

# 8

# Quantum theory: introduction and principles

This chapter introduces some of the basic principles of quantum mechanics. First, it reviews the experimental results that overthrew the concepts of classical physics. These experiments led to the conclusion that particles may not have an arbitrary energy and that the classical concepts of ‘particle’ and ‘wave’ blend together. The overthrow of classical mechanics inspired the formulation of a new set of concepts and led to the formulation of quantum mechanics. In quantum mechanics, all the properties of a system are expressed in terms of a wavefunction that is obtained by solving the Schrödinger equation. We see how to interpret wavefunctions. Finally, we introduce some of the techniques of quantum mechanics in terms of operators, and see that they lead to the uncertainty principle, one of the most profound departures from classical mechanics.

It was once thought that the motion of atoms and subatomic particles could be expressed using **classical mechanics**, the laws of motion introduced in the seventeenth century by Isaac Newton, for these laws were very successful at explaining the motion of everyday objects and planets. However, towards the end of the nineteenth century, experimental evidence accumulated showing that classical mechanics failed when it was applied to particles as small as electrons, and it took until the 1920s to discover the appropriate concepts and equations for describing them. We describe the concepts of this new mechanics, which is called **quantum mechanics**, in this chapter, and apply them throughout the remainder of the text.

## The origins of quantum mechanics

The basic principles of classical mechanics are reviewed in *Appendix 2*. In brief, they show that classical physics (1) predicts a precise trajectory for particles, with precisely specified locations and momenta at each instant, and (2) allows the translational, rotational, and vibrational modes of motion to be excited to any energy simply by controlling the forces that are applied. These conclusions agree with everyday experience. Everyday experience, however, does not extend to individual atoms, and careful experiments of the type described below have shown that classical mechanics fails when applied to the transfers of very small energies and to objects of very small mass.

We shall also investigate the properties of light. In classical physics, light is described as electromagnetic radiation, which is understood in terms of the **electromagnetic field**, an oscillating electric and magnetic disturbance that spreads as a harmonic wave through empty space, the vacuum. Such waves are generated by the acceleration of electric charge, as in the oscillating motion of electrons in the antenna of a radio transmitter. The wave travels at a constant speed called the *speed of light*,  $c$ , which

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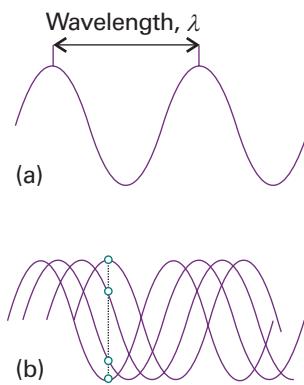
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**Fig. 8.1** The wavelength,  $\lambda$ , of a wave is the peak-to-peak distance. (b) The wave is shown travelling to the right at a speed  $c$ . At a given location, the instantaneous amplitude of the wave changes through a complete cycle (the four dots show half a cycle). The frequency,  $\nu$ , is the number of cycles per second that occur at a given point.

#### Comment 8.1

Harmonic waves are waves with displacements that can be expressed as sine or cosine functions. The physics of waves is reviewed in Appendix 3.

is about  $3 \times 10^8 \text{ m s}^{-1}$ . As its name suggests, an electromagnetic field has two components, an **electric field** that acts on charged particles (whether stationary or moving) and a **magnetic field** that acts only on moving charged particles. The electromagnetic field is characterized by a **wavelength**,  $\lambda$  (lambda), the distance between the neighbouring peaks of the wave, and its **frequency**,  $\nu$  (nu), the number of times per second at which its displacement at a fixed point returns to its original value (Fig. 8.1). The frequency is measured in **hertz**, where  $1 \text{ Hz} = 1 \text{ s}^{-1}$ . The wavelength and frequency of an electromagnetic wave are related by

$$\lambda\nu = c \quad [8.1]$$

Therefore, the shorter the wavelength, the higher the frequency. The characteristics of the wave are also reported by giving the **wavenumber**,  $\tilde{\nu}$  (nu tilde), of the radiation, where

$$\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} \quad [8.2]$$

Wavenumbers are normally reported in reciprocal centimetres ( $\text{cm}^{-1}$ ).

Figure 8.2 summarizes the **electromagnetic spectrum**, the description and classification of the electromagnetic field according to its frequency and wavelength. White light is a mixture of electromagnetic radiation with wavelengths ranging from about 380 nm to about 700 nm (1 nm =  $10^{-9} \text{ m}$ ). Our eyes perceive different wavelengths of radiation in this range as different colours, so it can be said that white light is a mixture of light of all different colours.

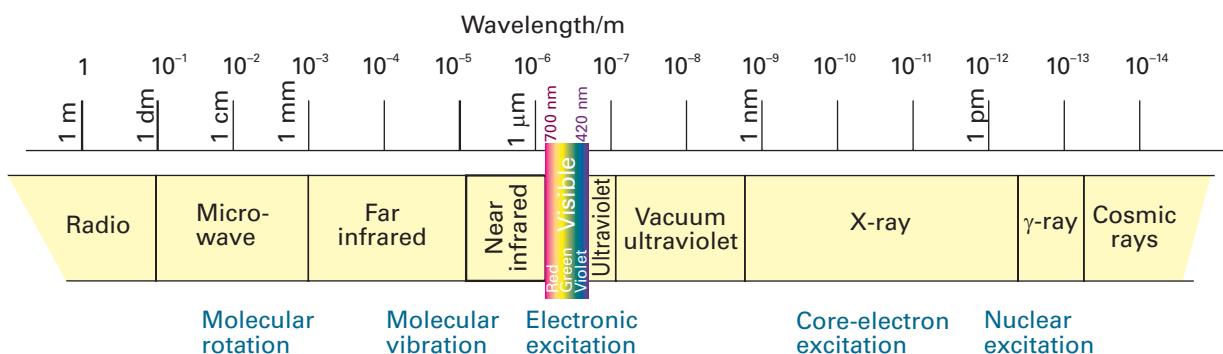
The wave model falls short of describing all the properties of radiation. So, just as our view of particles (and in particular small particles) needs to be adjusted, a new view of light also has to be developed.

### 8.1 The failures of classical physics

In this section we review some of the experimental evidence that showed that several concepts of classical mechanics are untenable. In particular, we shall see that observations of the radiation emitted by hot bodies, heat capacities, and the spectra of atoms and molecules indicate that systems can take up energy only in discrete amounts.

#### (a) Black-body radiation

A hot object emits electromagnetic radiation. At high temperatures, an appreciable proportion of the radiation is in the visible region of the spectrum, and a higher



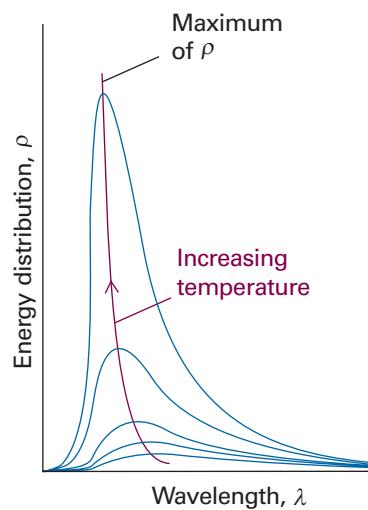
**Fig. 8.2** The electromagnetic spectrum and the classification of the spectral regions.

proportion of short-wavelength blue light is generated as the temperature is raised. This behaviour is seen when a heated iron bar glowing red hot becomes white hot when heated further. The dependence is illustrated in Fig. 8.3, which shows how the energy output varies with wavelength at several temperatures. The curves are those of an ideal emitter called a **black body**, which is an object capable of emitting and absorbing all frequencies of radiation uniformly. A good approximation to a black body is a pinhole in an empty container maintained at a constant temperature, because any radiation leaking out of the hole has been absorbed and re-emitted inside so many times that it has come to thermal equilibrium with the walls (Fig. 8.4).

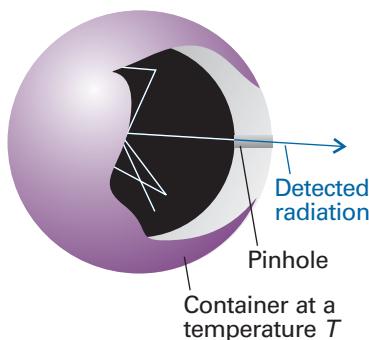
The explanation of black-body radiation was a major challenge for nineteenth-century scientists, and in due course it was found to be beyond the capabilities of classical physics. The physicist Lord Rayleigh studied it theoretically from a classical viewpoint, and thought of the electromagnetic field as a collection of oscillators of all possible frequencies. He regarded the presence of radiation of frequency  $\nu$  (and therefore of wavelength  $\lambda = c/\nu$ ) as signifying that the electromagnetic oscillator of that frequency had been excited (Fig. 8.5). Rayleigh used the equipartition principle (Section 2.2) to calculate the average energy of each oscillator as  $kT$ . Then, with minor help from James Jeans, he arrived at the **Rayleigh–Jeans law** (see *Further reading* for its justification):

$$dE = \rho d\lambda \quad \rho = \frac{8\pi kT}{\lambda^4} \quad (8.3)$$

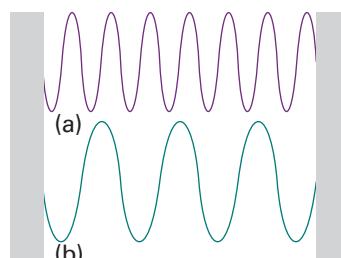
where  $\rho$  (rho), the **density of states**, is the proportionality constant between  $d\lambda$  and the energy density,  $dE$ , in the range of wavelengths between  $\lambda$  and  $\lambda + d\lambda$ ,  $k$  is Boltzmann's constant ( $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$ ). The units of  $\rho$  are typically joules per metre<sup>4</sup> ( $\text{J m}^{-4}$ ), to give an energy density  $dE$  in joules per cubic metre ( $\text{J m}^{-3}$ ) when multiplied by a wavelength range  $d\lambda$  in metres. A high density of states at the wavelength  $\lambda$  simply means that there is a lot of energy associated with wavelengths lying between  $\lambda$  and  $\lambda + d\lambda$ . The total energy density (in joules per cubic metre) in a region is obtained by integrating eqn 8.3 over all wavelengths between zero and infinity, and the total energy (in joules) within the region is obtained by multiplying that total energy density by the volume of the region.



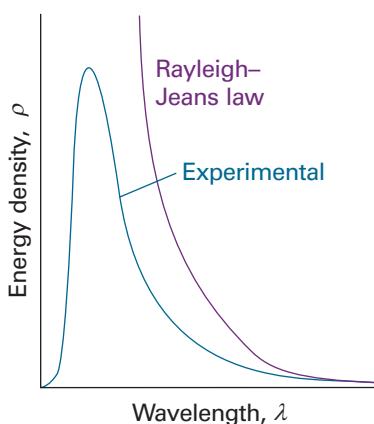
**Fig. 8.3** The energy distribution in a black-body cavity at several temperatures. Note how the energy density increases in the region of shorter wavelengths as the temperature is raised, and how the peak shifts to shorter wavelengths. The total energy density (the area under the curve) increases as the temperature is increased (as  $T^4$ ).



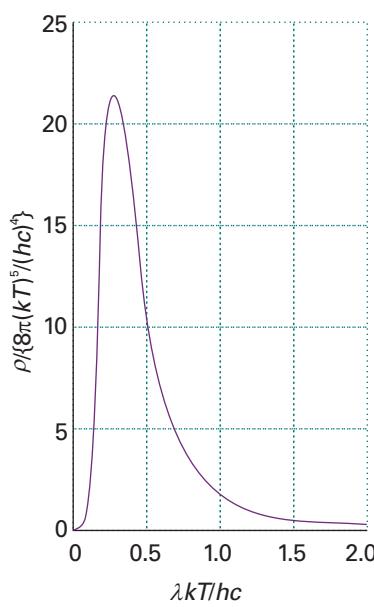
**Fig. 8.4** An experimental representation of a black-body is a pinhole in an otherwise closed container. The radiation is reflected many times within the container and comes to thermal equilibrium with the walls at a temperature  $T$ . Radiation leaking out through the pinhole is characteristic of the radiation within the container.



**Fig. 8.5** The electromagnetic vacuum can be regarded as able to support oscillations of the electromagnetic field. When a high frequency, short wavelength oscillator (a) is excited, that frequency of radiation is present. The presence of low frequency, long wavelength radiation (b) signifies that an oscillator of the corresponding frequency has been excited.



**Fig. 8.6** The Rayleigh–Jeans law (eqn 8.3) predicts an infinite energy density at short wavelengths. This approach to infinity is called the *ultraviolet catastrophe*.



**Fig. 8.7** The Planck distribution (eqn 8.5) accounts very well for the experimentally determined distribution of black-body radiation. Planck's quantization hypothesis essentially quenches the contributions of high frequency, short wavelength oscillators. The distribution coincides with the Rayleigh–Jeans distribution at long wavelengths.

 **Exploration** Plot the Planck distribution at several temperatures and confirm that eqn 8.5 predicts the behaviour summarized by Fig. 8.2.

Unfortunately (for Rayleigh, Jeans, and classical physics), although the Rayleigh–Jeans law is quite successful at long wavelengths (low frequencies), it fails badly at short wavelengths (high frequencies). Thus, as  $\lambda$  decreases,  $\rho$  increases without going through a maximum (Fig. 8.6). The equation therefore predicts that oscillators of very short wavelength (corresponding to ultraviolet radiation, X-rays, and even  $\gamma$ -rays) are strongly excited even at room temperature. This absurd result, which implies that a large amount of energy is radiated in the high-frequency region of the electromagnetic spectrum, is called the **ultraviolet catastrophe**. According to classical physics, even cool objects should radiate in the visible and ultraviolet regions, so objects should glow in the dark; there should in fact be no darkness.

