

# Chapter 5

## Wave Mechanics

The version of quantum mechanics based on studying the properties of the wave function is known as wave mechanics, and is the version that first found favour amongst early researchers in the quantum theory, in part because it involved setting up and solving a partial differential equation for the wave function, the famous Schrödinger equation, which was of a well-known and much studied form. As well as working in familiar mathematical territory, physicists and chemists were also working with something concrete in what was in other ways a very abstract theory – the wave function was apparently a wave in space which could be visualized, at least to a certain extent. But it must be borne in mind that the wave function is not an objectively real entity, the wave function does not represent waves occurring in some material substance. Furthermore, it turns out that the wave function is no more than one aspect of a more general theory, quantum theory, that is convenient for certain classes of problems, and entirely inappropriate (or indeed inapplicable) to others<sup>1</sup>. Nevertheless, wave mechanics offers a fairly direct route to some of the more important features of quantum mechanics, and for that reason, some attention is given here to some aspects of wave mechanics prior to moving on, in later chapters, to considering the more general theory.

### 5.1 The Probability Interpretation of the Wave Function

The probability interpretation of the wave function was introduced in the preceding Chapter. It is restated here for convenience: if a particle is described by a wave function  $\psi(x, t)$ , then

$$|\Psi(x, t)|^2 \delta x = \text{Probability of observing the particle in the region } (x, x + \delta x) \text{ at time } t.$$

---

<sup>1</sup>The wave function appears to be a wave in real space for a single particle, but that is only because it depends on  $x$  and  $t$ , in the same way as, say, the amplitude of a wave on a string can be written as a function of  $x$  and  $t$ . But, for a system of more than one particle, the wave function becomes a function of two space variables  $x_1$  and  $x_2$  say, as well as  $t$ :  $\Psi(x_1, x_2, t)$ . It then makes no sense to talk about the value of the wave function at some position in space. In fact, the wave function is a wave that ‘exists’ in an abstract space known as phase space.

Some obvious results follow immediately from this statement, one of the first being the requirement that the wave function be *normalized to unity* for all time:

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1. \quad (5.1)$$

This condition on the wave function follows directly from the fact that the particle must be somewhere, so the total probability of finding it anywhere in space must add up to unity.

An immediate consequence of this condition is that the wave function must vanish as  $x \rightarrow \pm\infty$  otherwise the integral will have no hope of being finite. This condition on the wave function is found to lead to one of the most important results of quantum mechanics, namely that the energy of the particle (and other observable quantities as well) is *quantized*, that is to say, it can only have certain discrete values in circumstances in which, classically, the energy can have any value.

We can note at this stage that the wave function that we have been mostly dealing with, the wave function of a free particle of given energy and momentum

$$\Psi(x, t) = A \sin(kx - \omega t), \quad A \cos(kx - \omega t), \quad Ae^{i(kx - \omega t)}, \quad \dots, \quad (5.2)$$

does not satisfy the normalization condition Eq. (5.1) – the integral of  $|\Psi(x, t)|^2$  is infinite. Thus it already appears that there is an inconsistency in what we have been doing. However, there is a place for such wave functions in the greater scheme of things, though this is an issue that cannot be considered here. It is sufficient to interpret this wave function as saying that because it has the same amplitude everywhere in space, the particle is equally likely to be found anywhere.

Finally we note that provided the wave function is normalized to unity, the probability of finding the particle over a finite region of space, say  $a < x < b$ , will be given by

$$\int_a^b |\Psi(x, t)|^2 dx. \quad (5.3)$$

## 5.2 Expectation Values and Uncertainties

Since  $|\Psi(x, t)|^2$  is a normalized probability density for the particle to be found in some region in space, it can be used to calculate various statistical properties of the position of the particle. In defining these quantities, we must make use of the notion of an ‘ensemble of identically prepared systems’. By this we mean that we imagine that we set up an experimental apparatus and use it to prepare an extremely large number  $N$  of particles all in the same state. We then propose to measure the position of each particle at some time  $t$  after the start of the preparation procedure. Presumably, because each particle has gone through exactly the same preparation, they will all be in the same state at time  $t$ , as given by the wave function  $\Psi(x, t)$ . The collection of particles is known as an ensemble, and it is common practice (and a point of contention) in quantum mechanics to refer to the wave function as the wave function of the ensemble, rather than the wave function of each individual particle. We will however frequently refer to the wave function as if

it is associated with a single particle, in part because this reflects the development of the point-of-view that the wave function represents the information that we have about a given particle (or system, in general).

