

## Chapter 12

# The Schrödinger Wave Equation

### Topics

*The double-slit experiment. Representing particles by waves. Heisenberg's Uncertainty Principle. Schrödinger's wave equation. Stationary states. Interpretation of the wave-function. One dimensional solutions for a particle in an infinite square potential well. General features of solutions of Schrödinger's wave equation. The correspondence principle.*

This chapter is the centrepiece of our development of quantum mechanics and the 'derivation' of the Schrödinger wave equation. Let us build up the equation, reviewing the clues provided in the previous chapters. We have established that the wave-particle duality works in both directions:

- waves have particle properties, most vividly demonstrated by the *photoelectric effect* and the derivation of the Planck distribution. For photons,

$$E = h\nu = \hbar\omega \quad p = \frac{h\nu}{c} = \frac{\hbar\omega}{c} = \hbar k.$$

- particles have wave properties as illustrated by *electron diffraction* experiments.

$$p = \hbar k = \frac{h}{\lambda}.$$

### 12.1 The Double-slit Experiment

The famous double-slit experiment was first carried out by Thomas Young in Emmanuel College in 1802 – the importance of the experiment was that it demonstrated beyond any reasonable doubt the correctness of the wave theory of light. A pair of narrow slits separated by distance  $d$  is illuminated by a uniform plane wave and the diffracted rays observed on a screen at some distance  $R$  from the slits. A series of light and dark bands is observed, corresponding to constructive and destructive interference between the light rays from the two slits. The geometry of the experiment is shown in Figure 12.1.

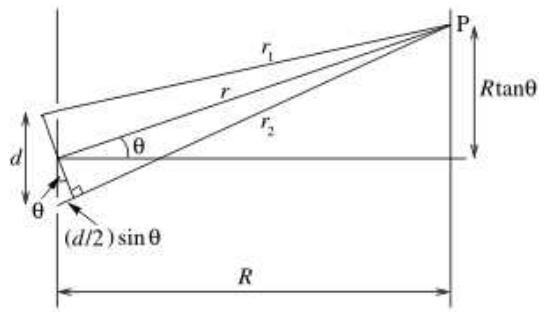


Figure 12.1. The geometry of Young's double-slit experiment.

Let us revise the calculation of the observed intensity, but now using complex wave notation

$$\psi = \Re[A e^{i(kx - \omega t)}] = \Re \{A \exp [i(kx - \omega t)]\} .$$

where  $\Re$  means 'take the real part of'. It will turn out that *this is not just a mathematical convenience*, but rather goes right to the heart of quantum mechanics. *Complex numbers are the natural language of quantum mechanics.*

For convenience, we will drop the explicit use of  $\Re$ . From Figure 12.1, provided  $R \gg d$ , the paths travelled from the two slits to the observation point P are:

$$r_1 \approx r - \frac{d}{2} \sin \theta \quad \text{and} \quad r_2 \approx r + \frac{d}{2} \sin \theta .$$

We use Huyghens' construction according to which we can replace the slits by sources of light which are in phase and have the same amplitude. Therefore, the amplitude of the wave at P is

$$\begin{aligned} \psi &= A \exp [i(kr_1 - \omega t)] + A \exp [i(kr_2 - \omega t)] \\ &\approx A \exp i[k(r - \frac{d}{2} \sin \theta) - \omega t] + A \exp i[k(r + \frac{d}{2} \sin \theta) - \omega t] \\ &= A \exp i(kr - \omega t) \{ \exp [ik(d/2) \sin \theta] + \exp [-ik(d/2) \sin \theta] \} \\ &= 2A \exp i(kr - \omega t) \cos[k(d/2) \sin \theta] . \end{aligned}$$

$$\begin{aligned} \exp(iq) &= \cos(q) + i \sin(q) \\ \exp(-iq) &= \cos(q) - i \sin(q) \end{aligned}$$

The intensity is proportional to the square of the

amplitude and so

$$I \propto 4A^2 \cos^2[k(d/2) \sin \theta] \quad (12.1)$$

(Figure 12.2). For small values of  $\theta$ ,  $\sin \theta \approx \theta$  and so the intensity distribution becomes

$$I \propto 4A^2 \cos^2\left(\frac{k\theta d}{2}\right). \quad (12.2)$$

There is an important piece of mathematics in what we have just done. In the complex representation, the intensity can be found by taking the square of the modulus of the complex function  $\psi$ , that is,

$$I = \psi\psi^* = |\psi|^2,$$

where  $\psi^*$  is the complex conjugate of  $\psi$ . *We do not need to take the real part at all.*

Let us repeat the double-slit experiment using a photon counting detector. In this case, the arrival of each photon on the screen is detected separately. When the light is of high intensity, we observe the usual  $\cos^2(k\theta d/2)$  variation of light intensity on the screen (Figure 12.3(c)). As the light intensity is decreased, we begin to see the pattern ‘shimmering’ as we begin to see the individual photons arriving (Figure 12.3(b)). At the very lowest light intensities, we observe individual photons arriving at the screen (Figure 12.3(a)). The extraordinary thing about this experiment is that the individual particles of light *know where to appear on the screen to produce the standard diffraction pattern*, despite the fact that they only arrive one at a time. To put it another way, the physics of light quanta must be such that there is zero probability that the individual photons will land on the screen at the nulls in the diffraction pattern. It is interesting to quote the words of Richard Feynman about the significance of the double-slit experiment for quantum mechanics.

‘We choose to examine a phenomenon which is impossible, absolutely impossible, to explain in any classical way, and which has in it the heart of quantum mechanics. In reality, it contains the only mystery.’