### (b) The Planck distribution

The German physicist Max Planck studied black-body radiation from the viewpoint of thermodynamics. In 1900 he found that he could account for the experimental observations by proposing that the energy of each electromagnetic oscillator is limited to discrete values and cannot be varied arbitrarily. This proposal is quite contrary to the viewpoint of classical physics (on which the equipartition principle used by Rayleigh is based), in which all possible energies are allowed. The limitation of energies to discrete values is called the **quantization of energy**. In particular, Planck found that he could account for the observed distribution of energy if he supposed that the permitted energies of an electromagnetic oscillator of frequency  $v$  are integer multiples of  $hv$ :

$$E = nhv \quad n = 0, 1, 2, \dots \quad (8.4)$$

where  $h$  is a fundamental constant now known as **Planck's constant**. On the basis of this assumption, Planck was able to derive the **Planck distribution**:

$$dE = \rho d\lambda \quad \rho = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)} \quad (8.5)$$

(For references to the derivation of this expression, see *Further reading*.) This expression fits the experimental curve very well at all wavelengths (Fig. 8.7), and the value of  $h$ , which is an undetermined parameter in the theory, may be obtained by varying its value until a best fit is obtained. The currently accepted value for  $h$  is  $6.626 \times 10^{-34}$  J s.

The Planck distribution resembles the Rayleigh–Jeans law (eqn 8.3) apart from the all-important exponential factor in the denominator. For short wavelengths,  $hc/\lambda kT \gg 1$  and  $e^{hc/\lambda kT} \rightarrow \infty$  faster than  $\lambda^5 \rightarrow 0$ ; therefore  $\rho \rightarrow 0$  as  $\lambda \rightarrow 0$  or  $v \rightarrow \infty$ . Hence, the energy density approaches zero at high frequencies, in agreement with observation. For long wavelengths,  $hc/\lambda kT \ll 1$ , and the denominator in the Planck distribution can be replaced by

$$e^{hc/\lambda kT} - 1 = \left( 1 + \frac{hc}{\lambda kT} + \dots \right) - 1 \approx \frac{hc}{\lambda kT}$$

When this approximation is substituted into eqn 8.5, we find that the Planck distribution reduces to the Rayleigh–Jeans law.

It is quite easy to see why Planck's approach was successful while Rayleigh's was not. The thermal motion of the atoms in the walls of the black body excites the oscillators of the electromagnetic field. According to classical mechanics, all the oscillators of the field share equally in the energy supplied by the walls, so even the highest frequencies are excited. The excitation of very high frequency oscillators results in the ultraviolet catastrophe. According to Planck's hypothesis, however, oscillators are excited only if

they can acquire an energy of at least  $h\nu$ . This energy is too large for the walls to supply in the case of the very high frequency oscillators, so the latter remain unexcited. The effect of quantization is to reduce the contribution from the high frequency oscillators, for they cannot be significantly excited with the energy available.

### (c) Heat capacities

In the early nineteenth century, the French scientists Pierre-Louis Dulong and Alexis Thérèse Petit determined the heat capacities of a number of monatomic solids. On the basis of some somewhat slender experimental evidence, they proposed that the molar heat capacities of all monatomic solids are the same and (in modern units) close to  $25 \text{ J K}^{-1} \text{ mol}^{-1}$ .

Dulong and Petit's law is easy to justify in terms of classical physics. If classical physics were valid, the equipartition principle could be used to calculate the heat capacity of a solid. According to this principle, the mean energy of an atom as it oscillates about its mean position in a solid is  $kT$  for each direction of displacement. As each atom can oscillate in three dimensions, the average energy of each atom is  $3kT$ ; for  $N$  atoms the total energy is  $3NkT$ . The contribution of this motion to the molar internal energy is therefore

$$U_m = 3N_A kT = 3RT$$

because  $N_A k = R$ , the gas constant. The molar constant volume heat capacity (see Comment 8.3) is then predicted to be

$$C_{V,m} = \left( \frac{\partial U_m}{\partial T} \right)_V = 3R \quad (8.6)$$

This result, with  $3R = 24.9 \text{ J K}^{-1} \text{ mol}^{-1}$ , is in striking accord with Dulong and Petit's value.

Unfortunately (this time, for Dulong and Petit), significant deviations from their law were observed when advances in refrigeration techniques made it possible to measure heat capacities at low temperatures. It was found that the molar heat capacities of all monatomic solids are lower than  $3R$  at low temperatures, and that the values approach zero as  $T \rightarrow 0$ . To account for these observations, Einstein (in 1905) assumed that each atom oscillated about its equilibrium position with a single frequency  $\nu$ . He then invoked Planck's hypothesis to assert that the energy of oscillation is confined to discrete values, and specifically to  $n\nu$ , where  $n$  is an integer. Einstein first calculated the contribution of the oscillations of the atoms to the total molar energy of the metal (by a method described in Section 16.4) and obtained

$$U_m = \frac{3N_A h\nu}{e^{h\nu/kT} - 1}$$

in place of the classical expression  $3RT$ . Then he found the molar heat capacity by differentiating  $U_m$  with respect to  $T$ . The resulting expression is now known as the **Einstein formula**:

$$C_{V,m} = 3Rf \quad f = \left( \frac{\theta_E}{T} \right)^2 \left( \frac{e^{\theta_E/2T}}{e^{\theta_E/T} - 1} \right)^2 \quad (8.7)$$

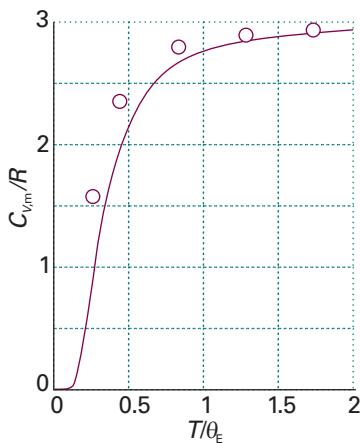
The **Einstein temperature**,  $\theta_E = h\nu/k$ , is a way of expressing the frequency of oscillation of the atoms as a temperature: a high frequency corresponds to a high Einstein temperature.

### Comment 8.2

The series expansion of an exponential function is  $e^x = 1 + x + \frac{1}{2}x^2 + \dots$ . If  $x \ll 1$ , a good approximation is  $e^x \approx 1 + x$ . For example,  $e^{0.01} = 1.010\ 050 \dots \approx 1 + 0.01$ .

### Comment 8.3

The internal energy,  $U$ , a concept from thermodynamics (Chapter 2), can be regarded as the total energy of the particles making up a sample of matter. The constant-volume heat capacity is defined as  $C_V = (\partial U / \partial T)_V$ . A small heat capacity indicates that a large rise in temperature results from a given transfer of energy.



**Fig. 8.8** Experimental low-temperature molar heat capacities and the temperature dependence predicted on the basis of Einstein's theory. His equation (eqn 8.7) accounts for the dependence fairly well, but is everywhere too low.

**Exploration** Using eqn 8.7, plot  $C_{V,m}$  against  $T$  for several values of the Einstein temperature  $\theta_E$ . At low temperature, does an increase in  $\theta_E$  result in an increase or decrease of  $C_{V,m}$ ? Estimate the temperature at which the value of  $C_{V,m}$  reaches the classical value given by eqn 8.6.

At high temperatures (when  $T \gg \theta_E$ ) the exponentials in  $f$  can be expanded as  $1 + \theta_E/T + \dots$  and higher terms ignored (see *Comment 8.2*). The result is

$$f = \left( \frac{\theta_E}{T} \right)^2 \left\{ \frac{1 + \theta_E/2T + \dots}{(1 + \theta_E/T + \dots) - 1} \right\}^2 \approx 1 \quad (8.8a)$$

Consequently, the classical result ( $C_{V,m} = 3R$ ) is obtained at high temperatures. At low temperatures, when  $T \ll \theta_E$ ,

$$f \approx \left( \frac{\theta_E}{T} \right)^2 \left( \frac{e^{\theta_E/2T}}{e^{\theta_E/T}} \right)^2 = \left( \frac{\theta_E}{T} \right)^2 e^{-\theta_E/T} \quad (8.8b)$$

The strongly decaying exponential function goes to zero more rapidly than  $1/T$  goes to infinity; so  $f \rightarrow 0$  as  $T \rightarrow 0$ , and the heat capacity therefore approaches zero too. We see that Einstein's formula accounts for the decrease of heat capacity at low temperatures. The physical reason for this success is that at low temperatures only a few oscillators possess enough energy to oscillate significantly. At higher temperatures, there is enough energy available for all the oscillators to become active: all  $3N$  oscillators contribute, and the heat capacity approaches its classical value.

Figure 8.8 shows the temperature dependence of the heat capacity predicted by the Einstein formula. The general shape of the curve is satisfactory, but the numerical agreement is in fact quite poor. The poor fit arises from Einstein's assumption that all the atoms oscillate with the same frequency, whereas in fact they oscillate over a range of frequencies from zero up to a maximum value,  $v_D$ . This complication is taken into account by averaging over all the frequencies present, the final result being the **Debye formula**:

$$C_{V,m} = 3Rf \quad f = 3 \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (8.9)$$

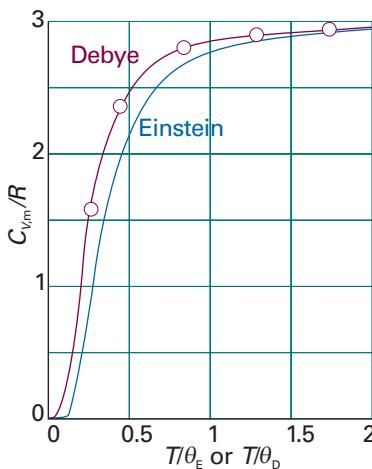
where  $\theta_D = h\nu_D/k$  is the **Debye temperature** (for a derivation, see *Further reading*). The integral in eqn 8.9 has to be evaluated numerically, but that is simple with mathematical software. The details of this modification, which, as Fig. 8.9 shows, gives improved agreement with experiment, need not distract us at this stage from the main conclusion, which is that quantization must be introduced in order to explain the thermal properties of solids.

#### Illustration 8.1 Assessing the heat capacity

The Debye temperature for lead is 105 K, corresponding to a vibrational frequency of  $2.2 \times 10^{12}$  Hz, whereas that for diamond and its much lighter, more rigidly bonded atoms, is 2230 K, corresponding to  $4.6 \times 10^{13}$  Hz. As we see from Fig. 8.9,  $f \approx 1$  for  $T > \theta_D$  and the heat capacity is almost classical. For lead at 25°C, corresponding to  $T/\theta_D = 2.8$ ,  $f = 0.99$  and the heat capacity has almost its classical value. For diamond at the same temperature,  $T/\theta_D = 0.13$ , corresponding to  $f = 0.15$ , and the heat capacity is only 15 per cent of its classical value.

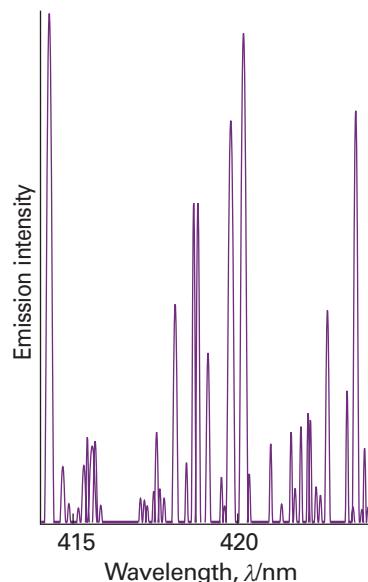
#### (d) Atomic and molecular spectra

The most compelling evidence for the quantization of energy comes from **spectroscopy**, the detection and analysis of the electromagnetic radiation absorbed, emitted, or scattered by a substance. The record of the intensity of light intensity transmitted

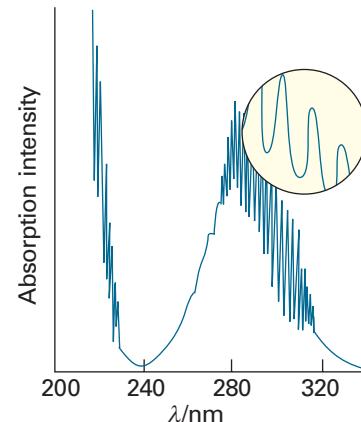


**Fig. 8.9** Debye's modification of Einstein's calculation (eqn 8.9) gives very good agreement with experiment. For copper,  $T/\theta_D = 2$  corresponds to about 170 K, so the detection of deviations from Dulong and Petit's law had to await advances in low-temperature physics.

 **Exploration** Starting with the Debye formula (eqn 8.9), plot  $dC_{V,m}/dT$ , the temperature coefficient of  $C_{V,m}$ , against  $T$  for  $\theta_D = 400$  K. At what temperature is  $C_{V,m}$  most sensitive to temperature?



**Fig. 8.10** A region of the spectrum of radiation emitted by excited iron atoms consists of radiation at a series of discrete wavelengths (or frequencies).



**Fig. 8.11** When a molecule changes its state, it does so by absorbing radiation at definite frequencies. This spectrum is part of that due to the electronic, vibrational, and rotational excitation of sulfur dioxide ( $\text{SO}_2$ ) molecules. This observation suggests that molecules can possess only discrete energies, not an arbitrary energy.

or scattered by a molecule as a function of frequency ( $v$ ), wavelength ( $\lambda$ ), or wavenumber ( $\tilde{v} = v/c$ ) is called its **spectrum** (from the Latin word for appearance).

