Module P10.3 Wavefunctions

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1 Opening items

1.1 Module introduction

Classical physics, in the shape of Newtonian mechanics and Maxwell’s electromagnetism, reached its culmination at around the turn of the 19th century. The theory seemed complete, except for a little tidying up, but cracks were about to open up and cause the downfall of the whole structure. The unfolding of these events was dramatic and rapid. In the space of 30 years, classical physics was replaced by quantum physics as the fundamental theory of the world, with classical physics surviving only as a special case — admittedly, adequate for most everyday situations. This module traces part of the story of those hectic years; other modules begin the story and others carry it further. Here we pick up after the demonstration of particle-like behaviour of electromagnetic radiation and the publication of the de Broglie hypothesis, that matter should show wave-like behaviour. The resolution of this wave and particle dual behaviour for both matter and electromagnetic radiation is the door to *quantum mechanics* or *wave mechanics* and this story begins with the idea of a *wavefunction* and how this can be used.

Section 2 reviews some some basic quantum ideas, including *de Broglie waves* and *Heisenberg uncertainty principle*. Section 3 introduces the concept of a *wavefunction* and relates this to the probability distribution associated with the position of a particle.

The wavefunction of a *free particle* is then modelled, first as a *complex travelling wave* and then as a *wave packet*. The total energy, the momentum and the kinetic energy of the particle are then related to the angular wavenumber and angular frequency of the associated travelling wave. The discussion of the wave packet representation includes the significance of the phenomenon of *dispersion* and the relationship between the phase and group speeds of the packet.

Section 4 concerns the wavefunction of a particle which is confined in one dimension. The idea of a *one-dimensional box* is introduced, along with the *stationary state* wavefunctions and discrete *energy levels* relevant to such a system. Again, the development is guided closely by classical models of confined waves. The superposition of stationary states is briefly considered, as is the significance of *transitions* between stationary states.

Section 5 extends the discussion to the case of a particle which is confined in two or three dimensions, introducing the idea of *degeneracy*.

The overall strategy of the module is to develop quantum wave models by analogy with the classical wave models, rather than to adopt a wave equation approach from first principles. A more rigorous mathematical treatment of these topics — using the Schrödinger equation — is included elsewhere in *FLAP*.

Study comment Having read the introduction you may feel that you are already familiar with the material covered by this module and that you do not need to study it. If so, try the *Fast track questions* given in Subsection 1.2. If not, proceed directly to *Ready to study?* in Subsection 1.3.

1.2 Fast track questions

Study comment Can you answer the following *Fast track questions*?. If you answer the questions successfully you need only glance through the module before looking at the *Module summary* (Subsection 6.1) and the *Achievements* listed in Subsection 6.2. If you are sure that you can meet each of these achievements, try the *Exit test* in Subsection 6.3. If you have difficulty with only one or two of the questions you should follow the guidance given in the answers and read the relevant parts of the module. However, *if you have difficulty with more than two of the Exit questions you are strongly advised to study the whole module*.

Question F1

A particle state is represented by a wave packet which extends over a distance $\Delta x = 5.0 \times 10^{-14}$ m. What is the uncertainty in the x-component of the particle's momentum Δp_x? (Take $h = 6.6 \times 10^{-34}$ J s.)

Question F2

A particle is confined in one dimension between $x = 0$ and $x = 5 \times 10^{-14}$ m, by rigid impenetrable walls. Give an expression for the wavefunctions corresponding to the standing waves between the walls.

Question F3

What is the energy of the ground state of the particle in the previous question, if the mass of the particle is 9.1×10^{-31} kg?

Is this energy level degenerate?

Study comment

Having seen the *Fast track questions* you may feel that it would be wiser to follow the normal route through the module and to proceed directly to *Ready to study?* in Subsection 1.3.

Alternatively, you may still be sufficiently comfortable with the material covered by the module to proceed directly to the *Closing items*.

1.3 Ready to study?

Study comment In order to study this module you will need to be familiar with the following terms: *de Broglie hypothesis*, *de Broglie wave*, *de Broglie wavelength*, *electron*, *energy*, *hydrogen atom* (including the *Bohr model*), *momentum*, *photon*, *Planck's constant* and *quanta*. You will need to be familiar with the basic characteristics of *waves* and *wave packets*, including; *amplitude*, *frequency*, *wavelength*, *propagation speed*, *phase speed* and *group speed*; and with wave phenomena such as *diffraction*, *interference*, and *superposition*; and to know the difference between a *travelling wave* and a *standing wave*. You also should be familiar with the *differentiation* and *integration* of simple functions of x, including *exponentials* and *trigonometric functions*. If you are uncertain about any of these terms then you can review them now by referring to the *Glossary*, which will also indicate where in *FLAP* they are developed. The following *Ready to study questions* will allow you to establish whether you need to review some of the topics before embarking on this module.

Question R1

A wave travelling along the x-axis consists of a moving disturbance that varies with time and position, which may be represented by a function of two variables $y(x, t)$. The 'shape' of the wave at any particular time $t = T$ is described by its *wave profile* at that time, $y(x, T)$, which depends on the single variable x since T is a given constant in this case. The profile may be thought of as an instantaneous snapshot of the wave at the given time.

(a) At $t = 0$, the wave profile of a particular wave is given by $y = A\sin(kx)$, where k is a constant called the *angular wavenumber* of the wave. Write down the amplitude and wavelength of the wave.

(b) If the wave in part (a) has a frequency f, write down the general relationship between the wavelength, the frequency and the speed of the wave. If the angular frequency of the wave is $\omega = 2\pi f$, write down the corresponding relationship between angular wavenumber, angular frequency and speed.

Question R2

At a particular time the transverse displacements due to two waves, acting at a common point, are $y_1 = 5\sin(2x)$ and $y_2 = 2\sin(2x)$. Use the principle of superposition to obtain the combined effect of the two waves at this time.

Question R3

What is the de Broglie wavelength associated with a particle with momentum magnitude $5.0 \times 10^{-21}\,\mathrm{kg\,m\,s^{-1}}$? [Take Planck's constant, h, to have the value $6.6 \times 10^{-34}\,\mathrm{J\,s}$]

Question R4

Write down and evaluate the definite integral of the function $f(x) = x^3$ between the limits $x = 3$ and $x = 4$.

Question R5

Give an expression for the indefinite integral $\int \sin(2x)\,dx$.

2 A review of basic quantum physics

2.1 Particle-like behaviour of electromagnetic radiation

Max Planck's ☞ interpretation (1900) of the distribution of light emitted by an idealized hot body, the so-called *black-body spectrum*, provided the first evidence that the interactions of radiation with matter were quantized. If a body is heated to a high temperature it emits light over a wide continuous range of wavelengths. When the *spectrum* of this radiation is examined and the relative brightness of the emission from unit area of the surface is plotted as a function of wavelength, it is found that the wavelength for peak emission and the total radiated power are determined mainly by the temperature of the body, not by its material. In the case of an ideal emitter, a so-called *black body*, the spectrum would be *entirely* determined by the temperature. An explanation for the detailed shape of the black-body spectrum proved impossible using classical physics, which predicted that the brightness should increase without limit at high frequencies. Planck was able to resolve this by assuming a quantum model for the interaction of matter and radiation. In particular he assumed that the interaction involved the emission and absorption of *quanta*, (which later become known as *photons*) with energy hf, where f is the frequency of the radiation and h is *Planck's constant*. The spectrum predicted on the basis of this assumption was in excellent agreement with the observed spectrum of black-body radiation. ☞

More direct evidence for photons was provided later through the *photoelectric effect* and the *Compton effect*. In the photoelectric effect, electrons are produced by shining ultraviolet radiation on to a metal surface. It is found that the maximum kinetic energy of the photoelectrons emitted from any particular surface depends only on the frequency of the incident radiation and not on the intensity of the radiation. In addition, there is a threshold frequency for a particular material and no photoelectrons are produced below this frequency, however intense the radiation. Classical wave models of electromagnetic radiation could not explain this and it was left to Einstein to interpret the observed behaviour in terms of a particle-like interaction between the radiation and the electrons in the material. In this interaction energy is absorbed from individual photons of discrete energy E given by:

photon energy $$E = hf \tag{1}$$

This result became known as the *Planck–Einstein formula*.

Some 20 years later, a crucial series of experiments, involving the scattering of X-rays by different targets showed that the scattered X-rays had a slightly longer wavelength (or a lower frequency) than the incident radiation and also that the shift in wavelength depended on the scattering angle. These observations were inexplicable using classical wave ideas. However, Arthur H. Compton (1892–1962) gave a quantum interpretation of these results, which involved the photon having a *momentum* as well as the energy given by Equation 1. (The collision between the X-ray photon and an essentially free electron in the material could then be treated as a particle–particle collision, conserving energy and momentum in the usual way.) The required expression for the photon momentum magnitude was:

photon momentum $$p = E/c = h/\lambda \qquad (2)$$

This scattering phenomenon later became known as the *Compton effect*.

2.2 Wave-like behaviour of matter

The next stage in the evolution of quantum physics came when Louis de Broglie (1892–1987) suggested that since the particles (i.e. photons) which make up electromagnetic radiation can exhibit wave-like behaviour, perhaps the same is true of every other particle. This suggestion became known as the *de Broglie hypothesis*, and the wave associated with a particle, the *de Broglie wave*, was expected to have its *de Broglie wavelength* set by the magnitude of the momentum p of the particle, according to the expression:

de Broglie wavelength $\lambda_{\rm dB} = h/p$ (3) ☞

The suggestion that particles of matter might exhibit wave-like behaviour implies that such particles might exhibit diffraction and interference. If so, the closely spaced planes of atoms in a crystalline solid might be used to diffract the de Broglie waves associated with an electron beam with particle energies of a few tens of electron volts. Such an experiment was carried out in 1927 by C. H. Davisson and L. H. Germer and they obtained a diffraction pattern in good agreement with de Broglie’s predicted wavelength. Subsequently, many other experiments have demonstrated that *all* particles, irrespective of charge, mass, shape or composition, produce a diffraction pattern which is consistent with the de Broglie hypothesis.

