Quantum theory: techniques and applications

9

To find the properties of systems according to quantum mechanics we need to solve the appropriate Schrödinger equation. This chapter presents the essentials of the solutions for three basic types of motion: translation, vibration, and rotation. We shall see that only certain wavefunctions and their corresponding energies are acceptable. Hence, quantization emerges as a natural consequence of the equation and the conditions imposed on it. The solutions bring to light a number of highly nonclassical, and therefore surprising, features of particles, especially their ability to tunnel into and through regions where classical physics would forbid them to be found. We also encounter a property of the electron, its spin, that has no classical counterpart. The chapter concludes with an introduction to the experimental techniques used to probe the quantization of energy in molecules.

The three basic modes of motion—translation (motion through space), vibration, and rotation—all play an important role in chemistry because they are ways in which molecules store energy. Gas-phase molecules, for instance, undergo translational motion and their kinetic energy is a contribution to the total internal energy of a sample. Molecules can also store energy as rotational kinetic energy and transitions between their rotational energy states can be observed spectroscopically. Energy is also stored as molecular vibration and transitions between vibrational states are responsible for the appearance of infrared and Raman spectra.

Translational motion

Section 8.5 introduced the quantum mechanical description of free motion in one dimension. We saw there that the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{9.1a}$$

or more succinctly

$$\hat{H}\psi = E\psi \qquad \hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{9.1b}$$

The general solutions of eqn 9.1 are

$$\psi_k = Ae^{ikx} + Be^{-ikx} \qquad E_k = \frac{k^2\hbar^2}{2m} \tag{9.2}$$

Note that we are now labelling both the wavefunctions and the energies (that is, the eigenfunctions and eigenvalues of $\hat{H}$) with the index k. We can verify that these
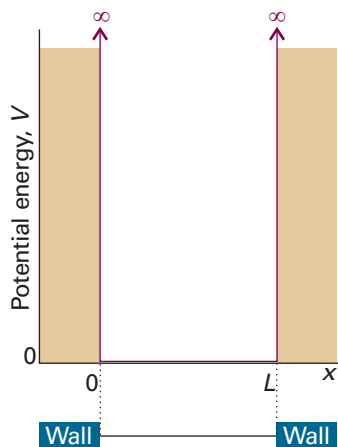
Fig. 9.1 A particle in a one-dimensional region with impenetrable walls. Its potential energy is zero between $x = 0$ and $x = L$, and rises abruptly to infinity as soon as it touches the walls.

functions are solutions by substituting ψ_k into the left-hand side of eqn 9.1a and showing that the result is equal to $E_k\psi_k$. In this case, all values of k, and therefore all values of the energy, are permitted. It follows that the translational energy of a free particle is not quantized.

We saw in Section 8.5b that a wavefunction of the form e^{ikx} describes a particle with linear momentum $p_x = +k\hbar$, corresponding to motion towards positive x (to the right), and that a wavefunction of the form e^{-ikx} describes a particle with the same magnitude of linear momentum but travelling towards negative x (to the left). That is, e^{ikx} is an eigenfunction of the operator $\hat{p}_x$ with eigenvalue $+k\hbar$, and e^{-ikx} is an eigenfunction with eigenvalue $-k\hbar$. In either state, $|\psi|^2$ is independent of x, which implies that the position of the particle is completely unpredictable. This conclusion is consistent with the uncertainty principle because, if the momentum is certain, then the position cannot be specified (the operators $\hat{x}$ and $\hat{p}_x$ do not commute, Section 8.6).

9.1 A particle in a box

In this section, we consider a **particle in a box**, in which a particle of mass m is confined between two walls at $x = 0$ and $x = L$: the potential energy is zero inside the box but rises abruptly to infinity at the walls (Fig. 9.1). This model is an idealization of the potential energy of a gas-phase molecule that is free to move in a one-dimensional container. However, it is also the basis of the treatment of the electronic structure of metals (Chapter 20) and of a primitive treatment of conjugated molecules. The particle in a box is also used in statistical thermodynamics in assessing the contribution of the translational motion of molecules to their thermodynamic properties (Chapter 16).

(a) The acceptable solutions

The Schrödinger equation for the region between the walls (where $V = 0$) is the same as for a free particle (eqn 9.1), so the general solutions given in eqn 9.2 are also the same. However, we can us $e^{\pm ix} = \cos x \pm i \sin x$ to write

$$\psi_k = Ae^{ikx} + Be^{-ikx} = A(\cos kx + i \sin kx) + B(\cos kx - i \sin kx)$$
$$= (A + B) \cos kx + (A - B)i \sin kx$$

If we absorb all numerical factors into two new coefficients C and D, then the general solutions take the form

$$\psi_k(x) = C \sin kx + D \cos kx \qquad E_k = \frac{k^2\hbar^2}{2m} \tag{9.3}$$

For a free particle, any value of E_k corresponds to an acceptable solution. However, when the particle is confined within a region, the acceptable wavefunctions must satisfy certain **boundary conditions**, or constraints on the function at certain locations. As we shall see when we discuss penetration into barriers, a wavefunction decays exponentially with distance inside a barrier, such as a wall, and the decay is infinitely fast when the potential energy is infinite. This behaviour is consistent with the fact that it is physically impossible for the particle to be found with an infinite potential energy. We conclude that the wavefunction must be zero where V is infinite, at $x < 0$ and $x > L$. The continuity of the wavefunction then requires it to vanish just inside the well at $x = 0$ and $x = L$. That is, the boundary conditions are $\psi_k(0) = 0$ and $\psi_k(L) = 0$. These boundary conditions imply quantization, as we show in the following *Justification*.

....

Justification 9.1 *The energy levels and wavefunctions of a particle in a one-dimensional box*

For an informal demonstration of quantization, we consider each wavefunction to be a de Broglie wave that must fit within the container. The permitted wavelengths satisfy

$$L = n \times \tfrac{1}{2}\lambda \qquad n = 1, 2, \ldots$$

and therefore

$$\lambda = \frac{2L}{n} \qquad \text{with } n = 1, 2, \ldots$$

According to the de Broglie relation, these wavelengths correspond to the momenta

$$p = \frac{h}{\lambda} = \frac{nh}{2L}$$

The particle has only kinetic energy inside the box (where $V = 0$), so the permitted energies are

$$E = \frac{p^2}{2m} = \frac{n^2 h^2}{8mL^2} \qquad \text{with } n = 1, 2, \ldots$$

A more formal and widely applicable approach is as follows. Consider the wall at $x = 0$. According to eqn 9.3, $\psi(0) = D$ (because $\sin 0 = 0$ and $\cos 0 = 1$). But because $\psi(0) = 0$ we must have $D = 0$. It follows that the wavefunction must be of the form $\psi_k(x) = C \sin kx$. The value of ψ at the other wall (at $x = L$) is $\psi_k(L) = C \sin kL$, which must also be zero. Taking $C = 0$ would give $\psi_k(x) = 0$ for all x, which would conflict with the Born interpretation (the particle must be somewhere). Therefore, kL must be chosen so that $\sin kL = 0$, which is satisfied by

$$kL = n\pi \qquad n = 1, 2, \ldots$$

The value $n = 0$ is ruled out, because it implies $k = 0$ and $\psi_k(x) = 0$ everywhere (because $\sin 0 = 0$), which is unacceptable. Negative values of n merely change the sign of $\sin kL$ (because $\sin(-x) = -\sin x$). The wavefunctions are therefore

$$\psi_n(x) = C \sin(n\pi x/L) \qquad n = 1, 2, \ldots$$

(At this point we have started to label the solutions with the index n instead of k.) Because k and E_k are related by eqn 9.3, and k and n are related by $kL = n\pi$, it follows that the energy of the particle is limited to $E_n = n^2 h^2/8mL^2$, the values obtained by the informal procedure.

....

We conclude that the energy of the particle in a one-dimensional box is quantized and that this quantization arises from the boundary conditions that ψ must satisfy if it is to be an acceptable wavefunction. This is a general conclusion: *the need to satisfy boundary conditions implies that only certain wavefunctions are acceptable, and hence restricts observables to discrete values.* So far, only energy has been quantized; shortly we shall see that other physical observables may also be quantized.

(b) Normalization

Before discussing the solution in more detail, we shall complete the derivation of the wavefunctions by finding the normalization constant (here written C and regarded as real, that is, does not contain i). To do so, we look for the value of C that ensures that the integral of ψ^2 over all the space available to the particle (that is, from $x = 0$ to $x = L$) is equal to 1:

$$\int_0^L \psi^2 \, dx = C^2 \int_0^L \sin^2 \frac{n\pi x}{L} = C^2 \times \frac{L}{2} = 1, \qquad \text{so } C = \left(\frac{2}{L}\right)^{1/2}$$
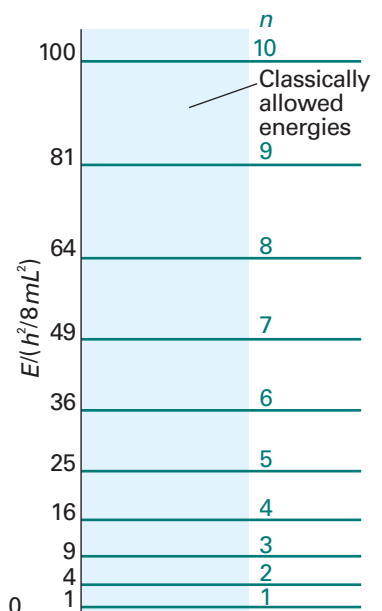
Fig. 9.2 The allowed energy levels for a particle in a box. Note that the energy levels increase as n^2, and that their separation increases as the quantum number increases.
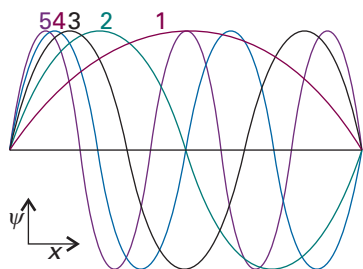

Fig. 9.3 The first five normalized wavefunctions of a particle in a box. Each wavefunction is a standing wave, and successive functions possess one more half wave and a correspondingly shorter wavelength.

Exploration Plot the probability density for a particle in a box with $n = 1, 2, \ldots 5$ and $n = 50$. How do your plots illustrate the correspondence principle?

Comment 9.1

It is sometimes useful to write

$$\cos x = (e^{ix} + e^{-ix})/2 \qquad \sin x = (e^{ix} - e^{-ix})/2i$$

for all n. Therefore, the complete solution to the problem is

$$E_n = \frac{n^2 h^2}{8mL^2} \qquad n = 1, 2, \ldots \tag{9.4a}$$

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \qquad \text{for } 0 \leq x \leq L \tag{9.4b}$$

Self-test 9.1 Provide the intermediate steps for the determination of the normalization constant C. *Hint.* Use the standard integral $\int \sin^2 ax \, dx = \frac{1}{2}x - (\frac{1}{4a}) \sin 2ax +$ constant and the fact that $\sin 2m\pi = 0$, with $m = 0, 1, 2, \ldots$.

The energies and wavefunctions are labelled with the 'quantum number' n. A **quantum number** is an integer (in some cases, as we shall see, a half-integer) that labels the state of the system. For a particle in a box there is an infinite number of acceptable solutions, and the quantum number n specifies the one of interest (Fig. 9.2). As well as acting as a label, a quantum number can often be used to calculate the energy corresponding to the state and to write down the wavefunction explicitly (in the present example, by using eqn 9.4).

(c) The properties of the solutions

Figure 9.3 shows some of the wavefunctions of a particle in a box: they are all sine functions with the same amplitude but different wavelengths. Shortening the wavelength results in a sharper average curvature of the wavefunction and therefore an increase in the kinetic energy of the particle. Note that the number of nodes (points where the wavefunction passes *through* zero) also increases as n increases, and that the wavefunction ψ_n has $n - 1$ nodes. Increasing the number of nodes between walls of a given separation increases the average curvature of the wavefunction and hence the kinetic energy of the particle.

The linear momentum of a particle in a box is not well defined because the wavefunction $\sin kx$ is a standing wave and, like the example of $\cos kx$ treated in Section 8.5d, not an eigenfunction of the linear momentum operator. However, each wavefunction is a superposition of momentum eigenfunctions:

$$\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\frac{n\pi x}{L} = \frac{1}{2i}\left(\frac{2}{L}\right)^{1/2} (e^{ikx} - e^{-ikx}) \qquad k = \frac{n\pi}{L} \tag{9.5}$$

It follows that measurement of the linear momentum will give the value $+k\hbar$ for half the measurements of momentum and $-k\hbar$ for the other half. This detection of opposite directions of travel with equal probability is the quantum mechanical version of the classical picture that a particle in a box rattles from wall to wall, and in any given period spends half its time travelling to the left and half travelling to the right.

Self-test 9.2 What is (a) the average value of the linear momentum of a particle in a box with quantum number n, (b) the average value of p^2?

$$[\text{(a) } \langle p \rangle = 0, \text{ (b) } \langle p^2 \rangle = n^2 h^2/4L^2]$$

Because n cannot be zero, the lowest energy that the particle may possess is not zero (as would be allowed by classical mechanics, corresponding to a stationary particle) but

$$E_1 = \frac{h^2}{8mL^2} \tag{9.6}$$

This lowest, irremovable energy is called the **zero-point energy**. The physical origin of the zero-point energy can be explained in two ways. First, the uncertainty principle requires a particle to possess kinetic energy if it is confined to a finite region: the location of the particle is not completely indefinite, so its momentum cannot be precisely zero. Hence it has nonzero kinetic energy. Second, if the wavefunction is to be zero at the walls, but smooth, continuous, and not zero everywhere, then it must be curved, and curvature in a wavefunction implies the possession of kinetic energy.

The separation between adjacent energy levels with quantum numbers n and $n+1$ is

$$E_{n+1} - E_n = \frac{(n+1)^2 h^2}{8mL^2} - \frac{n^2 h^2}{8mL^2} = (2n+1)\frac{h^2}{8mL^2} \tag{9.7}$$

This separation decreases as the length of the container increases, and is very small when the container has macroscopic dimensions. The separation of adjacent levels becomes zero when the walls are infinitely far apart. Atoms and molecules free to move in normal laboratory-sized vessels may therefore be treated as though their translational energy is not quantized. The translational energy of completely free particles (those not confined by walls) is not quantized.

**Illustration 9.1** *Accounting for the electronic absorption spectra of polyenes*

β-Carotene (**1**) is a linear polyene in which 10 single and 11 double bonds alternate along a chain of 22 carbon atoms. If we take each CC bond length to be about 140 pm, then the length L of the molecular box in β-carotene is $L = 0.294$ nm. For reasons that will be familiar from introductory chemistry, each C atom contributes one p-electron to the π orbitals and, in the lowest energy state of the molecule, each level up to $n = 11$ is occupied by two electrons. From eqn 9.7 it follows that the separation in energy between the ground state and the state in which one electron is promoted from $n = 11$ to $n = 12$ is

$$\Delta E = E_{12} - E_{11} = (2 \times 11 + 1)\frac{(6.626 \times 10^{-34}\text{ J s})^2}{8 \times (9.110 \times 10^{-31}\text{ kg}) \times (2.94 \times 10^{-10}\text{ m})^2}$$
$$= 1.60 \times 10^{-19}\text{ J}$$

It follows from the Bohr frequency condition (eqn 8.10, $\Delta E = h\nu$) that the frequency of radiation required to cause this transition is

$$\nu = \frac{\Delta E}{h} = \frac{1.60 \times 10^{-19}\text{ J}}{6.626 \times 10^{-34}\text{ J s}} = 2.41 \times 10^{14}\text{ s}^{-1}$$

The experimental value is $\nu = 6.03 \times 10^{14}$ s^{-1} ($\lambda = 497$ nm), corresponding to radiation in the visible range of the electromagnetic spectrum.
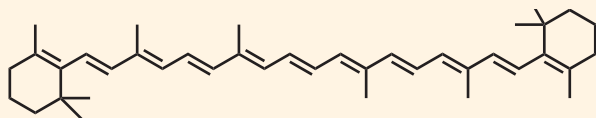
1 β-Carotene

Self-test 9.3 Estimate a typical nuclear excitation energy by calculating the first excitation energy of a proton confined to a square well with a length equal to the diameter of a nucleus (approximately 1 fm).   [0.6 GeV]
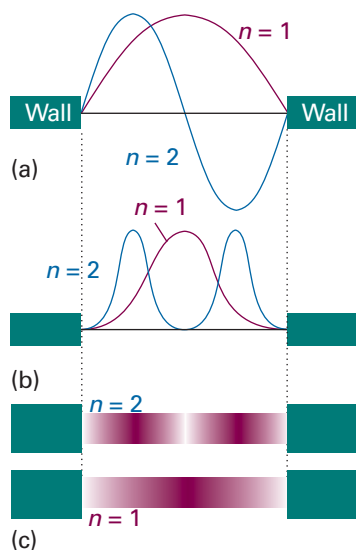
Fig. 9.4 (a) The first two wavefunctions, (b) the corresponding probability distributions, and (c) a representation of the probability distribution in terms of the darkness of shading.

The probability density for a particle in a box is

$$\psi^2(x) = \frac{2}{L}\sin^2\frac{n\pi x}{L} \tag{9.8}$$

and varies with position. The nonuniformity is pronounced when n is small (Fig. 9.4), but—provided we ignore the increasingly rapid oscillations—$\psi^2(x)$ becomes more uniform as n increases. The distribution at high quantum numbers reflects the classical result that a particle bouncing between the walls spends, on the average, equal times at all points. That the quantum result corresponds to the classical prediction at high quantum numbers is an illustration of the **correspondence principle**, which states that classical mechanics emerges from quantum mechanics as high quantum numbers are reached.

Example 9.1 *Using the particle in a box solutions*

The wavefunctions of an electron in a conjugated polyene can be approximated by particle-in-a-box wavefunctions. What is the probability, P, of locating the electron between $x = 0$ (the left-hand end of a molecule) and $x = 0.2$ nm in its lowest energy state in a conjugated molecule of length 1.0 nm?

Method The value of $\psi^2 dx$ is the probability of finding the particle in the small region dx located at x; therefore, the total probability of finding the electron in the specified region is the integral of $\psi^2 dx$ over that region. The wavefunction of the electron is given in eqn 9.4b with $n = 1$.

Answer The probability of finding the particle in a region between $x = 0$ and $x = l$ is

$$P = \int_0^l \psi_n^2 \, dx = \frac{2}{L}\int_0^l \sin^2\frac{n\pi x}{L} \, dx = \frac{l}{L} - \frac{1}{2n\pi}\sin\frac{2\pi n l}{L}$$

We then set $n = 1$ and $l = 0.2$ nm, which gives $P = 0.05$. The result corresponds to a chance of 1 in 20 of finding the electron in the region. As n becomes infinite, the sine term, which is multiplied by $1/n$, makes no contribution to P and the classical result, $P = l/L$, is obtained.

Self-test 9.4 Calculate the probability that an electron in the state with $n = 1$ will be found between $x = 0.25L$ and $x = 0.75L$ in a conjugated molecule of length L (with $x = 0$ at the left-hand end of the molecule). [0.82]

(d) Orthogonality

We can now illustrate a property of wavefunctions first mentioned in Section 8.5. Two wavefunctions are **orthogonal** if the integral of their product vanishes. Specifically, the functions ψ_n and $\psi_{n'}$ are orthogonal if

$$\int \psi_n^* \psi_{n'} \, d\tau = 0 \tag{9.9}$$

where the integration is over all space. A general feature of quantum mechanics, which we prove in the *Justification* below, is that *wavefunctions corresponding to different energies are orthogonal*; therefore, we can be confident that all the wavefunctions of a particle in a box are mutually orthogonal. A more compact notation for integrals of this kind is described in *Further information 9.1*.

Justification 9.2 *The orthogonality of wavefunctions*

Suppose we have two wavefunctions ψ_n and ψ_m corresponding to two different energies E_n and E_m, respectively. Then we can write

$$\hat{H}\psi_n = E_n\psi_n \qquad \hat{H}\psi_m = E_m\psi_m$$

Now multiply the first of these two Schrödinger equations by ψ_m^* and the second by ψ_n^* and integrate over all space:

$$\int \psi_m^* \hat{H}\psi_n \, d\tau = E_n \int \psi_m^* \psi_n \, d\tau \qquad \int \psi_n^* \hat{H}\psi_m \, d\tau = E_m \int \psi_n^* \psi_m \, d\tau$$

Next, noting that the energies themselves are real, form the complex conjugate of the second expression (for the state m) and subtract it from the first expression (for the state n):

$$\int \psi_m^* \hat{H}\psi_n \, d\tau - \left(\int \psi_n^* \hat{H}\psi_m \, d\tau\right)^* = E_n \int \psi_m^* \psi_n \, d\tau - E_m \int \psi_n \psi_m^* \, d\tau$$

By the hermiticity of the hamiltonian (Section 8.5c), the two terms on the left are equal, so they cancel and we are left with

$$0 = (E_n - E_m) \int \psi_m^* \psi_n \, d\tau$$

However, the two energies are different; therefore the integral on the right must be zero, which confirms that two wavefunctions belonging to different energies are orthogonal.
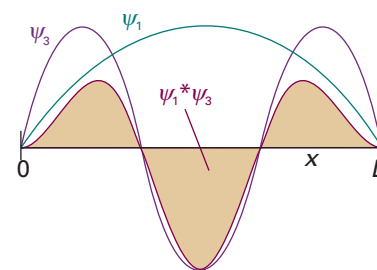

Fig. 9.5 Two functions are orthogonal if the integral of their product is zero. Here the calculation of the integral is illustrated graphically for two wavefunctions of a particle in a square well. The integral is equal to the total area beneath the graph of the product, and is zero.