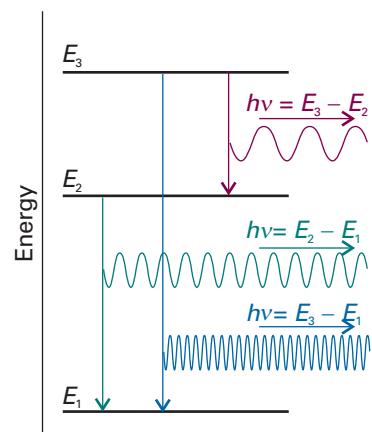
A typical atomic spectrum is shown in Fig. 8.10, and a typical molecular spectrum is shown in Fig. 8.11. The obvious feature of both is that radiation is emitted or absorbed at a series of discrete frequencies. This observation can be understood if the energy of the atoms or molecules is also confined to discrete values, for then energy can be discarded or absorbed only in discrete amounts (Fig. 8.12). Then, if the energy of an atom decreases by  $\Delta E$ , the energy is carried away as radiation of frequency  $v$ , and an emission 'line', a sharply defined peak, appears in the spectrum. We say that a molecule undergoes a **spectroscopic transition**, a change of state, when the **Bohr frequency condition**

$$\Delta E = h\nu \quad (8.10)$$

is fulfilled. We develop the principles and applications of atomic spectroscopy in Chapter 10 and of molecular spectroscopy in Chapters 13–15.

## 8.2 Wave–particle duality

At this stage we have established that the energies of the electromagnetic field and of oscillating atoms are quantized. In this section we shall see the experimental evidence that led to the revision of two other basic concepts concerning natural phenomena. One experiment shows that electromagnetic radiation—which classical physics treats as wave-like—actually also displays the characteristics of particles. Another experiment shows that electrons—which classical physics treats as particles—also display the characteristics of waves.



**Fig. 8.12** Spectroscopic transitions, such as those shown above, can be accounted for if we assume that a molecule emits a photon as it changes between discrete energy levels. Note that high-frequency radiation is emitted when the energy change is large.

**(a) The particle character of electromagnetic radiation**

The observation that electromagnetic radiation of frequency  $\nu$  can possess only the energies  $0, h\nu, 2h\nu, \dots$  suggests that it can be thought of as consisting of  $0, 1, 2, \dots$  particles, each particle having an energy  $h\nu$ . Then, if one of these particles is present, the energy is  $h\nu$ , if two are present the energy is  $2h\nu$ , and so on. These particles of electromagnetic radiation are now called **photons**. The observation of discrete spectra from atoms and molecules can be pictured as the atom or molecule generating a photon of energy  $h\nu$  when it discards an energy of magnitude  $\Delta E$ , with  $\Delta E = h\nu$ .

**Example 8.1** Calculating the number of photons

Calculate the number of photons emitted by a 100 W yellow lamp in 1.0 s. Take the wavelength of yellow light as 560 nm and assume 100 per cent efficiency.

**Method** Each photon has an energy  $h\nu$ , so the total number of photons needed to produce an energy  $E$  is  $E/h\nu$ . To use this equation, we need to know the frequency of the radiation (from  $\nu = c/\lambda$ ) and the total energy emitted by the lamp. The latter is given by the product of the power ( $P$ , in watts) and the time interval for which the lamp is turned on ( $E = P\Delta t$ ).

**Answer** The number of photons is

$$N = \frac{E}{h\nu} = \frac{P\Delta t}{h(c/\lambda)} = \frac{\lambda P\Delta t}{hc}$$

Substitution of the data gives

$$N = \frac{(5.60 \times 10^{-7} \text{ m}) \times (100 \text{ J s}^{-1}) \times (1.0 \text{ s})}{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})} = 2.8 \times 10^{20}$$

Note that it would take nearly 40 min to produce 1 mol of these photons.

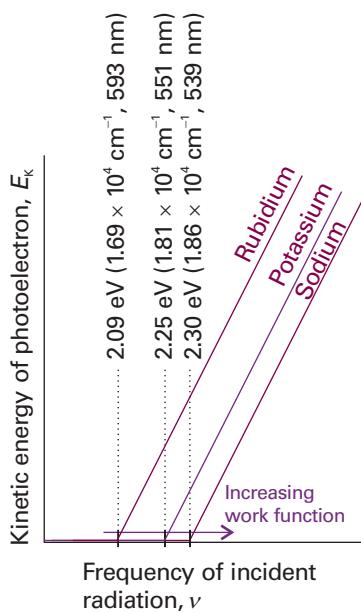
**A note on good practice** To avoid rounding and other numerical errors, it is best to carry out algebraic manipulations first, and to substitute numerical values into a single, final formula. Moreover, an analytical result may be used for other data without having to repeat the entire calculation.

**Self-test 8.1** How many photons does a monochromatic (single frequency) infrared rangefinder of power 1 mW and wavelength 1000 nm emit in 0.1 s?

[ $5 \times 10^{14}$ ]

Further evidence for the particle-like character of radiation comes from the measurement of the energies of electrons produced in the **photoelectric effect**. This effect is the ejection of electrons from metals when they are exposed to ultraviolet radiation. The experimental characteristics of the photoelectric effect are as follows:

- 1 No electrons are ejected, regardless of the intensity of the radiation, unless its frequency exceeds a threshold value characteristic of the metal.
- 2 The kinetic energy of the ejected electrons increases linearly with the frequency of the incident radiation but is independent of the intensity of the radiation.
- 3 Even at low light intensities, electrons are ejected immediately if the frequency is above the threshold.



**Fig. 8.13** In the photoelectric effect, it is found that no electrons are ejected when the incident radiation has a frequency below a value characteristic of the metal and, above that value, the kinetic energy of the photoelectrons varies linearly with the frequency of the incident radiation.

 **Exploration** Calculate the value of Planck's constant given that the following kinetic energies were observed for photoejected electrons irradiated by radiation of the wavelengths noted.

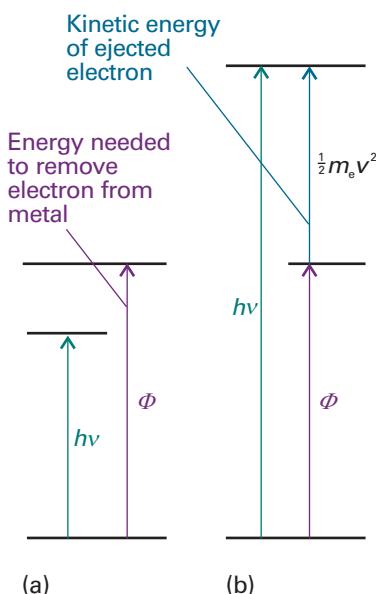
$\lambda_i/\text{nm}$	320	330	345	360	385
$E_K/\text{eV}$	1.17	1.05	0.885	0.735	0.511

Figure 8.13 illustrates the first and second characteristics.

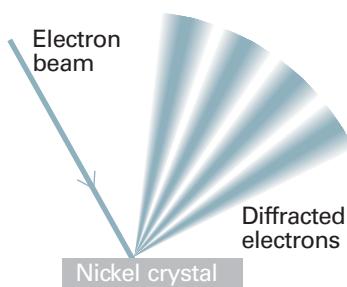
These observations strongly suggest that the photoelectric effect depends on the ejection of an electron when it is involved in a collision with a particle-like projectile that carries enough energy to eject the electron from the metal. If we suppose that the projectile is a photon of energy  $h\nu$ , where  $\nu$  is the frequency of the radiation, then the conservation of energy requires that the kinetic energy of the ejected electron should obey

$$\frac{1}{2}m_e v^2 = h\nu - \Phi \quad (8.11)$$

In this expression  $\Phi$  is a characteristic of the metal called its **work function**, the energy required to remove an electron from the metal to infinity (Fig. 8.14), the analogue of the ionization energy of an individual atom or molecule. Photoejection cannot occur if  $h\nu < \Phi$  because the photon brings insufficient energy: this conclusion accounts for observation (1). Equation 8.11 predicts that the kinetic energy of an ejected electron should increase linearly with frequency, in agreement with observation (2). When a photon collides with an electron, it gives up all its energy, so we should expect electrons to appear as soon as the collisions begin, provided the photons have sufficient energy;



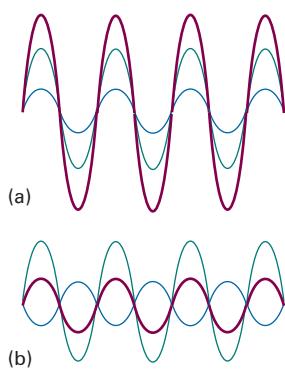
**Fig. 8.14** The photoelectric effect can be explained if it is supposed that the incident radiation is composed of photons that have energy proportional to the frequency of the radiation. (a) The energy of the photon is insufficient to drive an electron out of the metal. (b) The energy of the photon is more than enough to eject an electron, and the excess energy is carried away as the kinetic energy of the photoelectron (the ejected electron).



**Fig. 8.15** The Davisson–Germer experiment. The scattering of an electron beam from a nickel crystal shows a variation of intensity characteristic of a diffraction experiment in which waves interfere constructively and destructively in different directions.

#### Comment 8.4

A characteristic property of waves is that they interfere with one another, giving a greater displacement where peaks or troughs coincide, leading to constructive interference, and a smaller displacement where peaks coincide with troughs, leading to destructive interference (see the illustration: (a) constructive, (b) destructive).



this conclusion agrees with observation (3). A practical application of eqn 8.11 is that it provides a technique for the determination of Planck's constant, for the slopes of the lines in Fig. 8.13 are all equal to  $h$ .

#### (b) The wave character of particles

Although contrary to the long-established wave theory of light, the view that light consists of particles had been held before, but discarded. No significant scientist, however, had taken the view that matter is wave-like. Nevertheless, experiments carried out in 1925 forced people to consider that possibility. The crucial experiment was performed by the American physicists Clinton Davisson and Lester Germer, who observed the diffraction of electrons by a crystal (Fig. 8.15). Diffraction is the interference caused by an object in the path of waves. Depending on whether the interference is constructive or destructive, the result is a region of enhanced or diminished intensity of the wave. Davisson and Germer's success was a lucky accident, because a chance rise of temperature caused their polycrystalline sample to anneal, and the ordered planes of atoms then acted as a diffraction grating. At almost the same time, G.P. Thomson, working in Scotland, showed that a beam of electrons was diffracted when passed through a thin gold foil. Electron diffraction is the basis for special techniques in microscopy used by biologists and materials scientists (*Impact I8.1* and Section 20.4).

The Davisson–Germer experiment, which has since been repeated with other particles (including  $\alpha$  particles and molecular hydrogen), shows clearly that particles have wave-like properties, and the diffraction of neutrons is a well-established technique for investigating the structures and dynamics of condensed phases (see Chapter 20). We have also seen that waves of electromagnetic radiation have particle-like properties. Thus we are brought to the heart of modern physics. When examined on an atomic scale, the classical concepts of particle and wave melt together, particles taking on the characteristics of waves, and waves the characteristics of particles.

Some progress towards coordinating these properties had already been made by the French physicist Louis de Broglie when, in 1924, he suggested that any particle, not only photons, travelling with a linear momentum  $p$  should have (in some sense) a wavelength given by the **de Broglie relation**:

$$\lambda = \frac{h}{p} \quad (8.12)$$

That is, a particle with a high linear momentum has a short wavelength (Fig. 8.16). Macroscopic bodies have such high momenta (because their mass is so great), even when they are moving slowly, that their wavelengths are undetectably small, and the wave-like properties cannot be observed.

#### Example 8.2 Estimating the de Broglie wavelength

Estimate the wavelength of electrons that have been accelerated from rest through a potential difference of 40 kV.

**Method** To use the de Broglie relation, we need to know the linear momentum,  $p$ , of the electrons. To calculate the linear momentum, we note that the energy acquired by an electron accelerated through a potential difference  $V$  is  $eV$ , where  $e$  is the magnitude of its charge. At the end of the period of acceleration, all the acquired energy is in the form of kinetic energy,  $E_K = p^2/2m_e$ , so we can determine  $p$  by setting  $p^2/2m_e$  equal to  $eV$ . As before, carry through the calculation algebraically before substituting the data.

**Answer** The expression  $p^2/2m_e = eV$  solves to  $p = (2m_e eV)^{1/2}$ ; then, from the de Broglie relation  $\lambda = h/p$ ,

$$\lambda = \frac{h}{(2m_e eV)^{1/2}}$$

Substitution of the data and the fundamental constants (from inside the front cover) gives

$$\begin{aligned}\lambda &= \frac{6.626 \times 10^{-34} \text{ J s}}{\{2 \times (9.109 \times 10^{-31} \text{ kg}) \times (1.609 \times 10^{-19} \text{ C}) \times (4.0 \times 10^4 \text{ V})\}^{1/2}} \\ &= 6.1 \times 10^{-12} \text{ m}\end{aligned}$$

where we have used  $1 \text{ V C} = 1 \text{ J}$  and  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ . The wavelength of 6.1 pm is shorter than typical bond lengths in molecules (about 100 pm). Electrons accelerated in this way are used in the technique of electron diffraction for the determination of molecular structure (see Section 20.4).

**Self-test 8.2** Calculate (a) the wavelength of a neutron with a translational kinetic energy equal to  $kT$  at 300 K, (b) a tennis ball of mass 57 g travelling at 80 km/h.

[a] 178 pm, [b]  $5.2 \times 10^{-34} \text{ m}$

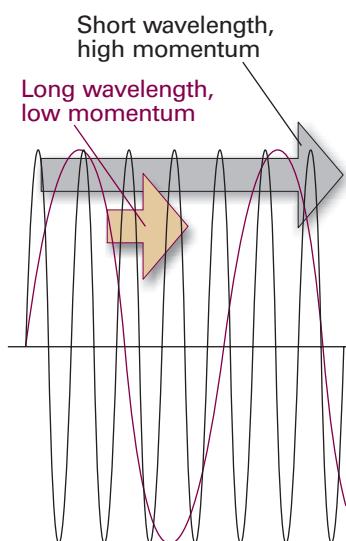
We now have to conclude that, not only has electromagnetic radiation the character classically ascribed to particles, but electrons (and all other particles) have the characteristics classically ascribed to waves. This joint particle and wave character of matter and radiation is called **wave-particle duality**. Duality strikes at the heart of classical physics, where particles and waves are treated as entirely distinct entities. We have also seen that the energies of electromagnetic radiation and of matter cannot be varied continuously, and that for small objects the discreteness of energy is highly significant. In classical mechanics, in contrast, energies could be varied continuously. Such total failure of classical physics for small objects implied that its basic concepts were false. A new mechanics had to be devised to take its place.