Figure 1 shows an instantaneous snapshot of the de Broglie wave for a particle with definite momentum p_x travelling along the x-direction.

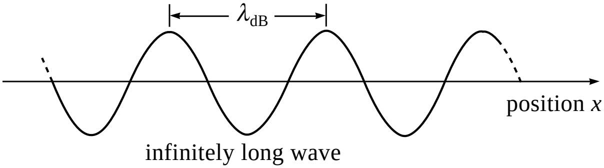


Figure 1 The profile of a de Broglie wave of fixed amplitude and wavelength λ_{dB}, corresponding to a particle moving in the positive x-direction with momentum p_x. Note that the figure shows a *snapshot* of the wave, which is actually travelling in the positive x-direction.

The precise nature of de Broglie waves and the exact sense in which such waves are to be associated with particles was left unclear by de Broglie. However, subsequent work by others, notably Erwin Schrödinger (1887–1961), Werner Heisenberg (1901–1976) and Max Born (1882–1970), put de Broglie's ideas onto a firmer mathematical footing and eventually brought about a complete revolution in physical thinking. Part of that revolution forms the main theme of this module, and we will come to it later.

In the meantime, we will continue to use the term 'de Broglie wave' to describe the wave aspect of a particle, and we will summarize later work by saying that the de Broglie wave of a particle determines the relative likelihood of detecting the particle in any given region of space. In particular, continuing to use this somewhat over-simplified language, we can say that *the probability of finding a particle in any small region of space is proportional to the square of the amplitude of the de Broglie wave in that region*. In this sense the disturbance that constitutes a de Broglie wave may be thought of as a disturbance in the probability of finding the associated particle.

A simple one-dimensional de Broglie wave of fixed amplitude and wavelength, extending to infinity along the x-direction, corresponds to a particle whose momentum magnitude is perfectly known. Unfortunately, such a wave is not localized in space; its amplitude is the same everywhere, and so it conveys no information at all about the position of the particle. If we wish to produce a wave of finite extent, with some implied localization of the particle, then we must construct a *wave packet* by superposing (adding) waves, and arrange for this superposition to diminish sharply outside the expected range of particle positions Δx. In discussing this process it is convenient to use as the variable the *angular wavenumber* k rather than the wavelength λ—the two are related by

angular wavenumber $$k = 2\pi/\lambda \tag{4}$$

Question T1

At time $t = 0$, the instantaneous profiles of two de Broglie waves are $\psi_1(x) = A_1\cos(k_1x)$ and $\psi_2(x) = A_2\cos(k_2x)$.

☞ These expressions show that the two are in phase at $x = 0$. (a) Write down an expression for the profile of their superposition at $t = 0$ and give its value at $x = 0$. (b) What are the values of x closest to zero for which $\psi_1(x)$ and $\psi_2(x)$ are exactly out of phase (in anti-phase) at $t = 0$? Express this value of x in terms of the difference in momentum of the corresponding particles. ❏

Answer T1 illustrates the principle that a more localized profile can be produced by superposing two other profiles, corresponding to two different angular wavenumbers, i.e. two different momenta, by using $\psi(x) = [\psi_1(x) + \psi_2(x)]$ as a new wave profile.

Such a case is illustrated in Figure 2. The answer also shows that a position of constructive interference is separated from a position of destructive interference by a distance Δx which is determined by the angular wavenumber difference Δk. The two quantities Δx and Δk being inversely related: $\Delta k \approx \pm \pi/\Delta x$.

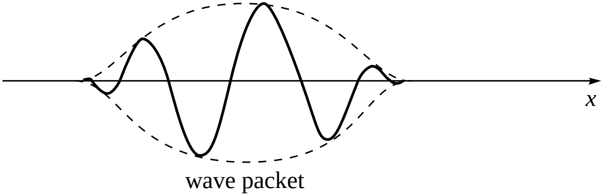


Figure 2 A wave packet constructed from a superposition of de Broglie waves of different wavelength. Again, note that the figure shows a *snapshot* of the wave, which is actually travelling since it describes the motion of particles. Note that although the figure shows an isolated wave packet the pattern is actually repeated all along the x-axis.

We can go further than this, and use more than two waves in the superposition, as shown in Figure 3. This figure shows an example of the construction of a finite wave packet by the superposition of (in this case eight) waves of *suitably chosen* amplitudes and wavelengths. Although *each* contributing wave has a well defined wavelength and associated momentum, the resultant superposition does not.

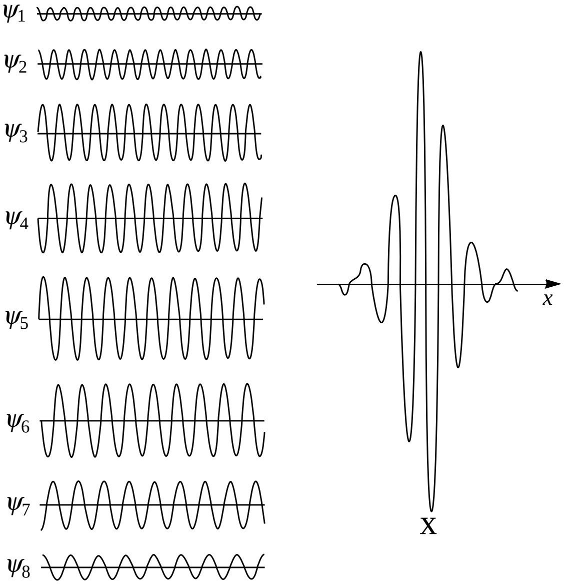


Figure 3 The localization of the wavefunction produced when eight waves with different amplitudes and wavelengths are added together using the principle of superposition.

The basic features arising from the mathematics are illustrated in Figure 4. It should be noted, in particular, that in order to localize the wave packet within a smaller and smaller region of space, there must be included in the superposition a wider and wider range of values of angular wavenumber for the contributing waves.

> The greater the spread of angular wavenumbers Δk, the narrower the width Δx, of the corresponding wave packet.

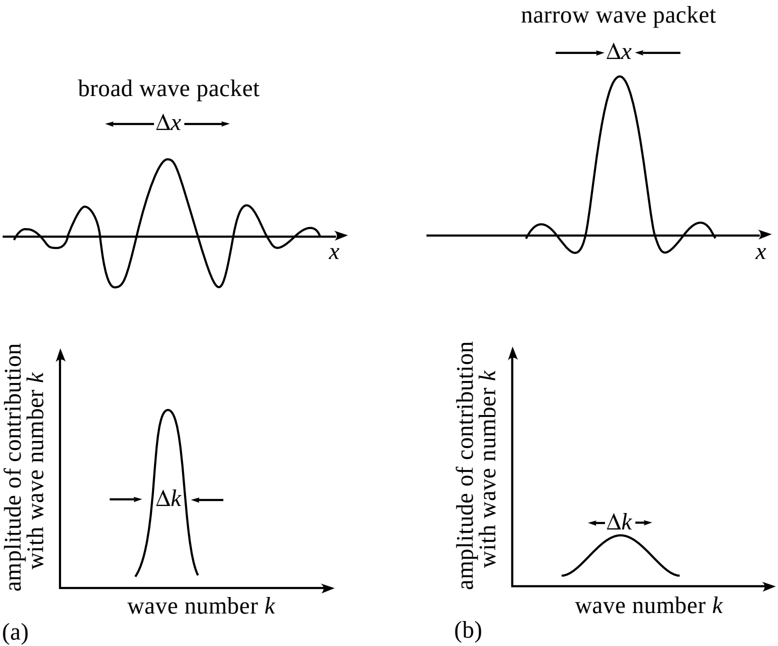


Figure 4 A *broad* wave packet can be constructed from the superposition of waves with a *narrow* range of angular wavenumbers. Conversely a *narrow* wave packet requires a *broad* range of angular wavenumbers for its construction.

Fourier analysis quantifies this relationship in the simple expression:

$$\Delta x\,\Delta k \approx 1 \qquad (5)$$

Notice that Equation 5 is not given as an equality since, as you will see by looking at Figure 4, Δx and Δk are only approximate measures of spread and have not been defined precisely. This relationship is very important however, as it shows a *trend* which is always satisfied, *irrespective of the shape* of the wave packet.

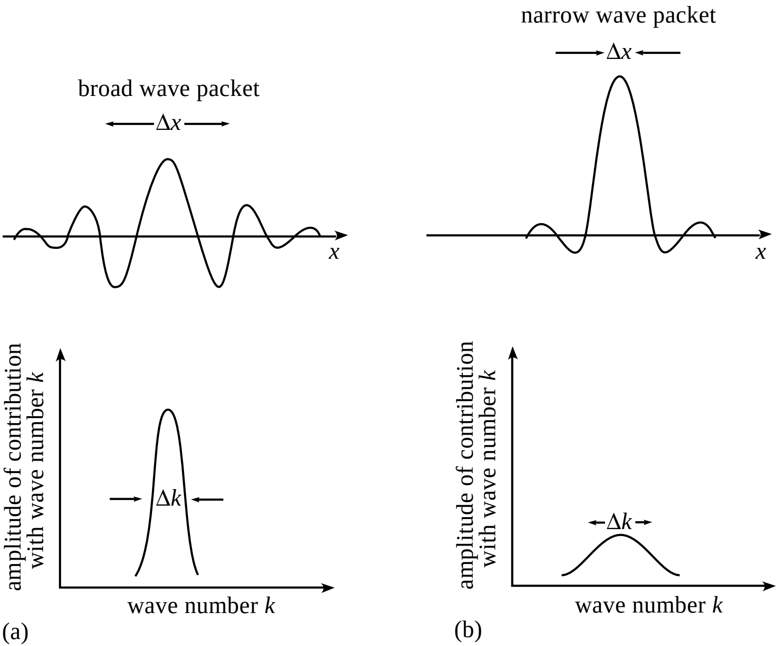


Figure 4 A *broad* wave packet can be constructed from the superposition of waves with a *narrow* range of angular wavenumbers. Conversely a *narrow* wave packet requires a *broad* range of angular wavenumbers for its construction.