Illustration 9.2 *Verifying the orthogonality of the wavefunctions for a particle in a box*

We can verify the orthogonality of wavefunctions of a particle in a box with $n = 1$ and $n = 3$ (Fig. 9.5):

$$\int_0^L \psi_1^* \psi_3 \, dx = \frac{2}{L} \int_0^L \sin \frac{\pi x}{L} \sin \frac{3\pi x}{L} \, dx = 0$$

We have used the standard integral given in *Illustration 8.2*.

The property of orthogonality is of great importance in quantum mechanics because it enables us to eliminate a large number of integrals from calculations. Orthogonality plays a central role in the theory of chemical bonding (Chapter 11) and spectroscopy (Chapter 14). Sets of functions that are normalized and mutually orthogonal are called **orthonormal**. The wavefunctions in eqn 9.4b are orthonormal.

9.2 Motion in two and more dimensions

Next, we consider a two-dimensional version of the particle in a box. Now the particle is confined to a rectangular surface of length L_1 in the x-direction and L_2 in the y-direction; the potential energy is zero everywhere except at the walls, where it is infinite (Fig. 9.6). The wavefunction is now a function of both x and y and the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2}\right) = E\psi \tag{9.10}$$
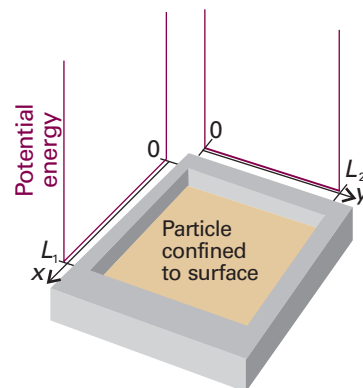

Fig. 9.6 A two-dimensional square well. The particle is confined to the plane bounded by impenetrable walls. As soon as it touches the walls, its potential energy rises to infinity.

We need to see how to solve this *partial* differential equation, an equation in more than one variable.

(a) Separation of variables

Some partial differential equations can be simplified by the **separation of variables technique**, which divides the equation into two or more ordinary differential equations, one for each variable. An important application of this procedure, as we shall see, is the separation of the Schrödinger equation for the hydrogen atom into equations that describe the radial and angular variation of the wavefunction. The technique is particularly simple for a two-dimensional square well, as can be seen by testing whether a solution of eqn 9.10 can be found by writing the wavefunction as a product of functions, one depending only on x and the other only on y:

$$\psi(x,y) = X(x)Y(y)$$

With this substitution, we show in the *Justification* below that eqn 9.10 separates into two ordinary differential equations, one for each coordinate:

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = E_X X \qquad -\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2} = E_Y Y \qquad E = E_X + E_Y \tag{9.11}$$

The quantity E_X is the energy associated with the motion of the particle parallel to the x-axis, and likewise for E_Y and motion parallel to the y-axis.

Justification 9.3 *The separation of variables technique applied to the particle in a two-dimensional box*

The first step in the justification of the separability of the wavefunction into the product of two functions X and Y is to note that, because X is independent of y and Y is independent of x, we can write

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial^2 XY}{\partial x^2} = Y\frac{d^2X}{dx^2} \qquad \frac{\partial^2\psi}{\partial y^2} = \frac{\partial^2 XY}{\partial y^2} = X\frac{d^2Y}{dy^2}$$

Then eqn 9.10 becomes

$$-\frac{\hbar^2}{2m}\left(Y\frac{d^2X}{dx^2} + X\frac{d^2Y}{dy^2}\right) = EXY$$

When both sides are divided by XY, we can rearrange the resulting equation into

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} = -\frac{2mE}{\hbar^2}$$

The first term on the left is independent of y, so if y is varied only the second term can change. But the sum of these two terms is a constant given by the right-hand side of the equation; therefore, even the second term cannot change when y is changed. In other words, the second term is a constant, which we write $-2mE_Y/\hbar^2$. By a similar argument, the first term is a constant when x changes, and we write it $-2mE_X/\hbar^2$, and $E = E_X + E_Y$. Therefore, we can write

$$\frac{1}{X}\frac{d^2X}{dx^2} = -\frac{2mE_X}{\hbar^2} \qquad \frac{1}{Y}\frac{d^2Y}{dy^2} = -\frac{2mE_Y}{\hbar^2}$$

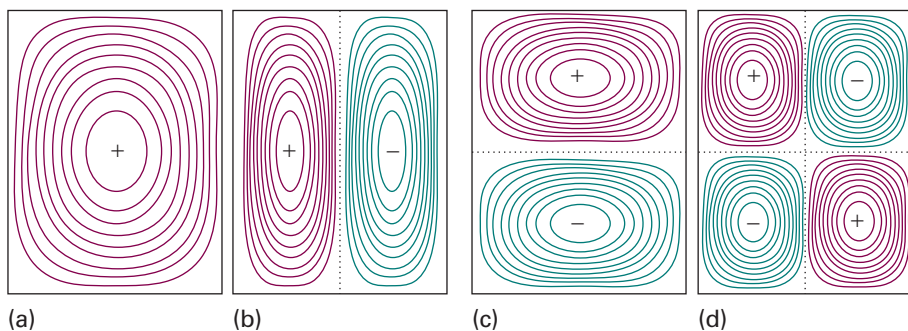which rearrange into the two ordinary (that is, single variable) differential equations in eqn 9.11.

Fig. 9.7 The wavefunctions for a particle confined to a rectangular surface depicted as contours of equal amplitude. (a) $n_1 = 1$, $n_2 = 1$, the state of lowest energy, (b) $n_1 = 1$, $n_2 = 2$, (c) $n_1 = 2$, $n_2 = 1$, and (d) $n_1 = 2$, $n_2 = 2$.

Exploration Use mathematical software to generate three-dimensional plots of the functions in this illustration. Deduce a rule for the number of nodal lines in a wavefunction as a function of the values of n_x and n_y.

Each of the two ordinary differential equations in eqn 9.11 is the same as the one-dimensional square-well Schrödinger equation. We can therefore adapt the results in eqn 9.4 without further calculation:

$$X_{n_1}(x) = \left(\frac{2}{L_1}\right)^{1/2} \sin \frac{n_1 \pi x}{L_1} \qquad Y_{n_2}(y) = \left(\frac{2}{L_2}\right)^{1/2} \sin \frac{n_2 \pi y}{L_2}$$

Then, because $\psi = XY$ and $E = E_X + E_Y$, we obtain

$$\psi_{n_1,n_2}(x,y) = \frac{2}{(L_1 L_2)^{1/2}} \sin \frac{n_1 \pi x}{L_1} \sin \frac{n_2 \pi y}{L_2} \qquad 0 \le x \le L_1, 0 \le y \le L_2$$

(9.12a)

$$E_{n_1 n_2} = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2}\right) \frac{h^2}{8m}$$

with the quantum numbers taking the values $n_1 = 1, 2, \ldots$ and $n_2 = 1, 2, \ldots$ independently. Some of these functions are plotted in Fig. 9.7. They are the two-dimensional versions of the wavefunctions shown in Fig. 9.3. Note that two quantum numbers are needed in this two-dimensional problem.

We treat a particle in a three-dimensional box in the same way. The wavefunctions have another factor (for the z-dependence), and the energy has an additional term in n_3^2/L_3^2. Solution of the Schrödinger equation by the separation of variables technique then gives

$$\psi_{n_1,n_2,n_3}(x,y,z) = \left(\frac{8}{L_1 L_2 L_3}\right)^{1/2} \sin \frac{n_1 \pi x}{L_1} \sin \frac{n_2 \pi y}{L_2} \sin \frac{n_3 \pi z}{L_3}$$

$$0 \le x \le L_1, 0 \le y \le L_2, 0 \le z \le L_3 \quad (9.12b)$$

$$E_{n_1 n_2 n_3} = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right) \frac{h^2}{8m}$$

(b) Degeneracy

An interesting feature of the solutions for a particle in a two-dimensional box is obtained when the plane surface is square, with $L_1 = L_2 = L$. Then eqn 9.12a becomes

$$\psi_{n_1,n_2}(x,y) = \frac{2}{L} \sin \frac{n_1 \pi x}{L} \sin \frac{n_2 \pi y}{L} \qquad E_{n_1 n_2} = (n_1^2 + n_2^2) \frac{h^2}{8mL^2} \qquad (9.13)$$
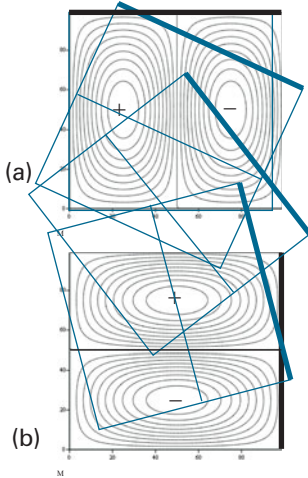
(a)

(b)

Fig. 9.8 The wavefunctions for a particle confined to a square surface. Note that one wavefunction can be converted into the other by a rotation of the box by 90°. The two functions correspond to the same energy. Degeneracy and symmetry are closely related.
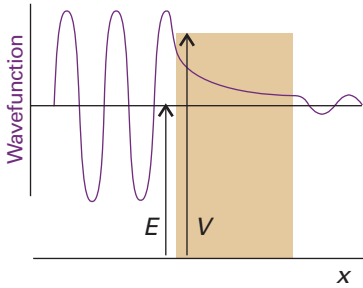

Fig. 9.9 A particle incident on a barrier from the left has an oscillating wave function, but inside the barrier there are no oscillations (for $E < V$). If the barrier is not too thick, the wavefunction is nonzero at its opposite face, and so oscillates begin again there. (Only the real component of the wavefunction is shown.)

Consider the cases $n_1 = 1$, $n_2 = 2$ and $n_1 = 2$, $n_2 = 1$:

$$\psi_{1,2} = \frac{2}{L} \sin \frac{\pi x}{L} \sin \frac{2\pi y}{L} \qquad E_{1,2} = \frac{5h^2}{8mL^2}$$

$$\psi_{2,1} = \frac{2}{L} \sin \frac{2\pi x}{L} \sin \frac{\pi y}{L} \qquad E_{2,1} = \frac{5h^2}{8mL^2}$$

We see that, although the wavefunctions are different, they are **degenerate**, meaning that they correspond to the same energy. In this case, in which there are two degenerate wavefunctions, we say that the energy level $5(h^2/8mL^2)$ is 'doubly degenerate'.

The occurrence of degeneracy is related to the symmetry of the system. Figure 9.8 shows contour diagrams of the two degenerate functions $\psi_{1,2}$ and $\psi_{2,1}$. Because the box is square, we can convert one wavefunction into the other simply by rotating the plane by 90°. Interconversion by rotation through 90° is not possible when the plane is not square, and $\psi_{1,2}$ and $\psi_{2,1}$ are then not degenerate. Similar arguments account for the degeneracy of states in a cubic box. We shall see many other examples of degeneracy in the pages that follow (for instance, in the hydrogen atom), and all of them can be traced to the symmetry properties of the system (see Section 12.4b).

9.3 **Tunnelling**

If the potential energy of a particle does not rise to infinity when it is in the walls of the container, and $E < V$, the wavefunction does not decay abruptly to zero. If the walls are thin (so that the potential energy falls to zero again after a finite distance), then the wavefunction oscillates inside the box, varies smoothly inside the region representing the wall, and oscillates again on the other side of the wall outside the box (Fig. 9.9). Hence the particle might be found on the outside of a container even though according to classical mechanics it has insufficient energy to escape. Such leakage by penetration through a classically forbidden region is called **tunnelling**.

The Schrödinger equation can be used to calculate the probability of tunnelling of a particle of mass m incident on a finite barrier from the left. On the left of the barrier (for $x < 0$) the wavefunctions are those of a particle with $V = 0$, so from eqn 9.2 we can write

$$\psi = Ae^{ikx} + Be^{-ikx} \qquad k\hbar = (2mE)^{1/2} \tag{9.14}$$

The Schrödinger equation for the region representing the barrier (for $0 \le x \le L$), where the potential energy is the constant V, is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi \tag{9.15}$$

We shall consider particles that have $E < V$ (so, according to classical physics, the particle has insufficient energy to pass over the barrier), and therefore $V - E$ is positive. The general solutions of this equation are

$$\psi = Ce^{\kappa x} + De^{-\kappa x} \qquad \kappa\hbar = \{2m(V-E)\}^{1/2} \tag{9.16}$$

as we can readily verify by differentiating ψ twice with respect to x. The important feature to note is that the two exponentials are now real functions, as distinct from the complex, oscillating functions for the region where $V = 0$ (oscillating functions would be obtained if $E > V$). To the right of the barrier ($x > L$), where $V = 0$ again, the wavefunctions are

$$\psi = A'e^{ikx} + B'e^{-ikx} \qquad k\hbar = (2mE)^{1/2} \tag{9.17}$$

The complete wavefunction for a particle incident from the left consists of an incident wave, a wave reflected from the barrier, the exponentially changing amplitudes inside the barrier, and an oscillating wave representing the propagation of the particle to the right after tunnelling through the barrier successfully (Fig. 9.10). The acceptable wavefunctions must obey the conditions set out in Section 8.4b. In particular, they must be continuous at the edges of the barrier (at $x = 0$ and $x = L$, remembering that $e^0 = 1$):

$$A + B = C + D \qquad Ce^{\kappa L} + De^{-\kappa L} = A'e^{ikL} + B'e^{-ikL} \tag{9.18}$$

Their slopes (their first derivatives) must also be continuous there (Fig. 9.11):

$$ikA - ikB = \kappa C - \kappa D \qquad \kappa Ce^{\kappa L} - \kappa De^{-\kappa L} = ikA'e^{ikL} - ikB'e^{-ikL} \tag{9.19}$$

At this stage, we have four equations for the six unknown coefficients. If the particles are shot towards the barrier from the left, there can be no particles travelling to the left on the right of the barrier. Therefore, we can set $B' = 0$, which removes one more unknown. We cannot set $B = 0$ because some particles may be reflected back from the barrier toward negative x.

The probability that a particle is travelling towards positive x (to the right) on the left of the barrier is proportional to $|A|^2$, and the probability that it is travelling to the right on the right of the barrier is $|A'|^2$. The ratio of these two probabilities is called the **transmission probability**, T. After some algebra (see Problem 9.9) we find

$$T = \left\{ 1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\varepsilon(1-\varepsilon)} \right\}^{-1} \tag{9.20a}$$

where $\varepsilon = E/V$. This function is plotted in Fig. 9.12; the transmission coefficient for $E > V$ is shown there too. For high, wide barriers (in the sense that $\kappa L \gg 1$), eqn 9.20a simplifies to

$$T \approx 16\varepsilon(1-\varepsilon)e^{-2\kappa L} \tag{9.20b}$$

The transmission probability decreases exponentially with the thickness of the barrier and with $m^{1/2}$. It follows that particles of low mass are more able to tunnel through barriers than heavy ones (Fig. 9.13). Tunnelling is very important for electrons and muons, and moderately important for protons; for heavier particles it is less important.
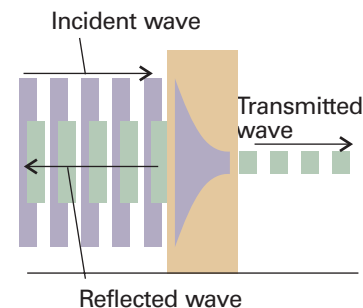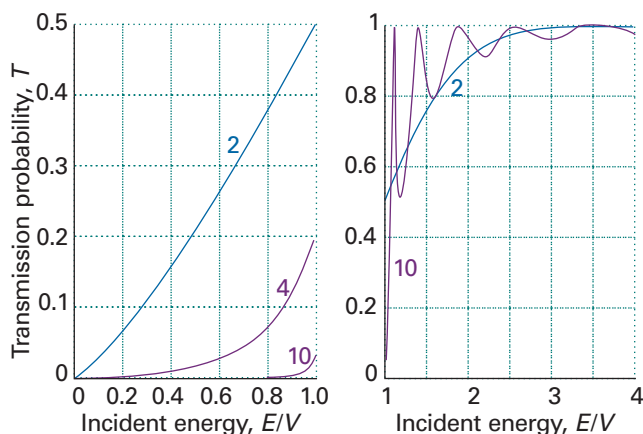

Fig. 9.10 When a particle is incident on a barrier from the left, the wavefunction consists of a wave representing linear momentum to the right, a reflected component representing momentum to the left, a varying but not oscillating component inside the barrier, and a (weak) wave representing motion to the right on the far side of the barrier.
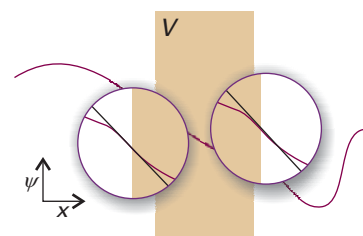
Fig. 9.11 The wavefunction and its slope must be continuous at the edges of the barrier. The conditions for continuity enable us to connect the wavefunctions in the three zones and hence to obtain relations between the coefficients that appear in the solutions of the Schrödinger equation.

Fig. 9.12 The transition probabilities for passage through a barrier. The horizontal axis is the energy of the incident particle expressed as a multiple of the barrier height. The curves are labelled with the value of $L(2mV)^{1/2}/\hbar$. The graph on the left is for $E < V$ and that on the right for $E > V$. Note that $T > 0$ for $E < V$ whereas classically T would be zero. However, $T < 1$ for $E > V$, whereas classically T would be 1.

Exploration Plot T against ε for a hydrogen molecule, a proton and an electron.

Heavy   Light
particle particle
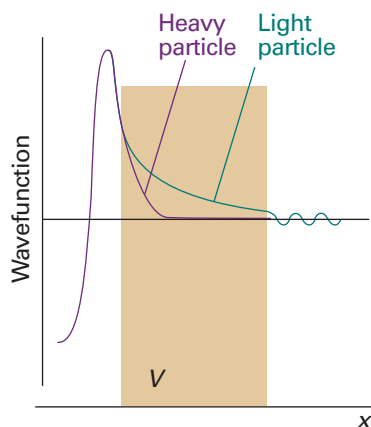
Fig. 9.13 The wavefunction of a heavy particle decays more rapidly inside a barrier than that of a light particle. Consequently, a light particle has a greater probability of tunnelling through the barrier.
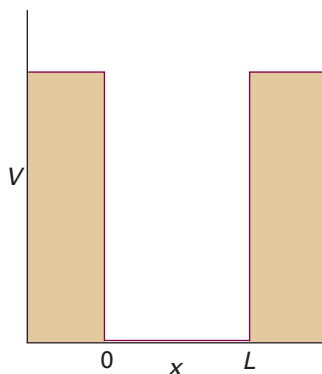
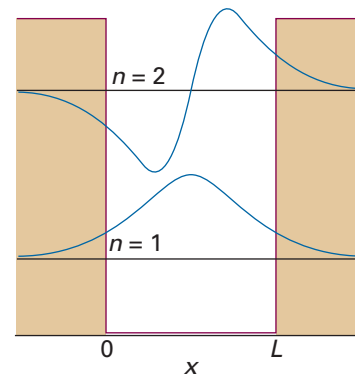**Fig. 9.14** A potential well with a finite depth.

$n = 2$

$n = 1$

Fig. 9.15 The lowest two bound-state wavefunctions for a particle in the well shown in Fig. 9.14 and one of the wavefunctions corresponding to an unbound state ($E > V$).

A number of effects in chemistry (for example, the isotope-dependence of some reaction rates) depend on the ability of the proton to tunnel more readily than the deuteron. The very rapid equilibration of proton transfer reactions is also a manifestation of the ability of protons to tunnel through barriers and transfer quickly from an acid to a base. Tunnelling of protons between acidic and basic groups is also an important feature of the mechanism of some enzyme-catalysed reactions. As we shall see in Chapters 24 and 25, electron tunnelling is one of the factors that determine the rates of electron transfer reactions at electrodes and in biological systems.

A problem related to the one just considered is that of a particle in a square-well potential of finite depth (Fig. 9.14). In this kind of potential, the wavefunction penetrates into the walls, where it decays exponentially towards zero, and oscillates within the well. The wavefunctions are found by ensuring, as in the discussion of tunnelling, that they and their slopes are continuous at the edges of the potential. Some of the lowest energy solutions are shown in Fig. 9.15. A further difference from the solutions for an infinitely deep well is that there is only a finite number of bound states. Regardless of the depth and length of the well, there is always at least one bound state. Detailed consideration of the Schrödinger equation for the problem shows that in general the number of levels is equal to N, with

$$N - 1 < \frac{(8mVL)^{1/2}}{h} < N \tag{9.21}$$

where V is the depth of the well and L is its length (for a derivation of this expression, see *Further reading*). We see that the deeper and wider the well, the greater the number of bound states. As the depth becomes infinite, so the number of bound states also becomes infinite, as we have already seen.

IMPACT ON NANOSCIENCE
I9.1 Scanning probe microscopy

Nanoscience is the study of atomic and molecular assemblies with dimensions ranging from 1 nm to about 100 nm and *nanotechnology* is concerned with the incorporation of such assemblies into devices. The future economic impact of nanotechnology could be very significant. For example, increased demand for very small digital electronic

devices has driven the design of ever smaller and more powerful microprocessors. However, there is an upper limit on the density of electronic circuits that can be incorporated into silicon-based chips with current fabrication technologies. As the ability to process data increases with the number of circuits in a chip, it follows that soon chips and the devices that use them will have to become bigger if processing power is to increase indefinitely. One way to circumvent this problem is to fabricate devices from nanometre-sized components.

We will explore several concepts of nanoscience throughout the text. We begin with the description of *scanning probe microscopy* (SPM), a collection of techniques that can be used to visualize and manipulate objects as small as atoms on surfaces. Consequently, SPM has far better resolution than electron microscopy (*Impact I8.1*).