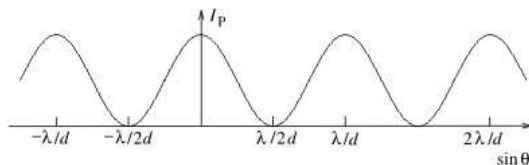


Figure 12.2 Diffraction pattern from double slits.

The experiment with light was first performed by G.I. Taylor in 1909, and the electron diffraction experiment was performed by Jönsson in 1961 using 50 keV electrons and a slit separation of only  $1 \mu\text{m}$ .

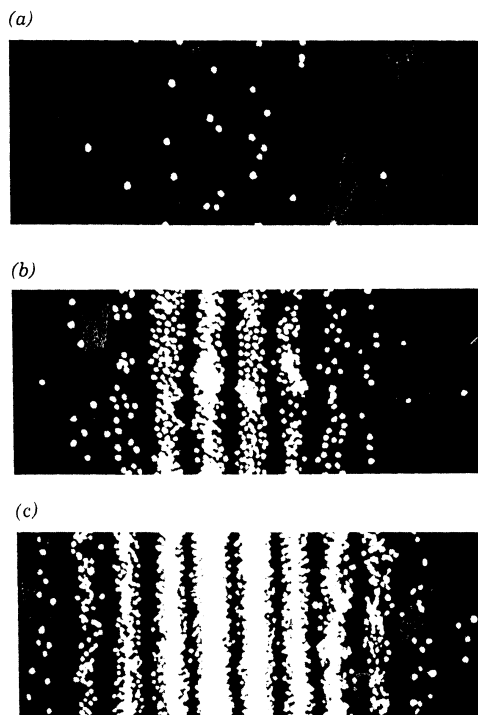


Figure 12.3. Young's double-slit experiment carried out using a photon counting detector.

These results provide the clue as to how we should interpret the  $\cos^2(k\theta d/2)$  intensity distribution. This function describes the *probability* that a single particle arrives at any particular location on the detector. Therefore, the *quantum mechanical wave function*  $\psi(x)$  will be used to describe a particle such as an electron with the property that the *probability of finding the particle in the interval  $x$  to  $x + dx$  is*

$$p(x) dx = |\psi|^2 dx = \psi\psi^* dx, \quad (12.3)$$

which has the form of a probability density function.

This represents a huge change from classical mechanics. According to classical physics we can specify precisely the position and momentum of a particle. This has been replaced by a *probabilistic description* of phenomena at the atomic level. This different perspective is forced upon us as a result of the need to describe particles by waves and *vice versa*. The consequences are very profound as we shall see.

Our next task is to determine the differential equation which determines the wave function  $\psi$  – that will turn out to be the *Schrödinger wave equation*. First, however, let us investigate how we go about representing particles by waves.

## 12.2 The Representation of Particles by Waves

We need a means of localising the particle in space – in other words, of finding a probability density which describes where the particle is located. This is done by developing the idea of a *wave packet* which we construct out of a *superposition of waves*. This leads to a consideration of the properties of *Fourier series* and *Fourier transforms*, which come only late in the mathematics course. We need only one key idea from these topics and that is that we can use sums of sine and cosine functions to represent any function  $f(x)$  within some range  $x_1 \leq x \leq x_2$ . The reason this works is that, mathematically,

### The Wave Function

The wave function is defined so that the probability of finding the particle in the interval  $x$  to  $x + dx$  is

$$p(x) dx = |\psi|^2 dx = \psi\psi^* dx$$

the sequences of sine waves

$$\sin k_0x, \sin 2k_0x, \sin 3k_0x, \dots$$

plus the series of cosine waves

$$\cos k_0x, \cos 2k_0x, \cos 3k_0x, \dots$$

form a *complete, orthogonal set of functions*, meaning that we can synthesise *any* pattern we like by selecting appropriately the constants  $A_0, A_1, A_2, \dots$  and  $B_1, B_2, \dots$  in the series expansion

$$\psi(x) = A_0 + \sum_{n=1}^{\infty} A_n \cos nk_0x + \sum_{n=1}^{\infty} B_n \sin nk_0x. \tag{12.4}$$

This sum is the *Fourier series* for the function  $\psi(x)$  defined in the interval  $x_1 \leq x \leq x_2$ .

These ideas suggest a way in which we can represent particles by waves. As an example, consider building up a gaussian distribution in the  $x$ -direction, which is to represent the probability density distribution of the particle in that coordinate. Suppose the particle has momentum  $p$ , so that, according to the de Broglie hypothesis, the wavelength associated with it is  $\lambda_0 = h/p$ . The corresponding wavevector is

$$k_0 = \frac{2\pi}{\lambda_0} = \frac{2\pi p}{h}. \tag{12.5}$$

The waves associated with  $k_0$  are sine or cosine waves,  $A \sin k_0x$  or  $A \cos k_0x$ , and they are not localised at all – the extend all the way from  $-\infty$  to  $+\infty$  and this is not very helpful.