In the context of a de Broglie wave packet, each of the superposed waves will have a different de Broglie wavelength, and hence a different associated particle momentum (Equation 3).

de Broglie wavelength $\lambda_{\rm dB} = h/p$ (Eqn 3)

A spread in angular wavenumber will therefore correspond to a spread in particle momentum. This implies that the wave packet corresponding to a particle whose position is known to within Δx must be composed of de Broglie waves associated with particle momenta in the range

$$\Delta p = \frac{h}{2\pi}\Delta k \approx \frac{h}{2\pi}\frac{1}{\Delta x}$$

This leads to the **Heisenberg uncertainty principle**:

Heisenberg uncertainty principle $$\Delta x\,\Delta p_x \gtrsim \frac{h}{2\pi} \qquad (6)$$ ☞

where Δp_x represents the irreducible uncertainty in the x-component of the momentum of a particle that is known to be localized within Δx.

We have replaced the approximation sign in Equation 5

$$\Delta x\,\Delta k \approx 1 \qquad \text{(Eqn 5)}$$

by a ‘greater than or approximately equal to’ sign in Equation 6

Heisenberg uncertainty principle

$$\Delta x\,\Delta p_x \gtrsim \frac{h}{2\pi} \qquad \text{(Eqn 6)}$$

to signify that in any *experiment* we can never obtain simultaneous information on position and momentum in a given direction to a precision which is better than the fundamental limit set by the wave nature of matter.

Question T2

In each of the two cases below, measurements are made simultaneously of position x, and x-component of momentum p_x. In each case the uncertainty Δx, is given. Estimate the percentage uncertainty in the momentum due to the Heisenberg uncertainty principle. Take Planck’s constant h, as $6.6 \times 10^{-34}\,\mathrm{J\,s}$.

(a) A bullet of mass 0.10 kg is travelling with a speed of $1.5\,\mathrm{km\,s^{-1}}$ and Δx is 0.10 mm.

(b) A proton of mass 1.7×10^{-27} kg is travelling with a speed of $1.0\,\mathrm{km\,s^{-1}}$ for which Δx is 1.0×10^{-10} m. ❏

We are now in a position to introduce the concept of a *wavefunction* and to begin the journey from the old de Broglie world to the new world of *quantum mechanics*. Our first task is to organize our vocabulary. So far, we have sometimes referred to electrons, protons, neutrons and other such entities rather loosely as ‘particles’. On other occasions we have had to accept that they exhibit wave-like behaviour. Neither the word ‘particle’ nor ‘wave’ conveys the full picture of their behaviour, so we will describe each of them simply as a **quantum**, indicating that they are neither waves nor particles but may exhibit features of either. ☞ This is a new technical definition of the term. It is natural then to describe the study of the motion and the interaction of these quanta as **quantum mechanics**. This new world of quantum mechanics is a good deal more mathematical than the old world of de Broglie waves, but we will try to maintain the contact with de Broglie waves as long as we can.

3 The wavefunction for a free particle

The principles of quantum mechanics were introduced in a series of papers by Heisenberg, Schrödinger, Born and Pascual Jordan (1902–1980) in the years 1925–1926. Initially there were two quite distinct formulations of quantum mechanics, but they were soon shown to be mathematically equivalent and Schrödinger's version (now known as **wave mechanics**) now provides the usual route of entry to the subject.

Central to Schrödinger's approach is a mathematical quantity called the **wavefunction**. This quantity varies with time and position, just like a wave, and replaces the more primitive (and ill-defined) concept of a de Broglie wave. It is conventional to use the upper-case Greek letter Ψ (pronounced 'psi') to represent the wavefunction, so in a one-dimensional problem where its value depends on position x and time t, the wavefunction is usually written $\Psi(x, t)$. The precise form of the wavefunction in any given situation is determined by solving a (complicated) equation known as the *time-dependent Schrödinger equation*. Learning how to formulate this equation to represent a given physical situation is an important skill, as is learning how to solve it, but we will not be concerned with either of those issues in this module. Instead, we will concentrate on the significance and physical interpretation of the wavefunctions that satisfy it.

In the conventional interpretation of quantum mechanics the wavefunction provides the most complete description of the behaviour of a system we can hope to have. This sounds rather grand, and it certainly has far reaching implications, but in practice we are often restricted to dealing with such simple systems that even their ‘complete description’ is fairly straightforward. In the case of a particle moving in one dimension, for instance, it usually boils down to knowing the energy and momentum, and something about the relative likelihood of finding the particle in various regions.

An important mathematical property of the wavefunction $\Psi(x, t)$ that clearly distinguishes it from a de Broglie wave is that it is generally a *complex* quantity. That is to say, given particular values for the variables x and t, the corresponding value of the wavefunction will generally be **complex number** and may therefore be written in the form

$$\Psi(x, t) = a + ib$$ ☞

where a and b are ordinary (*real*) numbers and i is a special algebraic quantity, usually referred to as the square root of –1, with the property

$$i^2 = -1$$

Complex numbers are used in many parts of physics, but often only as a convenience. In quantum mechanics, however, they play an essential role and are unavoidable. In this particular module we will use them as little as possible, but even here we cannot avoid them completely and you will certainly need to know more about them if you intend to pursue the study of quantum mechanics.

For the moment, the one additional fact you need to know about any complex quantity is that it may always be associated with a unique real number called its **modulus**. The modulus of $\Psi(x, t) = a + ib$ is written $|\Psi(x, t)|$ and is defined in the following way

if $\quad \Psi(x, t) = a + ib$

then $\quad |\Psi(x, t)| = (a^2 + b^2)^{1/2}$

In quantum mechanics the modulus of the wavefunction plays the role that we earlier (and over-simplistically) assigned to the square of the amplitude of a de Broglie wave. In other words, if the behaviour of a quantum is described by the wavefunction $\Psi(x, t)$

> The probability of finding the particle within the small interval Δx around the position x at time t is
>
> $$\propto |\Psi(x, t)|^2 \Delta x. \qquad (7)$$
>
> ☞

There are several points to note here:

- Since $|\Psi(x, t)|$ is a real quantity (it doesn't involve i), it must be the case that $|\Psi(x, t)|^2$ is positive. It is therefore at least possible that $|\Psi(x, t)|^2$ might represent a probability, since probabilities are represented by real numbers in the range 0 to 1 with 0 for no possibility and 1 for certainty.
- Since Δx is taken to be very small, $|\Psi(x, t)|^2$ can be thought of as the probability per unit length, or **probability density** around position x.
- $|\Psi(x, t)|^2\,\Delta x$ is a *statistical* indicator of behaviour. Given a large number of experiments to measure the position of a particle, set up under identical conditions, it represents the fraction of those experiments that will indicate a particle in the range Δx at a time t. The set up for the experiment is fixed but the results of individual experiments are not always the same.
- We may write an *equality* sign in place of the *proportionality* sign in Equation 6, provided we choose an appropriate scale of probability. For the moment, we do not need to be concerned with this refinement, but we will return to it in Subsection 4.2 when we discuss *normalization*.

Our task now is to introduce the appropriate wavefunctions for some simple situations and to determine how these wavefunctions may be used to obtain the characteristic properties of the associated particle—such as its position, momentum and kinetic energy. We begin with the case of a free particle.

3.1 A complex travelling wave to represent a free particle

If we are to represent a moving particle by a wave then it is reasonable to use a *travelling wave* and so we begin by reviewing how we represent a classical travelling wave, such as a transverse wave on a string. ☞

A classical travelling wave on a string

A wave travelling along a string is characterized by having an amplitude A, frequency f, angular frequency $\omega = 2\pi f$, wavelength λ and angular wavenumber $k = 2\pi/\lambda$. ☞ When such a wave propagates in the positive x-direction, the wave displacement $y(x, t)$ can be represented by:

travelling wave $$y(x, t) = A\cos(kx - \omega t) \qquad (8)$$ ☞

The wave represented by Equation 8 can be shown to be travelling in the positive x-direction, using the following argument. Consider the position of the wave at two times $t = 0$ and $t = \Delta t$, where Δt is very short compared to the *period* of the wave.

At $t = 0$: $y(x, 0) = A\cos(kx)$ and the wave has a maximum at $x = 0$.

At $t = \Delta t$: $y(x, \Delta t) = A\cos(kx - \omega\Delta t)$ and the wave has a maximum when $(kx - \omega\Delta t) = 0$. This maximum occurs at $x = \omega\Delta t/k$.

We deduce that the maximum of the wave has moved a distance $\Delta x = \omega\Delta t/k$ in the time Δt. It is apparent that the wave is travelling along the positive x-direction and that a point of fixed phase (e.g. a point of maximum displacement where $kx - \omega\Delta t = 0$) advances with a *phase speed* v_ϕ given by:

wave *phase speed*: $$v_\phi = \Delta x/\Delta t = \omega/k \tag{9}$$

We could rewrite Equation 8

travelling wave $$y(x,\, t) = A\cos(kx - \omega t) \qquad \text{(Eqn 8)}$$

in terms of the wave phase speed as:

travelling wave $$y(x,\, t) = A\cos[k(x - v_\phi t)] \tag{10}$$

This expression for the travelling wave makes the role of the phase speed clear.

The travelling wave is shown in Figure 5.