One modality of SPM is *scanning tunnelling microscopy* (STM), in which a platinum–rhodium or tungsten needle is scanned across the surface of a conducting solid. When the tip of the needle is brought very close to the surface, electrons tunnel across the intervening space (Fig. 9.16). In the constant-current mode of operation, the stylus moves up and down corresponding to the form of the surface, and the topography of the surface, including any adsorbates, can be mapped on an atomic scale. The vertical motion of the stylus is achieved by fixing it to a piezoelectric cylinder, which contracts or expands according to the potential difference it experiences. In the constant-z mode, the vertical position of the stylus is held constant and the current is monitored. Because the tunnelling probability is very sensitive to the size of the gap, the microscope can detect tiny, atom-scale variations in the height of the surface.

Figure 9.17 shows an example of the kind of image obtained with a surface, in this case of gallium arsenide, that has been modified by addition of atoms, in this case caesium atoms. Each 'bump' on the surface corresponds to an atom. In a further variation of the STM technique, the tip may be used to nudge single atoms around on the surface, making possible the fabrication of complex and yet very tiny nanometre-sized structures.

In *atomic force microscopy* (AFM) a sharpened stylus attached to a cantilever is scanned across the surface. The force exerted by the surface and any bound species pushes or pulls on the stylus and deflects the cantilever (Fig. 9.18). The deflection is monitored either by interferometry or by using a laser beam. Because no current is needed between the sample and the probe, the technique can be applied to non-conducting surfaces too. A spectacular demonstration of the power of AFM is given in Fig. 9.19, which shows individual DNA molecules on a solid surface.
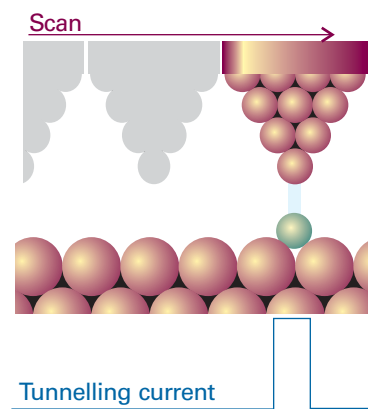
Fig. 9.16 A scanning tunnelling microscope makes use of the current of electrons that tunnel between the surface and the tip. That current is very sensitive to the distance of the tip above the surface.
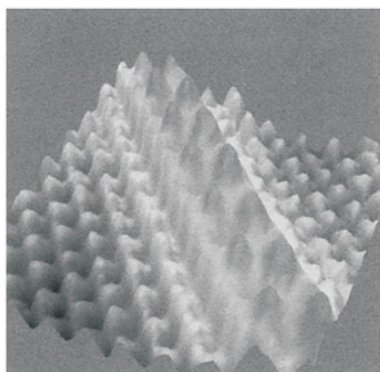
Fig. 9.17 An STM image of caesium atoms on a gallium arsenide surface.
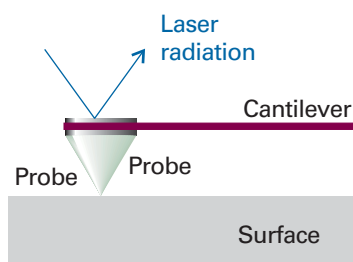
Fig. 9.18 In atomic force microscopy, a laser beam is used to monitor the tiny changes in the position of a probe as it is attracted to or repelled from atoms on a surface.
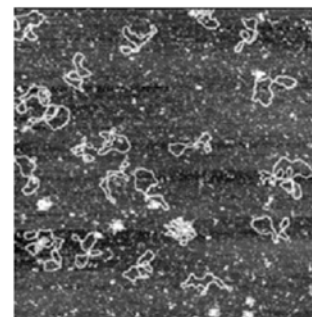
Fig. 9.19 An AFM image of bacterial DNA plasmids on a mica surface. (Courtesy of Veeco Instruments.)

Example 9.2 *Exploring the origin of the current in scanning tunnelling microscopy*

To get an idea of the distance dependence of the tunnelling current in STM, suppose that the wavefunction of the electron in the gap between sample and needle is given by $\psi = Be^{-\kappa x}$, where $\kappa = \{2m_e(V - E)/\hbar^2\}^{1/2}$; take $V - E = 2.0$ eV. By what factor would the current drop if the needle is moved from $L_1 = 0.50$ nm to $L_2 = 0.60$ nm from the surface?

Method We regard the tunnelling current to be proportional to the transmission probability T, so the ratio of the currents is equal to the ratio of the transmission probabilities. To choose between eqn 9.20a or 9.20b for the calculation of T, first calculate κL for the shortest distance L_1: if $\kappa L_1 > 1$, then use eqn 9.20b.

Answer When $L = L_1 = 0.50$ nm and $V - E = 2.0$ eV $= 3.20 \times 10^{-19}$ J the value of κL is

$$\kappa L_1 = \left\{ \frac{2m_e(V - E)}{\hbar^2} \right\}^{1/2} L_1$$

$$= \left\{ \frac{2 \times (9.109 \times 10^{-31} \text{ kg}) \times (3.20 \times 10^{-19} \text{ J})}{(1.054 \times 10^{-34} \text{ J s})^2} \right\}^{1/2} \times (5.0 \times 10^{-10} \text{ m})$$

$$= (7.25 \times 10^9 \text{ m}^{-1}) \times (5.0 \times 10^{-10} \text{ m}) = 3.6$$

Because $\kappa L_1 > 1$, we use eqn 9.20b to calculate the transmission probabilities at the two distances. It follows that

$$\frac{\text{current at } L_2}{\text{current at } L_1} = \frac{T(L_2)}{T(L_1)} = \frac{16\varepsilon(1 - \varepsilon)e^{-2\kappa L_2}}{16\varepsilon(1 - \varepsilon)e^{-2\kappa L_1}} = e^{-2\kappa(L_2 - L_1)}$$

$$= e^{-2 \times (7.25 \times 10^9 \text{ m}^{-1}) \times (1.0 \times 10^{-10} \text{ m})} = 0.23$$

We conclude that, at a distance of 0.60 nm between the surface and the needle, the current is 23 per cent of the value measured when the distance is 0.50 nm.

Self-test 9.5 The ability of a proton to tunnel through a barrier contributes to the rapidity of proton transfer reactions in solution and therefore to the properties of acids and bases. Estimate the relative probabilities that a proton and a deuteron can tunnel through the same barrier of height 1.0 eV (1.6×10^{-19} J) and length 100 pm when their energy is 0.9 eV. Any comment?

$[T_H/T_D = 3.7 \times 10^2$; we expect proton transfer reactions to be much faster than deuteron transfer reactions.]

Vibrational motion

A particle undergoes **harmonic motion** if it experiences a restoring force proportional to its displacement:

$$F = -kx \tag{9.22}$$

where k is the **force constant**: the stiffer the 'spring', the greater the value of k. Because force is related to potential energy by $F = -dV/dx$ (see *Appendix 3*), the force in eqn 9.22 corresponds to a potential energy

$$V = \tfrac{1}{2}kx^2 \tag{9.23}$$

This expression, which is the equation of a parabola (Fig. 9.20), is the origin of the term 'parabolic potential energy' for the potential energy characteristic of a harmonic oscillator. The Schrödinger equation for the particle is therefore

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+\tfrac{1}{2}kx^2\psi=E\psi \tag{9.24}$$

9.4 The energy levels

Equation 9.24 is a standard equation in the theory of differential equations and its solutions are well known to mathematicians (for details, see *Further reading*). Quantization of energy levels arises from the boundary conditions: the oscillator will not be found with infinitely large compressions or extensions, so the only allowed solutions are those for which $\psi=0$ at $x=\pm\infty$. The permitted energy levels are

$$E_v=(v+\tfrac{1}{2})\hbar\omega \qquad \omega=\left(\frac{k}{m}\right)^{1/2} \qquad v=0, 1, 2, \ldots \tag{9.25}$$

Note that ω (omega) increases with increasing force constant and decreasing mass. It follows that the separation between adjacent levels is

$$E_{v+1}-E_v=\hbar\omega \tag{9.26}$$

which is the same for all v. Therefore, the energy levels form a uniform ladder of spacing $\hbar\omega$ (Fig. 9.21). The energy separation $\hbar\omega$ is negligibly small for macroscopic objects (with large mass), but is of great importance for objects with mass similar to that of atoms.

Because the smallest permitted value of v is 0, it follows from eqn 9.26 that a harmonic oscillator has a zero-point energy

$$E_0=\tfrac{1}{2}\hbar\omega \tag{9.27}$$

The mathematical reason for the zero-point energy is that v cannot take negative values, for if it did the wavefunction would be ill-behaved. The physical reason is the same as for the particle in a square well: the particle is confined, its position is not completely uncertain, and therefore its momentum, and hence its kinetic energy, cannot be exactly zero. We can picture this zero-point state as one in which the particle fluctuates incessantly around its equilibrium position; classical mechanics would allow the particle to be perfectly still.
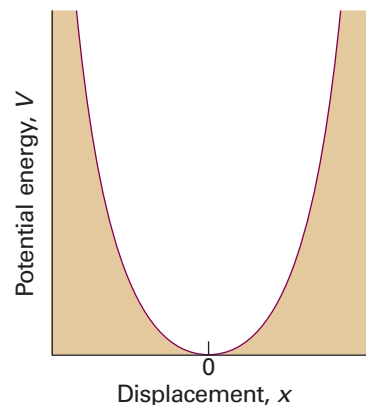
Fig. 9.20 The parabolic potential energy $V=\tfrac{1}{2}kx^2$ of a harmonic oscillator, where x is the displacement from equilibrium. The narrowness of the curve depends on the force constant k: the larger the value of k, the narrower the well.
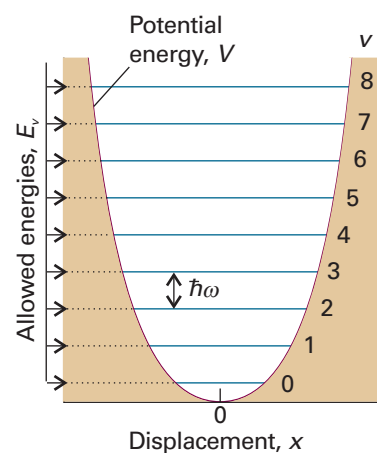
Fig. 9.21 The energy levels of a harmonic oscillator are evenly spaced with separation $\hbar\omega$, with $\omega=(k/m)^{1/2}$. Even in its lowest state, an oscillator has an energy greater than zero.

Illustration 9.3 *Calculating a molecular vibrational absorption frequency*

Atoms vibrate relative to one another in molecules with the bond acting like a spring. Consider an X—H chemical bond, where a heavy X atom forms a stationary anchor for the very light H atom. That is, only the H atom moves, vibrating as a simple harmonic oscillator. Therefore, eqn 9.25 describes the allowed vibrational energy levels of a X—H bond. The force constant of a typical X—H chemical bond is around 500 N m^{-1}. For example $k=516.3$ N m^{-1} for the $^1H^{35}Cl$ bond. Because the mass of a proton is about 1.7×10^{-27} kg, using $k=500$ N m^{-1} in eqn 9.25 gives $\omega\approx 5.4\times 10^{14}$ s^{-1} (5.4×10^2 THz). It follows from eqn 9.26 that the separation of adjacent levels is $\hbar\omega\approx 5.7\times 10^{-20}$ J (57 zJ, about 0.36 eV). This energy separation corresponds to 34 kJ mol^{-1}, which is chemically significant. From eqn 9.27, the zero-point energy of this molecular oscillator is about 3 zJ, which corresponds to 0.2 eV, or 15 kJ mol^{-1}.

The excitation of the vibration of the bond from one level to the level immediately above requires 57 zJ. Therefore, if it is caused by a photon, the excitation requires radiation of frequency $v = \Delta E/h = 86$ THz and wavelength $\lambda = c/v = 3.5$ μm. It follows that transitions between adjacent vibrational energy levels of molecules are stimulated by or emit infrared radiation. We shall see in Chapter 13 that the concepts just described represent the st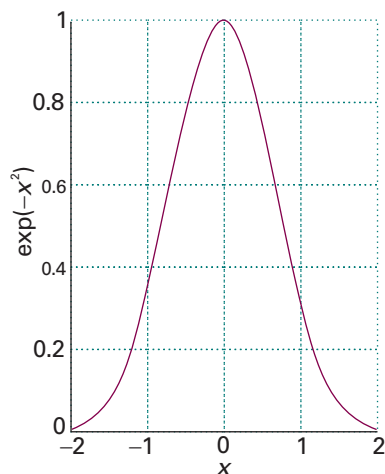arting point for the interpretation of vibrational spectroscopy, an important technique for the characterization of small and large molecules in the gas phase or in condensed phases.

9.5 The wavefunctions

It is helpful at the outset to identify the similarities between the harmonic oscillator and the particle in a box, for then we shall be able to anticipate the form of the oscillator wavefunctions without detailed calculation. Like the particle in a box, a particle undergoing harmonic motion is trapped in a symmetrical well in which the potential energy rises to large values (and ultimately to infinity) for sufficiently large displacements (compare Figs. 9.1 and 9.20). However, there are two important differences. First, because the potential energy climbs towards infinity only as x^2 and not abruptly, the wavefunction approaches zero more slowly at large displacements than for the particle in a box. Second, as the kinetic energy of the oscillator depends on the displacement in a more complex way (on account of the variation of the potential energy), the curvature of the wavefunction also varies in a more complex way.

(a) The form of the wavefunctions

The detailed solution of eqn 9.24 shows that the wavefunction for a harmonic oscillator has the form

$$\psi(x) = N \times (\text{polynomial in } x) \times (\text{bell-shaped Gaussian function})$$

where N is a normalization constant. A Gaussian function is a function of the form e^{-x^2} (Fig. 9.22). The precise form of the wavefunctions are

$$\psi_v(x) = N_v H_v(y) e^{-y^2/2} \qquad y = \frac{x}{\alpha} \qquad \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4} \tag{9.28}$$

The factor $H_v(y)$ is a **Hermite polynomial** (Table 9.1). For instance, because $H_0(y) = 1$, the wavefunction for the ground state (the lowest energy state, with $v = 0$) of the harmonic oscillator is

$$\psi_0(x) = N_0 e^{-y^2/2} = N_0 e^{-x^2/2\alpha^2} \tag{9.29a}$$

It follows that the probability density is the bell-shaped Gaussian function

$$\psi_0^2(x) = N_0^2 e^{-x^2/\alpha^2} \tag{9.29b}$$

The wavefunction and the probability distribution are shown in Fig. 9.23. Both curves have their largest values at zero displacement (at $x = 0$), so they capture the classical picture of the zero-point energy as arising from the ceaseless fluctuation of the particle about its equilibrium position.

The wavefunction for the first excited state of the oscillator, the state with $v = 1$, is obtained by noting that $H_1(y) = 2y$ (note that some of the Hermite polynomials are very simple functions!):

$$\psi_1(x) = N_1 \times 2y e^{-y^2/2} \tag{9.30}$$

Fig. 9.22 The graph of the Gaussian function, $f(x) = e^{-x^2}$.

Comment 9.2

The Hermite polynomials are solutions of the differential equation

$$H_v'' - 2yH_v' + 2vH_v = 0$$

where primes denote differentiation. They satisfy the recursion relation

$$H_{v+1} - 2yH_v + 2vH_{v-1} = 0$$

An important integral is

$$\int_{-\infty}^{\infty} H_{v'}H_v e^{-y^2} dy = \begin{cases} 0 & \text{if } v' \neq v \\ \pi^{1/2} 2^v v! & \text{if } v' = v \end{cases}$$

Hermite polynomials are members of a class of functions called *orthogonal polynomials*. These polynomials have a wide range of important properties that allow a number of quantum mechanical calculations to be done with relative ease. See *Further reading* for a reference to their properties.
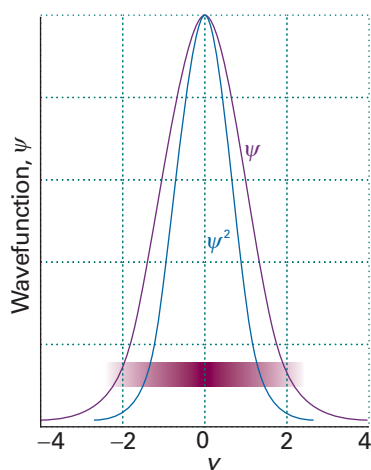
Fig. 9.23 The normalized wavefunction and probability distribution (shown also by shading) for the lowest energy state of a harmonic oscillator.
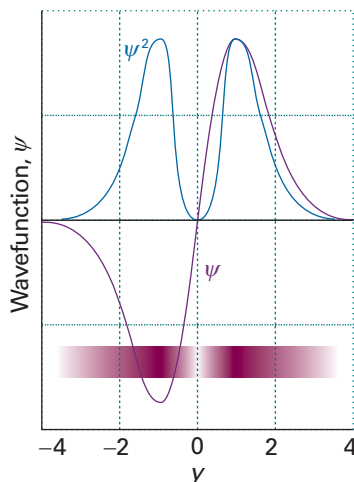

Fig. 9.24 The normalized wavefunction and probability distribution (shown also by shading) for the first excited state of a harmonic oscillator.

Table 9.1 The Hermite polynomials $H_v(y)$

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$

This function has a node at zero displacement ($x = 0$), and the probability density has maxima at $x = \pm \alpha$, corresponding to $y = \pm 1$ (Fig. 9.24).

Once again, we should interpret the mathematical expressions we have derived. In the case of the harmonic oscillator wavefunctions in eqn 9.28, we should note the following:

1. The Gaussian function goes very strongly to zero as the displacement increases (in either direction), so all the wavefunctions approach zero at large displacements.

2. The exponent y^2 is proportional to $x^2 \times (mk)^{1/2}$, so the wavefunctions decay more rapidly for large masses and stiff springs.

3. As v increases, the Hermite polynomials become larger at large displacements (as x^v), so the wavefunctions grow large before the Gaussian function damps them down to zero: as a result, the wavefunctions spread over a wider range as v increases.

The shapes of several wavefunctions are shown in Fig. 9.25. The shading in Fig. 9.26 that represents the probability density is based on the squares of these functions. At high quantum numbers, harmonic oscillator wavefunctions have their largest amplitudes near the turning points of the classical motion (the locations at which $V = E$, so

Fig. 9.25 The normalized wavefunctions for the first five states of a harmonic oscillator. Note that the number of nodes is equal to v and that alternate wavefunctions are symmetrical or antisymmetrical about $y = 0$ (zero displacement).
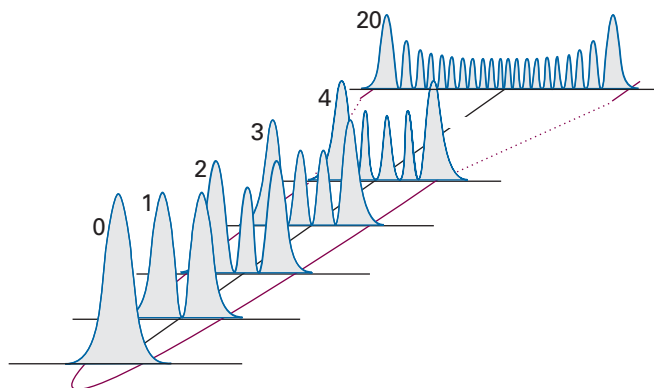
Fig. 9.26 The probability distributions for the first five states of a harmonic oscillator and the state with $v = 20$. Note how the regions of highest probability move towards the turning points of the classical motion as v increases.

Exploration To gain some insight into the origins of the nodes in the harmonic oscillator wavefunctions, plot the Hermite polynomials $H_v(y)$ for $v = 0$ through 5.

the kinetic energy is zero). We see classical properties emerging in the correspondence limit of high quantum numbers, for a classical particle is most likely to be found at the turning points (where it travels most slowly) and is least likely to be found at zero displacement (where it travels most rapidly).

Example 9.3 *Normalizing a harmonic oscillator wavefunction*

Find the normalization constant for the harmonic oscillator wavefunctions.

Method Normalization is always carried out by evaluating the integral of $|\psi|^2$ over all space and then finding the normalization factor from eqn 8.16. The normalized wavefunction is then equal to $N\psi$. In this one-dimensional problem, the volume element is dx and the integration is from $-\infty$ to $+\infty$. The wavefunctions are expressed in terms of the dimensionless variable $y = x/\alpha$, so begin by expressing the integral in terms of y by using $dx = \alpha dy$. The integrals required are given in *Comment 9.2*.

Answer The unnormalized wavefunction is

$$\psi_v(x) = H_v(y)e^{-y^2/2}$$

It follows from the integrals given in *Comment 9.2* that

$$\int_{-\infty}^{\infty} \psi_v^* \psi_v \, dx = \alpha \int_{-\infty}^{\infty} \psi_v^* \psi_v \, dy = \alpha \int_{-\infty}^{\infty} H_v^2(y)e^{-y^2} \, dy = \alpha \pi^{1/2} 2^v v!$$

where $v! = v(v-1)(v-2) \ldots 1$. Therefore,

$$N_v = \left(\frac{1}{\alpha \pi^{1/2} 2^v v!} \right)^{1/2}$$

Note that for a harmonic oscillator N_v is different for each value of v.

Self-test 9.6 Confirm, by explicit evaluation of the integral, that ψ_0 and ψ_1 are orthogonal.
  [Evaluate the integral $\int_{-\infty}^{\infty} \psi_0^* \psi_1 \, dx$ by using the information in *Comment 9.2*.]