### IMPACT ON BIOLOGY

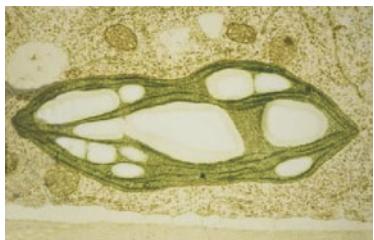
#### 18.1 Electron microscopy

The basic approach of illuminating a small area of a sample and collecting light with a microscope has been used for many years to image small specimens. However, the *resolution* of a microscope, the minimum distance between two objects that leads to two distinct images, is on the order of the wavelength of light used as a probe (see *Impact II 13.1*). Therefore, conventional microscopes employing visible light have resolutions in the micrometre range and are blind to features on a scale of nanometres.

There is great interest in the development of new experimental probes of very small specimens that cannot be studied by traditional light microscopy. For example, our understanding of biochemical processes, such as enzymatic catalysis, protein folding, and the insertion of DNA into the cell's nucleus, will be enhanced if it becomes possible to image individual biopolymers—with dimensions much smaller than visible wavelengths—at work. One technique that is often used to image nanometre-sized objects is *electron microscopy*, in which a beam of electrons with a well defined de Broglie wavelength replaces the lamp found in traditional light microscopes. Instead of glass or quartz lenses, magnetic fields are used to focus the beam. In *transmission electron microscopy* (TEM), the electron beam passes through the specimen and the



**Fig. 8.16** An illustration of the de Broglie relation between momentum and wavelength. The wave is associated with a particle (shortly this wave will be seen to be the wavefunction of the particle). A particle with high momentum has a wavefunction with a short wavelength, and vice versa.



**Fig. 8.17** A TEM image of a cross-section of a plant cell showing chloroplasts, organelles responsible for the reactions of photosynthesis (Chapter 23). Chloroplasts are typically 5  $\mu\text{m}$  long. (Image supplied by Brian Bowes.)

image is collected on a screen. In *scanning electron microscopy* (SEM), electrons scattered back from a small irradiated area of the sample are detected and the electrical signal is sent to a video screen. An image of the surface is then obtained by scanning the electron beam across the sample.

As in traditional light microscopy, the wavelength of and the ability to focus the incident beam—in this case a beam of electrons—govern the resolution. Electron wavelengths in typical electron microscopes can be as short as 10 pm, but it is not possible to focus electrons well with magnetic lenses so, in the end, typical resolutions of TEM and SEM instruments are about 2 nm and 50 nm, respectively. It follows that electron microscopes cannot resolve individual atoms (which have diameters of about 0.2 nm). Furthermore, only certain samples can be observed under certain conditions. The measurements must be conducted under high vacuum. For TEM observations, the samples must be very thin cross-sections of a specimen and SEM observations must be made on dry samples. A consequence of these requirements is that neither technique can be used to study living cells. In spite of these limitations, electron microscopy is very useful in studies of the internal structure of cells (Fig. 8.17).

## The dynamics of microscopic systems

Quantum mechanics acknowledges the wave–particle duality of matter by supposing that, rather than travelling along a definite path, a particle is distributed through space like a wave. This remark may seem mysterious: it will be interpreted more fully shortly. The mathematical representation of the wave that in quantum mechanics replaces the classical concept of trajectory is called a **wavefunction**,  $\psi$  (psi).

### 8.3 The Schrödinger equation

In 1926, the Austrian physicist Erwin Schrödinger proposed an equation for finding the wavefunction of any system. The **time-independent Schrödinger equation** for a particle of mass  $m$  moving in one dimension with energy  $E$  is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \quad (8.13)$$

The factor  $V(x)$  is the potential energy of the particle at the point  $x$ ; because the total energy  $E$  is the sum of potential and kinetic energies, the first term must be related (in a manner we explore later) to the kinetic energy of the particle;  $\hbar$  (which is read  $h$ -cross or  $h$ -bar) is a convenient modification of Planck's constant:

$$\hbar = \frac{h}{2\pi} = 1.05457 \times 10^{-34} \text{ J s} \quad (8.14)$$

For a partial justification of the form of the Schrödinger equation, see the *Justification* below. The discussions later in the chapter will help to overcome the apparent arbitrariness of this complicated expression. For the present, treat the equation as a quantum-mechanical postulate. Various ways of expressing the Schrödinger equation, of incorporating the time-dependence of the wavefunction, and of extending it to more dimensions, are collected in Table 8.1. In Chapter 9 we shall solve the equation for a number of important cases; in this chapter we are mainly concerned with its significance, the interpretation of its solutions, and seeing how it implies that energy is quantized.

**Table 8.1** The Schrödinger equation

For one-dimensional systems:

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

Where  $V(x)$  is the potential energy of the particle and  $E$  is its total energy. For three-dimensional systems

$$-\frac{\hbar^2}{2m} \nabla^2\psi + V\psi = E\psi$$

where  $V$  may depend on position and  $\nabla^2$  ('del squared') is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In systems with spherical symmetry three equivalent forms are

$$\begin{aligned}\nabla^2 &= \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2} \Lambda^2 \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2 \\ &= \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2\end{aligned}$$

where

$$\Lambda^2 = \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta}$$

In the general case the Schrodinger equation is written

$$\hat{H}\psi = E\psi$$

where  $\hat{H}$  is the hamiltonian operator for the system:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V$$

For the evolution of a system with time, it is necessary to solve the time-dependent Schrödinger equation:

$$\hat{H}\Psi = i\hbar \frac{\partial\Psi}{\partial t}$$

#### **Justification 8.1** Using the Schrödinger equation to develop the de Broglie relation

Although the Schrödinger equation should be regarded as a postulate, like Newton's equations of motion, it can be seen to be plausible by noting that it implies the de Broglie relation for a freely moving particle in a region with constant potential energy  $V$ . After making the substitution  $V(x) = V$ , we can rearrange eqn 8.13 into

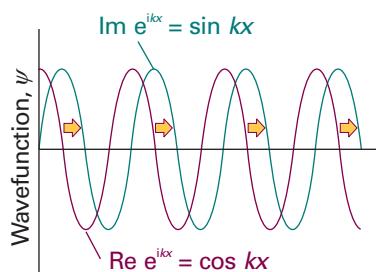
$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}(E - V)\psi$$

General strategies for solving differential equations of this and other types that occur frequently in physical chemistry are treated in *Appendix 2*. In the case at hand, we note that a solution is

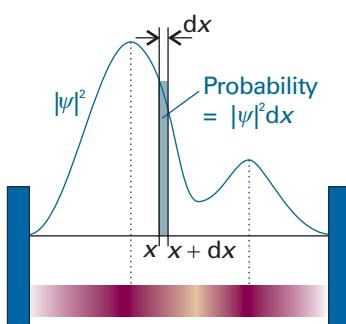
$$\psi = e^{ikx} \quad k = \left\{ \frac{2m(E - V)}{\hbar^2} \right\}^{1/2}$$

**Comment 8.5**

**Complex numbers and functions are discussed in Appendix 2.** Complex numbers have the form  $z = x + iy$ , where  $i = (-1)^{1/2}$  and the real numbers  $x$  and  $y$  are the real and imaginary parts of  $z$ , denoted  $\text{Re}(z)$  and  $\text{Im}(z)$ , respectively. Similarly, a complex function of the form  $f = g + ih$ , where  $g$  and  $h$  are functions of real arguments, has a real part  $\text{Re}(f) = g$  and an imaginary part  $\text{Im}(f) = h$ .



**Fig. 8.18** The real (purple) and imaginary (blue) parts of a free particle wavefunction corresponding to motion towards positive  $x$  (as shown by the arrow).



**Fig. 8.19** The wavefunction  $\psi$  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  $|\psi|^2 dx$ . We represent the probability density by the density of shading in the superimposed band.

**Comment 8.6**

To form the complex conjugate,  $\psi^*$ , of a complex function, replace  $i$  wherever it occurs by  $-i$ . For instance, the complex conjugate of  $e^{ikx}$  is  $e^{-ikx}$ . If the wavefunction is real,  $|\psi|^2 = \psi^* \psi$ .

In quantum mechanics, a wavefunction that describes the spatial distribution of a particle (a ‘spatial wavefunction’) is complex if the particle it describes has a net motion. In the present case, we can use the relation  $e^{i\theta} = \cos \theta + i \sin \theta$  to write

$$\psi = \cos kx + i \sin kx$$

The real and imaginary parts of  $\psi$  are drawn in Fig. 8.18, and we see that the imaginary component  $\text{Im}(\psi) = \sin kx$  is shifted in the direction of the particle’s motion. That is, both the real and imaginary parts of the wavefunction are ‘real’, in the sense of being present, and we express  $\psi$  as a complex function simply to help with the visualization of the motion of the particle the wavefunction describes.

Now we recognize that  $\cos kx$  (or  $\sin kx$ ) is a wave of wavelength  $\lambda = 2\pi/k$ , as can be seen by comparing  $\cos kx$  with the standard form of a harmonic wave,  $\cos(2\pi x/\lambda)$ . The quantity  $E - V$  is equal to the kinetic energy of the particle,  $E_K$ , so  $k = (2mE_K/\hbar^2)^{1/2}$ , which implies that  $E_K = k^2 \hbar^2 / 2m$ . Because  $E_K = p^2/2m$ , it follows that

$$p = k\hbar$$

Therefore, the linear momentum is related to the wavelength of the wavefunction by

$$p = \frac{2\pi}{\lambda} \times \frac{\hbar}{2\pi} = \frac{\hbar}{\lambda}$$

which is the de Broglie relation.

## 8.4 The Born interpretation of the wavefunction

A principal tenet of quantum mechanics is 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  $\psi$  is complex). It states that the value of  $|\psi|^2$  at a point is proportional to the probability of finding the particle in a region around that point. Specifically, for a one-dimensional system (Fig. 8.19):

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

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  $\psi$  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. 8.20):

If the wavefunction of a particle has the value  $\psi$  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  $\psi$  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. 8.21). 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 8.3 Interpreting a wavefunction

We shall see in Chapter 12 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  $1.0 \text{ pm}^3$ , 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  $\psi$  within it and write the probability,  $P$ , as proportional to the probability density ( $\psi^2$ ; note that  $\psi$  is real) evaluated at the point of interest multiplied by the volume of interest,  $\delta V$ . That is,  $P \propto \psi^2 \delta V$ , with  $\psi^2 \propto e^{-2r/a_0}$ .

**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,

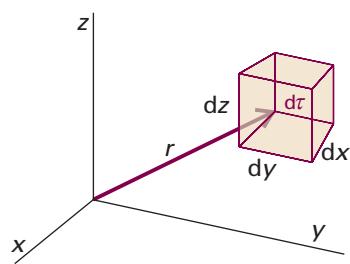
$$P \propto e^{-2} \times (1.0 \text{ pm}^3) = (0.14) \times (1.0 \text{ pm}^3)$$

Therefore, the ratio of probabilities is  $1.0/0.14 = 7.1$ . Note that it is more probable (by a factor of 7) that the electron will be found at the nucleus than in a volume element of the same size 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.

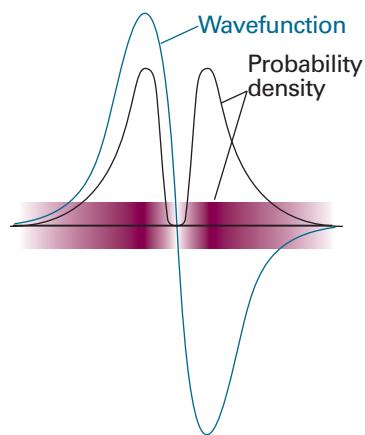
**A note on good practice** The square of a wavefunction is not a probability: it is a probability density, and (in three dimensions) has the dimensions of  $1/\text{length}^3$ . It becomes a (unitless) probability when multiplied by a volume. In general, we have to take into account the variation of the amplitude of the wavefunction over the volume of interest, but here we are supposing that the volume is so small that the variation of  $\psi$  in the region can be ignored.

**Self-test 8.3** The wavefunction for the electron in its lowest energy state in the ion  $\text{He}^+$  is proportional to  $e^{-2r/a_0}$ . Repeat the calculation for this ion. Any comment?