Question T3

Obtain an expression similar to Equation 8,

$$\textit{travelling wave } y(x, t) = A\cos(kx - \omega t) \quad \text{(Eqn 8)}$$

but representing a wave travelling in the negative x-direction. ❑

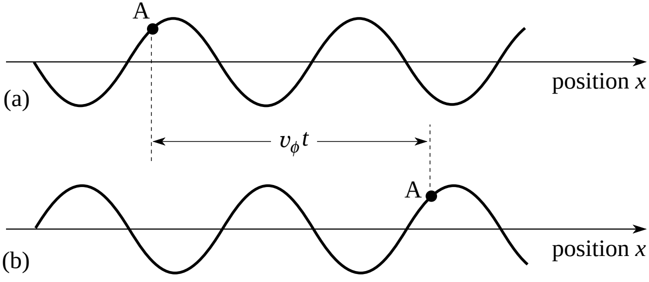


Figure 5 (a) An infinitely long wave at time $t = 0$. (b) The same wave at a later time t; the speed of the wave is v_ϕ from left to right so the wave has moved a distance $v_\phi t$ to the right, but its shape is unchanged.

A quantum travelling wave in one dimension

We can now write down the wavefunction of a freely moving quantum travelling in the $+x$-direction. (Remember, this is found by solving the time dependent Schrödinger equation, though we will not go into that in this module.)

$$\textit{free particle wavefunction}\quad \Psi(x,\,t) = A\cos(kx - \omega t) + i A\sin(kx - \omega t) \qquad (11)$$

As you can see, it owes a great deal to the expression for a one-dimensional travelling wave (Equation 8),

$$\textit{travelling wave}\qquad y(x,\,t) = A\cos(kx - \omega t) \qquad \text{(Eqn 8)}$$

but there is also a striking difference. This wavefunction involves i, the square root of -1, and is therefore intrinsically *complex*. We will examine the significance of this in a moment, but for the present let us exploit the similarities with a travelling wave.

As you might expect the total energy, the momentum and the kinetic energy of the quantum can all be expressed in terms of the parameters ω and k of the wavefunction, through Equations 1 and 3, as:

total energy: $$E = hf = \frac{h\omega}{2\pi} = \hbar\omega \qquad (12)$$ ☞

momentum: $$p_x = \frac{h}{\lambda_{\rm dB}} = \frac{hk}{2\pi} = \hbar k \qquad (13)$$

kinetic energy: $$E_{\rm kin} = \frac{mv_x^2}{2} = \frac{(mv_x)^2}{2m} = \frac{p_x^2}{2m} = \frac{\hbar^2 k^2}{2m} \qquad (14)$$

Where we have introduced the shorthand $\hbar$ for the commonly met quantity $h/2\pi$. Notice an important feature of quantum mechanics shown here — the properties of the quantum are derivable from the mathematical form of its wavefunction, in this case simply by inspection of the coefficients of x and t.

Now, let us see what information about the *position* of the quantum, can be derived from the wavefunction of Equation 11.

free particle wavefunction $\Psi(x,\,t) = A\cos(kx - \omega t) + iA\sin(kx - \omega t)$ (Eqn 11)

Using the general expression for the modulus of a complex quantity we see that in this case

$$|\,\Psi(x,\,t)\,| = [A^2\cos^2(kx - \omega t) + A^2\sin^2(kx - \omega t)]^{1/2}$$

But $\sin^2\theta + \cos^2\theta = 1$ for all values of θ

So $|\,\Psi(x,\,t)\,| = A$

and $|\,\Psi(x,\,t)\,|^2 = A^2$ (15)

Thus, the probability density is independent of x, and the likelihood of finding the quantum in a small region of fixed length Δx is the same everywhere. You shouldn't be surprised by this result: in the first place there is no reason why a freely moving quantum should be more likely to be found in one place than another; secondly this quantum has a well defined momentum magnitude so $\Delta p = 0$ and it follows from the uncertainty principle that Δx $(= \hbar/\Delta p)$ will be undefined.

We might now be tempted to calculate the phase velocity from the wavefunction in Equation 11.

free particle wavefunction $\Psi(x,t) = A\cos(kx - \omega t) + iA\sin(kx - \omega t)$ (Eqn 11)

When we do so we are in for a shock! By analogy with the wave on a string we find the phase speed of this wavefunction is:

$$\textit{phase speed}: \qquad v_\phi = \frac{\omega}{k} = \frac{E}{p} = \frac{\frac{1}{2}mv^2}{mv} = \frac{v}{2} \tag{16}$$

In Equation 16 we have used the usual expressions for the kinetic energy and momentum magnitude of a particle travelling with speed v. We have arrived at the disturbing conclusion that the phase speed of the wavefunction is *not the same* as the velocity of the associated particle, but half this value! We will resolve this apparent paradox in the next subsection.

3.2 A travelling wave packet to represent a free particle

Just as we were able to construct a wave packet from de Broglie waves to represent a localized particle, so too we can produce a localized wavefunction by superposing free particle wavefunctions like that of Equation 11.

free particle wavefunction $\Psi(x,\,t) = A\cos(kx - \omega t) + iA\sin(kx - \omega t)$ (Eqn 11)

If this quantum wave packet moves through space, its motion can represent the motion of the associated free particle. Of course, since the wave packet will involve a range of angular wavenumbers it will not describe a particle with precisely determined momentum but that, according to the uncertainty principle, is the price we must pay for having some idea where the particle is located.

When the phase speed of a wave depends on its wavelength or angular wavenumber, individual waves of a given k will move with different phase speeds whilst the wave packet itself will travel at the *group speed*. According to classical wave theory the group speed is the speed with which the energy is propagated and is given by the expression:

group speed $$v_{\rm g} = d\omega/dk \tag{17}$$ ☞

We will soon use Equation 17 to investigate the group speed of our quantum wave packet. However, before we do that let us clarify the meaning of the equation by using it to investigate a packet of (hopefully familiar) electromagnetic waves.

Group speed of an electromagnetic wave packet in a vacuum

For an electromagnetic wave of frequency f and wavelength λ travelling in a vacuum:

$$c = f\lambda \tag{18}$$

so the phase speed of a single electromagnetic wave is

$$\textit{phase speed}: \qquad v_\phi = \frac{\omega}{k} = \frac{2\pi f}{2\pi/\lambda} = f\lambda = c \tag{19}$$

The phase speed is constant, it is independent of k, and $\omega = kc$. In a vacuum, an electromagnetic wave packet composed of many such waves with different values of k moves with an overall speed known as its *group speed*, given by

$$\textit{group speed} \qquad v_{\rm g} = \frac{d\omega}{dk} = \frac{d}{dk}(ck) = c \tag{20}$$

Since the group speed is also c, the wave packet travels at the same speed as each of the constituent waves within it. The wave packet thus travels through a vacuum without change of shape.

In a medium the situation is rather different. If an electromagnetic wave packet travels through any material, other than vacuum, the phase speed of each constituent wave is reduced by the *refractive index*, which usually depends on k. In this case, the group speed and the various phase speeds differ and the wave packet changes its shape and spreads out as it propagates. This process is called **dispersion**. and the relation between ω and k is called the **dispersion relation** of the material.

Group speed of a quantum wave packet

To determine the group speed of the quantum wave packet representing a free particle we first need to determine its dispersion relation (i.e. the relationship between k and ω). We can do this by recognizing that for a free particle the total energy and the kinetic energy must be identical since it then follows from Equations 12 and 14

total energy: $$E = hf = \frac{h\omega}{2\pi} = \hbar\omega \tag{Eqn 12}$$

kinetic energy: $$E_{\text{kin}} = \frac{mv_x^2}{2} = \frac{(mv_x)^2}{2m} = \frac{p_x^2}{2m} = \frac{\hbar^2 k^2}{2m} \tag{Eqn 14}$$

that:

quantum dispersion relation: $$\omega = \frac{\hbar k^2}{2m} \tag{21}$$

so, *quantum group speed*: $$v_{\text{g}} = \frac{d\omega}{dk} = \frac{d}{dk}\left(\frac{\hbar k^2}{2m}\right) = \frac{\hbar k}{m} = \frac{p_x}{m} = v_x \tag{22}$$

We thus find that for a quantum wave packet, the group speed with which the packet moves (i.e. speed with which the energy is transmitted) is equal to the speed of the associated particle. This resolves the problem we had at the end of Subsection 3.1, where we wrongly associated particle speed with *phase speed* rather than *group speed*.

Question T4

An electromagnetic wave packet moves through a material in which the dispersion relation is:

$$k = b\omega(1 + a\omega)$$

where a and b are positive constants. Obtain expressions for:
(a) the phase speed and
(b) the group speed of the wave packet.

Which of these two speeds is the greater? ❏

4 The wavefunction for a particle confined in one dimension

We now turn our attention from freely moving particles (whether localized or not) to particles that are confined to a limited region of the *x*-axis. As with the travelling wave examples discussed earlier, we will approach the quantum wave problem through the familiar territory of classical waves, but we must now consider *standing waves*.

4.1 A particle confined in a one-dimensional box

A classical standing wave on a string

The simplest classical example of a one-dimensional *standing wave* is that of a vibrating string with fixed ends, such as occurs on the string of a musical instrument. For simplicity, we consider an elastic string which, in its rest state, is straight and taut with length *D*. It is fixed at each of its ends but may be made to vibrate at right angles to its length, if disturbed — for example, by plucking. A short while after being disturbed, a standing wave becomes established on the string and this wave can be analysed in terms of a superposition of oppositely directed travelling waves with various amplitudes; ☞ this result can again be understood mathematically in terms of a Fourier superposition.

The significant difference between the free moving wave packet, discussed in Subsection 3.2, and the *standing wave* here, is that the wavelengths involved in the superposition can now *have only certain particular values* and do not form a continuous range.

The origin of this restriction on the contributing wavelengths is easy to explain. Since the end points of the string are fixed the displacement of the string must be zero at either end. These are known as the **boundary conditions** on the standing wave, and all the travelling waves that contribute to the superposition must obey them. In this case, the boundary conditions of zero displacement require that the standing wave can be expressed as a sum of travelling sine waves of definite wavelengths and amplitudes.