So suppose we have this ensemble of particles all in the state  $\Psi(x, t)$ , and we measure the position of each particle at time  $t$ . In general, we will get a scatter of results, with a probability distribution given by  $P(x, t) = |\Psi(x, t)|^2$ . Suppose we divide the range of  $x$  values into regions of width  $\delta x$ , and measure the number of particles for which the value of  $x$  lies in the range  $(x, x + \delta x)$ ,  $\delta N(x)$  say. The fraction of particles that are observed to lie in this range will then be

$$\frac{\delta N(x)}{N} \approx P(x, t)\delta x \quad (5.4)$$

where the approximate equality will become more exact as the number of particles becomes larger. We can then calculate the average value of all these results in the usual way, i.e.

$$\langle x(t) \rangle = \sum_{\text{All } \delta x} x \frac{\delta N(x)}{N} \approx \sum_{\text{All } \delta x} x P(x, t)\delta x. \quad (5.5)$$

In the limit in which the number of particles becomes infinitely large, and as  $\delta x \rightarrow 0$ , this becomes an integral:

$$\langle x(t) \rangle = \int_{-\infty}^{+\infty} x P(x, t) dx = \int_{-\infty}^{+\infty} x |\Psi(x, t)|^2 dx \quad (5.6)$$

i.e. this is the average value of, in effect, an infinite number of measurements of the position of the particles all prepared in the same state described by the wave function  $\Psi(x, t)$ . It is usually referred to as the expectation value of  $x$ . Similarly, expectation values of functions of  $x$  can be derived. For  $f(x)$ , we have

$$\langle f(x) \rangle = \int_{-\infty}^{+\infty} f(x) |\Psi(x, t)|^2 dx. \quad (5.7)$$

In particular, we have

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 |\Psi(x, t)|^2 dx. \quad (5.8)$$

We can now define the uncertainty in the position of the particle by the usual statistical quantity, the standard deviation  $(\Delta x)^2$ , given by

$$(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2. \quad (5.9)$$

In order to illustrate the sort of results that can be obtained from the wave function, we will consider a particularly simple example about which much can be said, even with the limited understanding that we have at this stage. The model is that of a particle in an infinitely deep potential well.

### 5.3 Particle in an Infinite Potential Well

Suppose we have a single particle of mass  $m$  confined to within a region  $0 < x < L$  with potential energy  $V = 0$  bounded by infinitely high potential barriers, i.e.  $V = \infty$  for  $x < 0$

and  $x > L$ . This simple model is sufficient to describe (in one dimension), for instance, the properties of the conduction electrons in a metal (in the so-called free electron model), or the properties of gas particles in an ideal gas where the particles do not interact with each other. We want to learn as much about the properties of the particle using what we have learned about the wave function above.

The first point to note is that, because of the infinitely high barriers, the particle cannot be found in the regions  $x > L$  and  $x < 0$ . Consequently, the wave function has to be zero in these regions. If we make the not unreasonable assumption that the wave function has to be continuous, then we must conclude that

$$\Psi(0, t) = \Psi(L, t) = 0. \quad (5.10)$$

These conditions on  $\Psi(x, t)$  are known as boundary conditions. Between the barriers, the energy of the particle is purely kinetic. Suppose the energy of the particle is  $E$ , so that

$$E = \frac{p^2}{2m}. \quad (5.11)$$

Using the de Broglie relation  $E = \hbar k$  we then have that

$$k = \pm \frac{\sqrt{2mE}}{\hbar} \quad (5.12)$$

while, from  $E = \hbar\omega$  we have

$$\omega = E/\hbar. \quad (5.13)$$

In the region  $0 < x < L$  the particle is free, so the wave function must be of the form Eq. (5.2), or perhaps a combination of such wave functions, in the manner that gave us the wave packets in Section 3.2. In deciding on the possible form for the wave function, we are restricted by two requirements. First, the boundary conditions Eq. (5.10) must be satisfied and secondly, we note that the wave function must be normalized to unity, Eq. (5.1). The first of these conditions immediately implies that the wave function cannot be simply  $A \sin(kx - \omega t)$ ,  $A \cos(kx - \omega t)$ , or  $Ae^{i(kx - \omega t)}$  or so on, as none of these will be zero at  $x = 0$  and  $x = L$  for all time. The next step is therefore to try a combination of these wave functions. In doing so we note two things: first, from Eq. (5.12) we see there are two possible values for  $k$ , and further we note that any sin or cos function can be written as a sum of complex exponentials:

$$\cos \theta = \frac{e^{i\theta} + e^{-i\theta}}{2} \quad \sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}$$

which suggests that we can try combining the lot together and see if the two conditions above pick out the combination that works. Thus, we will try

$$\Psi(x, t) = Ae^{i(kx - \omega t)} + Be^{-i(kx - \omega t)} + Ce^{i(kx + \omega t)} + De^{-i(kx + \omega t)} \quad (5.14)$$

where  $A$ ,  $B$ ,  $C$ , and  $D$  are coefficients that we wish to determine from the boundary conditions and from the requirement that the wave function be normalized to unity for all time.