(b)   The properties of oscillators

With the wavefunctions that are available, we can start calculating the properties of a harmonic oscillator. For instance, we can calculate the expectation values of an observable Ω by evaluating integrals of the type

$$\langle \Omega \rangle = \int_{-\infty}^{\infty} \psi_v^* \hat{\Omega} \psi_v \, dx \tag{9.31}$$

(Here and henceforth, the wavefunctions are all taken to be normalized to 1.) When the explicit wavefunctions are substituted, the integrals look fearsome, but the Hermite polynomials have many simplifying features. For instance, we show in the following example that the mean displacement, $\langle x \rangle$, and the mean square displacement, $\langle x^2 \rangle$, of the oscillator when it is in the state with quantum number v are

$$\langle x \rangle = 0 \qquad \langle x^2 \rangle = (v + \tfrac{1}{2}) \frac{\hbar}{(mk)^{1/2}} \tag{9.32}$$

The result for $\langle x \rangle$ shows that the oscillator is equally likely to be found on either side of $x = 0$ (like a classical oscillator). The result for $\langle x^2 \rangle$ shows that the mean square displacement increases with v. This increase is apparent from the probability densities in Fig. 9.26, and corresponds to the classical amplitude of swing increasing as the oscillator becomes more highly excited.

Example 9.4 *Calculating properties of a harmonic oscillator*

We can imagine the bending motion of a CO_2 molecule as a harmonic oscillation relative to the linear conformation of the molecule. We may be interested in the extent to which the molecule bends. Calculate the mean displacement of the oscillator when it is in a quantum state v.

Method Normalized wavefunctions must be used to calculate the expectation value. The operator for position along x is multiplication by the value of x (Section 8.5b). The resulting integral can be evaluated either by inspection (the integrand is the product of an odd and an even function), or by explicit evaluation using the formulas in *Comment 9.2*. To give practice in this type of calculation, we illustrate the latter procedure. We shall need the relation $x = \alpha y$, which implies that $dx = \alpha dy$.

Answer The integral we require is

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_v^* x \psi_v \, dx = N_v^2 \int_{-\infty}^{\infty} (H_v e^{-y^2/2}) x (H_v e^{-y^2/2}) \, dx$$

$$= \alpha^2 N_v^2 \int_{-\infty}^{\infty} (H_v e^{-y^2/2}) y (H_v e^{-y^2/2}) \, dy$$

$$= \alpha^2 N_v^2 \int_{-\infty}^{\infty} H_v y H_v e^{-y^2} \, dy$$

Now use the recursion relation (see *Comment 9.2*) to form

$$y H_v = v H_{v-1} + \tfrac{1}{2} H_{v+1}$$

which turns the integral into

$$\int_{-\infty}^{\infty} H_v y H_v e^{-y^2} \, dy = v \int_{-\infty}^{\infty} H_{v-1} H_v e^{-y^2} \, dy + \tfrac{1}{2} \int_{-\infty}^{\infty} H_{v+1} H_v e^{-y^2} \, dy$$

Both integrals are zero, so $\langle x \rangle = 0$. As remarked in the text, the mean displacement is zero because the displacement occurs equally on either side of the equilibrium position. The following Self-test extends this calculation by examining the mean square displacement, which we can expect to be non-zero and to increase with increasing v.

Self-test 9.7 Calculate the mean square displacement $\langle x^2 \rangle$ of the particle from its equilibrium position. (Use the recursion relation twice.)   [eqn 9.32]

Comment 9.3

An even function is one for which $f(-x) = f(x)$; an odd function is one for which $f(-x) = -f(x)$. The product of an odd and even function is itself odd, and the integral of an odd function over a symmetrical range about $x = 0$ is zero.

The mean potential energy of an oscillator, the expectation value of $V = \tfrac{1}{2}kx^2$, can now be calculated very easily:

$$\langle V \rangle = \langle \tfrac{1}{2}kx^2 \rangle = \tfrac{1}{2}(v + \tfrac{1}{2})\hbar \left(\frac{k}{m} \right)^{1/2} = \tfrac{1}{2}(v + \tfrac{1}{2})\hbar\omega \tag{9.33}$$

Because the total energy in the state with quantum number v is $(v + \frac{1}{2})\hbar\omega$, it follows that

$$\langle V \rangle = \tfrac{1}{2} E_v \tag{9.34a}$$

The total energy is the sum of the potential and kinetic energies, so it follows at once that the mean kinetic energy of the oscillator is

$$\langle E_K \rangle = \tfrac{1}{2} E_v \tag{9.34b}$$

The result that the mean potential and kinetic energies of a harmonic oscillator are equal (and therefore that both are equal to half the total energy) is a special case of the **virial theorem**:

If the potential energy of a particle has the form $V = ax^b$, then its mean potential and kinetic energies are related by

$$2\langle E_K \rangle = b\langle V \rangle \tag{9.35}$$

For a harmonic oscillator $b = 2$, so $\langle E_K \rangle = \langle V \rangle$, as we have found. The virial theorem is a short cut to the establishment of a number of useful results, and we shall use it again.

An oscillator may be found at extensions with $V > E$ that are forbidden by classical physics, for they correspond to negative kinetic energy. For example, it follows from the shape of the wavefunction (see the *Justification* below) that in its lowest energy state there is about an 8 per cent chance of finding an oscillator stretched beyond its classical limit and an 8 per cent chance of finding it with a classically forbidden compression. These tunnelling probabilities are independent of the force constant and mass of the oscillator. The probability of being found in classically forbidden regions decreases quickly with increasing v, and vanishes entirely as v approaches infinity, as we would expect from the correspondence principle. Macroscopic oscillators (such as pendulums) are in states with very high quantum numbers, so the probability that they will be found in a classically forbidden region is wholly negligible. Molecules, however, are normally in their vibrational ground states, and for them the probability is very significant.

....

Justification 9.4 *Tunnelling in the quantum mechanical harmonic oscillator*

According to classical mechanics, the turning point, x_{tp}, of an oscillator occurs when its kinetic energy is zero, which is when its potential energy $\frac{1}{2}kx^2$ is equal to its total energy E. This equality occurs when

$$x_{tp}^2 = \frac{2E}{k} \qquad \text{or, } x_{tp} = \pm\left(\frac{2E}{k}\right)^{1/2}$$

with E given by eqn 9.25. The probability of finding the oscillator stretched beyond a displacement x_{tp} is the sum of the probabilities $\psi^2 dx$ of finding it in any of the intervals dx lying between x_{tp} and infinity:

$$P = \int_{x_{tp}}^{\infty} \psi_v^2 \, dx$$

The variable of integration is best expressed in terms of $y = x/\alpha$ with $\alpha = (\hbar^2/mk)^{1/2}$, and then the turning point on the right lies at

$$y_{tp} = \frac{x_{tp}}{\alpha} = \left\{ \frac{2(v + \frac{1}{2})\hbar\omega}{\alpha^2 k} \right\}^{1/2} = (2v + 1)^{1/2}$$

For the state of lowest energy ($v = 0$), $y_{tp} = 1$ and the probability is

$$P = \int_{x_{tp}}^{\infty} \psi_0^2 dx = \alpha N_0^2 \int_1^{\infty} e^{-y^2} dy$$

The integral is a special case of the *error function*, erf z, which is defined as follows:

$$\text{erf } z = 1 - \frac{2}{\pi^{1/2}} \int_z^{\infty} e^{-y^2} dy$$

The values of this function are tabulated and available in mathematical software packages, and a small selection of values is given in Table 9.2. In the present case

$$P = \tfrac{1}{2}(1 - \text{erf } 1) = \tfrac{1}{2}(1 - 0.843) = 0.079$$

It follows that, in 7.9 per cent of a large number of observations, any oscillator in the state $v = 0$ will be found stretched to a classically forbidden extent. There is the same probability of finding the oscillator with a classically forbidden compression. The total probability of finding the oscillator tunnelled into a classically forbidden region (stretched or compressed) is about 16 per cent. A similar calculation for the state with $v = 6$ shows that the probability of finding the oscillator outside the classical turning points has fallen to about 7 per cent.

Table 9.2 The error function

z	erf z
0	0
0.01	0.0113
0.05	0.0564
0.10	0.1125
0.50	0.5205
1.00	0.8427
1.50	0.9661
2.00	0.9953

Rotational motion

The treatment of rotational motion can be broken down into two parts. The first deals with motion in two dimensions and the second with rotation in three dimensions. It may be helpful to review the classical description of rotational motion given in *Appendix 3*, particularly the concepts of moment of inertia and angular momentum.

9.6 Rotation in two dimensions: a particle on a ring

We consider a particle of mass m constrained to move in a circular path of radius r in the xy-plane (Fig. 9.27). The total energy is equal to the kinetic energy, because $V = 0$ everywhere. We can therefore write $E = p^2/2m$. According to classical mechanics, the **angular momentum**, J_z, around the z-axis (which lies perpendicular to the xy-plane) is $J_z = \pm pr$, so the energy can be expressed as $J_z^2/2mr^2$. Because mr^2 is the **moment of inertia**, I, of the mass on its path, it follows that

$$E = \frac{J_z^2}{2I} \tag{9.36}$$

We shall now see that not all the values of the angular momentum are permitted in quantum mechanics, and therefore that both angular momentum and rotational energy are quantized.

Fig. 9.27 The angular momentum of a particle of mass m on a circular path of radius r in the xy-plane is represented by a vector J with the single non-zero component J_z of magnitude pr perpendicular to the plane.

(a) The qualitative origin of quantized rotation

Because $J_z = \pm pr$, and, from the de Broglie relation, $p = h/\lambda$, the angular momentum about the z-axis is

$$J_z = \pm \frac{hr}{\lambda}$$

Opposite signs correspond to opposite directions of travel. This equation shows that the shorter the wavelength of the particle on a circular path of given radius, the greater the angular momentum of the particle. It follows that, if we can see why the
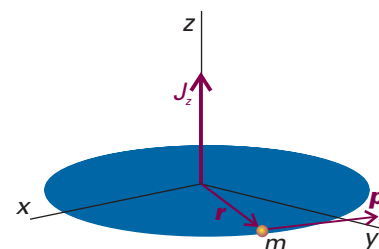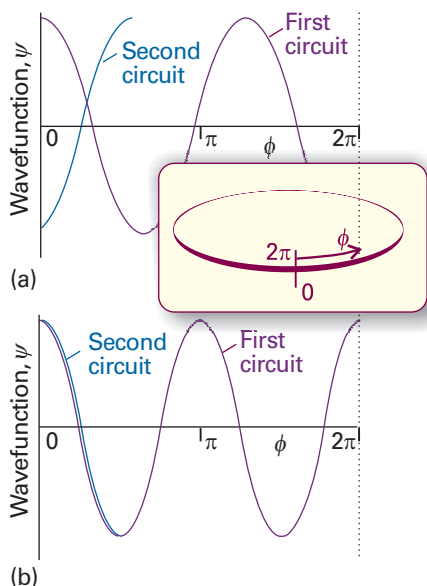
(a)

(b)

Fig. 9.28 Two solutions of the Schrödinger equation for a particle on a ring. The circumference has been opened out into a straight line; the points at $\phi = 0$ and 2π are identical. The solution in (a) is unacceptable because it is not single-valued. Moreover, on successive circuits it interferes destructively with itself, and does not survive. The solution in (b) is acceptable: it is single-valued, and on successive circuits it reproduces itself.
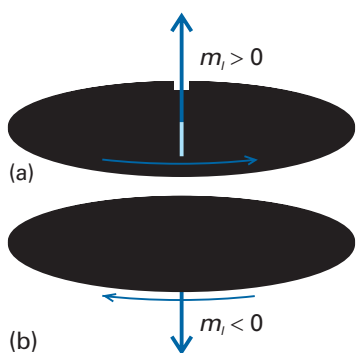

(a)

(b)

Fig. 9.29 The angular momentum of a particle confined to a plane can be represented by a vector of length $|m_l|$ units along the z-axis and with an orientation that indicates the direction of motion of the particle. The direction is given by the right-hand screw rule.

wavelength is restricted to discrete values, then we shall understand why the angular momentum is quantized.

Suppose for the moment that λ can take an arbitrary value. In that case, the wavefunction depends on the azimuthal angle ϕ as shown in Fig. 9.28a. When ϕ increases beyond 2π, the wavefunction continues to change, but for an arbitrary wavelength it gives rise to a different value at each point, which is unacceptable (Section 8.4b). An acceptable solution is obtained only if the wavefunction reproduces itself on successive circuits, as in Fig. 9.28b. Because only some wavefunctions have this property, it follows that only some angular momenta are acceptable, and therefore that only certain rotational energies exist. Hence, the energy of the particle is quantized. Specifically, the only allowed wavelengths are

$$\lambda = \frac{2\pi r}{m_l}$$

with m_l, the conventional notation for this quantum number, taking integral values including 0. The value $m_l = 0$ corresponds to $\lambda = \infty$; a 'wave' of infinite wavelength has a constant height at all values of ϕ. The angular momentum is therefore limited to the values

$$J_z = \pm\frac{hr}{\lambda} = \frac{m_l h r}{2\pi r} = \frac{m_l h}{2\pi}$$

where we have allowed m_l to have positive or negative values. That is,

$$J_z = m_l \hbar \qquad m_l = 0, \pm 1, \pm 2, \ldots \tag{9.37}$$

Positive values of m_l correspond to rotation in a clockwise sense around the z-axis (as viewed in the direction of z, Fig. 9.29) and negative values of m_l correspond to counter-clockwise rotation around z. It then follows from eqn 9.36 that the energy is limited to the values

$$E = \frac{J_z^2}{2I} = \frac{m_l^2 \hbar^2}{2I} \tag{9.38a}$$

We shall see shortly that the corresponding normalized wavefunctions are

$$\psi_{m_l}(\phi) = \frac{e^{im_l\phi}}{(2\pi)^{1/2}} \tag{9.38b}$$

The wavefunction with $m_l = 0$ is $\psi_0(\phi) = 1/(2\pi)^{1/2}$, and has the same value at all points on the circle.

We have arrived at a number of conclusions about rotational motion by combining some classical notions with the de Broglie relation. Such a procedure can be very useful for establishing the general form (and, as in this case, the exact energies) for a quantum mechanical system. However, to be sure that the correct solutions have been obtained, and to obtain practice for more complex problems where this less formal approach is inadequate, we need to solve the Schrödinger equation explicitly. The formal solution is described in the *Justification* that follows.

Justification 9.5 *The energies and wavefunctions of a particle on a ring*

The hamiltonian for a particle of mass m in a plane (with $V = 0$) is the same as that given in eqn 9.10:

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

and the Schrödinger equation is $H\psi = E\psi$, with the wavefunction a function of the angle ϕ. It is always a good idea to use coordinates that reflect the full symmetry of the system, so we introduce the coordinates r and ϕ (Fig. 9.30), where $x = r \cos \phi$ and $y = r \sin \phi$. By standard manipulations (see *Further reading*) we can write

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2} \tag{9.39}$$

However, because the radius of the path is fixed, the derivatives with respect to r can be discarded. The hamiltonian then becomes

$$\hat{H} = -\frac{\hbar^2}{2mr^2}\frac{d^2}{d\phi^2}$$

The moment of inertia $I = mr^2$ has appeared automatically, so H may be written

$$\hat{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2} \tag{9.40}$$

and the Schrödinger equation is

$$\frac{d^2\psi}{d\phi^2} = -\frac{2IE}{\hbar^2}\psi \tag{9.41}$$

The normalized general solutions of the equation are

$$\psi_{m_l}(\phi) = \frac{e^{im_l\phi}}{(2\pi)^{1/2}} \qquad m_l = \pm\frac{(2IE)^{1/2}}{\hbar} \tag{9.42}$$

The quantity m_l is just a dimensionless number at this stage.

We now select the acceptable solutions from among these general solutions by imposing the condition that the wavefunction should be single-valued. That is, the wavefunction ψ must satisfy a **cyclic boundary condition**, and match at points separated by a complete revolution: $\psi(\phi + 2\pi) = \psi(\phi)$. On substituting the general wavefunction into this condition, we find

$$\psi_{m_l}(\phi + 2\pi) = \frac{e^{im_l(\phi+2\pi)}}{(2\pi)^{1/2}} = \frac{e^{im_l\phi}e^{2\pi im_l}}{(2\pi)^{1/2}} = \psi_{m_l}(\phi)e^{2\pi im_l}$$

As $e^{i\pi} = -1$, this relation is equivalent to

$$\psi_{m_l}(\phi + 2\pi) = (-1)^{2m_l}\psi(\phi) \tag{9.43}$$

Because we require $(-1)^{2m_l} = 1$, $2m_l$ must be a positive or a negative even integer (including 0), and therefore m_l must be an integer: $m_l = 0, \pm 1, \pm 2, \dots$.

(b) Quantization of rotation

We can summarize the conclusions so far as follows. The energy is quantized and restricted to the values given in eqn 9.38a ($E = m_l^2\hbar^2/2I$). The occurrence of m_l as its square means that the energy of rotation is independent of the sense of rotation (the sign of m_l), as we expect physically. In other words, states with a given value of $|m_l|$ are doubly degenerate, except for $m_l = 0$, which is non-degenerate. Although the result has been derived for the rotation of a single mass point, it also applies to any body of moment of inertia I constrained to rotate about one axis.

We have also seen that the angular momentum is quantized and confined to the values given in eqn 9.37 ($J_z = m_l\hbar$). The increasing angular momentum is associated with the increasing number of nodes in the real and imaginary parts of the wavefunction: the wavelength decreases stepwise as $|m_l|$ increases, so the momentum with which the particle travels round the ring increases (Fig. 9.31). As shown in the following
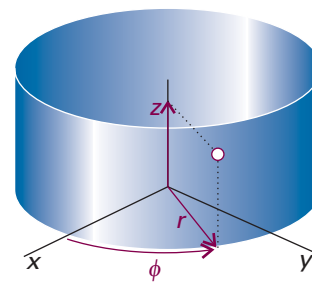
Fig. 9.30 The cylindrical coordinates z, r, and ϕ for discussing systems with axial (cylindrical) symmetry. For a particle confined to the xy-plane, only r and ϕ can change.

$|m_l| = 2$

$|m_l| = 1$

$m_l = 0$
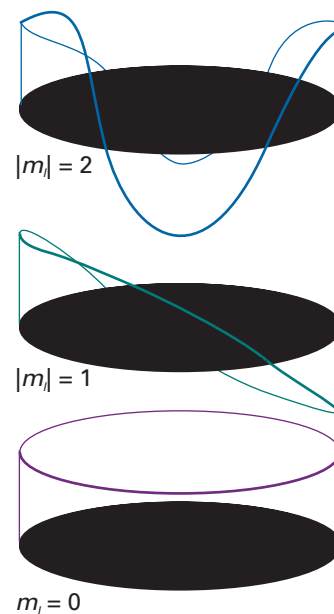
Fig. 9.31 The real parts of the wavefunctions of a particle on a ring. As shorter wavelengths are achieved, the magnitude of the angular momentum around the z-axis grows in steps of $\hbar$.

Comment 9.4

The complex function $e^{im_l\phi}$ does not have nodes; however, it may be written as $\cos m_l\phi + i \sin m_l\phi$, and the real ($\cos m_l\phi$) and imaginary ($\sin m_l\phi$) components do have nodes.

The angular momentum in three dimensions is defined as

$$l = r \times p = \begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$= (yp_z - zp_y)i - (xp_z - zp_x)j + (xp_y - yp_x)k$$

where i, j, and k are unit vectors pointing along the positive directions on the x-, y-, and z-axes. It follows that the z-component of the angular momentum has a magnitude given by eqn 9.44. For more information on vectors, see *Appendix 2*.

Angular momentum

Fig. 9.32 The basic ideas of the vector representation of angular momentum: the magnitude of the angular momentum is represented by the length of the vector, and the orientation of the motion in space by the orientation of the vector (using the right-hand screw rule).

Justification, we can come to the same conclusion more formally by using the argument about the relation between eigenvalues and the values of observables established in Section 8.5.

....

Justification 9.6 *The quantization of angular momentum*

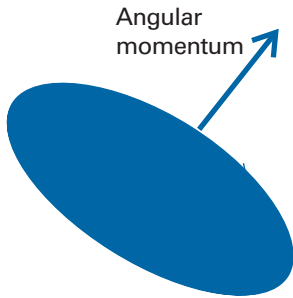In the discussion of translational motion in one dimension, we saw that the opposite signs in the wavefunctions e^{ikx} and e^{-ikx} correspond to opposite directions of travel, and that the linear momentum is given by the eigenvalue of the linear momentum operator. The same conclusions can be drawn here, but now we need the eigenvalues of the angular momentum operator. In classical mechanics the orbital angular momentum l_z about the z-axis is defined as

$$l_z = xp_y - yp_x \qquad [9.44]$$

where p_x is the component of linear motion parallel to the x-axis and p_y is the component parallel to the y-axis. The operators for the two linear momentum components are given in eqn 8.26, so the operator for angular momentum about the z-axis, which we denote $\hat{l}_z$, is

$$\hat{l}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) \qquad (9.45)$$

When expressed in terms of the coordinates r and ϕ, by standard manipulations this equation becomes

$$\hat{l}_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi} \qquad (9.46)$$

With the angular momentum operator available, we can test the wavefunction in eqn 9.38b. Disregarding the normalization constant, we find

$$\hat{l}_z \psi_{m_l} = \frac{\hbar}{i}\frac{d\psi_{m_l}}{d\phi} = im_l\frac{\hbar}{i}e^{im_l\phi} = m_l\hbar\psi_{m_l} \qquad (9.47)$$

That is, ψ_{m_l} is an eigenfunction of $\hat{l}_z$, and corresponds to an angular momentum $m_l\hbar$. When m_l is positive, the angular momentum is positive (clockwise when seen from below); when m_l is negative, the angular momentum is negative (counterclockwise when seen from below). These features are the origin of the vector representation of angular momentum, in which the magnitude is represented by the length of a vector and the direction of motion by its orientation (Fig. 9.32).

....

To locate the particle given its wavefunction in eqn 9.38b, we form the probability density:

$$\psi_{m_l}^{*}\psi_{m_l} = \left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}} \right)^{*}\left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}} \right) = \left(\frac{e^{-im_l\phi}}{(2\pi)^{1/2}} \right)\left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}} \right) = \frac{1}{2\pi}$$

Because this probability density is independent of ϕ, the probability of locating the particle somewhere on the ring is also independent of ϕ (Fig. 9.33). Hence the location of the particle is completely indefinite, and knowing the angular momentum precisely eliminates the possibility of specifying the particle's location. Angular momentum and angle are a pair of complementary observables (in the sense defined in Section 8.6), and the inability to specify them simultaneously with arbitrary precision is another example of the uncertainty principle.