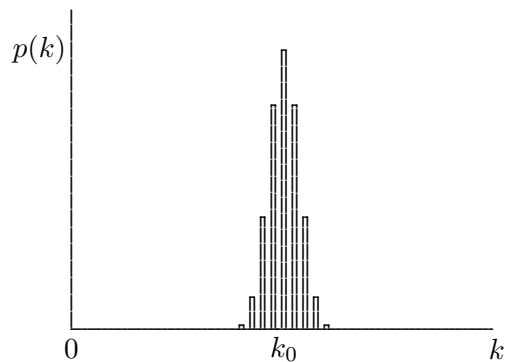
Now, let us start with  $A \cos k_0x$  and add some other cosine waves and, for illustrative purposes, let us add together a binomial sequence of terms, centred on  $k_0$ , but separated from it by  $\pm n \Delta k_0$ , where  $\Delta k_0 \ll k_0$ . Figure 12.4 shows the binomial distribution of amplitudes of cosine waves, which are the coefficients of the expansion of  $(1 + x)^8$ , that is,

$$(1 + x)^8 = 1 + 8x + 28x^2 + 56x^3 + 70x^4 + 56x^5 + 28x^6 + 8x^7 + x^8,$$

where we have chosen  $k_0 = 1$  and  $\Delta k_0 = 0.05$ .

Figure 12.4. The distribution of terms in the Fourier Series with  $\Delta k_0 = 0.05$ .

We are bearing in mind that in the limit of a large number of terms, the binomial series tends to a gaussian distribution.



The result of adding together this series of cosine waves is shown in Figure 12.5 by the oscillating line which has maximum at the origin, but tends rapidly to zero in a finite distance rather than oscillating to infinity. In terms of the units shown on the  $x$ -axis, the wave packet mostly lies between  $\pm 20$  units. Because we chose a binomial distribution of coefficients, the envelope of the wavepacket  $f(x)$  is approximately gaussian. In Figure 12.5, the envelope of the wave packet can be well described by a gaussian distribution of the form

$$f(x) = \exp [-x^2/(20)^2].$$

Thus, by adding together cosine waves with appropriate weightings, we can localise the wave packet.

Now, let us change the spacing of the waves in  $k$ -space from  $\Delta k_0 = 0.05$  to  $\Delta k_0 = 0.1$ . The corresponding pair of diagrams are shown in Figures 12.6 and 12.7. It can be seen that the width of the distribution of  $f(x)$  is shrunk and the envelope is described by

$$f(x) = \exp [-x^2/(10)^2].$$

Thus, the wave is now much better localised, but it is at the expense of a broader distribution of  $\Delta k_0$ .

Let us quantify this relation using the above examples. Let us determine the standard deviations of  $p(k)$  and the envelope  $f(x)$ . For the discrete distribution  $p(k)$ , we write

$$\begin{aligned} \sigma_k^2 &= \frac{1}{256} [1 \times 70 \times 0 \times (\Delta k_0)^2 + 2 \times 56 \times (1 \times \Delta k_0)^2 \\ &\quad + 2 \times 28 \times (2\Delta k_0)^2 + 2 \times 8 \times (3\Delta k_0)^2 \\ &\quad + 2 \times 1 \times (4\Delta k_0)^2] \\ &= 2(\Delta k_0)^2. \end{aligned}$$

Next, we evaluate the standard deviation of  $f(x) = \exp [-x^2/(20)^2]$

$$\begin{aligned} \sigma_x^2 &= \frac{\int_{-\infty}^{\infty} x^2 \exp [-x^2/(20)^2] dx}{\int_{-\infty}^{\infty} \exp [-x^2/(20)^2] dx} \\ &= 20^2/2. \end{aligned}$$

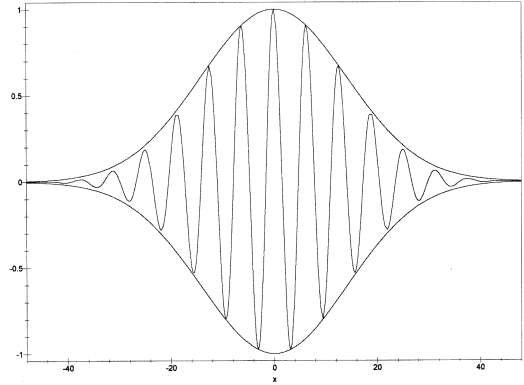
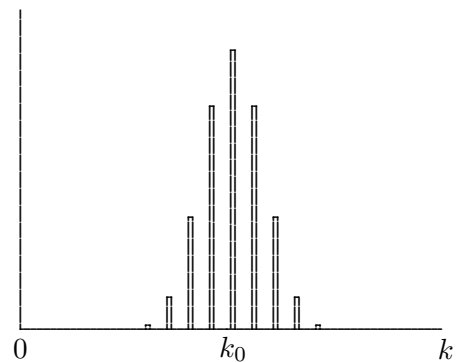


Figure 12.5. The wave packet  $f(x)$  corresponding to the sum of the Fourier components shown in Figure 12.6. The envelope is described by  $f(x) = \exp [-x^2/(20)^2]$ .

Figure 12.6. The distribution of terms in the Fourier Series with  $\Delta k_0 = 0.1$ .



But  $\Delta k_0 = 1/20$  and so we find

$$\sigma_k^2 \times \sigma_x^2 = 1, \quad \sigma_k \times \sigma_x = 1. \quad (12.6)$$

These calculations make it wholly plausible that, if we now represent the packet by a continuous gaussian distribution of wavevectors  $k$ , with some central wavevector  $k_0$  and standard deviation  $\Delta k$ ,

$$A(k) = \exp \left[ -\frac{(k - k_0)^2}{2(\Delta k)^2} \right],$$

the function  $f(x)$  has a Gaussian envelope

$$\exp \left[ -\frac{(x^2)}{2(\Delta x)^2} \right]$$

with standard deviation  $\Delta x$  which is related to the spread in wavenumbers  $\Delta k$  by the relation

$$\Delta x = (\Delta k)^{-1}$$

This envelope is modulated by a cosine (or sine) wave with wavenumber  $k_0$ . This is how we can represent a particle by a superposition of waves.