The particular wavelengths allowed are those for which an *integer number of half wavelengths* fits into the distance D, between the ends of the string.

Figure 6 shows ‘freeze-frame’ snapshots of some of these simplest standing waves that can arise. These elemental oscillations are known as the **standing wave modes** of the string. It is possible to excite a single mode, with a particular initial condition, but in general, several modes may be operating at the same time. When a single mode is excited, each point on the string oscillates at the same mode frequency but with an amplitude which depends on position along the string. Positions with zero amplitude are called **nodes** and positions with maximum amplitude are called **antinodes**; the ends of the string are nodes. The distance between a node and the adjacent antinode is one quarter of the wavelength for that mode. If the string is excited into *single mode* oscillation it will continue in that mode until it is disturbed in some way, although energy losses due to friction usually *damp* the oscillation away, eventually.

❖ How many half wavelengths are contained in the distance D for the wave form in the bottom picture of Figure 6?

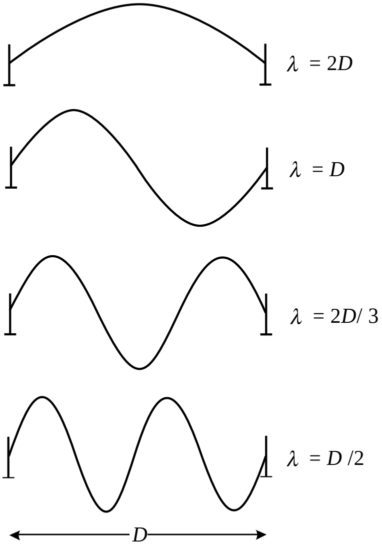


Figure 6 Four of the standing wave modes that may be set up on a taut, elastic string that is fixed at each end.

The vertical displacements in any one of the one-dimensional standing wave modes, shown in Figure 6, may be represented mathematically as follows:

$$\textit{Standing wave mode } n\text{:}\qquad y_n(x,t) = A_n \sin(k_n x)\cos(\omega_n t) \tag{23}$$

The wavelength ☞ of the mode n is determined by the condition:

$$D = \frac{n\lambda_n}{2}$$

for $n = 1, 2, 3, 4, \dots$ (i.e. n is a positive integer).

We can write the associated angular wavenumbers k_n as:

$$k_n = \frac{2\pi}{\lambda_n} = \frac{n\pi}{D} \tag{24}$$

so the modes become:

$$y_n(x,t) = A_n \sin\left(\frac{n\pi x}{D}\right)\cos(\omega_n t) \qquad \text{for } n = 1, 2, 3, \dots \tag{25}$$

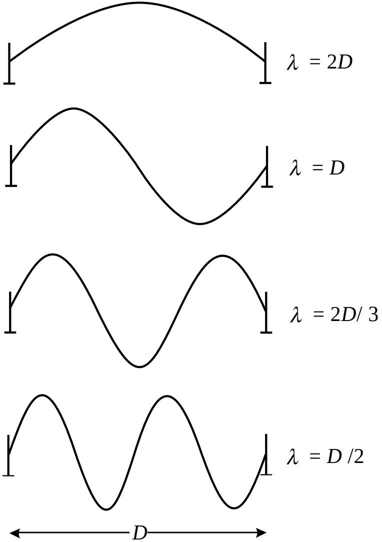


Figure 6 Four of the standing wave modes that may be set up on a taut, elastic string that is fixed at each end.

For a given mode Equation 23

$$\textit{Standing wave mode } n\text{:}\qquad y_n(x,t) = A_n \sin(k_n x)\cos(\omega_n t) \qquad (23)$$

does not lead to a travelling wave. Each point at position x on the string undergoes oscillation at the same angular frequency ω_n, but with an amplitude $A_n \sin(k_n x)$, which depends on position. At an antinode the amplitude is A_n. Since all points on the string oscillate in phase at the same frequency, the time dependence of this stationary wave is the same at each point and for many purposes is of less interest than the spatial dependence of the mode.

However, if we ask what happens when *two or more different modes operate simultaneously* then we find that a more interesting time-dependence emerges. In particular, interference between two standing waves of different frequencies produces *beats* ☞ at the difference frequency and the shape of the string is no longer a fixed sinusoid. Visually, the string appears to contain travelling waves which move back and forth along it.

A quantum wavefunction for one-dimensional confinement

For our quantum example, we will again consider the simplest case of one-dimensional confinement subject to appropriate boundary conditions. The wavefunction can then be completely specified in terms of a single position coordinate (x) and a time coordinate (t). The particle is not allowed outside of a finite range of x-values, say between $x = 0$ and $x = D$.

A realization of this situation could be a particle held in the space between two parallel infinite planes, separated by a distance D, measured along the x-axis. For example, we might locate one plane at $x = 0$ and the other at $x = D$, as shown in Figure 7a. This is usually called a **one-dimensional box** — it is actually a box in three-dimensional space, but the *confinement* is in one dimension only. The confinement of the particle means that the wavefunction must be zero everywhere outside the box, so there is no probability of finding the particle outside the box. It follows from this that we require the wavefunction to fall to zero at the boundary — in this case, at the walls of the box.

Thus the wavefunction must satisfy the boundary conditions:

$$\Psi(0, t) = 0 \quad \text{and} \quad \Psi(D, t) = 0 \qquad \text{for all } t$$

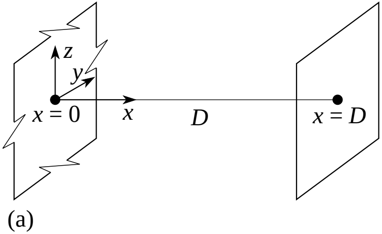


Figure 7a A particle of mass m is moving in the space between two parallel infinite planes, separated by a distance D, measured along the x-axis.

Before we consider this system in detail, let us examine whether the uncertainty principle has anything to say about this situation. When we make a mental picture of the situation we must be careful not to imply more information than we can legitimately claim from the Heisenberg uncertainty principle.

Question T5

Could we say that, in the realization of a one-dimensional box described above, the particle has only x-motion, i.e. that this is a one-dimensional problem, since the particle has no y- or z-components of velocity? Present your argument carefully. ☞ ❑

Question T6

In the situation described in Question T5, could we claim that the particle is moving *along the x-axis*? Present your argument carefully. ☞ ❑

The simplest wavefunctions describing a quantum confined between $x = 0$ and $x = D$, in a one-dimensional box may be written in the form:

confined wavefunction: ☞

$$\Psi_n(x,t) = \psi_n(x)[\cos(\omega_n t) + i\sin(\omega_n t)] = A_n \sin\left(\frac{n\pi x}{D}\right)[\cos(\omega_n t) + i\sin(\omega_n t)] \quad n = 1, 2, 3, \dots \qquad (26)$$

Note that these wavefunctions satisfy the boundary conditions, and that we can separate out the spatial and time dependencies, as we did for the classical wave. The part of the wavefunction that depends on position (x) is denoted by the *lower case* Greek letter ψ and is therefore written as $\psi_n(x)$ in each case. This is called the spatial part of the wavefunction, or simply the **spatial wavefunction**. (Note the distinction between the wavefunction $\Psi_n(x, t)$ and its spatial part $\psi_n(x)$.) In this particular case

spatial wavefunction:

$$\psi_n(x) = A_n \sin(k_n x) = A_n \sin\left(\frac{n\pi x}{D}\right) \qquad n = 1, 2, 3, \dots \qquad (27)$$

As for the classical case, the quantum wavefunctions consist of a set of modes for the system. The time-dependence is common to a particular mode and it is the spatial part of these wavefunctions which is of most interest. The spatial part of each of the first three wavefunctions, as given by Equation 27,

$$\psi_n(x) = A_n \sin(k_n x) = A_n \sin\left(\frac{n\pi x}{D}\right) \qquad n = 1, 2, 3, \ldots \text{(Eqn 27)}$$

is shown in Figure 7b. As in the classical case, if the system is excited into a particular single mode then it will continue with this same wavefunction indefinitely, unless it is perturbed in some way. These persisting single mode wavefunctions are called the **stationary states** of the system; they are the quantum equivalent of the modes of a classical system. Stationary states have the particular property that they correspond to a probability density $|\Psi_n(x, t)|^2$ that is independent of time.

✦ Confirm that $|\Psi(x, t)|^2$ is independent of time for these stationary states, and show that $|\Psi(x, t)|^2 = |\psi(x)|^2$.

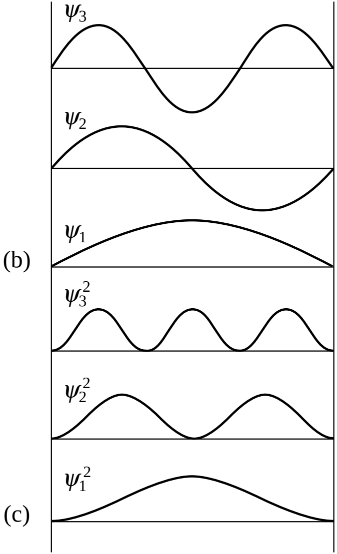


Figure 7b & c (b) The three lowest energy stationary state wavefunctions that can describe the particle. (c) The values of $|\psi(x)|^2$ for the three lowest energy stationary states shown in (b).