[55; more compact wavefunction]



**Fig. 8.20** 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.



**Fig. 8.21** 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  $\psi$  and depicted by the density of shading).

### (a) Normalization

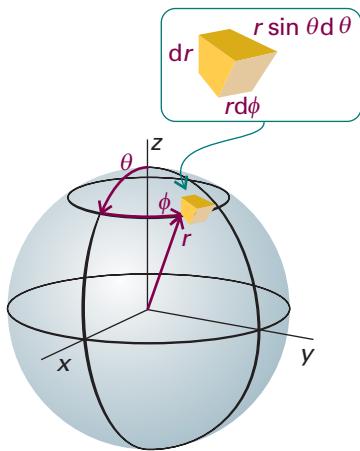
A mathematical feature of the Schrödinger equation is that, if  $\psi$  is a solution, then so is  $N\psi$ , where  $N$  is any constant. This feature is confirmed by noting that  $\psi$  occurs in every term in eqn 8.13, so any constant factor can be cancelled. This freedom to vary the wavefunction 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

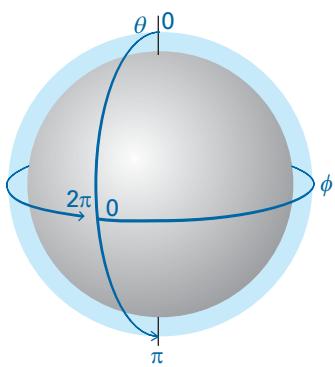
$$N^2 \int_{-\infty}^{\infty} \psi^* \psi dx = 1 \quad (8.15)$$

Almost all wavefunctions go to zero at sufficiently great distances so there is rarely any difficulty with the evaluation of this integral, and wavefunctions for which the integral in eqn 8.15 exists (in the sense of having a finite value) are said to be ‘square-integrable’. It follows that

$$N = \frac{1}{\left( \int_{-\infty}^{\infty} \psi^* \psi dx \right)^{1/2}} \quad (8.16)$$



**Fig. 8.22** The spherical polar coordinates used for discussing systems with spherical symmetry.



**Fig. 8.23** The surface of a sphere is covered by allowing  $\theta$  to range from 0 to  $\pi$ , and then sweeping that arc around a complete circle by allowing  $\phi$  to range from 0 to  $2\pi$ .

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  $\psi$  already includes a factor that ensures that (in one dimension)

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1 \quad (8.17a)$$

In three dimensions, the wavefunction is normalized if

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi^* \psi dx dy dz = 1 \quad (8.17b)$$

or, more succinctly, if

$$\int \psi^* \psi d\tau = 1 \quad (8.17c)$$

where  $d\tau = dx dy dz$  and the limits of this definite integral are not written explicitly: in all such integrals, the integration is over all the space accessible to the particle. For systems with spherical symmetry it is best to work in **spherical polar coordinates**  $r$ ,  $\theta$ , and  $\phi$  (Fig. 8.22):  $x = r \sin \theta \cos \phi$ ,  $y = r \sin \theta \sin \phi$ ,  $z = r \cos \theta$ . 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  $\infty$ , the colatitude,  $\theta$ , ranges from 0 to  $\pi$ , and the azimuth,  $\phi$ , ranges from 0 to  $2\pi$  (Fig. 8.23), so the explicit form of eqn 8.17c is

$$\int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \psi^* \psi r^2 \sin \theta dr d\theta d\phi = 1 \quad (8.17d)$$

#### Example 8.4 Normalizing a wavefunction

Normalize the wavefunction used for the hydrogen atom in Example 8.3.

**Method** We need to find the factor  $N$  that guarantees that the integral in eqn 8.17c is equal to 1. Because the system is spherical, it is most convenient to use spherical coordinates and to carry out the integrations specified in eqn 8.17d. Note that the

limits on the first integral sign refer to  $r$ , those on the second to  $\theta$ , and those on the third to  $\phi$ . 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 the product of three factors:

$$\int \psi^* \psi d\tau = N^2 \underbrace{\int_0^\infty r^2 e^{-2r/a_0} dr}_{\frac{1}{4}a_0^3} \underbrace{\int_0^\pi \sin \theta d\theta}_2 \underbrace{\int_0^{2\pi} d\phi}_{2\pi} = \pi a_0^3 N^2$$

Therefore, for this integral to equal 1, we must set

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

and the normalized wavefunction is

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

Note that, because  $a_0$  is a length, the dimensions of  $\psi$  are  $1/\text{length}^{3/2}$  and therefore those of  $\psi^2$  are  $1/\text{length}^3$  (for instance,  $1/\text{m}^3$ ) as is appropriate for a probability density.

If Example 8.3 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 10.1) that  $a_0 = 52.9$  pm, the results are (a)  $2.2 \times 10^{-6}$ , corresponding to 1 chance in about 500 000 inspections of finding the electron in the test volume, and (b)  $2.9 \times 10^{-7}$ , corresponding to 1 chance in 3.4 million.

**Self-test 8.4** Normalize the wavefunction given in Self-test 8.3.

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

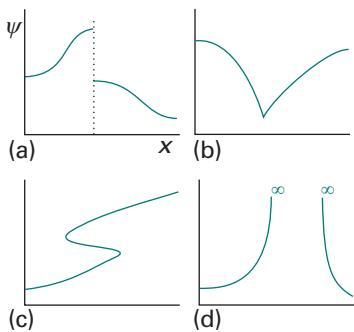
### (b) Quantization

The Born interpretation puts severe restrictions on the acceptability of wavefunctions. The principal constraint is that  $\psi$  must not be infinite anywhere. If it were, the integral in eqn 8.17 would be infinite (in other words,  $\psi$  would not be square-integrable) 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  $\psi$  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  $\psi$  is finite everywhere is not the only restriction implied by the Born interpretation. We could imagine (and in Section 9.6a 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.

### Comment 8.7

Ininitely sharp spikes are acceptable provided they have zero width, so it is more appropriate to state that the wavefunction must not be infinite over any finite region. In elementary quantum mechanics the simpler restriction, to finite  $\psi$ , is sufficient.



**Fig. 8.24** 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.

#### Comment 8.8

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.

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  $\psi$  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. 8.24) and if its first derivative, its slope, is continuous (so there are no kinks).

At this stage we see that  $\psi$  must be continuous, have a continuous slope, be single-valued, and be square-integrable. 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.

## Quantum mechanical principles

We have claimed that a wavefunction contains all the information it is possible to obtain about the dynamical properties of the particle (for example, its location and momentum). 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?

### 8.5 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 8.13 by setting  $V=0$ , and is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad (8.18)$$

The solutions of this equation have the form

$$\psi = A e^{ikx} + B e^{-ikx} \quad E = \frac{k^2 \hbar^2}{2m} \quad (8.19)$$

where  $A$  and  $B$  are constants. To verify that  $\psi$  is a solution of eqn 8.18, we simply substitute it into the left-hand side of the equation and confirm that we obtain  $E\psi$ :

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} (A e^{ikx} + B e^{-ikx}) \\ &= -\frac{\hbar^2}{2m} \{A(ik)^2 e^{ikx} + B(-ik)^2 e^{-ikx}\} \\ &= \frac{\hbar^2 k^2}{2m} (A e^{ikx} + B e^{-ikx}) = E\psi \end{aligned}$$

#### (a) The probability density

We shall see later what determines the values of  $A$  and  $B$ ; for the time being we can treat them as arbitrary constants. Suppose that  $B = 0$  in eqn 8.19, then the wavefunction is simply

$$\psi = A e^{ikx} \quad (8.20)$$

Where is the particle? To find out, we calculate the probability density:

$$|\psi|^2 = (Ae^{ikx})^*(Ae^{ikx}) = (A^*e^{-ikx})(Ae^{ikx}) = |A|^2 \quad (8.21)$$

This probability density is independent of  $x$ ; so, wherever we look along the  $x$ -axis, there is an equal probability of finding the particle (Fig. 8.25a). In other words, if the wavefunction of the particle is given by eqn 8.20, then we cannot predict where we will find the particle. The same would be true if the wavefunction in eqn 8.19 had  $A = 0$ ; then the probability density would be  $|B|^2$ , a constant.

Now suppose that in the wavefunction  $A = B$ . Then eqn 8.19 becomes

$$\psi = A(e^{ikx} + e^{-ikx}) = 2A \cos kx \quad (8.22)$$

The probability density now has the form

$$|\psi|^2 = (2A \cos kx)^*(2A \cos kx) = 4|A|^2 \cos^2 kx \quad (8.23)$$

This function is illustrated in Fig. 8.25b. 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 because it cannot be negative.

### (b) Operators, eigenvalues, and eigenfunctions

To formulate a systematic way of extracting information from the wavefunction, we first note that any Schrödinger equation (such as those in eqns 8.13 and 8.18) may be written in the succinct form

$$\hat{H}\psi = E\psi \quad (8.24a)$$

with (in one dimension)

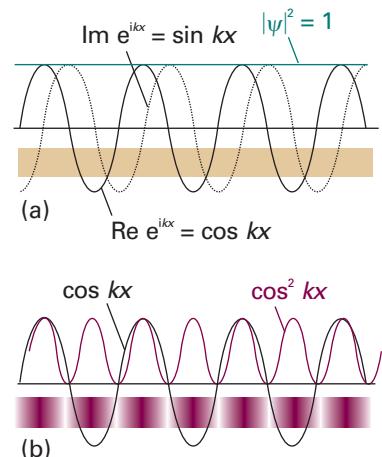
$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \quad (8.24b)$$

The quantity  $\hat{H}$  is an **operator**, something that carries out a mathematical operation on the function  $\psi$ . In this case, the operation is to take the second derivative of  $\psi$  and (after multiplication by  $-\hbar^2/2m$ ) to add the result to the outcome of multiplying  $\psi$  by  $V$ . The operator  $\hat{H}$  plays a special role in quantum mechanics, and is called the **hamiltonian operator** after the nineteenth century mathematician William Hamilton, who developed a form of classical mechanics that, it subsequently turned out, is well suited to the formulation of quantum mechanics. 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—as we anticipated in Section 8.3—that the first term in eqn 8.24b (the term proportional to the second derivative) must be the operator for the kinetic energy. When the Schrödinger equation is written as in eqn 8.24a, it is seen to be an **eigenvalue equation**, an equation of the form

$$(\text{Operator})(\text{function}) = (\text{constant factor}) \times (\text{same function}) \quad (8.25a)$$

If we denote a general operator by  $\hat{\Omega}$  (where  $\Omega$  is uppercase omega) and a constant factor by  $\omega$  (lowercase omega), then an eigenvalue equation has the form

$$\hat{\Omega}\psi = \omega\psi \quad (8.25b)$$



**Fig. 8.25** (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.

### Comment 8.9

If the probability density of a particle is a constant, then it follows that, with  $x$  ranging 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.

The factor  $\omega$  is called the **eigenvalue** of the operator  $\hat{\Omega}$ . The eigenvalue in eqn 8.24a is the energy. The function  $\psi$  in an equation of this kind is called an **eigenfunction** of the operator  $\hat{\Omega}$  and is different for each eigenvalue. The eigenfunction in eqn 8.24a is the wavefunction corresponding to the energy  $E$ . It follows that another way of saying ‘solve the Schrödinger equation’ is to say ‘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 8.5** 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  $\psi = e^{ax}$ :

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

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  $\psi$  occurs on the right, because  $\psi$  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 ( $2a$ ) times a *different* function.

**Self-test 8.5** 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 8.25b is then interpreted as an operator (for example, the hamiltonian,  $\hat{H}$ ) corresponding to an observable (for example, the energy), and the eigenvalue  $\omega$  is the value of that observable (for example, the value of the energy,  $E$ ). Therefore, if we know both the wavefunction  $\psi$  and the operator  $\hat{\Omega}$  corresponding to the observable  $\Omega$  of interest, and the wavefunction is an eigenfunction of the operator  $\hat{\Omega}$ , then we can predict the outcome of an observation of the property  $\Omega$  (for example, an atom’s energy) by picking out the factor  $\omega$  in the eigenvalue equation, eqn 8.25b.

A basic postulate of quantum mechanics tells us how to set up the operator corresponding to a given observable:

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

$$\hat{x} = x \quad \hat{p}_x = \frac{\hbar}{i} \frac{d}{dx} \quad [8.26]$$

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  $x$ .

### Comment 8.10

The rules summarized by eqn 8.26 apply to observables that depend on spatial variables; intrinsic properties, such as spin (see Section 9.8) are treated differently.

#### Example 8.6 Determining the value of an observable

What is the linear momentum of a particle described by the wavefunction in eqn 8.19 with (a)  $B = 0$ , (b)  $A = 0$ ?

**Method** We operate on  $\psi$  with the operator corresponding to linear momentum (eqn 8.26), and inspect the result. If the outcome is the original wavefunction multiplied by a constant (that is, we generate an eigenvalue equation), then the constant is identified with the value of the observable.

**Answer** (a) With the wavefunction given in eqn 8.19 with  $B = 0$ ,

$$\hat{p}_x \psi = \frac{\hbar}{i} \frac{d\psi}{dx} = \frac{\hbar}{i} A \frac{de^{ikx}}{dx} = \frac{\hbar}{i} B \times ik e^{ikx} = k\hbar B e^{-ikx} = k\hbar \psi$$

This is an eigenvalue equation, and by comparing it with eqn 8.25b we find that  $p_x = +k\hbar$ . (b) For the wavefunction with  $A = 0$ ,

$$\hat{p}_x \psi = \frac{\hbar}{i} \frac{d\psi}{dx} = \frac{\hbar}{i} B \frac{de^{-ikx}}{dx} = \frac{\hbar}{i} B \times (-ik) e^{-ikx} = -k\hbar B e^{-ikx} = -k\hbar \psi$$

The magnitude of the linear momentum is the same in each case ( $k\hbar$ ), but the signs are different: In (a) the particle is travelling to the right (positive  $x$ ) but in (b) it is travelling to the left (negative  $x$ ).