### 12.3 Heisenberg's Uncertainty Principle

We can now apply the above analysis to the physics of particles according to quantum mechanics. We can identify the classical particle with a *wave-packet* which is localised in space in the sense that it can be represented by a Gaussian function centred on  $x = 0$  with a dispersion, or probability distribution, about that value with standard deviation  $\Delta x$ . This wavepacket, which is modulated by a wave of wavevector  $k_0$ , is composed of a superposition of waves with a Gaussian distribution of amplitudes centred on the value  $k_0$  with a standard deviation about that value of  $\Delta k$ , where  $\Delta k = (\Delta x)^{-1}$ . But, we know from de Broglie's relation that

$$p = \frac{h}{\lambda} = \frac{k h}{2\pi} = k \hbar$$

Therefore  $\Delta p = \hbar \Delta k$  and so we find

$$\Delta p \Delta x = \hbar$$

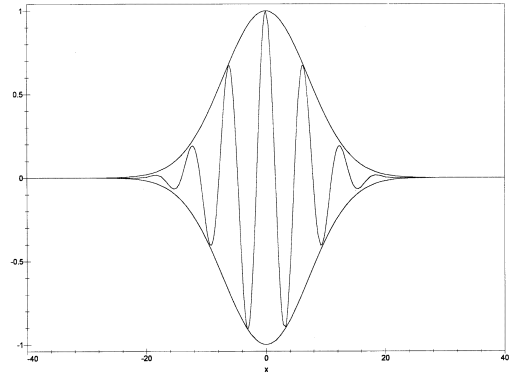


Figure 12.7. The wave packet corresponding to the Fourier components shown in Figure 12.6.

This is an example of *Heisenberg's Uncertainty Principle*. What it tells us is that, if we represent a particle by a superposition of waves, in order to localise it in the region of space  $\Delta x$ , there must inevitably be a range of wavenumbers and hence a limit to the precision with which we can determine its momentum  $\Delta p$ . This is the *fundamental limit* to the precision with which we can know simultaneously both the position and momentum of the particle. It is evident from the relation that, if we determine the position of the particle more precisely, that is, if we reduce  $\Delta x$ , then we require a broader range of wavenumbers  $\Delta k$ , corresponding to a larger range of momenta of the de Broglie waves.

Although we have treated the case of a gaussian wavepacket, which results in a gaussian spread of wave-numbers, the result is generally true for any function  $\psi(x)$ . In general, it can be shown that, for any form of wavepacket, *Heisenberg's Uncertainty Principle* has the form

$$\Delta p \Delta x \geq \frac{\hbar}{2}. \quad (12.7)$$

The consequences of Heisenberg's uncertainty principle are profound. Let us return to the photon or electron version of Young's double-slit experiment. If the light or flux of electrons is of very low intensity, we observe photons or electrons arriving separately and they define precisely the pattern expected from the classical interference experiment. But, then, the question arises, which hole did the individual photons pass through to reach the screen and how did they know where to arrive on the screen?

Part of the answer is that, if we perform any experiment by which we might determine which slit the light went through, we destroy the diffraction pattern and obtain only the interference pattern of each single slit. This is illustrated schematically in the diagrams. In Figure 12.8, we show the expected behaviour when electrons pass through a double slit experiment. If either hole 1 or hole 2 were blocked up, we would observe the diffraction pattern of each single slit  $P_1$  and  $P_2$ . Just as in the case of light

### Heisenberg's Uncertainty Principle

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

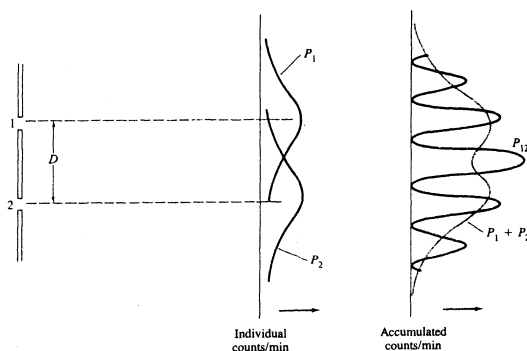


Figure 12.8. Illustrating schematically the interference patterns due to the two slits individually and when they are both open.



when both slits are open, we do *not* see the sum of these two diffraction patterns ( $P_1 + P_2$ ) but rather the characteristic interference pattern  $P_{12}$ .

If we place a light source behind the slits as shown in Figure 12.9, we might hope that, because of the light scattering by the electron, we could determine through which of the slits the electron passed. In fact, if we observe the scattered radiation, we do not obtain the interference pattern  $P_{12}$ . What happens is that, in the process of determining through which slit the electron passed, we have modified the wave function of the electron and so it no longer forms the characteristic interference pattern. A solution to the problem might be to reduce the frequency of the light until it no longer perturbs significantly the wavefunction of the electron. If, however, the frequency of the light is reduced to such a value that the characteristic diffraction pattern  $P_{12}$  reappears, the wavelength of the light is so long that we cannot determine which slit the electron passed through. We cannot determine simultaneously both the exact position and momentum of the electrons or the photons.

There is a much deeper way of thinking about this problem. In the case of both photons and electrons, what is physically important before they are detected on the screen, is the ways in which the *amplitudes* of the wave functions behave for propagation from the source to the screen. That amplitude is the linear sum of the amplitudes associated with all possible routes from the source to that point on the screen. It is only when the particle is detected on the screen that the process of taking the square of its amplitude takes place. Looked at in this way, it is perfectly sensible to state that the particle passed through both slits and that there are perfectly sensible wavefunctions which describe all possible routes to the screen. It is only when we transform from amplitudes to probabilities that we reconstruct the analogue of the classical particle.