9.7 Rotation in three dimensions: the particle on a sphere

We now consider a particle of mass m that is free to move anywhere on the surface of a sphere of radius r. We shall need the results of this calculation when we come to describe rotating molecules and the states of electrons in atoms and in small clusters of atoms. The requirement that the wavefunction should match as a path is traced over the poles as well as round the equator of the sphere surrounding the central point introduces a second cyclic boundary condition and therefore a second quantum number (Fig. 9.34).

(a) The Schrödinger equation

The hamiltonian for motion in three dimensions (Table 8.1) is

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V \qquad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad (9.48)$$

The symbol ∇^2 is a convenient abbreviation for the sum of the three second derivatives; it is called the **laplacian**, and read either 'del squared' or 'nabla squared'. For the particle confined to a spherical surface, $V = 0$ wherever it is free to travel, and the radius r is a constant. The wavefunction is therefore a function of the **colatitude**, θ, and the **azimuth**, ϕ (Fig. 9.35), and we write it $\psi(\theta,\phi)$. The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi \qquad (9.49)$$

As shown in the following *Justification*, this partial differential equation can be simplified by the separation of variables procedure by expressing the wavefunction (for constant r) as the product

$$\psi(\theta,\phi) = \Theta(\theta)\Phi(\phi) \qquad (9.50)$$

where Θ is a function only of θ and Φ is a function only of ϕ.

....

Justification 9.7 *The separation of variables technique applied to the particle on a sphere*

The laplacian in spherical polar coordinates is (see *Further reading*)

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2 \qquad (9.51a)$$

where the **legendrian**, Λ^2, is

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} \qquad (9.51b)$$

Because r is constant, we can discard the part of the laplacian that involves differentiation with respect to r, and so write the Schrödinger equation as

$$\frac{1}{r^2}\Lambda^2\psi = -\frac{2mE}{\hbar^2}\psi$$

or, because $I = mr^2$, as

$$\Lambda^2\psi = -\varepsilon\psi \qquad \varepsilon = \frac{2IE}{\hbar^2}$$
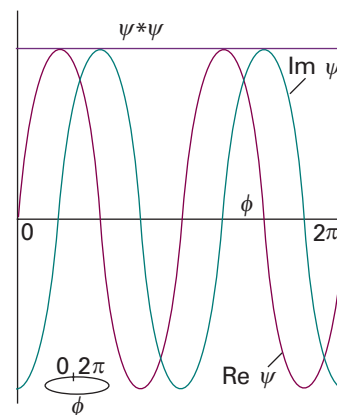
Fig. 9.33 The probability density for a particle in a definite state of angular momentum is uniform, so there is an equal probability of finding the particle anywhere on the ring.
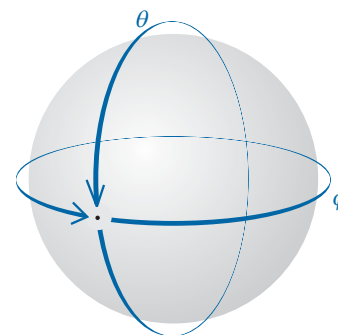
Fig. 9.34 The wavefunction of a particle on the surface of a sphere must satisfy two cyclic boundary conditions; this requirement leads to two quantum numbers for its state of angular momentum.
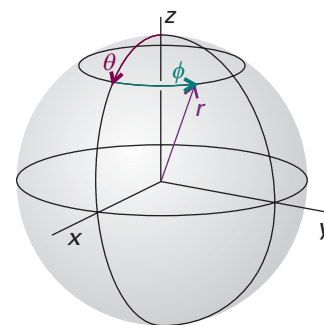
Fig. 9.35 Spherical polar coordinates. For a particle confined to the surface of a sphere, only the colatitude, θ, and the azimuth, ϕ, can change.

Table 9.3 The spherical harmonics

l	m_l	$Y_{l,m_l}(\theta,\varphi)$
0	0	$\left(\dfrac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\dfrac{3}{4\pi}\right)^{1/2}\cos\theta$
	± 1	$\mp\left(\dfrac{3}{8\pi}\right)^{1/2}\sin\theta\,e^{\pm i\phi}$
2	0	$\left(\dfrac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	± 1	$\mp\left(\dfrac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\,e^{\pm i\phi}$
	± 2	$\left(\dfrac{15}{32\pi}\right)^{1/2}\sin^2\theta\,e^{\pm 2i\phi}$
3	0	$\left(\dfrac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
	± 1	$\mp\left(\dfrac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\,e^{\pm i\phi}$
	± 2	$\left(\dfrac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\,e^{\pm 2i\phi}$
	± 3	$\mp\left(\dfrac{35}{64\pi}\right)^{1/2}\sin^3\theta\,e^{\pm 3i\phi}$

Comment 9.6

The spherical harmonics are orthogonal and normalized in the following sense:

$$\int_0^\pi\int_0^{2\pi} Y_{l',m_l'}(\theta,\phi)^* Y_{l,m_l}(\theta,\phi)\sin\theta\,d\theta\,d\phi$$

$$= \delta_{l'l}\delta_{m_l'm_l}$$

An important 'triple integral' is

$$\int_0^\pi\int_0^{2\pi} Y_{l',m_l''}(\theta,\phi)^* Y_{l',m_l'}(\theta,\phi) Y_{l,m_l}(\theta,\phi)$$

$$\sin\theta\,d\theta\,d\phi = 0$$

unless $m_l'' = m_l' + m_l$ and we can form a triangle with sides of lengths l'', l', and l (such as 1, 2, and 3 or 1, 1, and 1, but not 1, 2, and 4).

Comment 9.7

The real and imaginary components of the Φ component of the wavefunctions, $e^{im_l\phi} = \cos m_l\phi + i\sin m_l\phi$, each have $|m_l|$ angular nodes, but these nodes are not seen when we plot the probability density, because $|e^{im_l\phi}|^2 = 1$.

To verify that this expression is separable, we substitute $\psi = \Theta\Phi$:

$$\frac{1}{\sin^2\theta}\frac{\partial^2(\Theta\Phi)}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial(\Phi\Theta)}{\partial\theta} = -\varepsilon\Theta\Phi$$

We now use the fact that Θ and Φ are each functions of one variable, so the partial derivatives become complete derivatives:

$$\frac{\Theta}{\sin^2\theta}\frac{d^2\Phi}{d\phi^2} + \frac{\Phi}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} = -\varepsilon\Theta\Phi$$

Division through by $\Theta\Phi$, multiplication by $\sin^2\theta$, and minor rearrangement gives

$$\frac{\Phi}{}\frac{d^2\Phi}{d\phi^2} + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + \varepsilon\sin^2\theta = 0$$

The first term on the left depends only on ϕ and the remaining two terms depend only on θ. We met a similar situation when discussing a particle on a rectangular surface (*Justification 9.3*), and by the same argument, the complete equation can be separated. Thus, if we set the first term equal to the numerical constant $-m_l^2$ (using a notation chosen with an eye to the future), the separated equations are

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m_l^2 \qquad \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\sin\theta\frac{d\Theta}{d\theta} + \varepsilon\sin^2\theta = m_l^2$$

The first of these two equations is the same as that in *Justification 9.5*, so it has the same solutions (eqn 9.38b). The second is much more complicated to solve, but the solutions are tabulated as the *associated Legendre functions*. The cyclic boundary conditions on Θ result in the introduction of a second quantum number, l, which identifies the acceptable solutions. The presence of the quantum number m_l in the second equation implies, as we see below, that the range of acceptable values of m_l is restricted by the value of l.

As indicated in *Justification 9.7*, solution of the Schrödinger equation shows that the acceptable wavefunctions are specified by two quantum numbers l and m_l that are restricted to the values

$$l = 0, 1, 2, \ldots \qquad m_l = l, l-1, \ldots, -l \tag{9.52}$$

Note that the **orbital angular momentum quantum number** l is non-negative and that, for a given value of l, there are $2l+1$ permitted values of the **magnetic quantum number**, m_l. The normalized wavefunctions are usually denoted $Y_{l,m_l}(\theta,\phi)$ and are called the **spherical harmonics** (Table 9.3).

Figure 9.36 is a representation of the spherical harmonics for $l = 0$ to 4 and $m_l = 0$ which emphasizes how the number of angular nodes (the positions at which the wavefunction passes through zero) increases as the value of l increases. There are no angular nodes around the z-axis for functions with $m_l = 0$, which corresponds to there being no component of orbital angular momentum about that axis. Figure 9.37 shows the distribution of the particle of a given angular momentum in more detail. In this representation, the value of $|Y_{l,m_l}|^2$ at each value of θ and ϕ is proportional to the distance of the surface from the origin. Note how, for a given value of l, the most probable location of the particle migrates towards the xy-plane as the value of $|m_l|$ increases.

It also follows from the solution of the Schrödinger equation that the energy E of the particle is restricted to the values

$$E = l(l+1)\frac{\hbar^2}{2I} \qquad l = 0, 1, 2, \ldots \tag{9.53}$$
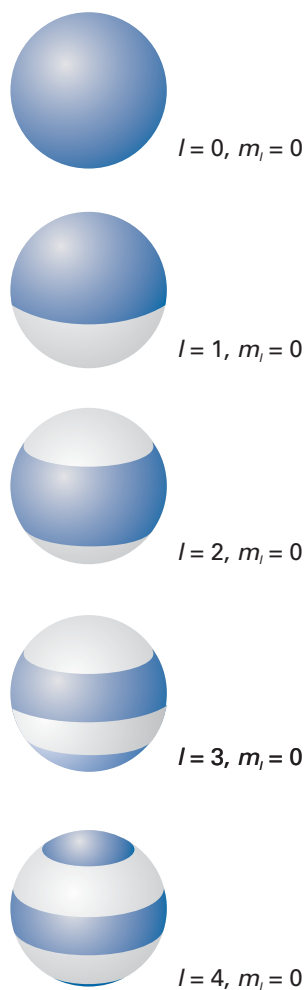
Fig. 9.36 A representation of the wavefunctions of a particle on the surface of a sphere which emphasizes the location of angular nodes: dark and light shading correspond to different signs of the wavefunction. Note that the number of nodes increases as the value of l increases. All these wavefunctions correspond to $m_l = 0$; a path round the vertical z-axis of the sphere does not cut through any nodes.
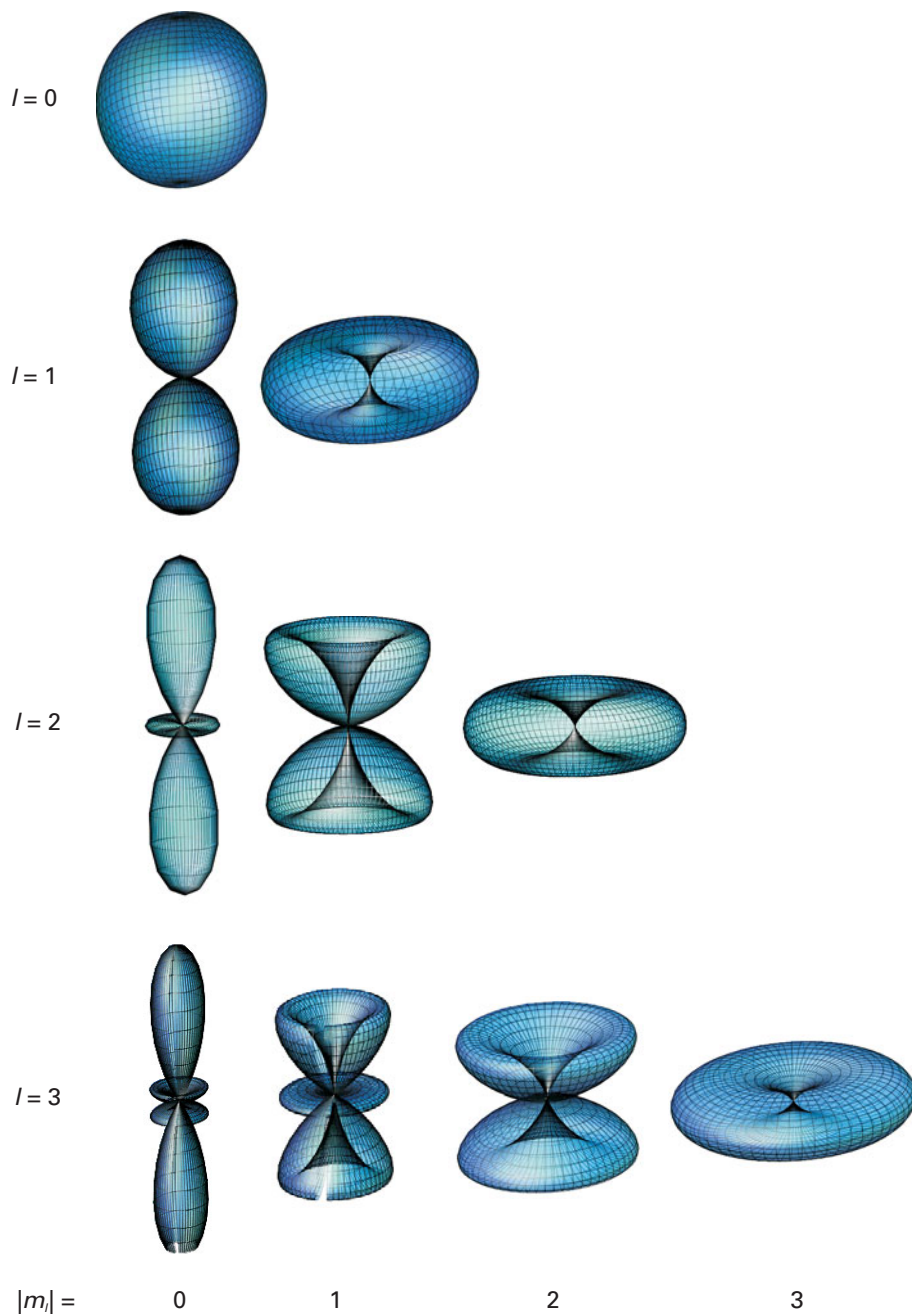
Fig. 9.37 A more complete representation of the wavefunctions for $l = 0$, 1, 2, and 3. The distance of a point on the surface from the origin is proportional to the square modulus of the amplitude of the wavefunction at that point.

Exploration Plot the variation with the radius r of the first ten energy levels of a particle on a sphere. Which of the following statements are true: (a) for a given value of r, the energy separation between adjacent levels decreases with increasing l, (b) increasing r leads to an decrease in the value of the energy for each level, (c) the energy difference between adjacent levels increases as r increases.

We see that the energy is quantized, and that it is independent of m_l. Because there are $2l + 1$ different wavefunctions (one for each value of m_l) that correspond to the same energy, it follows that a level with quantum number l is $(2l + 1)$-fold degenerate.

(b) Angular momentum

The energy of a rotating particle is related classically to its angular momentum J by $E = J^2/2I$ (see *Appendix 3*). Therefore, by comparing this equation with eqn 9.53, we can deduce that, because the energy is quantized, then so too is the magnitude of the angular momentum, and confined to the values

$$\text{Magnitude of angular momentum} = \{l(l+1)\}^{1/2}\hbar \qquad l = 0, 1, 2 \ldots \qquad (9.54a)$$

We have already seen (in the context of rotation in a plane) that the angular momentum about the z-axis is quantized, and that it has the values

$$z\text{-Component of angular momentum} = m_l\hbar \qquad m_l = l, l-1, \ldots, -l \qquad (9.54b)$$

The fact that the number of nodes in $\psi_{l,m_l}(\theta,\phi)$ increases with l reflects the fact that higher angular momentum implies higher kinetic energy, and therefore a more sharply buckled wavefunction. We can also see that the states corresponding to high angular momentum around the z-axis are those in which most nodal lines cut the equator: a high kinetic energy now arises from motion parallel to the equator because the curvature is greatest in that direction.

Illustration 9.4 *Calculating the frequency of a molecular rotational transition*

Under certain circumstances, the particle on a sphere is a reasonable model for the description of the rotation of diatomic molecules. Consider, for example, the rotation of a $^1\text{H}^{127}\text{I}$ molecule: because of the large difference in atomic masses, it is appropriate to picture the ^1H atom as orbiting a stationary ^{127}I atom at a distance $r = 160$ pm, the equilibrium bond distance. The moment of inertia of $^1\text{H}^{127}\text{I}$ is then $I = m_\text{H}r^2 = 4.288 \times 10^{-47}$ kg m^2. It follows that

$$\frac{\hbar^2}{2I} = \frac{(1.054\ 57 \times 10^{-34}\ \text{J s})^2}{2 \times (4.288 \times 10^{-47}\ \text{kg m}^2)} = 1.297 \times 10^{-22}\ \text{J}$$

or 0.1297 zJ. This energy corresponds to 78.09 J mol^{-1}. From eqn 9.53, the first few rotational energy levels are therefore 0 ($l = 0$), 0.2594 zJ ($l = 1$), 0.7782 zJ ($l = 2$), and 1.556 zJ ($l = 3$). The degeneracies of these levels are 1, 3, 5, and 7, respectively (from $2l + 1$), and the magnitudes of the angular momentum of the molecule are 0, $2^{1/2}\hbar$, $6^{1/2}\hbar$, and $(12)^{1/2}\hbar$ (from eqn 9.54a). It follows from our calculations that the $l = 0$ and $l = 1$ levels are separated by $\Delta E = 0.2594$ zJ. A transition between these two rotational levels of the molecule can be brought about by the emission or absorption of a photon with a frequency given by the Bohr frequency condition (eqn 8.10):

$$\nu = \frac{\Delta E}{h} = \frac{2.594 \times 10^{-22}\ \text{J}}{6.626 \times 10^{-34}\ \text{J s}} = 3.915 \times 10^{11}\ \text{Hz} = 391.5\ \text{GHz}$$

Radiation with this frequency belongs to the microwave region of the electromagnetic spectrum, so microwave spectroscopy is a convenient method for the study of molecular rotations. Because the transition energies depend on the moment of inertia, microwave spectroscopy is a very accurate technique for the determination of bond lengths. We discuss rotational spectra further in Chapter 13.

Self-test 9.8 Repeat the calculation for a $^2H^{127}I$ molecule (same bond length as $^1H^{127}I$).

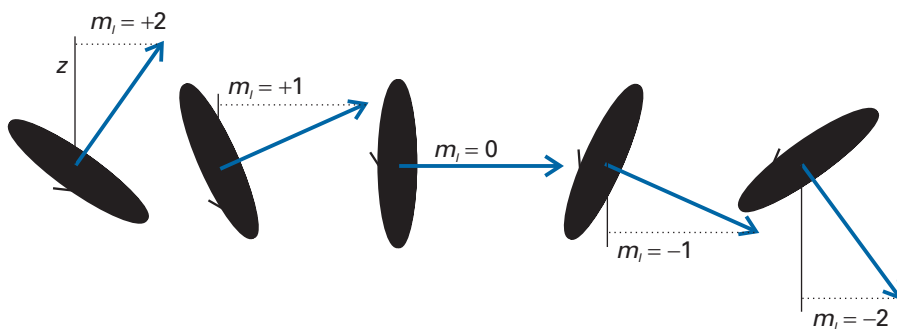[Energies are smaller by a factor of two; same angular momenta and numbers of components]

Fig. 9.38 The permitted orientations of angular momentum when $l = 2$. We shall see soon that this representation is too specific because the azimuthal orientation of the vector (its angle around z) is indeterminate.

(c) Space quantization

The result that m_l is confined to the values $l, l - 1, \ldots, -l$ for a given value of l means that the component of angular momentum about the z-axis may take only $2l + 1$ values. If the angular momentum is represented by a vector of length proportional to its magnitude (that is, of length $\{l(l + 1)\}^{1/2}$ units), then to represent correctly the value of the component of angular momentum, the vector must be oriented so that its projection on the z-axis is of length m_l units. In classical terms, this restriction means that the plane of rotation of the particle can take only a discrete range of orientations (Fig. 9.38). The remarkable implication is that *the orientation of a rotating body is quantized*.

The quantum mechanical result that a rotating body may not take up an arbitrary orientation with respect to some specified axis (for example, an axis defined by the direction of an externally applied electric or magnetic field) is called **space quantization**. It was confirmed by an experiment first performed by Otto Stern and Walther Gerlach in 1921, who shot a beam of silver atoms through an inhomogeneous magnetic field (Fig. 9.39). The idea behind the experiment was that a rotating, charged body behaves like a magnet and interacts with the applied field. According to classical mechanics, because the orientation of the angular momentum can take any value, the associated magnet can take any orientation. Because the direction in which the magnet is driven by the inhomogeneous field depends on the magnet's orientation, it follows that a broad band of atoms is expected to emerge from the region where the magnetic field acts. According to quantum mechanics, however, because the angular momentum is quantized, the associated magnet lies in a number of discrete orientations, so several sharp bands of atoms are expected.

In their first experiment, Stern and Gerlach appeared to confirm the classical prediction. However, the experiment is difficult because collisions between the atoms in the beam blur the bands. When the experiment was repeated with a beam of very low intensity (so that collisions were less frequent) they observed discrete bands, and so confirmed the quantum prediction.

Fig. 9.39 (a) The experimental arrangement for the Stern–Gerlach experiment: the magnet provides an inhomogeneous field. (b) The classically expected result. (c) The observed outcome using silver atoms.