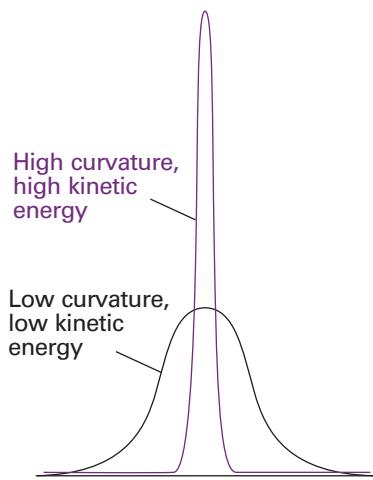
**Self-test 8.6** The operator for the angular momentum of a particle travelling in a circle in the  $xy$ -plane is  $\hat{l}_z = (\hbar/i)d/d\phi$ , where  $\phi$  is its angular position. What is the angular momentum of a particle described by the wavefunction  $e^{-2i\phi}$ ?

$$[l_z = -2\hbar]$$

We use the definitions in eqn 8.26 to construct operators for other spatial observables. For example, suppose we wanted the operator for a potential energy of the form  $V = \frac{1}{2}kx^2$ , with  $k$  a constant (later, we shall see that this potential energy describes the vibrations of atoms in molecules). Then it follows from eqn 8.26 that the operator corresponding to  $V$  is multiplication by  $x^2$ :

$$\hat{V} = \frac{1}{2}kx^2 \quad (8.27)$$

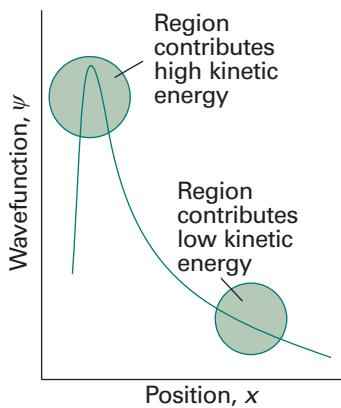
In normal practice, the multiplication sign is omitted. To construct the operator for kinetic energy, we make use of the classical relation between kinetic energy and linear



**Fig. 8.26** 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.

#### Comment 8.11

We are using the term ‘curvature’ informally: the precise technical definition of the curvature of a function  $f$  is  $(d^2f/dx^2)/\{1 + (df/dx)^2\}^{3/2}$ .



**Fig. 8.27** 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.

momentum, which in one dimension is  $E_K = p_x^2/2m$ . Then, by using the operator for  $p_x$  in eqn 8.26 we find:

$$\hat{E}_K = \frac{1}{2m} \left( i \frac{d}{dx} \right) \left( \frac{\hbar}{i} \frac{d}{dx} \right) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad (8.28)$$

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

$$\hat{H} = \hat{E}_K + \hat{V} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \hat{V} \quad (8.29)$$

with  $\hat{V}$  the multiplicative operator in eqn 8.27 (or some other relevant potential energy).

The expression for the kinetic energy operator, eqn 8.28, enables us to develop the point made earlier concerning the interpretation 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. 8.26). 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. 8.26. 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. 8.27). 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. Hence, we can expect a particle to have a high kinetic energy if the average curvature of its wavefunction is high. Locally there can be both positive and negative contributions to the kinetic energy (because the curvature can be either positive,  $\curvearrowleft$ , or negative,  $\curvearrowright$ ), but the average is always positive (see Problem 8.22).

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. 8.28). 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.

#### (c) Hermitian operators

All the quantum mechanical operators that correspond to observables have a very special mathematical property: they are ‘hermitian’. An **hermitian operator** is one for which the following relation is true:

$$\text{Hermiticity: } \int \psi_i^* \hat{Q} \psi_j dx = \left\{ \int \psi_j^* \hat{Q} \psi_i dx \right\}^* \quad [8.30]$$

It is easy to confirm that the position operator ( $x \times$ ) is hermitian because we are free to change the order of the factors in the integrand:

$$\int_{-\infty}^{\infty} \psi_i^* x \psi_j dx = \int_{-\infty}^{\infty} \psi_j x \psi_i^* dx = \left\{ \int_{-\infty}^{\infty} \psi_j^* x \psi_i dx \right\}^*$$

The demonstration that the linear momentum operator is hermitian is more involved because we cannot just alter the order of functions we differentiate, but it is hermitian, as we show in the following *Justification*.

**Justification 8.2** *The hermiticity of the linear momentum operator*

Our task is to show that

$$\int_{-\infty}^{\infty} \psi_i^* \hat{p}_x \psi_j dx = \left\{ \int_{-\infty}^{\infty} \psi_j^* \hat{p}_x \psi_i dx \right\}^*$$

with  $\hat{p}_x$  given in eqn 8.26. To do so, we use ‘integration by parts’, the relation

$$\int f \frac{dg}{dx} dx = fg - \int g \frac{df}{dx} dx$$

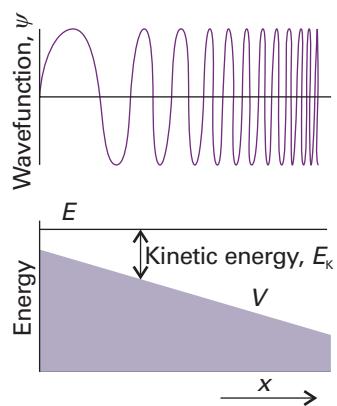
In the present case we write

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_i^* \hat{p}_x \psi_j dx &= \frac{\hbar}{i} \int_{-\infty}^{\infty} \psi_i^* \frac{d\psi_j}{dx} dx \\ &= \frac{\hbar}{i} \psi_i^* \psi_j \Big|_{-\infty}^{\infty} - \frac{\hbar}{i} \int_{-\infty}^{\infty} \psi_j \frac{d\psi_i^*}{dx} dx \end{aligned}$$

The first term on the right is zero, because all wavefunctions are zero at infinity in either direction, so we are left with

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_i^* \hat{p}_x \psi_j dx &= - \frac{\hbar}{i} \int_{-\infty}^{\infty} \psi_j \frac{d\psi_i^*}{dx} dx = \left\{ \frac{\hbar}{i} \int_{-\infty}^{\infty} \psi_j^* \frac{d\psi_i}{dx} dx \right\}^* \\ &= \left\{ \int_{-\infty}^{\infty} \psi_j^* \hat{p}_x \psi_i dx \right\}^* \end{aligned}$$

as we set out to prove.



**Fig. 8.28** 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.

**Self-test 8.7** Confirm that the operator  $d^2/dx^2$  is hermitian.

Hermitian operators are enormously important by virtue of two properties: their eigenvalues are real (as we prove in the *Justification* below), and their eigenfunctions are ‘orthogonal’. All observables have real values (in the mathematical sense, such as  $x = 2 \text{ m}$  and  $E = 10 \text{ J}$ ), so all observables are represented by hermitian operators. To say that two different functions  $\psi_i$  and  $\psi_j$  are **orthogonal** means that the integral (over all space) of their product is zero:

$$\text{Orthogonality: } \int \psi_i^* \psi_j d\tau = 0 \quad [8.31]$$

For example, the hamiltonian operator is hermitian (it corresponds to an observable, the energy). Therefore, if  $\psi_1$  corresponds to one energy, and  $\psi_2$  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.

**Justification 8.3** *The reality of eigenvalues*

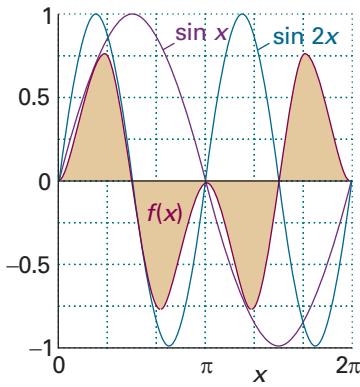
For a wavefunction  $\psi$  that is normalized and is an eigenfunction of an hermitian operator  $\hat{Q}$  with eigenvalue  $\omega$ , we can write

$$\int \psi^* \hat{Q} \psi d\tau = \int \psi^* \omega \psi d\tau = \omega \int \psi^* \psi d\tau = \omega$$

However, by taking the complex conjugate we can write

$$\omega^* = \left\{ \int \psi^* \hat{Q} \psi d\tau \right\}^* = \int \psi^* \hat{Q} \psi d\tau = \omega$$

where in the second equality we have used the hermiticity of  $\hat{Q}$ . The conclusion that  $\omega^* = \omega$  confirms that  $\omega$  is real.



**Fig. 8.29** The integral of the function  $f(x) = \sin x \sin 2x$  is equal to the area (tinted) below the brown curve, and is zero, as can be inferred by symmetry. The function—and the value of the integral—repeats itself for all replications of the section between 0 and  $2\pi$ , so the integral from  $-\infty$  to  $\infty$  is zero.

**Illustration 8.2** *Confirming orthogonality*

The wavefunctions  $\sin x$  and  $\sin 2x$  are eigenfunctions of the hermitian 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  $x = 2\pi$ , because both functions repeat themselves outside that range. Hence proving that the integral of their product is zero within that range implies that the integral over the whole of space is also zero (Fig. 8.29). A useful integral for this calculation is

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

It follows that, for  $a = 1$  and  $b = 2$ , and given the fact that  $\sin 0 = 0$ ,  $\sin 2\pi = 0$ , and  $\sin 6\pi = 0$ ,

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

and the two functions are mutually orthogonal.

**Self-test 8.8** Confirm that the functions  $\sin x$  and  $\sin 3x$  are mutually orthogonal.

$$\left[ \int_{-\infty}^{\infty} \sin x \sin 3x dx = 0 \right]$$

**(d) Superpositions and expectation values**

Suppose now that the wavefunction is the one given in eqn 8.19 (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  $p_x$ , we find

$$\frac{\hbar}{i} \frac{d\psi}{dx} = \frac{2\hbar}{i} A \frac{d \cos kx}{dx} = -\frac{2k\hbar}{i} A \sin kx \quad (8.32)$$

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

$$\psi = \psi_{\rightarrow} + \psi_{\leftarrow}$$

Particle with	
linear	linear
momentum	momentum
+ $k\hbar$	- $k\hbar$

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, if the particle is described by this wavefunction, then 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

$$\psi = c_1 \psi_1 + c_2 \psi_2 + \dots = \sum_k c_k \psi_k \quad (8.33)$$

where the  $c_k$  are numerical (possibly complex) coefficients and the  $\psi_k$  correspond to different momentum states. The functions  $\psi_k$  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  $\psi_k$  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

$$\langle \Omega \rangle = \int \psi^* \hat{\Omega} \psi d\tau \quad [8.34]$$

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.

### Comment 8.12

In general, a **linear combination** of two functions  $f$  and  $g$  is  $c_1 f + c_2 g$ , where  $c_1$  and  $c_2$  are numerical coefficients, so a linear combination is a more general term than 'sum'. In a sum,  $c_1 = c_2 = 1$ . A linear combination might have the form  $0.567f + 1.234g$ , for instance, so it is more general than the simple sum  $f + g$ .

**Justification 8.4** *The expectation value of an operator*

If  $\psi$  is an eigenfunction of  $\hat{\Omega}$  with eigenvalue  $\omega$ , the expectation value of  $\hat{\Omega}$  is

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

because  $\omega$  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  $\Omega$  results in the value  $\omega$  (because the wavefunction is an eigenfunction of  $\hat{\Omega}$ ), the mean value of all the observations is also  $\omega$ .

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 8.33, can easily be developed). Then

$$\begin{aligned} \langle \hat{\Omega} \rangle &= \int (c_1 \psi_1 + c_2 \psi_2)^* \hat{\Omega} (c_1 \psi_1 + c_2 \psi_2) d\tau \\ &= \int (c_1 \psi_1 + c_2 \psi_2)^* (c_1 \hat{\Omega} \psi_1 + c_2 \hat{\Omega} \psi_2) d\tau \\ &= \int (c_1 \psi_1 + c_2 \psi_2)^* (c_1 \omega_1 \psi_1 + c_2 \omega_2 \psi_2) d\tau \\ &= c_1^* c_1 \underbrace{\int \psi_1^* \psi_1 d\tau}_1 + c_2^* c_2 \underbrace{\int \psi_2^* \psi_2 d\tau}_1 \\ &\quad + c_2^* c_1 \underbrace{\int \psi_2^* \psi_1 d\tau}_0 + c_1^* c_2 \underbrace{\int \psi_1^* \psi_2 d\tau}_0 \end{aligned}$$

The first two integrals on the right are both equal to 1 because the wavefunctions are individually normalized. Because  $\psi_1$  and  $\psi_2$  correspond to different eigenvalues of an hermitian operator, they are orthogonal, so the third and fourth integrals on the right are zero. We can conclude that

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

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 8.7** *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 8.4) and then evaluate the integral in eqn 8.34.

**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 8.4 gives

$$\langle r \rangle = \frac{1}{\pi a_0^3} \overbrace{\int_0^\infty r^3 e^{-2r/a_0} dr}^{3!a_0^3/2^4} \overbrace{\int_0^\pi \sin \theta d\theta}^2 \overbrace{\int_0^{2\pi} d\phi}^{2\pi} = \frac{3}{2} a_0$$

Because  $a_0 = 52.9$  pm (see Section 10.1),  $\langle r \rangle = 79.4$  pm. This result means that, if a very large number of measurements of the distance of the electron from the nucleus are made, then 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 8.9** Evaluate the root mean square distance,  $\langle r^2 \rangle^{1/2}$ , of the electron from the nucleus in the hydrogen atom. [ $3^{1/2}a_0 = 91.6$  pm]

The mean kinetic energy of a particle in one dimension is the expectation value of the operator given in eqn 8.28. Therefore, we can write

$$\langle E_K \rangle = \int \psi^* \hat{E}_K \psi d\tau = -\frac{\hbar^2}{2m} \int \psi^* \frac{d^2\psi}{dx^2} d\tau \quad (8.35)$$

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  $\psi^*$  is large too).

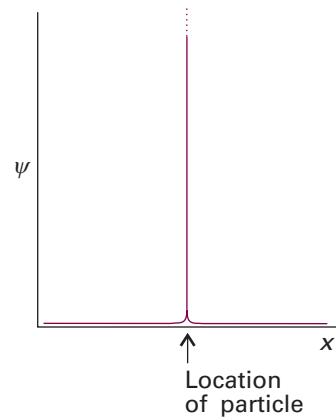
## 8.6 The uncertainty principle

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:

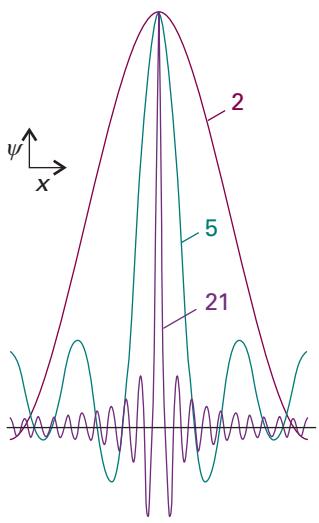
It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.