Let us apply Heisenberg's Uncertainty Principle to electrons in the Bohr model of the atom. The speed of an electron in the ground state of the hydrogen atom,  $n = 1$ , is  $2.2 \times 10^6 \text{ m s}^{-1}$  and

**Pedantic note** Strictly speaking, in order to observe a diffraction pattern in which the minima of  $P_{12}$  go to zero, the intensities from the two slits should be equal. Figure 12.8 has exaggerated the separation of the paths from holes 1 and 2 for the sake of clarity.

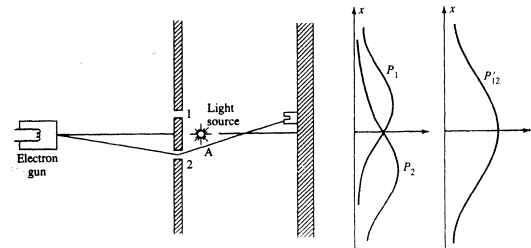


Figure 12.9. Illustrating an attempt to determine through which slit the photon or electron passed in the double slit experiment.

hence its momentum is  $p = m_e v = 2 \times 10^{-24}$  kg m s<sup>-1</sup>. Therefore, setting  $\Delta p \Delta x = \hbar$ , we find  $\Delta x = \hbar / \Delta p = 0.5 \times 10^{-10}$  m. This is just the size of the first Bohr orbit and is no accident. What this calculation is telling us is that, on the scale of atoms, we cannot know precisely where the electron is at any moment — we can only describe very precisely where it is likely to be statistically.

## 12.4 The Schrödinger Wave Equation

The next stage in our development of quantum mechanics is to find an equation for the wave function  $\psi(x, t)$ ; this analysis leads to the *Schrödinger Wave Equation*. Let us consider the general form which such an equation should have.

- The results of the diffraction experiments suggest that for free particles, that is, those not acted on by a force, the solution should be similar to the harmonic waves you have met already as solutions of the classical wave equation:

$$\frac{\partial^2 A(x, t)}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 A(x, t)}{\partial t^2},$$

where  $\omega/k = c$ . This equation is not quite adequate as we shall see below, but the equation we are seeking must be similar.

- De Broglie postulated that the wavevector  $k$  associated with the momentum of a particle should be  $p = \hbar k$ . He further postulated that the relation between the energy of the particle  $E$  and angular frequency  $\omega$  should be similar to that for photons,  $E = \hbar \omega$  (see margin note). Now, for a free particle, the energy is the kinetic energy

$$E = \frac{1}{2} m v^2 = \frac{p^2}{2m},$$

where  $p = mv$ . Therefore,

$$E = \hbar \omega = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}, \quad (12.8)$$

or

$$\omega = \frac{\hbar k^2}{2m}. \quad (12.9)$$

This relationship, known as a *dispersion relation*, must be the solution of our quantum mechanical wave equation for a free particle.

Let us start by postulating that the wave function for a free particle is a sine wave of the form  $\Psi(x, t) = A \sin(kx - \omega t)$ . Taking the second differential of  $\Psi$  with respect to  $x$ , we find an expression in  $\sin(kx - \omega t)$  multiplied by  $k^2$ :

$$\frac{\partial^2 \Psi(x, t)}{\partial x^2} = -Ak^2 \sin(kx - \omega t). \quad (12.10)$$

To obtain a factor containing  $\omega$ , we take the first derivative with respect to  $t$

$$\frac{\partial \Psi(x)}{\partial t} = -\omega A \cos(kx - \omega t). \quad (12.11)$$

This is encouraging, but we are not going to be able to find an equation involving a second derivative with respect to  $x$  and a first derivative with respect to  $t$  if the solution is to be simply a sine wave of the form  $\sin(kx - \omega t)$  since the first derivative turns it into a cosine. There is however a simple way around this difficulty by postulating instead that the solution for a free particle is to be a complex wave of the form:

$$\Psi(x, t) = A \exp[i(kx - \omega t)]. \quad (12.12)$$

Then, taking partial derivatives with respect to  $x$  twice and once with respect to  $t$ , we find

$$\frac{\partial^2 \Psi}{\partial x^2} = -k^2 A e^{i(kx - \omega t)} = -\frac{p^2}{\hbar^2} \Psi, \quad (12.13)$$

$$\frac{\partial \Psi}{\partial t} = -i\omega A e^{i(kx - \omega t)} = -\frac{iE}{\hbar} \Psi. \quad (12.14)$$

From (12.8), we can also write

$$E\Psi = \frac{p^2}{2m} \Psi. \quad (12.15)$$

Therefore, substituting for  $p$  from (12.13) and  $E$  from (12.14), we find the following equations

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = i\hbar \frac{\partial \Psi}{\partial t}, \quad (12.16)$$

$$E\Psi = i\hbar \frac{\partial \Psi}{\partial t}. \quad (12.17)$$

### De Broglie's relation between energy and angular frequency

The expression

$$\omega = \frac{\hbar k^2}{2m}$$

is significantly different from the dispersion relation for light waves,  $\omega = ck$ . The reason de Broglie adopted this relation for a free particle is connected with the requirement that *wave packet* which represents the particle should propagate at the speed  $v$  of the particle. You will find out next year that the speed of any wave packet is given by the *group velocity*,  $v_g = d\omega/dk$ . If we insert the expression (12.9) into this expression, we find

$$v_g = \frac{d\omega}{dk} = \frac{\hbar k}{m} = \frac{p}{m} = v,$$

the speed of the particle.