(d) The vector model

Throughout the preceding discussion, we have referred to the z-component of angular momentum (the component about an arbitrary axis, which is conventionally denoted z), and have made no reference to the x- and y-components (the components
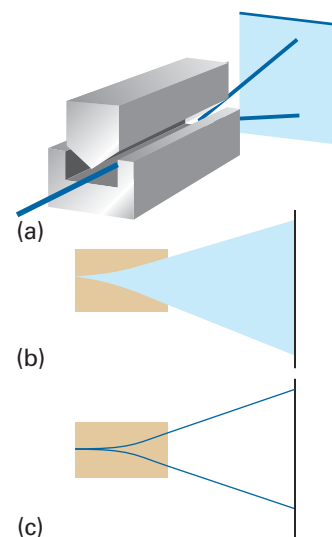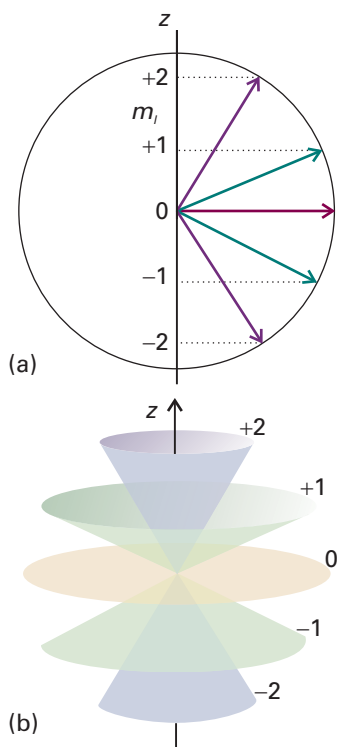
(a)

(b)

Fig. 9.40 (a) A summary of Fig. 9.38. However, because the azimuthal angle of the vector around the z-axis is indeterminate, a better representation is as in (b), where each vector lies at an unspecified azimuthal angle on its cone.

about the two axes perpendicular to z). The reason for this omission is found by examining the operators for the three components, each one being given by a term like that in eqn 9.45:

$$\hat{l}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \qquad \hat{l}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \qquad \hat{l}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \quad (9.55)$$

As you are invited to show in Problem 9.27, these three operators do not commute with one another:

$$[\hat{l}_x,\hat{l}_y] = i\hbar\hat{l}_z \qquad [\hat{l}_y,\hat{l}_z] = i\hbar\hat{l}_x \qquad [\hat{l}_z,\hat{l}_x] = i\hbar\hat{l}_y \qquad (9.56a)$$

Therefore, we cannot specify more than one component (unless $l=0$). In other words, l_x, l_y, and l_z are complementary observables. On the other hand, the operator for the square of the magnitude of the angular momentum is

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 = \hbar^2\Lambda^2 \qquad (9.56b)$$

where Λ^2 is the legendrian in eqn 9.51b. This operator does commute with all three components:

$$[\hat{l}^2,\hat{l}_q] = 0 \qquad q = x, y, \text{ and } z \qquad (9.56c)$$

(See Problem 9.29.) Therefore, although we may specify the magnitude of the angular momentum and any of its components, if l_z is known, then it is impossible to ascribe values to the other two components. It follows that the illustration in Fig. 9.38, which is summarized in Fig. 9.40a, gives a false impression of the state of the system, because it suggests definite values for the x- and y-components. A better picture must reflect the impossibility of specifying l_x and l_y if l_z is known.

The **vector model** of angular momentum uses pictures like that in Fig. 9.40b. The cones are drawn with side $\{l(l+1)\}^{1/2}$ units, and represent the magnitude of the angular momentum. Each cone has a definite projection (of m_l units) on the z-axis, representing the system's precise value of l_z. The l_x and l_y projections, however, are indefinite. The vector representing the state of angular momentum can be thought of as lying with its tip on any point on the mouth of the cone. At this stage it should not be thought of as sweeping round the cone; that aspect of the model will be added later when we allow the picture to convey more information.

IMPACT ON NANOSCIENCE
I9.2 Quantum dots

In *Impact I9.1* we outlined some advantages of working in the nanometre regime. Another is the possibility of using quantum mechanical effects that render the properties of an assembly dependent on its size. Here we focus on the origins and consequences of these quantum mechanical effects.

Consider a sample of a metal, such as copper or gold. It carries an electrical current because the electrons are delocalized over all the atomic nuclei. That is, we may treat the movement of electrons in metals with a particle in a box model, though it is necessary to imagine that the electrons move independently of each other. Immediately, we predict from eqn 9.6 that the energy levels of the electrons in a large box, such as a copper wire commonly used to make electrical connections, form a continuum so we are justified in neglecting quantum mechanical effects on the properties of the material. However, consider a *nanocrystal*, a small cluster of atoms with dimensions in the nanometre scale. Again using eqn 9.6, we predict that the electronic energies are quantized and that the separation between energy levels decreases with increasing size of the cluster. This quantum mechanical effect can be observed in 'boxes' of any

shape. For example, you are invited to show in Problem 9.39 that the energy levels of an electron *in* a sphere of radius R are given by

$$E_n = \frac{n^2 h^2}{8 m_e R^2} \tag{9.57}$$

The quantization of energy in nanocrystals has important technological implications when the material is a semiconductor, in which the electrical conductivity increases with increasing temperature or upon excitation by light (see Chapter 20 for a more detailed discussion). Transfer of energy to a semiconductor increases the mobility of electrons in the material. However, for every electron that moves to a different site in the sample, a unit of positive charge, called a *hole*, is left behind. The holes are also mobile, so to describe electrical conductivity in semiconductors we need to consider the movement of electron–hole pairs, also called **excitons**, in the material.

The electrons and holes may be regarded as particles trapped in a box, so eqn 9.6 can give us qualitative insight into the origins of conductivity in semiconductors. We conclude as before that only in nanocrystals are the energies of the charge carriers quantized. Now we explore the impact of energy quantization on the optical and electronic properties of semiconducting nanocrystals.

Three-dimensional nanocrystals of semiconducting materials containing 10^3 to 10^5 atoms are called **quantum dots**. They can be made in solution or by depositing atoms on a surface, with the size of the nanocrystal being determined by the details of the synthesis (see, for example, *Impact I20.2*). A quantitative but approximate treatment that leads to the energy of the exciton begins with the following hamiltonian for a spherical quantum dot of radius R:

$$\hat{H} = -\frac{\hbar^2}{2 m_e} \nabla_e^2 - \frac{\hbar^2}{2 m_h} \nabla_h^2 + V(\boldsymbol{r}_e, \boldsymbol{r}_h) \tag{9.58}$$

where the first two terms are the kinetic energy operators for the electron and hole (with masses m_e and m_h, respectively), and the third term is the potential energy of interaction between electron and hole, which are located at positions $\boldsymbol{r}_e$ and $\boldsymbol{r}_h$ from the centre of the sphere. Taking into account only the Coulomb attraction between the hole, with charge $+e$, and the electron, with charge $-e$, we write (see Chapter 9 and *Appendix 3* for details):

$$V(\boldsymbol{r}_e, \boldsymbol{r}_h) = -\frac{e^2}{4\pi\varepsilon |\boldsymbol{r}_e - \boldsymbol{r}_h|} \tag{9.59}$$

where $|\boldsymbol{r}_e - \boldsymbol{r}_h|$ is the distance between the electron and hole and ε is the permittivity of the medium (we are ignoring the effect of polarization of the medium due to the presence of charges). Solving the Schrödinger equation in this case is not a trivial task, but the final expression for the energy of the exciton, E_{ex}, is relatively simple (see *Further reading* for details):

$$E_{ex} = \frac{h^2}{8 R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8 e^2}{4\pi\varepsilon R} \tag{9.60}$$

As expected, we see that the energy of the exciton decreases with increasing radius of the quantum dot. Moreover, for small R, the second term on the right of the preceding equation is smaller than the first term and the energy of the exciton is largely kinetic, with the resulting expression resembling the case for a particle in a sphere.

The expression for E_{ex} has important consequences for the optical properties of quantum dots. First, we see that the energy required to create mobile charge carriers and to induce electrical conductivity depends on the size of the quantum dot. The

electrical properties of large, macroscopic samples of semiconductors cannot be tuned in this way. Second, in many quantum dots, such as the nearly spherical nanocrystals of cadmium selenide (CdSe), the exciton can be generated by absorption of visible light. Therefore, we predict that, as the radius of the quantum dot decreases, the excitation wavelength increases. That is, as the size of the quantum dot varies, so does the colour of the material. This phenomenon is indeed observed in suspensions of CdSe quantum dots of different sizes.

Because quantum dots are semiconductors with tunable electrical properties, it is easy to imagine uses for these materials in the manufacture of transistors. But the special optical properties of quantum dots can also be exploited. Just as the generation of an electron–hole pair requires absorption of light of a specific wavelength, so does recombination of the pair result in the emission of light of a specific wavelength. This property forms the basis for the use of quantum dots in the visualization of biological cells at work. For example, a CdSe quantum dot can be modified by covalent attachment of an organic spacer to its surface. When the other end of the spacer reacts specifically with a cellular component, such as a protein, nucleic acid, or membrane, the cell becomes labelled with a light-emitting quantum dot. The spatial distribution of emission intensity and, consequently, of the labelled molecule can then be measured with a microscope. Though this technique has been used extensively with organic molecules as labels, quantum dots are more stable and are stronger light emitters.

9.8 Spin

Stern and Gerlach observed *two* bands of Ag atoms in their experiment. This observation seems to conflict with one of the predictions of quantum mechanics, because an angular momentum l gives rise to $2l + 1$ orientations, which is equal to 2 only if $l = \frac{1}{2}$, contrary to the conclusion that l must be an integer. The conflict was resolved by the suggestion that the angular momentum they were observing was not due to orbital angular momentum (the motion of an electron around the atomic nucleus) but arose instead from the motion of the electron about its own axis. This intrinsic angular momentum of the electron is called its **spin**. The explanation of the existence of spin emerged when Dirac combined quantum mechanics with special relativity and established the theory of relativistic quantum mechanics.

The spin of an electron about its own axis does not have to satisfy the same boundary conditions as those for a particle circulating around a central point, so the quantum number for spin angular momentum is subject to different restrictions. To distinguish this spin angular momentum from orbital angular momentum we use the **spin quantum number** s (in place of l; like l, s is a non-negative number) and m_s, the **spin magnetic quantum number**, for the projection on the z-axis. The magnitude of the spin angular momentum is $\{s(s + 1)\}^{1/2}\hbar$ and the component $m_s\hbar$ is restricted to the $2s + 1$ values

$$m_s = s, s - 1, \ldots, -s \tag{9.61}$$

The detailed analysis of the spin of a particle is sophisticated and shows that the property should not be taken to be an actual spinning motion. It is better to regard 'spin' as an intrinsic property like mass and charge. However, the picture of an actual spinning motion can be very useful when used with care. For an electron it turns out that only one value of s is allowed, namely $s = \frac{1}{2}$, corresponding to an angular momentum of magnitude $(\frac{3}{4})^{1/2}\hbar = 0.866\hbar$. This spin angular momentum is an intrinsic property of the electron, like its rest mass and its charge, and every electron has exactly the same value: the magnitude of the spin angular momentum of an electron cannot be changed. The spin may lie in $2s + 1 = 2$ different orientations (Fig. 9.41).

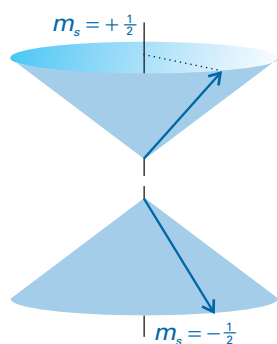**Fig. 9.41** An electron spin ($s = \frac{1}{2}$) can take only two orientations with respect to a specified axis. An α electron (top) is an electron with $m_s = +\frac{1}{2}$; a β electron (bottom) is an electron with $m_s = -\frac{1}{2}$. The vector representing the spin angular momentum lies at an angle of 55° to the z-axis (more precisely, the half-angle of the cones is $\arccos(1/3^{1/2})$).

One orientation corresponds to $m_s = +\frac{1}{2}$ (this state is often denoted α or $\uparrow$); the other orientation corresponds to $m_s = -\frac{1}{2}$ (this state is denoted β or $\downarrow$).

The outcome of the Stern–Gerlach experiment can now be explained if we suppose that each Ag atom possesses an angular momentum due to the spin of a single electron, because the two bands of atoms then correspond to the two spin orientations. Why the atoms behave like this is explained in Chapter 10 (but it is already probably familiar from introductory chemistry that the ground-state configuration of a silver atom is $[Kr]4d^{10}5s^1$, a single unpaired electron outside a closed shell).

Like the electron, other elementary particles have characteristic spin. For example, protons and neutrons are spin-$\frac{1}{2}$ particles (that is, $s = \frac{1}{2}$) and invariably spin with angular momentum $(\frac{3}{4})^{1/2}\hbar = 0.866\hbar$. Because the masses of a proton and a neutron are so much greater than the mass of an electron, yet they all have the same spin angular momentum, the classical picture would be of these two particles spinning much more slowly than an electron. Some elementary particles have $s = 1$, and so have an intrinsic angular momentum of magnitude $2^{1/2}\hbar$. Some mesons are spin-1 particles (as are some atomic nuclei), but for our purposes the most important spin-1 particle is the photon. From the discussion in this chapter, we see that the photon has zero rest mass, zero charge, an energy $h\nu$, a linear momentum h/λ or $h\nu/c$, an intrinsic angular momentum of $2^{1/2}\hbar$, and travels at the speed c. We shall see the importance of photon spin in the next chapter.

Particles with half-integral spin are called **fermions** and those with integral spin (including 0) are called **bosons**. Thus, electrons and protons are fermions and photons are bosons. It is a very deep feature of nature that all the elementary particles that constitute matter are fermions whereas the elementary particles that are responsible for the forces that bind fermions together are all bosons. Photons, for example, transmit the electromagnetic force that binds together electrically charged particles. Matter, therefore, is an assembly of fermions held together by forces conveyed by bosons.

The properties of angular momentum that we have developed are set out in Table 9.4. As mentioned there, when we use the quantum numbers l and m_l we shall mean orbital angular momentum (circulation in space). When we use s and m_s we shall mean spin angular momentum (intrinsic angular momentum). When we use j and m_j we shall mean either (or, in some contexts to be described in Chapter 10, a combination of orbital and spin momenta).

Table 9.4 Properties of angular momentum

Quantum number	Symbol	Values*	Specifies
Orbital angular momentum	l	$0, 1, 2, \ldots$	Magnitude, $\{l(l+1)\}^{1/2}\hbar$
Magnetic	m_l	$l, l-1, \ldots, -l$	Component on z-axis, $m_l\hbar$
Spin	s	$\frac{1}{2}$	Magnitude, $\{s(s+1)\}^{1/2}\hbar$
Spin magnetic	m_s	$\pm\frac{1}{2}$	Component on z-axis, $m_s\hbar$
Total	j	$l+s, l+s-1, \ldots, \lvert l-s \rvert$	Magnitude, $\{j(j+1)\}^{1/2}\hbar$
Total magnetic	m_j	$j, j-1, \ldots, -j$	Component on z-axis, $m_j\hbar$

To combine two angular momenta, use the Clebsch–Gordan series:

$$j = j_1 + j_2, j_1 + j_2 - 1, \ldots, \lvert j_1 - j_2 \rvert$$

For many-electron systems, the quantum numbers are designated by uppercase letters (L, M_L, S, M_S, etc.).

*Note that the quantum numbers for magnitude (l, s, j, etc.) are never negative.

Techniques of approximation

All the applications treated so far have had exact solutions. However, many problems —and almost all the problems of interest in chemistry—do not have exact solutions. To make progress with these problems we need to develop techniques of approximation. There are two major approaches, *variation theory* and *perturbation theory*. Variation theory is most commonly encountered in the context of molecular orbital theory, and we consider it there (Chapter 11). Here, we concentrate on perturbation theory.

9.9 Time-independent perturbation theory

In **perturbation theory**, we suppose that the hamiltonian for the problem we are trying to solve, $\hat{H}$, can be expressed as the sum of a simple hamiltonian, $\hat{H}^{(0)}$, which has known eigenvalues and eigenfunctions, and a contribution, $\hat{H}^{(1)}$, which represents the extent to which the true hamiltonian differs from the 'model' hamiltonian:

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} \tag{9.62}$$

In **time-independent perturbation theory**, the perturbation is always present and unvarying. For example, it might represent a dip in the potential energy of a particle in a box in some region along the length of the box.

In time-independent perturbation theory, we suppose that the true energy of the system differs from the energy of the simple system, and that we can write

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \ldots \tag{9.63}$$

where $E^{(1)}$ is the 'first-order correction' to the energy, a contribution proportional to $\hat{H}^{(1)}$, and $E^{(2)}$ is the 'second-order correction' to the energy, a contribution proportional to $\hat{H}^{(1)2}$, and so on. The true wavefunction also differs from the 'simple' wavefunction, and we write

$$\psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \ldots \tag{9.64}$$

In practice, we need to consider only the 'first-order correction' to the wavefunction, $\psi^{(1)}$. As we show in *Further information 9.2*, the first- and second-order corrections to the energy of the ground state (with the wavefunction ψ_0 and energy E_0), are

$$E_0^{(1)} = \int \psi_0^{(0)\star} \hat{H}^{(1)} \psi_0^{(0)} d\tau = H_{00}^{(1)} \tag{9.65a}$$

and

$$E_0^{(2)} = \sum_{n\neq0} \frac{\left| \int \psi_0^{(0)\star} \hat{H}^{(1)} \psi_0^{(0)} d\tau \right|^2}{E_0^{(0)} - E_n^{(0)}} = \sum_{n\neq0} \frac{|H_{n0}^{(1)}|^2}{E_0^{(0)} - E_n^{(0)}} \tag{9.65b}$$

where we have introduced the **matrix element**

$$\Omega_{nm} = \int \psi_n^{\star} \hat{\Omega} \psi_m d\tau \tag{9.65c}$$

in a convenient compact notation for integrals that we shall use frequently.

As usual, it is important to be able to interpret these equations physically. We can interpret $E^{(1)}$ as the average value of the perturbation, calculated by using the unperturbed wavefunction. An analogy is the shift in energy of vibration of a violin string

when small weights are hung along its length. The weights hanging close to the nodes have little effect on its energy of vibration. Those hanging at the antinodes, however, have a pronounced effect (Fig. 9.42a). The second-order energy represents a similar average of the perturbation, but now the average is taken over the *perturbed* wavefunctions. In terms of the violin analogy, the average is now taken over the distorted waveform of the vibrating string, in which the nodes and antinodes are slightly shifted (Fig. 9.42b).

We should note the following three features of eqn 9.65b:

1. Because $E_n(0) > E_0(0)$, all the terms in the denominator are negative and, because the numerators are all positive, the second-order correction is negative, which represents a *lowering* of the energy of the ground state.

2. The perturbation appears (as its square) in the numerator; so the stronger the perturbation, the greater the lowering of the ground-state energy.

3. If the energy levels of the system are widely spaced, all the denominators are large, so the sum is likely to be small; in which case the perturbation has little effect on the energy of the system: the system is 'stiff', and unresponsive to perturbations. The opposite is true when the energy levels lie close together.
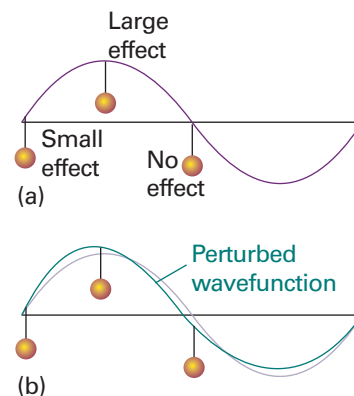

Fig. 9.42 (a) The first-order energy is an average of the perturbation (represented by the hanging weights) over the unperturbed wavefunction. (b) The second-order energy is a similar average, but over the distortion induced by the perturbation.

Example 9.5 *Using perturbation theory*

Find the first-order correction to the ground-state energy for a particle in a well with a variation in the potential of the form $V = -\varepsilon \sin(\pi x/L)$, as in Fig. 9.43.

Method Identify the first-order perturbation hamiltonian and evaluate $E_0^{(1)}$ from eqn 9.65a. We can expect a small lowering of the energy because the average potential energy of the particle is lower in the distorted box.

Answer The perturbation hamiltonian is

$$\hat{H}^{(1)} = -\varepsilon \sin(\pi x/L)$$

Therefore, the first-order correction to the energy is

$$E_0^{(1)} = \int_0^L \psi_1 \hat{H}^{(1)} \psi_1 \mathrm{d}x = -\frac{2\varepsilon}{L} \overbrace{\int_0^L \sin^3 \frac{\pi x}{L} \mathrm{d}x}^{4L/3\pi} = -\frac{8\varepsilon}{3\pi}$$

Note that the energy is lowered by the perturbation, as would be expected for the shape shown in Fig. 9.43.

Self-test 9.9 Suppose that only ψ_3 contributes to the distortion of the wavefunction: calculate the coefficient c_3 and the second-order correction to the energy by using eqn 9.65b and eqn 9.76 in *Further information 9.2*.

$$[c_3 = -8\varepsilon mL^2/15\pi h^2, \, E_0^{(2)} = -64\varepsilon^2 mL^2/225\pi^2 h^2]$$
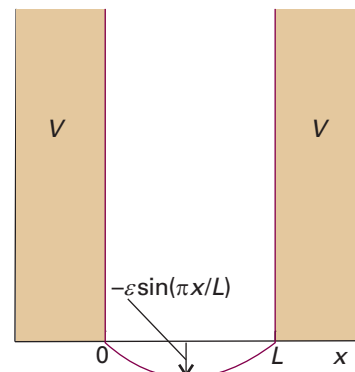
Fig. 9.43 The potential energy for a particle in a box with a potential that varies as $-\varepsilon \sin(\pi x/L)$ across the floor of the box. We can expect the particle to accumulate more in the centre of the box (in the ground state at least) than in the unperturbed box.

