

A.3 Quantum mechanics

The wavefunction is of central importance in quantum mechanics. For example, you will recall from Section 4.3 on p. 39 that the square of the wavefunction gives us the probability density – a property we have used constantly to talk about how the electrons are distributed in atoms and molecules.

This section describes how the mathematical form of wavefunctions are determined. To avoid the mathematics becoming too complicated we will have to restrict ourselves to some rather simple situations, but the principles we will describe are generally applicable.

We will start by considering the simplest case which is a particle of mass m moving in one dimension, x ; the wavefunction will simply be a function of x , and so we will denote it $\psi(x)$.

It is an assumption of quantum mechanics that the wavefunction is a solution to the *Schrödinger equation* (SE):

$$\frac{-h^2}{8\pi^2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (\text{A.4})$$

where h is Planck's constant, $V(x)$ is the potential energy at position x and E is the total energy.

The solution to this equation depends on how the potential energy varies with x ; we will look at two simple examples. The first is when the potential energy is zero everywhere – this situation is often referred to as a ‘free particle’ as there are no constraints on it. The SE then reduces to:

$$\frac{-h^2}{8\pi^2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x). \quad (\text{A.5})$$

This is a differential equation of a well-known type for which it is known that $\psi(x) = A \sin(kx)$ is a solution, where A and k are constants to be determined.

We can show that $\psi(x) = A \sin(kx)$ is a solution by first substituting it into the left-hand side of Eq. A.5:

$$\begin{aligned} \frac{-h^2}{8\pi^2m} \frac{d^2\psi(x)}{dx^2} &= \frac{-h^2}{8\pi^2m} \frac{d^2[A \sin(kx)]}{dx^2} \\ &= \frac{-h^2}{8\pi^2m} \frac{d[Ak \cos(kx)]}{dx} \\ &= \frac{-h^2}{8\pi^2m} [-Ak^2 \sin(kx)] \\ &= \frac{k^2h^2}{8\pi^2m} [A \sin(kx)] \\ &= \frac{k^2h^2}{8\pi^2m} \psi(x). \end{aligned}$$

From this we see that the left-hand side of Eq. A.5 is of the form of a constant times $\psi(x)$. The right-hand side of Eq. A.5 is E times $\psi(x)$, so we have confirmed that $\psi(x)$ is a solution to the SE, and that for this $\psi(x)$ the energy, E , is given by

$$E = \frac{k^2h^2}{8\pi^2m}. \quad (\text{A.6})$$

The energy is determined by the value of k , but there are no restrictions on k so that the energy can have any value, i.e. the system does not show quantization. The value of the constant A has no effect on the energy.

What we find in quantum mechanics is that quantization is a result of the particle being constrained by the potential. A simple example of this is to suppose that the potential energy is infinite when x is less than zero or greater than L ; this is illustrated in Fig. A.3.

The particle cannot go into a region of infinite potential and, as the square of the wavefunction gives the probability density, it follows that the wavefunction must be zero in these regions. So, the wavefunction must go to zero when $x = 0$ and when $x = L$ as the potential is infinite at these points. This arrangement is often called a 'particle in a box' simply because the particle is confined to a particular region defined by steep walls.

There is no problem at $x = 0$ as $A \sin(kx)$ is zero at this point for all values of k . However, at $x = L$ the wavefunction has the value $A \sin(kL)$ and this will only be zero if (kL) is an *integer multiple* of π ; this comes about because $\sin(\theta) = 0$ for $\theta = 0, \pi, 2\pi, 3\pi, \dots$ (radians). Expressed mathematically this condition is

$$kL = n\pi \quad n = 1, 2, 3, \dots$$

It follows that

$$k = \frac{n\pi}{L} \quad n = 1, 2, 3, \dots,$$

and if we substitute this value for k into $\psi(x) = A \sin(kx)$ and into the expression for the energy, Eq. A.6, we find that, for the particle in a box,

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right) \quad \text{and} \quad E_n = \frac{n^2 h^2}{8mL^2} \quad n = 1, 2, 3, \dots$$

We have added the subscript n to both the wavefunction and the energy to indicate that these depend on the value of n . The particle in a box shows quantization; n must be an integer and so only particular values of the energy are possible. The integer n is a *quantum number*.