The time dependence of the n^{th} wavefunction in Equation 26

confined wavefunction:

$$\Psi_n(x,t) = \psi_n(x)[\cos(\omega_n t) + i\sin(\omega_n t)] = A_n \sin\left(\frac{n\pi x}{D}\right)[\cos(\omega_n t) + i\sin(\omega_n t)] \quad \text{n} = 1, 2, 3, \ldots \qquad \text{(Eqn 26)}$$

is determined by the particle's total energy, E_n through Equation 12:

total energy: $$E_n = \hbar\omega_n \qquad \text{(Eqn 12)}$$

Equation 13 gives the momentum in the n^{th} mode as:

momentum: $$p_x = \hbar k_n \qquad \text{(Eqn 13)}$$ ☞

Equation 14 gives the kinetic energy in n^{th} mode as:

kinetic energy: $$E_{\text{kin}} = \frac{\hbar^2 k_n^2}{2m} \qquad \text{(Eqn 14)}$$

For this situation, there are no changes in potential energy in the box and so we may set the potential energy equal to zero everywhere in the box. This means that the kinetic energy is the same as the total energy E_n, which is:

The *total energy*:
$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mD^2} = \frac{n^2 h^2}{8mD^2} \tag{28}$$

where n can take on any positive integer value ($n \geq 1$). These allowed values of E_n are known as the **energy levels** of the system.

Figure 8 shows the first four such energy levels. The stationary state of lowest energy is called the **ground state** and the associated energy level is called the **ground level**. States with higher energy are called **excited states** and their energies are **excited levels**. Equation 28

The *total energy*: $$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mD^2} = \frac{n^2 h^2}{8mD^2} \qquad \text{(Eqn 28)}$$

represents a very important and characteristic feature of quantum mechanics. It shows that, if a particle is constrained (the constraint being represented by boundary conditions on the wavefunction) then its energy may not take on any arbitrary value. Only certain discrete energies determined by the integer n in Equation 28 are permitted. The energy is said to be **quantized** and n is referred to as a **quantum number**.

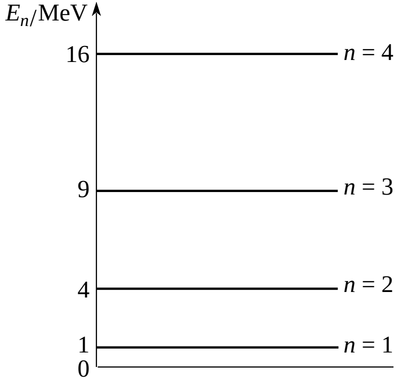


Figure 8 The first four allowed energy levels of a particle in a one-dimensional box. $E_n = n^2h^2/(8mD^2)$.

4.2 Comparison between the classical and quantum cases

We have now arrived at the predictions of quantum mechanics for a particle in a one-dimensional box. These predictions are in striking conflict with classical physics so we should take time to reflect on them and draw out just how fundamental the differences are. Before we draw together the conclusions of the quantum model, let us look briefly at how classical physics would model a particle trapped between these two impenetrable walls.

Question T7

Explain how classical physics could describe a particle with fixed kinetic energy, trapped in a one-dimensional box, given that there is no motion in the *y*- or *z*-directions. Comment on the speed and direction of the motion and whether the speed or energy is restricted in any way by the box. ❏

In contrast, the summary conclusions of our quantum treatment are as follows:

1 The system has available to it certain *stationary states*, or discrete states, each described by the appropriate wavefunction for that state. For the *n*th state:

$$\Psi_n(x,t) = \psi_n(x)[\cos(\omega_n t) + i\sin(\omega_n t)] = A_n \sin\left(\frac{n\pi x}{D}\right)[\cos(\omega_n t) + i\sin(\omega_n t)]$$

2 Each stationary state has an associated definite discrete total energy:

$E_n = \dfrac{n^2h^2}{8mD^2}$. These are known as the *energy levels* of the system.

3 The system's *lowest energy is not zero* but equal to $E_1 = \dfrac{h^2}{8mD^2}$.

4 For the stationary states the wavefunctions are complex standing waves, which do not travel and so imply *no particular direction of motion for the associated particle* in the box.

These conclusions differ at almost every point from the classical model!

❖ The energy becomes zero if we were to set $n = 0$ in the expression for E_n. Why does this give a result which is not physically sensible?

1 The system has available to it certain *stationary states*, or discrete states, each described by the appropriate wavefunction for that state. For the nth state:

$$\Psi_n(x,t) = \psi_n(x)[\cos(\omega_n t) + i\sin(\omega_n t)] = A_n \sin\left(\frac{n\pi x}{D}\right)[\cos(\omega_n t) + i\sin(\omega_n t)]$$

2 Each stationary state has an associated definite discrete total energy:

$E_n = \dfrac{n^2h^2}{8mD^2}$. These are known as the *energy levels* of the system.

3 The system's *lowest energy is not zero* but equal to $E_1 = \dfrac{h^2}{8mD^2}$.

4 For the stationary states the wavefunctions are complex standing waves, which do not travel and so imply *no particular direction of motion for the associated particle* in the box.

These claims seem outrageous (particularly points 3 and 4), but before we are tempted to abandon this quantum model as being unrealistic, we should reflect on the fact that these discrete energy levels, which are a consequence of the confinement of the particle to a given region of space, are broadly similar what is observed to happen when an electron is confined within a hydrogen atom. Indeed, it was the discrete energy levels and the fixed transitions between them which were an integral part of the Bohr model of hydrogen and which were completely inexplicable using classical physics. Clearly, our one-dimensional box doesn’t look much like a hydrogen atom, but it shows some encouraging features as an atomic model. ☞

Question T8

In the state $n = 1$, as described by Equation 28,

The *total energy*:
$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mD^2} = \frac{n^2 h^2}{8mD^2} \tag{Eqn 28}$$

the kinetic energy is known exactly. Since the motion is one-dimensional this appears to imply, by Equation 14,

kinetic energy:
$$E_{\rm kin} = \frac{mv_x^2}{2} = \frac{(mv_x)^2}{2m} = \frac{p_x^2}{2m} = \frac{\hbar^2 k^2}{2m} \tag{Eqn 14}$$

that the momentum p_x is known exactly. We then appear to have the particle located in x to within $\Delta x = D$ but with the momentum p_x known exactly ($\Delta p_x = 0$). Are we claiming more information than is allowed by the Heisenberg uncertainty principle? Present your argument carefully. ❏

Location of the particle in the one-dimensional box

Now we ask where the particle is most likely to be found within the box. From the general principle given in Equation 7, the probability of finding the particle in the interval between x and $x + \Delta x$ is proportional to $|\,\Psi(x, t)\,|^2\,\Delta x$. Since we are dealing with a stationary state, this is proportional to the square of the spatial part of the wavefunction, $|\,\psi(x)\,|^2\,\Delta x$.

✧ At which places is the particle most likely to be detected, when in its ground state?

To find the actual numerical value of the probability near any point we must first of all *normalize* the wavefunction. This means that we must ensure that the *total* probability of finding the particle *somewhere* in the box is 1 (i.e. certainty). Mathematically, this implies

$$\int_0^D |\,\psi_n(x)|^2\,dx = A_n^2\int_0^D \sin^2\left(\frac{n\pi x}{D}\right)dx = 1 \tag{29}$$

i.e. $$\frac{A_n^2}{2}\int\limits_0^D\left[1-\cos\left(\frac{2n\pi x}{D}\right)\right]dx = \frac{A_n^2}{2}\left[x-\left(\frac{D}{2n\pi}\right)\sin\left(\frac{2n\pi x}{D}\right)\right]_0^D = A_n^2\,\frac{D}{2} = 1$$

so that we must take $A_n = \sqrt{2/D}$ ☞ and the **normalized** spatial wavefunction for the state n is therefore:

normalized spatial wavefunction: $$\psi_n(x) = \sqrt{\frac{2}{D}}\sin\left(\frac{n\pi x}{D}\right) \qquad (30)$$ ☞

where $n = 1, 2, 3, 4, \dots$

Question T9

What is the probability that a particle in the $n = 5$ state will be detected between $x = 0$ and $x = +0.1D$? ❏

4.3 Energy changes or transitions in the one-dimensional box ☞

The quantum model for a particle in a one-dimensional box shows the existence of a set of stationary states of different energy. If the particle in one of these states is unperturbed, it will remain in the state indefinitely, in just the same way that a single standing wave mode on a string will continue with fixed energy indefinitely. If either system is perturbed, for example by gaining or losing energy, then the state of oscillation will change. In the classical case, other wave modes will become excited as the energy changes; in the quantum case, the system may make a **transition** between stationary states as the energy changes.

In Subsection 4.2 we noted that classically, when two standing wave modes are simultaneously operating on a string, the resulting disturbance has a time dependence at the difference frequency of the two modes. Visually, the string shows the presence of a disturbance which oscillates back and forth on the string, at this difference frequency. In the quantum case, the mixing of two stationary states with different characteristic angular frequencies ω_n and ω_m produces a *superposition state* which is no longer a stationary state and in which the probability density consequently depends on time. If we calculate the probability of finding the particle at a given position in the box we find that the probability density oscillates at the *angular beat frequency* $|\,\omega_n - \omega_m\,|$. This corresponds to a real oscillation of the particle between the walls — rather as the classical picture suggested.

Since an electron is a charged particle, any oscillation that it exhibits should, according to classical physics, be accompanied by radiation. The oscillating electron would either be radiating away its energy (emission), or gaining energy (absorption) from an incoming electromagnetic wave. It is natural, therefore, to try to associate the emission and absorption of radiation by an atom with the presence of an electron in a superposition state, mixing two stationary states of the system. At some initial time the system is in one of these two states and at some later time it will be in the other state, having made a *transition* between the two states; in the interim the state is a non-stationary superposition state in which the proportions of the two stationary states are changing with time. The energy change may then be associated with a photon of frequency $f = |\,\omega_n - \omega_m\,|/2\pi$, and so corresponds to energy change

$$\Delta E = hf = h|\,\omega_n - \omega_m\,|/2\pi = |\,E_n - E_m\,|$$ ☞

Question T10

An electron is confined in the one-dimensional box in Figure 7a.

(a) Sketch the spatial wavefunction that describes the electron when its total energy is $E = \dfrac{9h^2}{8m_\text{e}D^2}$.