9.10 Time-dependent perturbation theory

In **time-dependent perturbation theory**, the perturbation is either switched on and allowed to rise to its final value or is varying in time. Many of the perturbations encountered in chemistry are time-dependent. The most important is the effect of an oscillating electromagnetic field, which is responsible for spectroscopic transitions between quantized energy levels in atoms and molecules.

Classically, for a molecule to be able to interact with the electromagnetic field and absorb or emit a photon of frequency ν, it must possess, at least transiently, a dipole oscillating at that frequency. In this section, we develop the quantum mechanical view and begin by writing the hamiltonian for the system as

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}(t) \tag{9.66}$$

where $\hat{H}^{(1)}(t)$ is the time-dependent perturbation. Because the perturbation arises from the effect of an oscillating electric field with the electric dipole moment, we write

$$\hat{H}^{(1)}(t) = -\mu_z \mathcal{E} \cos \omega t \tag{9.67}$$

where ω is the frequency of the field and $\mathcal{E}$ is its amplitude. We suppose that the perturbation is absent until $t = 0$, and then it is turned on.

We show in *Further information 9.2* that the rate of change of population of the state ψ_f due to transitions from state ψ_i, $w_{f \leftarrow i}$, is proportional to the square modulus of the matrix element of the perturbation between the two states:

$$w_{f \leftarrow i} \propto |H_{fi}^{(1)}|^2 \tag{9.68}$$

Because in our case the perturbation is that of the interaction of the electromagnetic field with a molecule (eqn 9.67), we conclude that

$$w_{f \leftarrow i} \propto |\mu_{z,fi}|^2 \mathcal{E}^2 \tag{9.69}$$

Therefore, the rate of transition, and hence the intensity of absorption of the incident radiation, is proportional to the square of the **transition dipole moment**:

$$\mu_{z,fi} = \int \psi_f^* \mu_z \psi_i \, d\tau \tag{9.70}$$

The size of the transition dipole can be regarded as a measure of the charge redistribution that accompanies a transition.

The rate of transition is also proportional to $\mathcal{E}^2$, and therefore the intensity of the incident radiation (because the intensity is proportional to $\mathcal{E}^2$; see *Appendix 3*). This result will be the basis of most of our subsequent discussion of spectroscopy in Chapters 10 and 13–15 and of the kinetics of electron transfer in Chapter 24.

Comment 9.8

An electric dipole consists of two electric charges $+q$ and $-q$ separated by a distance R. The electric dipole moment vector μ has a magnitude $\mu = qR$.

Checklist of key ideas

☐ 1. The wavefunction of a free particle is $\psi_k = Ae^{ikx} + Be^{-ikx}$, $E_k = k^2\hbar^2/2m$.

☐ 2. The wavefunctions and energies of a particle in a one-dimensional box of length L are, respectively, $\psi_n(x) = (2/L)^{1/2} \sin(n\pi x/L)$ and $E_n = n^2h^2/8mL^2$, $n = 1, 2, \ldots$. The zero-point energy, the lowest possible energy is $E_1 = h^2/8mL^2$.

☐ 3. The correspondence principle states that classical mechanics emerges from quantum mechanics as high quantum numbers are reached.

☐ 4. The functions ψ_n and $\psi_{n'}$ are orthogonal if $\int \psi_n^* \psi_{n'} d\tau = 0$; all wavefunctions corresponding to different energies of a system are orthogonal. Orthonormal functions are sets of functions that are normalized and mutually orthogonal.

☐ 5. The wavefunctions and energies of a particle in a two-dimensional box are given by eqn 9.12a.

☐ 6. Degenerate wavefunctions are different wavefunctions corresponding to the same energy.

☐ 7. Tunnelling is the penetration into or through classically forbidden regions. The transmission probability is given by eqn 9.20a.

☐ 8. Harmonic motion is the motion in the presence of a restoring force proportional to the displacement, $F = -kx$, where k is the force constant. As a consequence, $V = \frac{1}{2}kx^2$.

☐ 9. The wavefunctions and energy levels of a quantum mechanical harmonic oscillator are given by eqns 9.28 and 9.25, respectively.

☐ 10. The virial theorem states that, if the potential energy of a particle has the form $V = ax^b$, then its mean potential and kinetic energies are related by $2\langle E_K \rangle = b \langle V \rangle$.

☐ 11. Angular momentum is the moment of linear momentum around a point.

12. The wavefunctions and energies of a particle on a ring are, respectively, $\psi_{m_l}(\phi) = (1/2\pi)^{1/2}e^{im_l\phi}$ and $E = m_l^2\hbar^2/2I$, with $I = mr^2$ and $m_l = 0, \pm1, \pm2, \ldots$.

13. The wavefunctions of a particle on a sphere are the spherical harmonics, the functions $Y_{l,m_l}(\theta,\phi)$ (Table 9.3). The energies are $E = l(l+1)\hbar^2/2I$, $l = 0, 1, 2, \ldots$.

14. For a particle on a sphere, the magnitude of the angular momentum is $\{l(l+1)\}^{1/2}\hbar$ and the z-component of the angular momentum is $m_l\hbar$, $m_l = l, l-1, \ldots, -l$.

15. Space quantization is the restriction of the component of angular momentum around an axis to discrete values.

16. Spin is an intrinsic angular momentum of a fundamental particle. A fermion is a particle with a half-integral spin quantum number; a boson is a particle with an integral spin quantum number.

17. For an electron, the spin quantum number is $s = \frac{1}{2}$.

18. The spin magnetic quantum number is $m_s = s, s-1, \ldots, -s$; for an electron, $m_s = +\frac{1}{2}, -\frac{1}{2}$.

19. Perturbation theory is a technique that supplies approximate solutions to the Schrödinger equation and in which the hamiltonian for the problem is expressed as a sum of simpler hamiltonians.

20. In time-independent perturbation theory, the perturbation is always present and unvarying. The first- and second-order corrections to the energy are given by eqns 9.65a and 9.65b, respectively. In time-dependent perturbation theory, the perturbation is either switched on and allowed to rise to its final value or is varying in time.

21. The rate of change of population of the state ψ_f due to transitions from state ψ_i is $w_{f\leftarrow i} \propto |\mu_{z,fi}|^2 \mathcal{E}^2$, where $\mu_{z,fi} = \int \psi_f^* \mu_z \psi_i \mathrm{d}\tau$ is the transition dipole moment.

Further reading

Articles and texts

P.W. Atkins and R.S. Friedman, *Molecular quantum mechanics.* Oxford University Press (2005).

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

I.N. Levine, *Quantum chemistry.* Prentice–Hall, Upper Saddle River (2000).

D.A. McQuarrie, *Mathematical methods for scientists and engineers.* University Science Books, Mill Valley (2003).

J.J.C. Mulder, Closed-form spherical harmonics: explicit polynomial expression for the associated legendre functions. *J. Chem. Educ.* **77**, 244 (2000).

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

Further information

Further information 9.1 *Dirac notation*

The integral in eqn 9.9 is often written

$$\langle n | n' \rangle = 0 \qquad (n' \neq n)$$

This **Dirac bracket notation** is much more succinct than writing out the integral in full. It also introduces the words 'bra' and 'ket' into the language of quantum mechanics. Thus, the **bra** $\langle n |$ corresponds to ψ_n^* and the **ket** $| n' \rangle$ corresponds to the wavefunction $\psi_{n'}$. When the bra and ket are put together as in this expression, the integration over all space is understood. Similarly, the normalization condition in eqn 8.17c becomes simply

$$\langle n | n \rangle = 1$$

in bracket notation. These two expressions can be combined into one:

$$\langle n | n' \rangle = \delta_{nn'} \tag{9.71}$$

Here $\delta_{nn'}$, which is called the **Kronecker delta**, is 1 when $n' = n$ and 0 when $n' \neq n$.

Integrals of the form $\int \psi_n^* \hat{\Omega} \psi_m \mathrm{d}\tau$, which we first encounter in connection with perturbation theory (Section 9.9) and which are commonly called 'matrix elements', are incorporated into the bracket notation by writing

$$\langle n | \hat{\Omega} | m \rangle = \int \psi_n^* \hat{\Omega} \psi_m \mathrm{d}\tau \tag{9.72}$$

Note how the operator stands between the bra and the ket (which may denote different states), in the place of the c in $\langle \mathrm{bra} | c | \mathrm{ket} \rangle$. An integration is implied whenever a complete bracket is written. In this notation, an expectation value is

$$\langle \Omega \rangle = \langle n | \hat{\Omega} | n \rangle \tag{9.73}$$

with the bra and the ket corresponding to the same state (with quantum number n and wavefunction ψ_n). In this notation, an operator is hermitian (eqn 8.30) if

$$\langle n | \hat{\Omega} | m \rangle = \langle m | \hat{\Omega} | n \rangle^* \tag{9.74}$$

Further information 9.2 *Perturbation theory*

Here we treat perturbation theory in detail. Our first task is to develop the results of time-independent perturbation theory, in which a system is subjected to a perturbation that does not vary with

time. Then, we go on to discuss time-dependent perturbation theory, in which a perturbation is turned on at a specific time and the system is allowed to evolve.

1 Time-independent perturbation theory

To develop expressions for the corrections to the wavefunction and energy of a system subjected to a time-independent perturbation, we write

$$\psi = \psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \ldots$$

where the power of λ indicates the order of the correction. Likewise, we write

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}^{(1)}$$

and

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots$$

When these expressions are inserted into the Schrödinger equation, $\hat{H}\psi = E\psi$, we obtain

$$(\hat{H}^{(0)} + \lambda\hat{H}^{(1)})(\psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \ldots)$$
$$= (E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots)(\psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \ldots)$$

which we can rewrite as

$$\hat{H}^{(0)}\psi^{(0)} + \lambda(\hat{H}^{(1)}\psi^{(0)} + \hat{H}^{(0)}\psi^{(1)}) + \lambda^2(\hat{H}^{(0)}\psi^{(2)} + \hat{H}^{(1)}\psi^{(1)}) + \ldots$$
$$= E^{(0)}\psi^{(0)} + \lambda(E^{(0)}\psi^{(1)} + E^{(1)}\psi^{(0)}) + \lambda^2(E^{(2)}\psi^{(0)} + E^{(1)}\psi^{(1)}$$
$$+ E^{(0)}\psi^{(2)}) + \ldots$$

By comparing powers of λ, we find

Terms in λ^0: $\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$

Terms in λ: $\hat{H}^{(1)}\psi^{(0)} + \hat{H}^{(0)}\psi^{(1)} = E^{(0)}\psi^{(1)} + E^{(1)}\psi^{(0)}$

Terms in λ^2: $\hat{H}^{(0)}\psi^{(2)} + \hat{H}^{(1)}\psi^{(1)} = E^{(2)}\psi^{(0)} + E^{(1)}\psi^{(1)} + E^{(0)}\psi^{(2)}$

and so on.

The equations we have derived are applicable to any state of the system. From now on we shall consider only the ground state ψ_0 with energy E_0. The first equation, which we now write

$$\hat{H}^{(0)}\psi_0^{(0)} = E_0^{(0)}\psi_0^{(0)}$$

is the Schrödinger equation for the ground state of the unperturbed system, which we assume we can solve (for instance, it might be the equation for the ground state of the particle in a box, with the solutions given in eqn 9.7). To solve the next equation, which is now written

$$\hat{H}^{(1)}\psi_0^{(0)} + \hat{H}^{(0)}\psi_0^{(1)} = E_0^{(0)}\psi^{(1)} + E_0^{(1)}\psi_0^{(0)}$$

we suppose that the first-order correction to the wavefunction can be expressed as a linear combination of the wavefunctions of the unperturbed system, and write

$$\psi_0^{(1)} = \sum_n c_n \psi_n^{(0)} \tag{9.75}$$

Substitution of this expression gives

$$\hat{H}^{(1)}\psi_0^{(0)} + \sum_n c_n \hat{H}^{(0)}\psi_n^{(0)} = \sum_n c_n E_0^{(0)}\psi_n^{(0)} + E_0^{(1)}\psi_0^{(0)}$$

We can isolate the term in $E_0^{(1)}$ by making use of the fact that the $\psi_n^{(0)}$ form a complete orthogonal and normalized set in the sense that

$$\int \psi_0^{(0)\star}\psi_n^{(0)}\mathrm{d}\tau = 0 \qquad \text{if } n \neq 0, \qquad \text{but 1 if } n = 0$$

Therefore, when we multiply through by $\psi_0^{(0)\star}$ and integrate over all space, we get

$$\int \psi_0^{(0)\star}\hat{H}^{(1)}\psi_0^{(0)}\mathrm{d}\tau + \sum_n c_n \overbrace{\int \psi_0^{(0)\star}\hat{H}^{(0)}\psi_n^{(0)}\mathrm{d}\tau}^{E_0^{(0)} \text{ if } n=0, \, 0 \text{ otherwise}}$$
$$= \sum_n c_n E_0^{(0)} \overbrace{\int \psi_0^{(0)\star}\psi_n^{(0)}\,\mathrm{d}\tau}^{1 \text{ if } n=0, \, 0 \text{ otherwise}} + E_0^{(1)} \overbrace{\int \psi_0^{(0)\star}\psi_0^{(0)}\mathrm{d}\tau}^{1}$$

That is,

$$\int \psi_0^{(0)\star}\hat{H}^{(1)}\psi_0^{(0)}\mathrm{d}\tau = E_0^{(1)}$$

which is eqn 9.65a.

To find the coefficients c_n, we multiply the same expression through by $\psi_k^{(0)\star}$, where now $k \neq 0$, which gives

$$\int \psi_k^{(0)\star}\hat{H}^{(1)}\psi_0^{(0)}\mathrm{d}\tau + \sum_n c_n \overbrace{\int \psi_k^{(0)\star}\hat{H}^{(0)}\psi_n^{(0)}\mathrm{d}\tau}^{E_k^{(0)}\delta_{kn}}$$
$$= \sum_n c_n E_0^{(0)} \overbrace{\int \psi_k^{(0)\star}\psi_n^{(0)}\,\mathrm{d}\tau}^{1 \text{ if } n=k, \, 0 \text{ otherwise}} + E_0^{(1)} \overbrace{\int \psi_k^{(0)\star}\psi_0^{(0)}\mathrm{d}\tau}^{0}$$

That is,

$$\int \psi_k^{(0)\star}\hat{H}^{(1)}\psi_0^{(0)}\mathrm{d}\tau + c_k E_k^{(0)} = c_k E_0^{(0)}$$

which we can rearrange into

$$c_k = -\frac{\displaystyle\int \psi_k^{(0)\star}\hat{H}^{(1)}\psi_0^{(0)}\mathrm{d}\tau}{E_k^{(0)} - E_0^{(0)}} \tag{9.76}$$

The second-order energy is obtained starting from the second-order expression, which for the ground state is

$$\hat{H}^{(0)}\psi_0^{(2)} + \hat{H}^{(1)}\psi_0^{(1)} = E_0^{(2)}\psi_0^{(0)} + E_0^{(1)}\psi_0^{(1)} + E_0^{(0)}\psi_0^{(2)}$$

To isolate the term $E_0^{(2)}$ we multiply both sides by $\psi_0^{(0)\star}$, integrate over all space, and obtain

$$\overbrace{\int \psi_0^{(0)\star}\hat{H}^{(0)}\psi_0^{(2)}\mathrm{d}\tau}^{E_0^{(0)}\int\psi_0^{(0)\star}\psi_0^{(2)}\mathrm{d}\tau} + \int \psi_0^{(0)\star}\hat{H}^{(1)}\psi_0^{(1)}\mathrm{d}\tau$$
$$= E_0^{(2)} \underbrace{\int \psi_0^{(0)\star}\psi_0^{(0)}\mathrm{d}\tau}_{1} + E_0^{(1)} \int \psi_0^{(0)\star}\psi_0^{(1)}\mathrm{d}\tau + E_0^{(0)} \int \psi_0^{(0)\star}\psi_0^{(2)}\,\mathrm{d}\tau$$

The first and last terms cancel, and we are left with

$$E_0^{(2)} = \int \psi_0^{(0)\star}\hat{H}^{(1)}\psi_0^{(1)}\mathrm{d}\tau - E_0^{(1)}\int \psi_0^{(0)\star}\psi_0^{(1)}\mathrm{d}\tau$$

We have already found the first-order corrections to the energy and the wavefunction, so this expression could be regarded as an explicit expression for the second-order energy. However, we can go one step further by substituting eqn 9.75:

$$E_0^{(2)} = \sum_n c_n \overbrace{\int \psi_0^{(0)\star} \hat{H}^{(1)} \psi_n^{(0)} d\tau}^{H_{0n}^{(1)}} - \sum_n c_n E_0^{(1)} \overbrace{\int \psi_0^{(0)\star} \psi_n^{(0)} d\tau}^{\delta_{0n}}$$

$$= \sum_n c_n H_{0n}^{(1)} - c_0 E_0^{(1)}$$

The final term cancels the term $c_0 H_{00}^{(1)}$ in the sum, and we are left with

$$E_0^{(2)} = \sum_{n \neq 0} c_n H_{0n}^{(1)}$$

Substitution of the expression for c_n in eqn 9.76 now produces the final result, eqn 9.65b.

2 Time-dependent perturbation theory

To cope with a perturbed wavefunction that evolves with time, we need to solve the time-dependent Schrödinger equation,

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t} \tag{9.77}$$

We confirm below, that if we write the first-order correction to the wavefunction as

$$\Psi_0^{(1)}(t) = \sum_n c_n(t) \Psi_n(t) = \sum_n c_n(t) \psi_n^{(0)} e^{-iE_n^{(0)}t/\hbar} \tag{9.78a}$$

then the coefficients in this expansion are given by

$$c_n(t) = \frac{1}{i\hbar} \int_0^t H_{n0}^{(1)}(t) e^{i\omega_{n0}t} dt \tag{9.78b}$$

The formal demonstration of eqn 9.78 is quite lengthy (see *Further reading*). Here we shall show that, given eqn 9.78b, a perturbation that is switched on very slowly to a constant value gives the same expression for the coefficients as we obtained for time-independent perturbation theory. For such a perturbation, we write

$$\hat{H}^{(1)}(t) = \hat{H}^{(1)}(1 - e^{-t/\tau})$$

and take the time constant τ to be very long (Fig. 9.44). Substitution of this expression into eqn 9.78b gives

$$c_n(t) = \frac{1}{i\hbar} H_{n0}^{(1)} \int_0^t (1 - e^{-t/\tau}) e^{i\omega_{n0}t} dt$$

$$= \frac{1}{i\hbar} H_{n0}^{(1)} \left\{ \frac{e^{i\omega_{n0}t} - 1}{i\omega_{n0}} - \frac{e^{(i\omega_{n0} - 1/\tau)t} - 1}{i\omega_{n0} - 1/\tau} \right\}$$

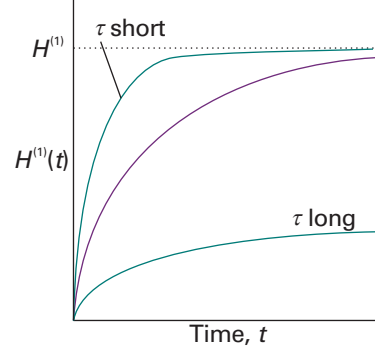**Fig. 9.44** The time-dependence of a slowly switched perturbation. A large value of τ corresponds to very slow switching.

At this point we suppose that the perturbation is switched slowly, in the sense that $\tau \gg 1/\omega_{n0}$ (so that the $1/\tau$ in the second denominator can be ignored). We also suppose that we are interested in the coefficients long after the perturbation has settled down into its final value, when $t \gg \tau$ (so that the exponential in the second numerator is close to zero and can be ignored). Under these conditions,

$$c_n(t) = -\frac{H_{n0}^{(0)}}{\hbar\omega_{n0}} e^{i\omega_{n0}t}$$

Now we recognize that $\hbar\omega_{n0} = E_n^{(0)} - E_0^{(0)}$, which gives

$$c_n(t) = -\frac{H_{n0}^{(0)}}{E_n^{(0)} - E_0^{(0)}} e^{iE_n^{(0)}t} e^{-iE_0^{(0)}t}$$

When this expression is substituted into eqn 9.78a, we obtain the time-independent expression, eqn 9.76 (apart from an irrelevant overall phase factor).

In accord with the general rules for the interpretation of wavefunctions, the probability that the system will be found in the state n is proportional to the square modulus of the coefficient of the state, $|c_n(t)|^2$. Therefore, the rate of change of population of a final state ψ_f due to transitions from an initial state ψ_i is

$$w_{f \leftarrow i} = \frac{d|c_f|^2}{dt} = \frac{dc_f^\star c_f}{dt} = c_f \frac{dc_f^\star}{dt} + c_f^\star \frac{dc_f}{dt}$$

Because the coefficients are proportional to the matrix elements of the perturbation, $w_{f \leftarrow i}$ is proportional to the square modulus of the matrix element of the perturbation between the two states:

$$w_{f \leftarrow i} \propto |H_{fi}^{(1)}|^2$$

which is eqn 9.68.

Discussion questions

9.1 Discuss the physical origin of quantization energy for a particle confined to moving inside a one-dimensional box or on a ring.

9.2 Discuss the correspondence principle and provide two examples.

9.3 Define, justify, and provide examples of zero-point energy.

9.4 Discuss the physical origins of quantum mechanical tunnelling. Why is tunnelling more likely to contribute to the mechanisms of electron transfer and proton transfer processes than to mechanisms of group transfer reactions, such as AB + C → A + BC (where A, B, and C are large molecular groups)?

9.5 Distinguish between a fermion and a boson. Provide examples of each type of particle.

9.6 Describe the features that stem from nanometre-scale dimensions that are not found in macroscopic objects.

Exercises

9.1a Calculate the energy separations in joules, kilojoules per mole, electronvolts, and reciprocal centimetres between the levels (a) $n = 2$ and $n = 1$, (b) $n = 6$ and $n = 5$ of an electron in a box of length 1.0 nm.