In fact, we could have run this argument backwards and, by requiring the speed of the particle to be the group velocity of the wavepacket, derive the dispersion relation (12.9) and the expression  $E = \hbar\omega$ .

These are the equations we have been seeking for a free particle. In general, however, we need to consider particles which move in some potential. We can extend the above analysis by considering the total energy of the particle  $E$  to be the sum of its kinetic energy  $T$  and potential energy  $V(x)$ :

$$\begin{aligned} E &= T + V(x) = \frac{p^2}{2m} + V(x) \\ &= \frac{k^2 \hbar^2}{2m} + V(x) \\ k^2 &= \frac{2m}{\hbar^2} [E - V(x)] \end{aligned} \quad (12.18)$$

Therefore, we can substitute for  $k^2$  in (12.13) and find

$$\begin{aligned} \frac{\partial^2 \Psi(x)}{\partial x^2} &= -\frac{2m}{\hbar^2} [E - V(x)] \Psi \\ -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} + V(x) \Psi(x) &= E \Psi(x). \end{aligned} \quad (12.19)$$

If  $E$  and  $V$  do not change with time, then the form of the equation means that we must be able to write the wave function in the form  $\Psi(x, t) = \psi(x) g(t)$ . Substituting this expression into (12.19), we see that the function  $g(t)$  cancels through and we arrive at the final form for the *time-independent Schrödinger wave equation*. Simplifying the notation,

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = E\psi \quad (12.20)$$

where it is understood that  $V$ ,  $E$  and  $\psi$  depend only on  $x$ .

It is best to regard the above ‘derivation’ of the Schrödinger wave equation as a *rationalisation* rather than a *proof*. We can no more ‘prove’ Schrödinger’s wave equation than we can ‘prove’ Newton’s laws of motion. The test of whether or not they are useful is simply how well they can account for experiments and observations. Notice that we have implicitly built the conservation of energy into our rationalisation of the form of the wave equation since  $E$  is the total energy of the system in the non-relativistic sense.

Notice that, in developing the time-independent form of the wave equation, we have dropped the

**The time-independent Schrödinger wave equation**

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

**Note**

We will use capital psi  $\Psi$  for the time dependent wavefunction and lower case  $\psi$  for the time-independent wave function.

time dependence in the equations (12.13) to (12.17). Following a similar analysis to the above, we can find the *time-dependent Schrödinger wave equation* in which the total energy  $E$  and the potential  $V$  vary with time

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x, t) \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}, \quad (12.21)$$

where the function  $\Psi$  depends upon both  $x$  and  $t$ .

The obvious extension to three dimensions is to replace the operator  $\partial^2/\partial x^2$  by the three dimensional operator  $\nabla^2$  and the pair of equations becomes

$$\begin{aligned} -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi &= E\psi \\ -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi &= i\hbar \frac{\partial \Psi}{\partial t} \end{aligned}$$

where  $\psi$ ,  $V$  and  $E$  can depend upon both space and time coordinates.

Notice also that these equations are *non-relativistic* and so they are the quantum equivalents of Newton's laws of motion. Relativistic quantum mechanics takes a little bit more work.

### 12.4.1 Stationary States

When the energy is a constant, we call a solution of the wave equation which satisfies the boundary conditions a *stationary state*. This does not mean that  $\Psi$  has no time dependence as we now demonstrate. We begin with (12.17):

$$E\Psi = i\hbar \frac{\partial \Psi}{\partial t}.$$

We have already noted that when  $E$  is constant we can write  $\Psi(x, t) = \psi(x)g(t)$  and so

$$E\psi(x)g(t) = i\hbar \frac{\partial[\psi(x)g(t)]}{\partial t} = i\hbar\psi(x) \frac{\partial g(t)}{\partial t}.$$

$\psi(x)$  cancels out and we obtain a simple first order equation for  $g(t)$

$$Eg(t) = i\hbar \frac{\partial g(t)}{\partial t}$$

#### The time-dependent Schrödinger wave equation

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x, t) \Psi(x, t) \\ = i\hbar \frac{\partial \Psi(x, t)}{\partial t}. \end{aligned}$$

#### The $\nabla$ operator

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

which has solution

$$g(t) = e^{-i\omega t},$$

where  $\omega = E/\hbar$ .

Hence for stationary states of the system, the wave function has the form

$$\Psi(x, t) = \psi(x) e^{-i\omega t} \quad (12.22)$$

and  $\psi$  satisfies the time independent equation. These solutions are *stationary* in that the probability distribution is independent of time since

$$\Psi\Psi^* = \psi e^{-i\omega t} \psi^* e^{i\omega t} = \psi\psi^*. \quad (12.23)$$

## 12.5 The Interpretation of the Schrödinger Wave Equation

We started this argument by introducing the wave function so that the modulus squared of the wave function,  $|\psi|^2 = \psi\psi^*$ , is the *probability density* of finding the particle in the interval  $x$  to  $x + dx$ . In the three-dimensional case it becomes the probability of finding the particle in a given element of volume. The total probability of the particle being found anywhere in space must be unity and so the wave-function has to be *normalised* so that

$$\int_{-\infty}^{\infty} \psi(x)\psi^*(x) dx = 1 \quad (12.24)$$

The wave function  $\psi$  must also satisfy the boundary conditions of the problem as well as being a continuous function, *both in  $\psi$  and in  $\partial\psi/\partial x$* . We will return to these important points in the next chapter.