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. 8.30). 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



**Fig. 8.30** 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.



**Fig. 8.31** 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.

 **Exploration** Use mathematical software or an electronic spreadsheet to construct superpositions of cosine functions as

$$\psi(x) = \sum_{k=1}^N (1/N) \cos(k\pi x), \text{ where the}$$

constant  $1/N$  is introduced to keep the superpositions with the same overall magnitude. Explore how the probability density  $\psi^2(x)$  changes with the value of  $N$ .

wavefunction, called a **wave packet**, by forming a linear combination of wavefunctions that correspond to many different linear momenta. The superposition of a few harmonic functions gives a wavefunction that spreads over a range of locations (Fig. 8.31). 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

$$\Delta p \Delta q \geq \frac{1}{2}\hbar \quad (8.36a)$$

In this expression  $\Delta p$  is the ‘uncertainty’ in the linear momentum parallel to the axis  $q$ , and  $\Delta q$  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:

$$\Delta p = \{\langle p^2 \rangle - \langle p \rangle^2\}^{1/2} \quad \Delta q = \{\langle q^2 \rangle - \langle q \rangle^2\}^{1/2} \quad (8.36b)$$

If there is complete certainty about the position of the particle ( $\Delta q = 0$ ), then the only way that eqn 8.36a can be satisfied is for  $\Delta p = \infty$ , which implies complete uncertainty about the momentum. Conversely, if the momentum parallel to an axis is known exactly ( $\Delta p = 0$ ), then the position along that axis must be completely uncertain ( $\Delta q = \infty$ ).

The  $p$  and  $q$  that appear in eqn 8.36 refer to the same direction in space. Therefore, whereas simultaneous specification of the 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. The restrictions that the uncertainty principle implies are summarized in Table 8.2.

#### Example 8.8 Using the uncertainty principle

Suppose 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  $\Delta p$  from  $m\Delta v$ , where  $\Delta v$  is the uncertainty in the speed; then use eqn 8.36a to estimate the minimum uncertainty in position,  $\Delta q$ .

**Answer** The minimum uncertainty in position is

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

where we have used  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ . The uncertainty is completely negligible for all practical purposes concerning macroscopic objects. However, if the mass is that of an electron, then the same uncertainty in speed implies an uncertainty in

position far larger than the diameter of an atom (the analogous calculation gives  $\Delta q = 60 \text{ m}$ ); so the concept of a trajectory, the simultaneous possession of a precise position and momentum, is untenable.

**Self-test 8.10** Estimate the minimum uncertainty in the speed of an electron in a one-dimensional region of length  $2a_0$ . [500 km s<sup>-1</sup>]

The Heisenberg uncertainty principle is more general than eqn 8.36 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  $\Omega_1$  and  $\Omega_2$  are complementary if

$$\hat{\Omega}_1(\hat{\Omega}_2\psi) \neq \hat{\Omega}_2(\hat{\Omega}_1\psi) \quad (8.37)$$

When the effect of two operators depends on their order (as this equation implies), we say that they 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

$$[\hat{\Omega}_1, \hat{\Omega}_2] = \hat{\Omega}_1\hat{\Omega}_2 - \hat{\Omega}_2\hat{\Omega}_1 \quad [8.38]$$

We can conclude from *Illustration 8.3* that the commutator of the operators for position and linear momentum is

$$[\hat{x}, \hat{p}_x] = i\hbar \quad (8.39)$$

### Illustration 8.3 Evaluating a commutator

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  $\psi$ :

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

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):

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

For this step we have used the standard rule about differentiating a product of functions. The second expression is clearly different from the first, so the two operators do not commute. Subtraction of the second expression from the first gives eqn 8.39.

**Table 8.2\*** Constraints of the uncertainty principle

Variable 2	$x$	$y$	$z$	$p_x$	$p_y$	$p_z$
$x$						
$y$						
$z$						
$p_x$						
$p_y$						
$p_z$						

\* Pairs of observables that cannot be determined simultaneously with arbitrary precision are marked with a white rectangle; all others are unrestricted.

The commutator in eqn 8.39 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 may be 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 8.26.

### Comment 8.13

For two functions  $f$  and  $g$ ,  
 $d(fg) = f dg + g df$ .

**Comment 8.14**

The ‘modulus’ notation  $|\dots|$  means take the magnitude of the term the bars enclose: for a real quantity  $x$ ,  $|x|$  is the magnitude of  $x$  (its value without its sign); for an imaginary quantity  $iy$ ,  $|iy|$  is the magnitude of  $y$ ; and—most generally—for a complex quantity  $z = x + iy$ ,  $|z|$  is the value of  $(z^*z)^{1/2}$ . For example,  $|-2| = 2$ ,  $|3i| = 3$ , and  $|-2 + 3i| = \{(-2 - 3i)(-2 + 3i)\}^{1/2} = 13^{1/2}$ . Physically, the modulus on the right of eqn 8.40 ensures that the product of uncertainties has a real, non-negative value.

With the concept of commutator established, the Heisenberg uncertainty principle can be given its most general form. For *any* two pairs of observables,  $\Omega_1$  and  $\Omega_2$ , the uncertainties (to be precise, the root mean square deviations of their values from the mean) in simultaneous determinations are related by

$$\Delta\Omega_1\Delta\Omega_2 \geq \frac{1}{2} |\langle [\hat{\Omega}_1, \hat{\Omega}_2] \rangle| \quad (8.40)$$

We obtain the special case of eqn 8.36a when we identify the observables with  $x$  and  $p_x$  and use eqn 8.39 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.

## 8.7 The postulates of quantum mechanics

For convenience, we collect here the postulates on which quantum mechanics is based and which have been introduced in the course of this chapter.

*The wavefunction.* All dynamical information is contained in the wavefunction  $\psi$  for the system, which is a mathematical function found by solving the Schrödinger equation for the system. In one dimension:

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

*The Born interpretation.* If the wavefunction of a particle has the value  $\psi$  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  $|\psi|^2 d\tau$ .

*Acceptable wavefunctions.* An acceptable wavefunction must be continuous, have a continuous first derivative, be single-valued, and be square-integrable.

*Observables.* Observables,  $\Omega$ , are represented by operators,  $\hat{\Omega}$ , built from position and momentum operators of the form

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

or, more generally, from operators that satisfy the commutation relation  $[\hat{x}, \hat{p}_x] = i\hbar$ .

*The Heisenberg uncertainty principle.* It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle and, more generally, any pair of observable with operators that do not commute.

## Checklist of key ideas

- 1. In classical physics, radiation is described in terms of an oscillating electromagnetic disturbance that travels through vacuum at a constant speed  $c = \lambda v$ .
- 2. A black body is an object that emits and absorbs all frequencies of radiation uniformly.
- 3. The variation of the energy output of a black body with wavelength is explained by invoking quantization of energy, the limitation of energies to discrete values, which in turn leads to the Planck distribution, eqn 8.5.
- 4. The variation of the molar heat capacity of a solid with temperature is explained by invoking quantization of energy, which leads to the Einstein and Debye formulas, eqns 8.7 and 8.9.
- 5. Spectroscopic transitions are changes in populations of quantized energy levels of a system involving the absorption, emission, or scattering of electromagnetic radiation,  $\Delta E = h\nu$ .
- 6. The photoelectric effect is the ejection of electrons from metals when they are exposed to ultraviolet radiation:  $\frac{1}{2}m_e v^2 = h\nu - \Phi$ , where  $\Phi$  is the work function, the energy required to remove an electron from the metal to infinity.
- 7. The photoelectric effect and electron diffraction are phenomena that confirm wave–particle duality, the joint particle and wave character of matter and radiation.
- 8. The de Broglie relation,  $\lambda = h/p$ , relates the momentum of a particle with its wavelength.
- 9. A wavefunction is a mathematical function obtained by solving the Schrödinger equation and which contains all the dynamical information about a system.
- 10. The time-independent Schrödinger equation in one dimension is  $-(\hbar^2/2m)(d^2\psi/dx^2) + V(x)\psi = E\psi$ .
- 11. The Born interpretation of the wavefunction states that the value of  $|\psi|^2$ , the probability density, at a point is proportional to the probability of finding the particle at that point.
- 12. Quantization is the confinement of a dynamical observable to discrete values.
- 13. An acceptable wavefunction must be continuous, have a continuous first derivative, be single-valued, and be square-integrable.
- 14. An operator is something that carries out a mathematical operation on a function. The position and momentum operators are  $\hat{x} = x \times$  and  $\hat{p}_x = (\hbar/i)d/dx$ , respectively.
- 15. The hamiltonian operator is the operator for the total energy of a system,  $\hat{H}\psi = E\psi$  and is the sum of the operators for kinetic energy and potential energy.
- 16. An eigenvalue equation is an equation of the form  $\hat{Q}\psi = \omega\psi$ . The eigenvalue is the constant  $\omega$  in the eigenvalue equation; the eigenfunction is the function  $\psi$  in the eigenvalue equation.
- 17. The expectation value of an operator is  $\langle \hat{Q} \rangle = \int \psi^* \hat{Q} \psi d\tau$ .
- 18. An hermitian operator is one for which  $\int \psi_i^* \hat{Q} \psi_i dx = (\int \psi_j^* \hat{Q} \psi_j dx)^*$ . The eigenvalues of hermitian operators are real and correspond to observables, measurable properties of a system. The eigenfunctions of hermitian operations are orthogonal, meaning that  $\int \psi_i^* \psi_j d\tau = 0$ .
- 19. The Heisenberg uncertainty principle states that it is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle;  $\Delta p \Delta q \geq \frac{1}{2}\hbar$ .
- 20. Two operators commute when  $[\hat{Q}_1, \hat{Q}_2] = \hat{Q}_1 \hat{Q}_2 - \hat{Q}_2 \hat{Q}_1 = 0$ .
- 21. Complementary observables are observables corresponding to non-commuting operators.
- 22. The general form of the Heisenberg uncertainty principle is  $\Delta Q_1 \Delta Q_2 \geq \frac{1}{2} |\langle [\hat{Q}_1, \hat{Q}_2] \rangle|$ .

## Further reading

### Articles and texts

- P.W. Atkins, *Quanta: A handbook of concepts*. Oxford University Press (1991).
- P.W. Atkins and R.S. Friedman, *Molecular quantum mechanics*. Oxford University Press (2005).
- D. Bohm, *Quantum theory*. Dover, New York (1989).

R.P. Feynman, R.B. Leighton, and M. Sands, *The Feynman lectures on physics*. Volume III. Addison-Wesley, Reading (1965).

C.S. Johnson, Jr. and L.G. Pedersen, *Problems and solutions in quantum chemistry and physics*. Dover, New York, 1986.

L. Pauling and E.B. Wilson, *Introduction to quantum mechanics with applications to chemistry*. Dover, New York (1985).

## Discussion questions

- 8.1** Summarize the evidence that led to the introduction of quantum mechanics.
- 8.2** Explain why Planck's introduction of quantization accounted for the properties of black-body radiation.
- 8.3** Explain why Einstein's introduction of quantization accounted for the properties of heat capacities at low temperatures.
- 8.4** Describe how a wavefunction determines the dynamical properties of a system and how those properties may be predicted.
- 8.5** Account for the uncertainty relation between position and linear momentum in terms of the shape of the wavefunction.
- 8.6** Suggest how the general shape of a wavefunction can be predicted without solving the Schrödinger equation explicitly.

