ :

$$\hat{x}\hat{p}_x\psi = x \times \frac{\hbar}{i} \frac{d\psi}{dx}$$

Next, we consider the effect of $\hat{p}_x\hat{x}$ on the same function (that is, the effect of multiplication by x followed by the effect of \hat{p}_x on the outcome):

$$\hat{p}_x\hat{x}\psi = \frac{\hbar}{i} \frac{d}{dx} x\psi = \frac{\hbar}{i} \left(\psi + x \frac{d\psi}{dx} \right)$$

For this step we have used the standard rule about differentiating a product of functions (see *Further information 1*). The second expression is clearly different from the first, so the two operators do not commute.

The different outcomes of the effect of applying $\hat{\Omega}_1$ and $\hat{\Omega}_2$ in a different order are expressed by introducing the **commutator** of the two operators, which is defined as

$$[\hat{\Omega}_1, \hat{\Omega}_2] = \hat{\Omega}_1\hat{\Omega}_2 - \hat{\Omega}_2\hat{\Omega}_1 \quad [11.44]$$

We can conclude from Illustration 11.2 that the commutator of the operators for position and linear momentum is

$$[\hat{x}, \hat{p}_x] = i\hbar \quad (11.45)$$

This commutator is of such vital significance in quantum mechanics that it is taken as a fundamental distinction between classical mechanics and quantum mechanics. In fact, this commutator is taken as a postulate of quantum mechanics, and is used to justify the choice of the operators for position and linear momentum given in eqn 32.

With the concept of commutator established, the Heisenberg uncertainty principle can be given its most general form. For any two pairs of observables, Ω_1 and Ω_2 , the uncertainties (to be precise, the root mean square deviations of their values from the mean) in simultaneous determinations are related by

$$\Delta\Omega_1 \Delta\Omega_2 \geq \frac{1}{2} |\langle [\hat{\Omega}_1, \hat{\Omega}_2] \rangle| \quad (11.46)$$

We obtain the special case of eqn 41 when we identify the observables with x and p_x and use eqn 45 for their commutator.

Complementary observables are observables with non-commuting operators. With the discovery that some pairs of observables are complementary (we meet more examples in the next chapter), we are at the heart of the difference between classical and quantum mechanics. Classical mechanics supposed, falsely as we now know, that the position and momentum of a particle could be specified simultaneously with arbitrary precision. However, quantum mechanics shows that position and momentum are complementary, and that we have to make a choice: we can specify position at the expense of momentum, or momentum at the expense of position.

The realization that some observables are complementary allows us to make considerable progress with the calculation of atomic and molecular properties; but it does away with some of the most cherished concepts of classical physics.

Checklist of key ideas

- classical mechanics, the laws of motion introduced in the seventeenth century by Isaac Newton
- quantum mechanics, the laws of motion introduced in the twentieth century by Heisenberg and Schrödinger

The origins of quantum mechanics

11.1 The failures of classical physics

- black body, an object capable of emitting and absorbing all frequencies of radiation uniformly
- Wien displacement law, $T\lambda_{\max} = \frac{1}{5}c_2$
- second radiation constant, $c_2 = hc/k = 1.44 \text{ cm K}$

- Stefan-Boltzmann law, $E = aT^4$, $a = 4\sigma/c$
- excitation, the power emitted by a region of surface divided by the area of the surface
- Stefan-Boltzmann constant, $\sigma = 2\pi^5 k^4 / 15 c^2 h^3 = 56.7 \text{ nW m}^{-2} \text{ K}^{-4}$
- Rayleigh-Jeans law, $dE = \rho d\lambda$, $\rho = 8\pi kT/\lambda^4$
- quantization of energy, the limitation of energies to discrete values
- Planck's constant, $\hbar = 6.626 \text{ } 08 \times 10^{-34} \text{ J s}$
- Planck distribution, $dE = \rho d\lambda$, $\rho = (8\pi\hbar c/\lambda^5)/(e^{hc/\lambda kT} - 1)$
- Dulong and Petit's law: the molar heat capacities of all monatomic solids are the same, and close to $25 \text{ J K}^{-1} \text{ mol}^{-1}$

- Einstein formula, $C_{V,m} = 3Rf^2$, $f = (\theta_E/T)e^{\theta_E/2T}/(e^{\theta_E/T} - 1)$
- Einstein temperature, $\theta_E = hv/k$

- Debye formula, $C_{V,m} = 3Rf$, $f = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$
- Debye temperature, $\theta_D = hv_D/k$

11.2 Wave-particle duality

- photoelectric effect, the ejection of electrons from metals when they are exposed to ultraviolet radiation: $\frac{1}{2}m_e v^2 = hv - \Phi$
- work function, the energy required to remove an electron from the metal to infinity