These requirements on the properties of the wave functions provide very stringent restrictions upon possible forms for the wavefunction  $\psi$ . If we inspect the wave equation again

$$\begin{aligned} -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi &= E\psi \\ \left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\psi &= E\psi \end{aligned}$$

### The stationary states of a system

The wavefunction can be written

$$\Psi(x, t) = \psi(x) e^{-i\omega t},$$

where  $\omega = E/\hbar$  and  $\psi$  satisfies the time independent equation.

we see that, on the left-hand side, there is a second-order *differential operator* acting on the wavefunction  $\psi$ . Once we are given the potential energy function  $V(x)$ , the problem reduces to what is known as an *eigenvalue equation* in which it is only possible to find solutions for  $\psi(x)$  for certain discrete values of the energy  $E$ , which are known as the *energy eigenvalues*. This process is similar to that which we followed when we worked out the modes of oscillation of electromagnetic waves in a box — only certain modes of oscillation were allowed, consistent with the boundary conditions. As an example, let us consider a particle moving in an infinitely deep one-dimensional potential well.

## 12.6 A Particle in an Infinite Square Potential Well

This is the simplest example of a confined particle in quantum mechanics, and the solution is closely related to the standing waves you have already met. This example illustrates many of the procedures which are necessary in much more complicated solutions of the wave equation.

In this example, the potential in which the particle finds itself is

$$V(x) = 0 \quad 0 \leq x \leq L ; \quad V(x) = \infty \quad x < 0, x > L$$

(Figure 12.10). The particle can never escape from the well and so, in the regions  $x < 0$  and  $x > L$ ,  $\psi(x) = 0$ . Inside the box,  $V(x) = 0$  and so Schrödinger's time-independent wave equation becomes

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} = E\psi(x).$$

This is simply the equation of simple harmonic motion and the general solution has the form

$$\psi(x) = A \sin kx + B \cos kx \quad \text{with} \quad k^2 = \frac{2mE}{\hbar^2}.$$

We need to find the constants  $A$  and  $B$  which satisfy the boundary conditions. The wavefunction  $\psi$  has to be zero at  $x = 0$  and  $x = L$  and therefore

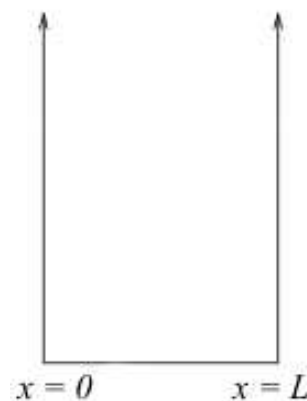


Figure 12.10. An infinitely deep square potential well.

$B = 0$  and  $A \sin kL = 0$ . The boundary conditions, therefore, restrict the possible values of  $k$  to

$$kL = n\pi \quad \text{where } n = 1, 2, 3, \dots$$

Therefore, since  $k^2 = (2mE/\hbar^2)$ , the energy eigenvalues, or the energies of the stationary states, are

$$E = \frac{\hbar^2 k^2}{2m} = n^2 \frac{\hbar^2 \pi^2}{2mL^2} \quad \text{where } n = 1, 2, 3, \dots$$

Thus, the energy levels are *quantised*. The mathematics is exactly the same as that of standing waves between two fixed walls.

Next, we have to *normalise* the wave function so that  $\int \psi^2(x) dx = 1$ . Thus,

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

Changing variable to  $y = 2n\pi x/L$ ,  $dy = (2n\pi/L) dx$ , we find

$$\begin{aligned} A^2 \frac{L}{4n\pi} \int_0^{2n\pi} (1 - \cos y) dy &= 1 \\ A^2 \frac{L}{4n\pi} \times 2n\pi &= 1, \quad A = \sqrt{\frac{2}{L}} \end{aligned}$$

Therefore, the wavefunctions for the stationary states of the particle in the infinite square potential well are

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad (12.25)$$

These wave functions  $\psi_n(x)$  and the corresponding probability distributions  $|\psi_n(x)|^2$  are shown in Figure 12.11. The wave functions are shown by the solid curves, and the shaded region gives the *probability density* for each level.

Thus, suppose we place an electron in such a potential well in the ground state energy  $E_0$  corresponding to  $n = 1$ . Then, when we measure the position of the electron, it is most likely to be found near the centre of the well, at  $x \approx L/2$ . If the electron