(b) Where is the electron most likely to be detected when it has this energy?

(c) If the electron makes a transition from this state to the ground state, obtain an expression for the reduction of its energy.

(d) If this energy is given out as a quantum of radiation, what will be the frequency f of its associated radiation? ❑

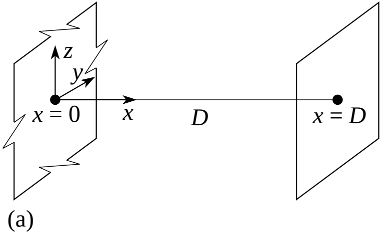


Figure 7a A particle of mass m is moving in the space between two parallel infinite planes, separated by a distance D, measured along the x-axis.

5 A particle confined in two or three dimensions

The quantum treatment of a particle confined in one dimension has shown many encouraging features in relation to explaining the observed behaviour of an atom. The Heisenberg uncertainty principle explains why an atom is stable against collapse into the nucleus and the confined wave model predicts quantized energies of a confined electron and associates transitions between these with the emission or absorption of electromagnetic radiation. Now we need to extend the model to confinement in *three* dimensions.

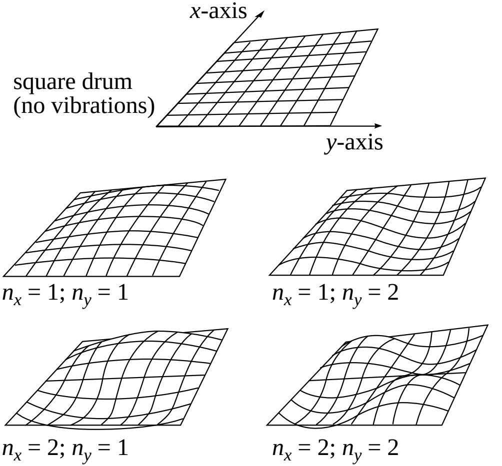
5.1 Extension to two-dimensional confinement

We have seen from Section 4 that when a particle is confined in one dimension it may be found in certain quantum states labelled by a single *quantum number*, the integer n, and described by a wavefunction $\Psi_n(x, t)$. Extending this idea to two dimensions means that the wavefunction must involve *two* spatial coordinates (e.g. x and y) as well as t. As usual, our deliberations will be guided by the classical analogue.

A classical standing wave on a square membrane

Consider a flexible two-dimensional surface, such as a taut square drum membrane stretched over and fixed to a square framework of side D (see Figure 9). Vibrations in this surface may be set up and there will be boundary conditions in both x- and y-directions, such that there can be no vibration along the perimeter of the square.

The displacement must be zero along both the lines $y = 0$ (the x-axis) and $y = D$ for any value of x between 0 and D, and along both the lines $x = 0$ (the y-axis) and $x = D$ for any value of y between 0 and D. These boundary conditions are complicated to write down, but they will affect the possible vibrations of the membrane in a way that is a simple extension of the one-dimensional case.



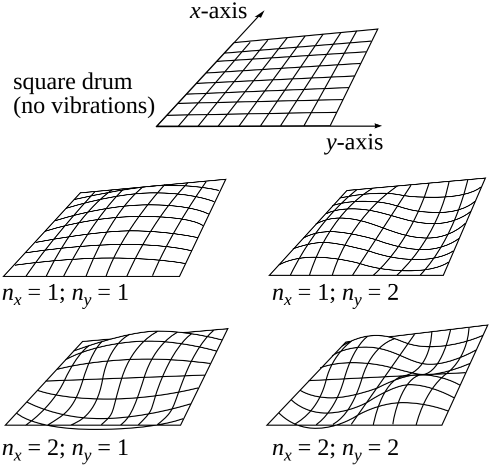
$n_x = 1; n_y = 1$ $n_x = 1; n_y = 2$

$n_x = 2; n_y = 1$ $n_x = 2; n_y = 2$

Figure 9 Four standing waves on a square, two-dimensional membrane. The integers n_x and n_y indicate the number of half wavelengths in the x- and y-directions, respectively.

The standing waves that can be set up will involve an integer number of half wavelengths in *each* of the two *independent* spatial dimensions. Thus there will be two integers that define a particular mode of vibration of the drum, n_x for the x-direction and n_y for the y-direction. This may be most clearly seen by looking at the examples shown in Figure 9.

The integers n_x and n_y simply designate the number of half-wavelengths of the standing wave between the two boundaries along the relevant axis. The oscillations in the two dimensions are *independent* in the sense that any valid value of n_x can be combined with any valid value of n_y to produce a valid wave mode, labelled (n_x, n_y) on the membrane.



$n_x = 1; n_y = 1$

$n_x = 1; n_y = 2$

$n_x = 2; n_y = 1$

$n_x = 2; n_y = 2$

Figure 9 Four standing waves on a square, two-dimensional membrane. The integers n_x and n_y indicate the number of half wavelengths in the x- and y-directions, respectively.

A quantum wavefunction for two-dimensional confinement

We need a two-dimensional box in which to confine our particle. A realization of this might involve using *two pairs* of parallel infinite planes, one pair separated by a distance D along the x-axis and the other pair separated by a distance D along the y-axis. The particle is completely unrestricted in z but is confined in x and y. Because we have not constrained the particle in z (Δz is undefined) we may legitimately claim that $p_z = 0$, or $\Delta p_z = 0$; the particle can then be said to have no motion along z, or to have only motion along x and y. These two motions will be completely independent and each will have an associated kinetic energy, with the total kinetic energy given by the sum of the two independent kinetic energies. ☞

Treating the two contributions to the kinetic energy as being independent will require that we use two independent quantum numbers, n_x and n_y, to describe each stationary state. The energy levels of those states will then be given by an extension of Equation 28:

The *total energy*: $$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mD^2} = \frac{n^2 h^2}{8mD^2} \qquad \text{(Eqn 28)}$$

$$E_{n_x, n_y} = \frac{h^2}{8mD^2}\left(n_x^2 + n_y^2\right) \qquad (31)$$

where $n_x = 1, 2, 3, 4, \ldots$ and $n_y = 1, 2, 3, 4, \ldots$

The corresponding spatial wavefunctions now also require two quantum numbers to label them

$$\psi_{n_x,n_y}(x,y) = A\sin\left(\frac{n_x\pi x}{D}\right)\sin\left(\frac{n_y\pi y}{D}\right) \tag{32}$$

where $n_x = 1, 2, 3, 4, \dots$ and $n_y = 1, 2, 3, 4, \dots$

Compare Equations 31 and 32

$$E_{n_x,n_y} = \frac{h^2}{8mD^2}\left(n_x^2 + n_y^2\right) \qquad \text{(Eqn 31)}$$

with Equations 28 and 27, respectively.

$$\psi_n(x) = A_n\sin(k_n x) = A_n\sin\left(\frac{n\pi x}{D}\right) \qquad n = 1, 2, 3, \qquad \text{(Eqn 27)}$$

The *total energy*: $$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 n^2\pi^2}{2mD^2} = \frac{n^2h^2}{8mD^2} \qquad \text{(Eqn 28)}$$

Equation 32 obviously satisfies the boundary conditions at $x = 0$ and $x = D$ and also at $y = 0$ and $y = D$.

Shared energy levels — degeneracy

Equations 31 and 32

$$E_{n_x,n_y} = \frac{h^2}{8mD^2}\left(n_x^2 + n_y^2\right) \qquad \text{(Eqn 31)}$$

$$\psi_{n_x,n_y}(x,y) = A\sin\left(\frac{n_x\pi x}{D}\right)\sin\left(\frac{n_y\pi y}{D}\right) \qquad \text{(Eqn 32)}$$

also show a feature which did not occur for the one-dimensional case. Since the energy does not depend separately on n_x and n_y but on the special combination $(n_x^2 + n_y^2)$, if we exchange the values of n_x and n_y we leave the energy unchanged. For example, the spatial wavefunctions $\psi_{1,2}$ and $\psi_{2,1}$ will correspond to the same energy level even though they are different functions. When different wavefunctions share the same energy level the wavefunctions are said to be **degenerate** and the system is said to exhibit **degeneracy**. In this case we see that the degeneracy arises as a consequence of the symmetry between the x and y variables. ☞

Table 1 shows the energies, expressed in units of $h^2/(8mD^2)$, for the states ψ_{n_x,n_y} for a range of values of n_x and n_y, you should be able to see several examples of degeneracy.

Degeneracies usually arise in systems with symmetries — here, it is the symmetry between the x- and y-motion. If we were to break the symmetry, for example by allowing the box to have different dimensions in x and y, we would remove the degeneracy, since the energy depends on n_x^2 and n_y^2 *separately* but not on $(n_x^2 + n_y^2)$. Symmetry and symmetry breaking are important considerations in quantum mechanics.

Table 1 Energies, expressed in units of $h^2/(8mD^2)$, for a particle confined in two-dimensions.