Putting $n = 0$ will give a wavefunction which is zero everywhere; as the square of the wavefunction gives the probability density, having $\psi(x) = 0$ everywhere is not acceptable as it would mean that the particle has zero probability of being located at any position. The solution with $n = 0$ is therefore rejected and so the lowest energy wavefunction is the one with $n = 1$.

Figure A.4 shows plots of the four lowest energy wavefunctions for the particle in a box. Note how the number of *nodes* (the values of x for which $\psi(x) = 0$) increases with n , which in turn corresponds to increasing energy.

Normalization

We know that the probability density of the particle is given by the square of the wavefunction; we also know that the particle must be *somewhere* in the box. Therefore, if we add up the total probability density in the box we must get the answer 1, i.e. there is 100% probability of finding the particle somewhere in the box.

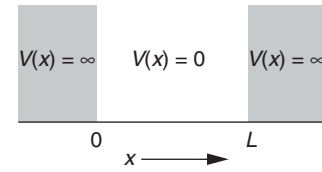


Fig. A.3 Visualization of a potential energy function which is zero between $x = 0$ and $x = L$, and infinity elsewhere (indicated by the shaded regions). The particle cannot go into the region of infinite potential, and so is constrained to be in the region $x = 0$ to L . This arrangement is often called a 'particle in a box'.

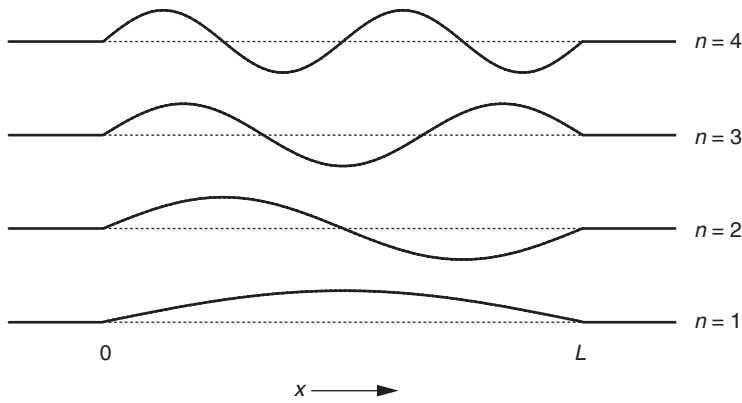


Fig. A.4 Plots of the four lowest energy wavefunctions for the potential energy function shown in Fig. A.3 (the particle in a box). The wavefunctions have been displaced vertically so that they can be seen clearly; the dotted horizontal line gives the position of $\psi = 0$ in each case. Note how the wavefunctions are zero for x less than 0 and greater than L , and how the number of nodes increases with n .

Mathematically, adding up this probability density in the box corresponds to integrating the square of the wavefunction in the range 0 to L :

$$\begin{aligned} \int_0^L [\psi_n(x)]^2 dx &= \int_0^L \left[A \sin\left(\frac{n\pi x}{L}\right) \right]^2 dx \\ &= A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx. \end{aligned}$$

To find the integral we use the identity $\sin^2 \theta = \frac{1}{2}[1 - \cos 2\theta]$:

$$\begin{aligned} A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx &= \frac{1}{2} A^2 \int_0^L 1 - \cos\left(\frac{2n\pi x}{L}\right) dx \\ &= \frac{1}{2} A^2 \left\{ \left[x \right]_0^L - \left[-\frac{L}{2n\pi} \sin\left(\frac{2n\pi x}{L}\right) \right]_0^L \right\} \\ &= \frac{1}{2} A^2 L \end{aligned}$$

where to go to the last line we have recalled that as n is an integer, $\sin(2n\pi)$ is zero.