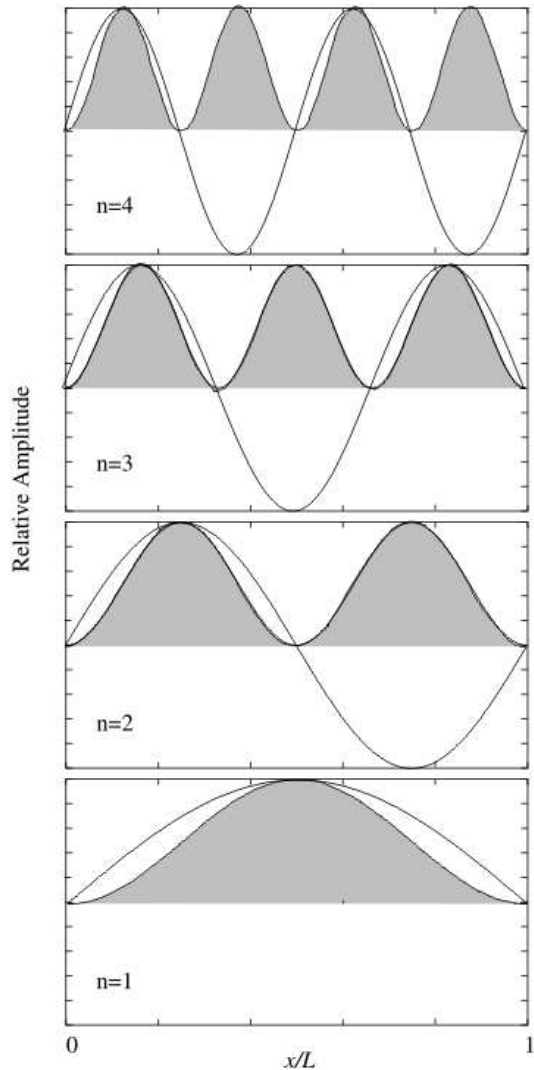


Figure 12.11. Wavefunction  $\psi(x)$  (solid line) and probability distribution  $|\psi(x)|^2$  (shaded) for  $n = 1, 2, 3$  and  $4$ .



is in the  $n = 2$  state with energy  $E = 4E_0$ , there is zero probability of the electron being found at exactly  $x = L/2$ . This arises because of the wave properties of the particle and is quite unlike the expectations of classical physics.

There are a number of important deductions we can make from this example which are generally applicable.

- The energy is clearly quantised. This quantisation comes from the fact that the particle is confined. Physically we see that the confinement limits the possible wavelengths of the wave function giving discrete admissible values for the wavevector  $k_n$ . The quantisation of the energy follows since  $E = (\hbar^2 k^2 / 2m) + V$  in this case.
- As  $n$  increases the number of zeros of the wave function increases. Between the boundaries, the ground state  $n = 0$  has no zeros, the  $n = 1$  state one zero and so on. This is a general result – the greater the energy of state the more zeros there are. Physically, this again follows from considering how  $k_n$  changes with  $n$ . The higher quantum states have larger values of  $k_n$  and so have shorter wavelengths and more zeros within the bounds of the potential well.
- The lowest energy state, the ground state  $n = 1$ , does not have zero energy. We say that the system has a *zero point energy* which in this case is  $(\hbar^2 \pi^2) / (2mL^2)$ . This is very different from the classical case in which a stationary particle in the potential well can have zero kinetic energy. Physically the zero point energy is unavoidable for a confined particle. The particle must be somewhere between the two walls and  $\psi$  must be zero *at* the walls. Therefore  $\psi$  must change and  $\partial^2 \psi / \partial x^2$  cannot be zero everywhere. This means that the particle must have some kinetic energy even in the ground state.
- We need to check that the solution satisfies Heisenberg's uncertainty principle. We start

by calculating the uncertainty in the particle's position:

$$\langle(\Delta x)^2\rangle = \int_0^L (x - \bar{x})^2 \psi^2 dx. \quad (12.26)$$

From symmetry,  $\bar{x} = L/2$  and, inserting the wavefunction (12.25), we can perform the integral to give:

$$\langle(\Delta x)^2\rangle = \frac{L^2}{12} \left(1 - \frac{6}{n^2\pi^2}\right) \quad (12.27)$$

What about the uncertainty in  $p$ ? Naively we might think that, since  $p = \hbar k$  and  $k$  is given by  $kL = n\pi$ ,  $\Delta p = 0$ . This argument is not correct since the wave function in this case is a standing wave which is the superposition of two travelling waves with  $p = \pm\hbar k$ . We can think of the momentum distribution as two delta-function centred on zero. Therefore the mean is zero and  $\langle(\Delta p)^2\rangle = \frac{1}{2}(\hbar^2 k^2 + \hbar^2 k^2)$ . Therefore  $\Delta p = \hbar k$ . This satisfies the uncertainty principle in its accurate form,  $\Delta p \Delta x \geq \hbar/2$ . We find, for any value of  $n$ ,  $\Delta p \Delta x \geq \hbar/2$ .

- Consider what happens when  $n$  becomes very large. The wavelength of the standing wave becomes very small,  $\lambda = 2L/n$  and the wavefunction oscillates ever more rapidly in space (Figure 12.12). For very large  $n$ , the probability of finding the particle approaches ever more closely to a uniform distribution, albeit with very fast oscillations. A uniform distribution is exactly what is expected for a particle classically. Thus, for large  $n$  we approach the classical limit. As in Section 9.2, for a uniform distribution,  $p(x) dx = dx/L$  and so

$$\langle(\Delta x_c)^2\rangle = \int_0^L (x - \bar{x})^2 \frac{1}{L} dx.$$

$\bar{x} = L/2$  and so we find  $\langle(\Delta x_c)^2\rangle = L^2/12$ . The quantum result (12.27) tends to this result in the limit of large  $n$ . This is an example of what is known as the *correspondence principle*, according to which quantum physics approaches classical physics for large quantum numbers.

The integral (12.26) is good practice in integration by parts. Try it if you have time.

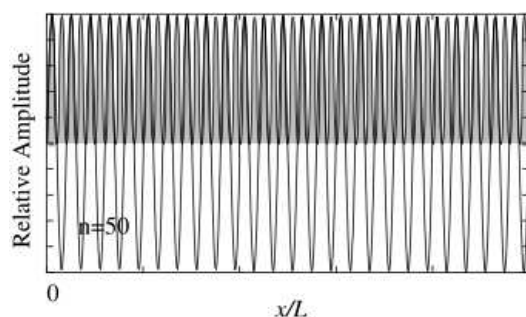


Figure 12.12. Wavefunction (solid line) and probability distribution (shaded) for  $n = 50$ ; for large  $n$  the distribution is approaching the classical result.