## Exercises

- 8.1a** To what speed must an electron be accelerated for it to have a wavelength of 3.0 cm?
- 8.1b** To what speed must a proton be accelerated for it to have a wavelength of 3.0 cm?
- 8.2a** The fine-structure constant,  $\alpha$ , plays a special role in the structure of matter; its approximate value is  $1/137$ . What is the wavelength of an electron travelling at a speed  $\alpha c$ , where  $c$  is the speed of light? (Note that the circumference of the first Bohr orbit in the hydrogen atom is 331 pm.)
- 8.2b** Calculate the linear momentum of photons of wavelength 350 nm. What speed does a hydrogen molecule need to travel to have the same linear momentum?
- 8.3a** The speed of a certain proton is  $0.45 \text{ Mm s}^{-1}$ . If the uncertainty in its momentum is to be reduced to 0.0100 per cent, what uncertainty in its location must be tolerated?
- 8.3b** The speed of a certain electron is  $995 \text{ km s}^{-1}$ . If the uncertainty in its momentum is to be reduced to 0.0010 per cent, what uncertainty in its location must be tolerated?
- 8.4a** Calculate the energy per photon and the energy per mole of photons for radiation of wavelength (a) 600 nm (red), (b) 550 nm (yellow), (c) 400 nm (blue).
- 8.4b** Calculate the energy per photon and the energy per mole of photons for radiation of wavelength (a) 200 nm (ultraviolet), (b) 150 pm (X-ray), (c) 1.00 cm (microwave).
- 8.5a** Calculate the speed to which a stationary H atom would be accelerated if it absorbed each of the photons used in Exercise 8.4a.
- 8.5b** Calculate the speed to which a stationary  ${}^4\text{He}$  atom (mass 4.0026 u) would be accelerated if it absorbed each of the photons used in Exercise 8.4b.
- 8.6a** A glow-worm of mass 5.0 g emits red light (650 nm) with a power of 0.10 W entirely in the backward direction. To what speed will it have accelerated after 10 y if released into free space and assumed to live?
- 8.6b** A photon-powered spacecraft of mass 10.0 kg emits radiation of wavelength 225 nm with a power of 1.50 kW entirely in the backward direction. To what speed will it have accelerated after 10.0 y if released into free space?
- 8.7a** A sodium lamp emits yellow light (550 nm). How many photons does it emit each second if its power is (a) 1.0 W, (b) 100 W?
- 8.7b** A laser used to read CDs emits red light of wavelength 700 nm. How many photons does it emit each second if its power is (a) 0.10 W, (b) 1.0 W?
- 8.8a** The work function for metallic caesium is 2.14 eV. Calculate the kinetic energy and the speed of the electrons ejected by light of wavelength (a) 700 nm, (b) 300 nm.
- 8.8b** The work function for metallic rubidium is 2.09 eV. Calculate the kinetic energy and the speed of the electrons ejected by light of wavelength (a) 650 nm, (b) 195 nm.
- 8.9a** Calculate the size of the quantum involved in the excitation of (a) an electronic oscillation of period 1.0 fs, (b) a molecular vibration of period 10 fs, (c) a pendulum of period 1.0 s. Express the results in joules and kilojoules per mole.
- 8.9b** Calculate the size of the quantum involved in the excitation of (a) an electronic oscillation of period 2.50 fs, (b) a molecular vibration of period 2.21 fs, (c) a balance wheel of period 1.0 ms. Express the results in joules and kilojoules per mole.
- 8.10a** Calculate the de Broglie wavelength of (a) a mass of 1.0 g travelling at  $1.0 \text{ cm s}^{-1}$ , (b) the same, travelling at  $100 \text{ km s}^{-1}$ , (c) an He atom travelling at  $1000 \text{ m s}^{-1}$  (a typical speed at room temperature).
- 8.10b** Calculate the de Broglie wavelength of an electron accelerated from rest through a potential difference of (a) 100 V, (b) 1.0 kV, (c) 100 kV.
- 8.11a** Confirm that the operator  $\hat{l}_z = (\hbar/i)d/d\phi$ , where  $\phi$  is an angle, is hermitian.
- 8.11b** Show that the linear combinations  $\hat{A} + i\hat{B}$  and  $\hat{A} - i\hat{B}$  are not hermitian if  $\hat{A}$  and  $\hat{B}$  are hermitian operators.
- 8.12a** Calculate the minimum uncertainty in the speed of a ball of mass 500 g that is known to be within  $1.0 \mu\text{m}$  of a certain point on a bat. What is the minimum uncertainty in the position of a bullet of mass 5.0 g that is known to have a speed somewhere between  $350.000\ 01 \text{ m s}^{-1}$  and  $350.000\ 00 \text{ m s}^{-1}$ ?
- 8.12b** An electron is confined to a linear region with a length of the same order as the diameter of an atom (about 100 pm). Calculate the minimum uncertainties in its position and speed.
- 8.13a** In an X-ray photoelectron experiment, a photon of wavelength 150 pm ejects an electron from the inner shell of an atom and it emerges with a speed of  $21.4 \text{ Mm s}^{-1}$ . Calculate the binding energy of the electron.
- 8.13b** In an X-ray photoelectron experiment, a photon of wavelength 121 pm ejects an electron from the inner shell of an atom and it emerges with a speed of  $56.9 \text{ Mm s}^{-1}$ . Calculate the binding energy of the electron.
- 8.14a** Determine the commutators of the operators (a)  $d/dx$  and  $1/x$ , (b)  $d/dx$  and  $x^2$ .
- 8.14b** Determine the commutators of the operators  $a$  and  $a^\dagger$ , where  $a = (\hat{x} + i\hat{p})/2^{1/2}$  and  $a^\dagger = (\hat{x} - i\hat{p})/2^{1/2}$ .

# Problems\*

## Numerical problems

**8.1** The Planck distribution gives the energy in the wavelength range  $d\lambda$  at the wavelength  $\lambda$ . Calculate the energy density in the range 650 nm to 655 nm inside a cavity of volume 100 cm<sup>3</sup> when its temperature is (a) 25°C, (b) 3000°C.

**8.2** For a black body, the temperature and the wavelength of emission maximum,  $\lambda_{\max}$ , are related by Wien's law,  $\lambda_{\max}T = \frac{1}{3}c_2$ , where  $c_2 = hc/k$  (see Problem 8.10). Values of  $\lambda_{\max}$  from a small pinhole in an electrically heated container were determined at a series of temperatures, and the results are given below. Deduce a value for Planck's constant.

$\theta/^\circ\text{C}$	1000	1500	2000	2500	3000	3500
$\lambda_{\max}/\text{nm}$	2181	1600	1240	1035	878	763

**8.3** The Einstein frequency is often expressed in terms of an equivalent temperature  $\theta_E$ , where  $\theta_E = h\nu/k$ . Confirm that  $\theta_E$  has the dimensions of temperature, and express the criterion for the validity of the high-temperature form of the Einstein equation in terms of it. Evaluate  $\theta_E$  for (a) diamond, for which  $\nu = 46.5$  THz and (b) for copper, for which  $\nu = 7.15$  THz. What fraction of the Dulong and Petit value of the heat capacity does each substance reach at 25°C?

**8.4** The ground-state wavefunction for a particle confined to a one-dimensional box of length  $L$  is

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

Suppose the box is 10.0 nm long. Calculate the probability that the particle is (a) between  $x = 4.95$  nm and 5.05 nm, (b) between  $x = 1.95$  nm and 2.05 nm, (c) between  $x = 9.90$  nm and 10.00 nm, (d) in the right half of the box, (e) in the central third of the box.

**8.5** The ground-state wavefunction of a hydrogen atom is

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

where  $a_0 = 53$  pm (the Bohr radius). (a) Calculate the probability that the electron will be found somewhere within a small sphere of radius 1.0 pm centred on the nucleus. (b) Now suppose that the same sphere is located at  $r = a_0$ . What is the probability that the electron is inside it?

**8.6** The normalized wavefunctions for a particle confined to move on a circle are  $\psi(\phi) = (1/2\pi)^{1/2} e^{-im\phi}$ , where  $m = 0, \pm 1, \pm 2, \pm 3, \dots$  and  $0 \leq \phi \leq 2\pi$ . Determine  $\langle \phi \rangle$ .

**8.7** A particle is in a state described by the wavefunction  $\psi(x) = (2a/\pi)^{1/4} e^{-ax^2}$ , where  $a$  is a constant and  $-\infty \leq x \leq \infty$ . Verify that the value of the product  $\Delta p \Delta x$  is consistent with the predictions from the uncertainty principle.

**8.8** A particle is in a state described by the wavefunction  $\psi(x) = a^{1/2} e^{-ax}$ , where  $a$  is a constant and  $0 \leq x \leq \infty$ . Determine the expectation value of the commutator of the position and momentum operators.

## Theoretical problems

**8.9** Demonstrate that the Planck distribution reduces to the Rayleigh–Jeans law at long wavelengths.

**8.10** Derive Wien's law, that  $\lambda_{\max}T$  is a constant, where  $\lambda_{\max}$  is the wavelength corresponding to maximum in the Planck distribution at the temperature  $T$ , and deduce an expression for the constant as a multiple of the second radiation constant,  $c_2 = hc/k$ .

**8.11** Use the Planck distribution to deduce the Stefan–Boltzmann law that the total energy density of black-body radiation is proportional to  $T^4$ , and find the constant of proportionality.

**8.12‡** Prior to Planck's derivation of the distribution law for black-body radiation, Wien found empirically a closely related distribution function which is very nearly but not exactly in agreement with the experimental results, namely,  $\rho = (a/\lambda^5)e^{-b/\lambda T}$ . This formula shows small deviations from Planck's at long wavelengths. (a) By fitting Wien's empirical formula to Planck's at short wavelengths determine the constants  $a$  and  $b$ .

(b) Demonstrate that Wien's formula is consistent with Wien's law (Problem 8.10) and with the Stefan–Boltzmann law (Problem 8.11).

**8.13** Normalize the following wavefunctions: (a)  $\sin(n\pi x/L)$  in the range  $0 \leq x \leq L$ , where  $n = 1, 2, 3, \dots$ , (b) a constant in the range  $-L \leq x \leq L$ , (c)  $e^{-r/a}$  in three-dimensional space, (d)  $xe^{-r/2a}$  in three-dimensional space. Hint: The volume element in three dimensions is  $d\tau = r^2 dr \sin \theta d\theta d\phi$ , with  $0 \leq r < \infty$ ,  $0 \leq \theta \leq \pi$ ,  $0 \leq \phi \leq 2\pi$ . Use the integral in Example 8.4.

**8.14** (a) Two (unnormalized) excited state wavefunctions of the H atom are

$$(i) \psi = \left(2 - \frac{r}{a_0}\right) e^{-r/a_0} \quad (ii) \psi = r \sin \theta \cos \phi e^{-r/2a_0}$$

Normalize both functions to 1. (b) Confirm that these two functions are mutually orthogonal.

**8.15** Identify which of the following functions are eigenfunctions of the operator  $d/dx$ : (a)  $e^{ikx}$ , (b)  $\cos kx$ , (c)  $k$ , (d)  $kx$ , (e)  $e^{-\alpha x^2}$ . Give the corresponding eigenvalue where appropriate.

**8.16** Determine which of the following functions are eigenfunctions of the inversion operator  $i$  (which has the effect of making the replacement  $x \rightarrow -x$ ): (a)  $x^3 - kx$ , (b)  $\cos kx$ , (c)  $x^2 + 3x - 1$ . State the eigenvalue of  $i$  when relevant.

**8.17** Which of the functions in Problem 8.15 are (a) also eigenfunctions of  $d^2/dx^2$  and (b) only eigenfunctions of  $d^2/dx^2$ ? Give the eigenvalues where appropriate.

**8.18** A particle is in a state described by the wavefunction  $\psi = (\cos \chi)e^{ikx} + (\sin \chi)e^{-ikx}$ , where  $\chi$  (chi) is a parameter. What is the probability that the particle will be found with a linear momentum (a)  $+k\hbar$ , (b)  $-k\hbar$ ? What form would the wavefunction have if it were 90 per cent certain that the particle had linear momentum  $+k\hbar$ ?

**8.19** Evaluate the kinetic energy of the particle with wavefunction given in Problem 8.18.

**8.20** Calculate the average linear momentum of a particle described by the following wavefunctions: (a)  $e^{ikx}$ , (b)  $\cos kx$ , (c)  $e^{-\alpha x^2}$ , where in each one  $x$  ranges from  $-\infty$  to  $+\infty$ .

**8.21** Evaluate the expectation values of  $r$  and  $r^2$  for a hydrogen atom with wavefunctions given in Problem 8.14.

**8.22** Calculate (a) the mean potential energy and (b) the mean kinetic energy of an electron in the ground state of a hydrogenic atom.

\* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

**8.23** Use mathematical software to construct superpositions of cosine functions and determine the probability that a given momentum will be observed. If you plot the superposition (which you should), set  $x = 0$  at the centre of the screen and build the superposition there. Evaluate the root mean square location of the packet,  $\langle x^2 \rangle^{1/2}$ .

**8.24** Show that the expectation value of an operator that can be written as the square of an hermitian operator is positive.

**8.25** (a) Given that any operators used to represent observables must satisfy the commutation relation in eqn 8.38, what would be the operator for position if the choice had been made to represent linear momentum parallel to the  $x$ -axis by multiplication by the linear momentum? These different choices are all valid ‘representations’ of quantum mechanics. (b) With the identification of  $\hat{x}$  in this representation, what would be the operator for  $1/x$ ? *Hint.* Think of  $1/x$  as  $x^{-1}$ .

### Applications: to biology, environmental science, and astrophysics

**8.26‡** The temperature of the Sun’s surface is approximately 5800 K. On the assumption that the human eye evolved to be most sensitive at the wavelength of light corresponding to the maximum in the Sun’s radiant energy distribution, determine the colour of light to which the eye is most sensitive. *Hint:* See Problem 8.10.

**8.27** We saw in *Impact I8.1* that electron microscopes can obtain images with several hundredfold higher resolution than optical microscopes because of the short wavelength obtainable from a beam of electrons. For electrons moving at speeds close to  $c$ , the speed of light, the expression for the de Broglie wavelength (eqn 8.12) needs to be corrected for relativistic effects:

$$\lambda = \frac{h}{\left\{ 2m_e eV \left( 1 + \frac{eV}{2m_e c^2} \right) \right\}^{1/2}}$$

where  $c$  is the speed of light in vacuum and  $V$  is the potential difference through which the electrons are accelerated. (a) Use the expression above to calculate the de Broglie wavelength of electrons accelerated through 50 kV. (b) Is the relativistic correction important?

**8.28‡** Solar energy strikes the top of the Earth’s atmosphere at a rate of  $343 \text{ W m}^{-2}$ . About 30 per cent of this energy is reflected directly back into space by the Earth or the atmosphere. The Earth–atmosphere system absorbs the remaining energy and re-radiates it into space as black-body radiation. What is the average black-body temperature of the Earth? What is the wavelength of the most plentiful of the Earth’s black-body radiation? *Hint.* Use Wien’s law, Problem 8.10.

**8.29‡** A star too small and cold to shine has been found by S. Kulkarni, K. Matthews, B.R. Oppenheimer, and T. Nakajima (*Science* **270**, 1478 (1995)). The spectrum of the object shows the presence of methane, which, according to the authors, would not exist at temperatures much above 1000 K. The mass of the star, as determined from its gravitational effect on a companion star, is roughly 20 times the mass of Jupiter. The star is considered to be a brown dwarf, the coolest ever found. (a) From available thermodynamic data, test the stability of methane at temperatures above 1000 K. (b) What is  $\lambda_{\max}$  for this star? (c) What is the energy density of the star relative to that of the Sun (6000 K)? (d) To determine whether the star will shine, estimate the fraction of the energy density of the star in the visible region of the spectrum.