9.1b Calculate the energy separations in joules, kilojoules per mole, electronvolts, and reciprocal centimetres between the levels (a) $n = 3$ and $n = 1$, (b) $n = 7$ and $n = 6$ of an electron in a box of length 1.50 nm.

9.2a Calculate the probability that a particle will be found between $0.49L$ and $0.51L$ in a box of length L when it has (a) $n = 1$, (b) $n = 2$. Take the wavefunction to be a constant in this range.

9.2b Calculate the probability that a particle will be found between $0.65L$ and $0.67L$ in a box of length L when it has (a) $n = 1$, (b) $n = 2$. Take the wavefunction to be a constant in this range.

9.3a Calculate the expectation values of p and p^2 for a particle in the state $n = 1$ in a square-well potential.

9.3b Calculate the expectation values of p and p^2 for a particle in the state $n = 2$ in a square-well potential.

9.4a An electron is confined to a a square well of length L. What would be the length of the box such that the zero-point energy of the electron is equal to its rest mass energy, $m_e c^2$? Express your answer in terms of the parameter $\lambda_C = h/m_e c$, the 'Compton wavelength' of the electron.

9.4b Repeat Exercise 9.4a for a general particle of mass m in a cubic box.

9.5a What are the most likely locations of a particle in a box of length L in the state $n = 3$?

9.5b What are the most likely locations of a particle in a box of length L in the state $n = 5$?

9.6a Consider a particle in a cubic box. What is the degeneracy of the level that has an energy three times that of the lowest level?

9.6b Consider a particle in a cubic box. What is the degeneracy of the level that has an energy $\frac{14}{3}$ times that of the lowest level?

9.7a Calculate the percentage change in a given energy level of a particle in a cubic box when the length of the edge of the cube is decreased by 10 per cent in each direction.

9.7b A nitrogen molecule is confined in a cubic box of volume 1.00 m^3. Assuming that the molecule has an energy equal to $\frac{3}{2}kT$ at $T = 300$ K, what is the value of $n = (n_x^2 + n_y^2 + n_z^2)^{1/2}$ for this molecule? What is the energy separation between the levels n and $n + 1$? What is its de Broglie wavelength? Would it be appropriate to describe this particle as behaving classically?

9.8a Calculate the zero-point energy of a harmonic oscillator consisting of a particle of mass 2.33×10^{-26} kg and force constant 155 N m^{-1}.

9.8b Calculate the zero-point energy of a harmonic oscillator consisting of a particle of mass 5.16×10^{-26} kg and force constant 285 N m^{-1}.

9.9a For a harmonic oscillator of effective mass 1.33×10^{-25} kg, the difference in adjacent energy levels is 4.82 zJ. Calculate the force constant of the oscillator.

9.9b For a harmonic oscillator of effective mass 2.88×10^{-25} kg, the difference in adjacent energy levels is 3.17 zJ. Calculate the force constant of the oscillator.

9.10a Calculate the wavelength of a photon needed to excite a transition between neighbouring energy levels of a harmonic oscillator of effective mass equal to that of a proton (1.0078 u) and force constant 855 N m^{-1}.

9.10b Calculate the wavelength of a photon needed to excite a transition between neighbouring energy levels of a harmonic oscillator of effective mass equal to that of an oxygen atom (15.9949 u) and force constant 544 N m^{-1}.

9.11a Refer to Exercise 9.10a and calculate the wavelength that would result from doubling the effective mass of the oscillator.

9.11b Refer to Exercise 9.10b and calculate the wavelength that would result from doubling the effective mass of the oscillator.

9.12a Calculate the minimum excitation energies of (a) a pendulum of length 1.0 m on the surface of the Earth, (b) the balance-wheel of a clockwork watch ($\nu = 5$ Hz).

9.12b Calculate the minimum excitation energies of (a) the 33 kHz quartz crystal of a watch, (b) the bond between two O atoms in O_2, for which $k = 1177$ N m^{-1}.

9.13a Confirm that the wavefunction for the ground state of a one-dimensional linear harmonic oscillator given in Table 9.1 is a solution of the Schrödinger equation for the oscillator and that its energy is $\frac{1}{2}\hbar\omega$.

9.13b Confirm that the wavefunction for the first excited state of a one-dimensional linear harmonic oscillator given in Table 9.1 is a solution of the Schrödinger equation for the oscillator and that its energy is $\frac{3}{2}\hbar\omega$.

9.14a Locate the nodes of the harmonic oscillator wavefunction with $\nu = 4$.

9.14b Locate the nodes of the harmonic oscillator wavefunction with $\nu = 5$.

9.15a Assuming that the vibrations of a $^{35}Cl_2$ molecule are equivalent to those of a harmonic oscillator with a force constant $k = 329$ N m^{-1}, what is the zero-point energy of vibration of this molecule? The mass of a ^{35}Cl atom is 34.9688 u.

9.15b Assuming that the vibrations of a $^{14}N_2$ molecule are equivalent to those of a harmonic oscillator with a force constant $k = 2293.8$ N m^{-1}, what is the zero-point energy of vibration of this molecule? The mass of a ^{14}N atom is 14.0031 u.

9.16a The wavefunction, $\psi(\phi)$, for the motion of a particle in a ring is of the form $\psi = N e^{im_l\phi}$. Determine the normalization constant, N.

9.16b Confirm that wavefunctions for a particle in a ring with different values of the quantum number m_l are mutually orthogonal.

9.17a A point mass rotates in a circle with $l = 1$, Calculate the magnitude of its angular momentum and the possible projections of the angular momentum on an arbitrary axis.

9.17b A point mass rotates in a circle with $l = 2$, Calculate the magnitude of its angular momentum and the possible projections of the angular momentum on an arbitrary axis.

9.18a Draw scale vector diagrams to represent the states (a) $s = \frac{1}{2}$, $m_s = +\frac{1}{2}$, (b) $l = 1$, $m_l = +1$, (c) $l = 2$, $m_l = 0$.

9.18b Draw the vector diagram for all the permitted states of a particle with $l = 6$.

Problems*

Numerical problems

9.1 Calculate the separation between the two lowest levels for an O_2 molecule in a one-dimensional container of length 5.0 cm. At what value of n does the energy of the molecule reach $\frac{1}{2}kT$ at 300 K, and what is the separation of this level from the one immediately below?

9.2 The mass to use in the expression for the vibrational frequency of a diatomic molecule is the effective mass $\mu = m_A m_B/(m_A + m_B)$, where m_A and m_B are the masses of the individual atoms. The following data on the infrared absorption wavenumbers (in cm^{-1}) of molecules are taken from *Spectra of diatomic molecules*, G. Herzberg, van Nostrand (1950):

$H^{35}Cl$	$H^{81}Br$	HI	CO	NO
2990	2650	2310	2170	1904

Calculate the force constants of the bonds and arrange them in order of increasing stiffness.

9.3 The rotation of an $^1H^{127}I$ molecule can be pictured as the orbital motion of an H atom at a distance 160 pm from a stationary I atom. (This picture is quite good; to be precise, both atoms rotate around their common centre of mass, which is very close to the I nucleus.) Suppose that the molecule rotates only in a plane. Calculate the energy needed to excite the molecule into rotation. What, apart from 0, is the minimum angular momentum of the molecule?

9.4 Calculate the energies of the first four rotational levels of $^1H^{127}I$ free to rotate in three dimensions, using for its moment of inertia $I = \mu R^2$, with $\mu = m_H m_I/(m_H + m_I)$ and $R = 160$ pm.

9.5 A small step in the potential energy is introduced into the one-dimensional square-well problem as in Fig. 9.45. (a) Write a general
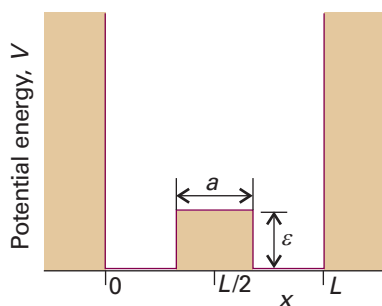

Fig. 9.45

expression for the first-order correction to the ground-state energy, $E_0^{(1)}$. (b) Evaluate the energy correction for $a = L/10$ (so the blip in the potential occupies the central 10 per cent of the well), with $n = 1$.

9.6 We normally think of the one-dimensional well as being horizontal. Suppose it is vertical; then the potential energy of the particle depends on x because of the presence of the gravitational field. Calculate the first-order correction to the zero-point energy, and evaluate it for an electron in a box on the surface of the Earth. Account for the result. *Hint.* The energy of the particle depends on its height as mgh, where $g = 9.81$ m s^{-2}. Because g is so small, the energy correction is small; but it would be significant if the box were near a very massive star.

9.7 Calculate the second-order correction to the energy for the system described in Problem 9.6 and calculate the ground-state wavefunction. Account for the shape of the distortion caused by the perturbation. *Hint.* The following integrals are useful

$$\int x \sin ax \sin bx \, dx = -\frac{d}{da} \int \cos ax \sin bx \, dx$$

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

Theoretical problems

9.8 Suppose that 1.0 mol perfect gas molecules all occupy the lowest energy level of a cubic box. How much work must be done to change the volume of the box by ΔV? Would the work be different if the molecules all occupied a state $n \neq 1$? What is the relevance of this discussion to the expression for the expansion work discussed in Chapter 2? Can you identify a distinction between adiabatic and isothermal expansion?

9.9 Derive eqn 9.20a, the expression for the transmission probability.

9.10‡ Consider the one-dimensional space in which a particle can experience one of three potentials depending upon its position. They are: $V = 0$ for $-\infty < x \leq 0$, $V = V_2$ for $0 \leq x \leq L$, and $V = V_3$ for $L \leq x < \infty$. The particle wavefunction is to have both a component e^{ik_1x} that is incident upon the barrier V_2 and a reflected component e^{-ik_1x} in region 1 ($-\infty < x \leq 0$). In region 3 the wavefunction has only a forward component, e^{ik_3x}, which represents a particle that has traversed the barrier. The energy of the particle, E, is somewhere in the range of the $V_2 > E > V_3$. The transmission probability, T, is the ratio of the square modulus of the region 3 amplitude to the square modulus of the incident amplitude. (a) Base your calculation on the continuity of the amplitudes and the slope of the wavefunction at the locations of the zone boundaries and derive a general equation for T. (b) Show that the general equation for T reduces to eqn 9.20b in the high, wide barrier limit when

---

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

$V_1 = V_3 = 0$. (c) Draw a graph of the probability of proton tunnelling when $V_3 = 0$, $L = 50$ pm, and $E = 10$ kJ mol^{-1} in the barrier range $E < V_2 < 2E$.

9.11 The wavefunction inside a long barrier of height V is $\psi = Ne^{-\kappa x}$. Calculate (a) the probability that the particle is inside the barrier and (b) the average penetration depth of the particle into the barrier.

9.12 Confirm that a function of the form e^{-gx^2} is a solution of the Schrödinger equation for the ground state of a harmonic oscillator and find an expression for g in terms of the mass and force constant of the oscillator.

9.13 Calculate the mean kinetic energy of a harmonic oscillator by using the relations in Table 9.1.

9.14 Calculate the values of $\langle x^3 \rangle$ and $\langle x^4 \rangle$ for a harmonic oscillator by using the relations in Table 9.1.

9.15 Determine the values of $\delta x = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$ and $\delta p = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2}$ for (a) a particle in a box of length L and (b) a harmonic oscillator. Discuss these quantities with reference to the uncertainty principle.

9.16 We shall see in Chapter 13 that the intensities of spectroscopic transitions between the vibrational states of a molecule are proportional to the square of the integral $\int \psi_{v'} x \psi_v dx$ over all space. Use the relations between Hermite polynomials given in Table 9.1 to show that the only permitted transitions are those for which $v' = v \pm 1$ and evaluate the integral in these cases.

9.17 The potential energy of the rotation of one CH$_3$ group relative to its neighbour in ethane can be expressed as $V(\varphi) = V_0 \cos 3\varphi$. Show that for small displacements the motion of the group is harmonic and calculate the energy of excitation from $v = 0$ to $v = 1$. What do you expect to happen to the energy levels and wavefunctions as the excitation increases?

9.18 Show that, whatever superposition of harmonic oscillator states is used to construct a wavepacket, it is localized at the same place at the times 0, T, $2T$, . . . , where T is the classical period of the oscillator.

9.19 Use the virial theorem to obtain an expression for the relation between the mean kinetic and potential energies of an electron in a hydrogen atom.

9.20 Evaluate the z-component of the angular momentum and the kinetic energy of a particle on a ring that is described by the (unnormalized) wavefunctions (a) $e^{i\phi}$, (b) $e^{-2i\phi}$, (c) $\cos \phi$, and (d) $(\cos \chi)e^{i\phi} + (\sin \chi)e^{-i\phi}$.

9.21 Is the Schrödinger equation for a particle on an elliptical ring of semimajor axes a and b separable? *Hint.* Although r varies with angle φ, the two are related by $r^2 = a^2 \sin^2\phi + b^2 \cos^2\phi$.

9.22 Use mathematical software to construct a wavepacket of the form

$$\Psi(\phi,t) = \sum_{m_l=0}^{m_{l,max}} c_{m_l} e^{i(m_l \phi - E_{m_l} t/\hbar)} \qquad E_{m_l} = m_l^2 \hbar^2 / 2I$$

with coefficients c of your choice (for example, all equal). Explore how the wavepacket migrates on the ring but spreads with time.

9.23 Confirm that the spherical harmonics (a) $Y_{0,0}$, (b) $Y_{2,-1}$, and (c) $Y_{3,+3}$ satisfy the Schrödinger equation for a particle free to rotate in three dimensions, and find its energy and angular momentum in each case.

9.24 Confirm that $Y_{3,+3}$ is normalized to 1. (The integration required is over the surface of a sphere.)

9.25 Derive an expression in terms of l and m_l for the half-angle of the apex of the cone used to represent an angular momentum according to the vector model. Evaluate the expression for an α spin. Show that the minimum possible angle approaches 0 as $l \rightarrow \infty$.

9.26 Show that the function $f = \cos ax \cos cos cz$ is an eigenfunction of ∇^2, and determine its eigenvalue.

9.27 Derive (in Cartesian coordinates) the quantum mechanical operators for the three components of angular momentum starting from the classical definition of angular momentum, $\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}$. Show that any two of the components do not mutually commute, and find their commutator.

9.28 Starting from the operator $l_z = x p_y - y p_x$, prove that in spherical polar coordinates $l_z = -i\hbar \partial/\partial\phi$.

9.29 Show that the commutator $[l^2, l_z] = 0$, and then, without further calculation, justify the remark that $[l^2, l_q] = 0$ for all $q = x$, y, and z.

9.30‡ A particle is confined to move in a one-dimensional box of length L. (a) If the particle is classical, show that the average value of x is $\frac{1}{2}L$ and that the root-mean square value is $L/3^{1/2}$. (b) Show that for large values of n, a quantum particle approaches the classical values. This result is an example of the correspondence principle, which states that, for very large values of the quantum numbers, the predictions of quantum mechanics approach those of classical mechanics.

Applications: to biology and nanotechnology

9.31 When β-carotene is oxidized *in vivo*, it breaks in half and forms two molecules of retinal (vitamin A), which is a precursor to the pigment in the retina responsible for vision (*Impact I14.1*). The conjugated system of retinal consists of 11 C atoms and one O atom. In the ground state of retinal, each level up to $n = 6$ is occupied by two electrons. Assuming an average internuclear distance of 140 pm, calculate (a) the separation in energy between the ground state and the first excited state in which one electron occupies the state with $n = 7$, and (b) the frequency of the radiation required to produce a transition between these two states. (c) Using your results and *Illustration 9.1*, choose among the words in parentheses to generate a rule for the prediction of frequency shifts in the absorption spectra of linear polyenes:

> The absorption spectrum of a linear polyene shifts to (higher/lower) frequency as the number of conjugated atoms (increases/decreases).

9.32 Many biological electron transfer reactions, such as those associated with biological energy conversion, may be visualized as arising from electron tunnelling between protein-bound co-factors, such as cytochromes, quinones, flavins, and chlorophylls. This tunnelling occurs over distances that are often greater than 1.0 nm, with sections of protein separating electron donor from acceptor. For a specific combination of donor and acceptor, the rate of electron tunnelling is proportional to the transmission probability, with $\kappa \approx 7$ nm^{-1} (eqn 9.20). By what factor does the rate of electron tunnelling between two co-factors increase as the distance between them changes from 2.0 nm to 1.0 nm?

9.33 Carbon monoxide binds strongly to the Fe^{2+} ion of the haem group of the protein myoglobin. Estimate the vibrational frequency of CO bound to myoglobin by using the data in Problem 9.2 and by making the following assumptions: the atom that binds to the haem group is immobilized, the protein is infinitely more massive than either the C or O atom, the C atom binds to the Fe^{2+} ion, and binding of CO to the protein does not alter the force constant of the C≡O bond.

9.34 Of the four assumptions made in Problem 9.33, the last two are questionable. Suppose that the first two assumptions are still reasonable and that you have at your disposal a supply of myoglobin, a suitable buffer in which to suspend the protein, ^{12}C^{16}O, ^{13}C^{16}O, ^{12}C^{18}O, ^{13}C^{18}O, and an infrared spectrometer. Assuming that isotopic substitution does not affect the force constant of the C≡O bond, describe a set of experiments that: (a) proves which atom, C or O, binds to the haem group of myoglobin, and (b) allows for the determination of the force constant of the C≡O bond for myoglobin-bound carbon monoxide.

9.35 The particle on a ring is a useful model for the motion of electrons around the porphine ring (**2**), the conjugated macrocycle that forms the
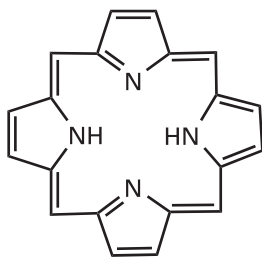
2 Porphine (free base form)

structural basis of the haem group and the chlorophylls. We may treat the group as a circular ring of radius 440 pm, with 22 electrons in the conjugated system moving along the perimeter of the ring. As in *Illustration 9.1*, we assume that in the ground state of the molecule quantized each state is occupied by two electrons. (a) Calculate the energy and angular momentum of an electron in the highest occupied level. (b) Calculate the frequency of radiation that can induce a transition between the highest occupied and lowest unoccupied levels.

9.36 When in Chapter 19 we come to study macromolecules, such as synthetic polymers, proteins, and nucleic acids, we shall see that one conformation is that of a random coil. For a one-dimensional random coil of N units, the restoring force at small displacements and at a temperature T is

$$F = -\frac{kT}{2l} \ln\left(\frac{N+n}{N-n}\right)$$

where l is the length of each monomer unit and nl is the distance between the ends of the chain (see Section 19.8). Show that for small extensions ($n \ll N$) the restoring force is proportional to n and therefore the coil undergoes harmonic oscillation with force constant kT/Nl^2. Suppose that the mass to use for the vibrating chain is its total mass Nm, where m is the mass of one monomer unit, and deduce the root mean square separation of the ends of the chain due to quantum fluctuations in its vibrational ground state.

9.37 The forces measured by AFM arise primarily from interactions between electrons of the stylus and on the surface. To get an idea of the magnitudes of these forces, calculate the force acting between two electrons separated by 2.0 nm. *Hints*. The Coulombic potential energy of a charge q_1 at a distance r from another charge q_2 is

$$V = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

where $\varepsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$ is the vacuum permittivity. To calculate the force between the electrons, note that $F = -dV/dr$.

9.38 Here we explore further the idea introduced in *Impact I9.2* that quantum mechanical effects need to be invoked in the description of the electronic properties of metallic nanocrystals, here modelled as three-dimensional boxes. (a) Set up the Schrödinger equation for a particle of mass m in a three-dimensional rectangular box with sides L_1, L_2, and L_3. Show that the Schrödinger equation is separable. (b) Show that the wavefunction and the energy are defined by three quantum numbers. (c) Specialize the result from part (b) to an electron moving in a cubic box of side $L = 5$ nm and draw an energy diagram resembling Fig. 9.2 and showing the first 15 energy levels. Note that each energy level may consist of degenerate energy states. (d) Compare the energy level diagram from part (c) with the energy level diagram for an electron in a one-dimensional box of length $L = 5$ nm. Are the energy levels become more or less sparsely distributed in the cubic box than in the one-dimensional box?

9.39 We remarked in *Impact I9.2* that the particle *in* a sphere is a reasonable starting point for the discussion of the electronic properties of spherical metal nanoparticles. Here, we justify eqn 9.54, which shows that the energy of an electron in a sphere is quantized. (a) The Hamiltonian for a particle free to move inside a sphere of radius R is

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

Show that the Schrödinger equation is separable into radial and angular components. That is, begin by writing $\psi(r,\theta,\phi) = X(r)Y(\theta,\phi)$, where $X(r)$ depends only on the distance of the particle away from the centre of the sphere, and $Y(\theta,\phi)$ is a spherical harmonic. Then show that the Schrödinger equation can be separated into two equations, one for X, the radial equation, and the other for Y, the angular equation:

$$-\frac{\hbar^2}{2m}\left(\frac{d^2 X(r)}{dr^2} + \frac{2}{r}\frac{dX(r)}{dr}\right) + \frac{l(l+1)\hbar^2}{2mr^2}X(r) = EX(r)$$

$$\Lambda^2 Y = -l(l+1)Y$$

You may wish to consult *Further information 10.1* for additional help. (c) Consider the case $l = 0$. Show by differentiation that the solution of the radial equation has the form

$$X(r) = (2\pi R)^{-1/2}\frac{\sin(n\pi r/R)}{r}$$

(e) Now go on to show that the allowed energies are given by:

$$E_n = \frac{n^2 h^2}{8mR^2}$$

This result for the energy (which is eqn 9.54 after substituting m_e for m) also applies when $l \neq 0$.