This integral of $[\psi(x)]^2$ gives the total probability, and so should have the value 1; this is plainly not the case. However, since we have shown that $\psi(x) = A \sin(kx)$ solves the SE for *any* value of the constant A , we can choose the value of A so that the integral is equal to 1:

$$\begin{aligned} 1 &= \frac{1}{2} A^2 L \\ \text{thus } A &= \left(\frac{2}{L} \right)^{1/2}. \end{aligned}$$

With this choice of A the wavefunction is said to be *normalized*, meaning that the total probability it predicts is indeed equal to one. A is called the *normalization constant* or *normalization factor*.

Other potential energy functions

It is particularly simple to solve the SE for the particle in a box as the potential, $V(x)$, is zero (inside the box). Other physical situations have more complex forms of the potential, which make the corresponding SE more difficult to solve.

It turns out that the SE can only be solved exactly for a few simple potential energy functions. One of these is the *harmonic potential* which has

$$V(x) = \frac{1}{2}k_f x^2$$

where k_f is the *force constant*; the potential is plotted in Fig. A.5 (a).

In classical mechanics such a potential would give rise to a force $-k_f x$. The force is proportional to the displacement from the origin ($x = 0$) and the minus sign means that the force is directed towards the origin. A mass experiencing such a force will execute what is called *harmonic motion* in which the mass oscillates about $x = 0$ at a frequency $\omega = \sqrt{k_f/m}$ (in rad s^{-1}).

The SE equation can be solved for this potential function, although it is not such an easy task as for the particle in a box. The lowest energy wavefunction turns out to be

$$\psi_0 = A \exp(-\alpha x^2)$$

where A is the normalization constant and

$$\alpha = \frac{\pi}{h} \sqrt{mk_f}.$$

This wavefunction is plotted in Fig. A.5 (b). In contrast to the particle on a box, the wavefunctions for the harmonic oscillator do not stop abruptly but decay away gradually as x increases.

The energy associated with this wavefunction can be shown to be $\frac{1}{2}h(\omega/2\pi)$. It turns out that this is just the first of a set of wavefunctions with energies given by

$$E_v = (v + \frac{1}{2}) \frac{h\omega}{2\pi},$$

where the quantum number v takes the values 0, 1, 2, ...; the lowest energy wavefunction is the one with $v = 0$.

The harmonic oscillator can be used as a simple model for the stretching of a chemical bond. All we do is to imagine that the coordinate x is the displacement of the bond length, R , from its equilibrium value, R_e :

$$x = R - R_e.$$

Absorption of a photon can cause the vibrating bond to move from the lowest energy state ($v = 0$) to the next highest energy state ($v = 1$). The energy difference between these two states, which must match the energy of the photon, is given by

$$\begin{aligned} E_1 - E_0 &= \frac{3}{2} \frac{h\omega}{2\pi} - \frac{1}{2} \frac{h\omega}{2\pi} \\ &= \frac{h\omega}{2\pi}. \end{aligned}$$

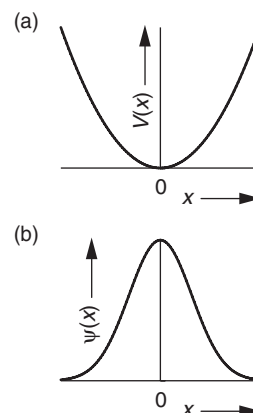


Fig. A.5 The potential energy function for the harmonic oscillator is shown in (a) and the lowest energy wavefunction for this particular form of $V(x)$ is shown in (b). Note that, in contrast to the wavefunctions for the particle in a box (Fig. A.4 on p. A-8), the wavefunction does not stop abruptly but tapers off toward zero as x increases.

From this we see that the energy of the absorbed photon is a direct measure of the frequency, ω , at which the bond is vibrating. These photons turn out to be in the infra-red (IR) part of the spectrum. Thus, by looking at the absorption in the IR, we can make direct measurements of the frequencies at which a bond is vibrating.