	$n_x = 1$	$n_x = 2$	$n_x = 3$	$n_x = 4$
$n_y = 1$	2	5	10	17
$n_y = 2$	5	8	13	20
$n_y = 3$	10	13	18	25
$n_y = 4$	17	20	25	32

5.2 Extension to three-dimensional confinement

The extension to three dimensions — where the complete specification of the wavefunction of the particle requires three spatial coordinates (x, y, z) — is now straightforward. The particle is confined to a cube of side D in which standing waves may be formed, as in Figure 10. The energy levels in this case are:

$$E_{n_x,n_y,n_z} = \frac{h^2}{8mD^2}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{33}$$

where $n_x = 1, 2, 3, 4, \dots$; $n_y = 1, 2, 3, 4, \dots$; $n_z = 1, 2, 3, 4, \dots$

The spatial wavefunctions are:

$$\psi_{n_x,n_y,n_z}(x, y, z) = A\sin\left(\frac{n_x\pi x}{D}\right)\sin\left(\frac{n_y\pi y}{D}\right)\sin\left(\frac{n_z\pi z}{D}\right) \tag{34}$$

where $n_x = 1, 2, 3, 4, \dots$; $n_y = 1, 2, 3, 4, \dots$; $n_z = 1, 2, 3, 4, \dots$

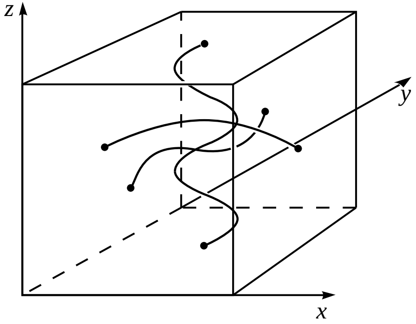


Figure 10 Standing waves confined to a cube in three dimensions.
$n_x = 1$, $n_y = 2$ and $n_z = 4$.

In three dimensions, a far richer range of degeneracies becomes possible. First, we have the symmetry due to the three spatial coordinates; for each set of three quantum numbers there will be six permutations of these three which give the same energy. There are also now a whole range of *accidental* degeneracies, based on the accidental equality of $(n_x^2 + n_y^2 + n_z^2)$ for two or more sets of three quantum numbers. For example, the state $n_x = 8$, $n_y = 6$, $n_z = 5$, has the same energy as the state $n_x = 4$, $n_y = 3$, $n_z = 10$. There are now many cases where several independent wavefunctions share a common energy level; the *number* of such wavefunctions sharing a given energy level is said to be the **order of degeneracy** of the energy level.

Question T11

(a) Write down an expression for the energy of the ground state of a particle confined in three dimensions. Explain whether or not this state is degenerate.

(b) What is the energy of the *first* excited state? Is this state degenerate and, if so, what is its order of degeneracy? ❏

6 Closing items

6.1 Module summary

1 Indications of the particle-like behaviour of electromagnetic radiation, include evidence for the photon as a particle with energy $E = hf$ and momentum $p = E/c = h/\lambda$.

2 Indications of the wave-like behaviour of matter, as predicted by the de Broglie hypothesis ($\lambda_{\rm dB} = h/p$), include a variety of particle diffraction experiments. The *Heisenberg uncertainty principle* states that the simultaneous uncertainties in the position and momentum of a particle obey the restriction

$$\Delta x\,\Delta p_x \gtrsim \frac{h}{2\pi} \qquad \text{(Eqn 6)}$$

3 The quantum mechanical *wavefunction* $\Psi(x,\,t)$, of a particle moving in one dimension is a *complex* quantity found by solving the time-dependent Schrödinger equation. The *probability* of finding the particle within the small interval Δx around the position x at time t being $\propto |\,\Psi(x,\,t)\,|^2\,\Delta x$, where $|\,\Psi(x,\,t)\,|^2$ is the *probability density* at position x.

4 An unlocalized free particle may be represented by a wavefunction of the form

$$\psi_n(x,t) = A\cos(kx - \omega t) + iA\sin(kx - \omega t)$$

this describes a particle for which the total energy $E = \hbar\omega$, the momemtum $p_x = \hbar k$ and the kinetic energy $E_{\rm kin} = \hbar^2 k^2/2m$.

5 The probability density for finding an unlocalized free particle at any value of x is constant and does not depend of x.

6 A localized free particle may be represented by a wavefunction constructed from a superposition of unlocalized free particle wavefunctions. Analysis of the *dispersion relation* for these wavefunctions shows that the superposition has a group speed that is equal to speed of the associated particle.

7 The quantum analogue to the confined wave on a stretched string is the particle confined in a *one-dimensional box*. The wavefunctions for this system consist of a set of *stationary states* for which the probability density is independent of time. The *spatial wavefunctions* of these states must satisfy *boundary conditions* that require them to vanish at the edges of the box. The spatial wavefunctions form a discrete set and are given by

$$\psi_n(x) = A_n \sin\left(\frac{n\pi x}{D}\right) \quad n = 1, 2, 3, \dots \qquad \text{(Eqn 27)}$$

8 These spatial wavefunctions correspond to a restricted range of energy values for the particle. The allowed *energy levels* are

$$E_n = \frac{n^2h^2}{8mD^2} \quad n = 1, 2, 3, \dots$$

where n is known as a *quantum number*. The *ground state* has a non-zero energy, which confirms that quantum mechanics forbids the idea of a confined particle at rest.

9 The stationary states imply no particular direction of motion for the confined particle and have a constant energy. If the system is perturbed and the energy does change, this can be associated with a *transition* between two stationary states. For an electron in a box, such a classical oscillation would be accompanied by the *emission* or *absorption* of electromagnetic radiation. This idea can be extended, in a modified way, to the quantum case.

10 A particle confined in two or three dimensions can be treated similarly, except that two or three independent quantum numbers are needed to specify the states and the energy levels. The energy levels are now:

$$E_{n_x,n_y,n_z} = \frac{h^2}{8mD^2}\left(n_x^2 + n_y^2 + n_z^2\right) \qquad \text{(Eqn 33)}$$

and the stationary state spatial wavefunctions are:

$$\psi_{n_x,n_y,n_z}(x,y,z) = A\sin\left(\frac{n_x\pi x}{D}\right)\sin\left(\frac{n_y\pi y}{D}\right)\sin\left(\frac{n_z\pi z}{D}\right) \qquad \text{(Eqn 34)}$$

The symmetry of the system produces some shared energy levels for several independent wavefunctions, an effect known as *degeneracy*, and some accidental degeneracies also occur.

Study comment As a final cautionary note we must admit that our approach in this module has been *inspirational* rather than rigorous. We have presented plausible arguments, based on analogies with classical wave ideas and have developed self-consistent models which throw some light on the quantum world. However, the classical models on which we have placed such reliance were themselves based on the rigorous solution of a *wave equation*, to which we have given scant reference here. The justification for the wavefunctions presented here also rests on the rigorous solution of an equation, the *Schrödinger equation* — but this must be left to other *FLAP* modules.

6.2 Achievements

Having completed this module, you should be able to:

A1 Define the terms that are emboldened and flagged in the margins of the module.

A2 State and use the relationship between a wavefunction $\Psi(x, t)$ and the probability of detecting the particle to which it relates.

A3 Describe how a free particle may be represented either by a wavefunction consisting of a single complex travelling wave of definite wavelength, or by a wave packet constructed from such travelling waves and explain how these representations conform with the Heisenberg uncertainty principle.

A4 In the representation of a free particle by a single wavelength wavefunction, recall and use expressions for the total energy, the momentum and the kinetic energy of the particle in terms of the angular wavenumber and the wave angular frequency.

A5 Apply the Heisenberg uncertainty principle in simple cases.

A6 Write down the spatial wavefunctions for a particle constrained in a one-dimensional box.

A7 Show that the energy levels for a particle constrained in a one-dimensional box are $E_n = \dfrac{n^2h^2}{8mD^2}$ and use this expression to discuss transitions between quantized energy levels.

A8 Explain what is meant by degeneracy of the energy levels of a particle confined in a two- or three-dimensional box. Determine orders of degeneracy in simple cases.

Study comment You may now wish to take the *Exit test* for this module which tests these Achievements. If you prefer to study the module further before taking this test then return to the *Module contents* to review some of the topics.

6.3 Exit test

Study comment Having completed this module, you should be able to answer the following questions each of which tests one or more of the Achievements.

Question E1

(*A2*) A particle in a stationary state is represented by the spatial wavefunction $\psi(x) = \exp(-3x^2)$.

(a) Is this spatial wavefunction normalized?

[You may use the following standard integral, $\int\limits_{-\infty}^{+\infty} \exp(-ax^2)\,dx = \sqrt{\pi/a}$.]

(b) If it is not, write down a normalized spatial wavefunction that represents the particle in the same state.

(c) What is the probability that the particle will be detected between x and $x + \Delta x$ (for small Δx)?

Question E2

(*A3*, *A4* and *A5*) Explain why a particle represented by a wave packet may not simultaneously have both its position and momentum known to arbitrarily high precision. What is the relationship between Δx and Δp_x, the uncertainties in the measurements of position and momentum, respectively?
(*Hint*: No mathematical derivations are required.)

Question E3

(*A7*) A helium nucleus has a mass of 6.6×10^{-27} kg. What is its minimum energy if it is confined in one dimension within a box of length 7.2 fm? (1 fm = 10^{-15} m) Explain the reasoning involved.

Question E4

(*A4*, *A6* and *A7*) A particle is confined in a one-dimensional box of dimension D.

(a) Write down the spatial wavefunction that is analogous to a standing wave that has five half wavelengths within the box.

(b) What is the momentum of a particle in the stationary state described by this spatial wavefunction?

(c) Show that the energy of the particle is $25h^2/(8mD^2)$ in this case.

Question E5

(*A8*) A particle confined to be within a cube of side D is in a stationary state with a spatial wavefunction:

$$\psi_{n_x,n_y,n_z}(x,y,z) = A\sin\left(\frac{n_x\pi x}{D}\right)\sin\left(\frac{n_y\pi y}{D}\right)\sin\left(\frac{n_z\pi z}{D}\right)$$

and with energy $E_{n_x,n_y,n_z} = \dfrac{h^2}{8mD^2}\left(n_x^2 + n_y^2 + n_z^2\right)$.

(a) What does it mean to say that an energy level is degenerate?

(b) The energy level $7h^2/(4mD^2)$ is degenerate. Determine the order of degeneracy and give expressions for the corresponding wavefunctions.

Study comment This is the final *Exit test* question. When you have completed the *Exit test* go back to Subsection 1.2 and try the *Fast track questions* if you have not already done so.

If you have completed **both** the *Fast track questions* and the *Exit test*, then you have finished the module and may leave it here.