First, consider the boundary condition at  $x = 0$ . Here, we must have

$$\begin{aligned} \Psi(0, t) &= Ae^{-i\omega t} + Be^{i\omega t} + Ce^{i\omega t} + De^{-i\omega t} \\ &= (A + D)e^{-i\omega t} + (B + C)e^{i\omega t} \\ &= 0. \end{aligned} \quad (5.15)$$

This must hold true for all time, which can only be the case if  $A + D = 0$  and  $B + C = 0$ . Thus we conclude that we must have

$$\begin{aligned}\Psi(x, t) &= Ae^{i(kx-\omega t)} + Be^{-i(kx-\omega t)} - Be^{i(kx+\omega t)} - Ae^{-i(kx+\omega t)} \\ &= A(e^{ikx} - e^{-ikx})e^{-i\omega t} - B(e^{ikx} - e^{-ikx})e^{i\omega t} \\ &= 2i \sin(kx)(Ae^{-i\omega t} - Be^{i\omega t}).\end{aligned}\quad (5.16)$$

Now check for normalization:

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 4|Ae^{-i\omega t} - Be^{i\omega t}|^2 \int_0^L \sin^2(kx) dx \quad (5.17)$$

where we note that the limits on the integral are  $(0, L)$  since the wave function is zero outside that range.

This integral must be equal to unity for all time. But, since

$$\begin{aligned}|Ae^{-i\omega t} - Be^{i\omega t}|^2 &= (Ae^{-i\omega t} - Be^{i\omega t})(A^*e^{i\omega t} - B^*e^{-i\omega t}) \\ &= AA^* + BB^* - AB^*e^{-2i\omega t} - A^*Be^{2i\omega t}\end{aligned}\quad (5.18)$$

what we have instead is a time dependent result, unless we have either  $A = 0$  or  $B = 0$ . It turns out that either choice can be made – we will make the conventional choice and put  $B = 0$  to give

$$\Psi(x, t) = 2iA \sin(kx)e^{-i\omega t}. \quad (5.19)$$

We can now check on the other boundary condition, i.e. that  $\Psi(L, t) = 0$ , which leads to:

$$\sin(kL) = 0 \quad (5.20)$$

and hence

$$kL = n\pi \quad n \text{ an integer} \quad (5.21)$$

which implies that  $k$  can have only a restricted set of values given by

$$k_n = \frac{n\pi}{L}. \quad (5.22)$$

An immediate consequence of this is that the energy of the particle is limited to the values

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\pi^2 n^2 \hbar^2}{2mL^2} = \hbar\omega_n \quad (5.23)$$

i.e. the energy is ‘quantized’.

Using these values of  $k$  in the normalization condition leads to

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 4|A|^2 \int_0^L \sin^2(k_n x) dx = 2|A|^2 L \quad (5.24)$$

so that by making the choice

$$A = \sqrt{\frac{1}{2L}} e^{i\phi} \quad (5.25)$$

where  $\phi$  is an unknown phase factor, we ensure that the wave function is indeed normalized to unity. Nothing we have seen above can give us a value for  $\phi$ , but whatever choice

is made, it always found to cancel out in any calculation of a physically observable result, so its value can be set to suit our convenience. Here, we will choose  $\phi = -\pi/2$  and hence

$$A = -i\sqrt{\frac{1}{2L}}. \quad (5.26)$$

The wave function therefore becomes

$$\begin{aligned} \Psi_n(x, t) &= \sqrt{\frac{2}{L}} \sin(n\pi x/L) e^{-i\omega_n t} & 0 < x < L \\ &= 0 & x < 0, \quad x > L. \end{aligned} \quad (5.27)$$

with associated energies

$$E_n = \frac{\pi^2 n^2 \hbar^2}{2mL^2} \quad n = 1, 2, 3, \dots \quad (5.28)$$

where the wave function and the energies has been labelled by the quantity  $n$ , known as a quantum number. It can have the values  $n = 1, 2, 3, \dots$ , i.e.  $n = 0$  is excluded, for then the wave function vanishes everywhere, and also excluded are the negative integers since they yield the same set of wave functions, and the same energies.

We see that the particle can only have the energies  $E_n$ , and in particular, the lowest energy,  $E_1$  is greater than zero, as is required by the uncertainty principle. Thus the energy of the particle is quantized, in contrast to the classical situation in which the particle can have any energy  $\geq 0$ .

### 5.3.1 Some Properties of Infinite Well Wave Functions

The wave functions derived above define the probability distributions for finding the particle of a given energy in some region in space. But the wave functions also possess other important properties, some of them of a purely mathematical nature that prove to be extremely important in further development of the theory, but also providing other information about the physical properties of the particle.

#### Energy Eigenvalues and Eigenfunctions

The above wave functions can be written in the form

$$\Psi_n(x, t) = \psi_n(x) e^{-iE_n t/\hbar} \quad (5.29)$$

where we note the time dependence factors out of the overall wave function as a complex exponential of the form  $\exp[-iE_n t/\hbar]$ . As will be seen later, the time dependence of the wave function for any system in a state of given energy is always of this form. The energy of the particle is limited to the values specified in Eq. (5.28). This phenomenon of energy quantization is to be found in all systems in which a particle is confined by an attractive potential such as the Coulomb potential binding an electron to a proton in the hydrogen atom, or the attractive potential of a simple harmonic oscillator. In all cases, the boundary condition that the wave function vanish at infinity guarantees that only a discrete set of

wave functions are possible, and each is associated with a certain energy – hence the energy levels of the hydrogen atom, for instance.

The remaining factor  $\psi_n(x)$  contains all the spatial dependence of the wave function. We also note a ‘pairing’ of the wave function  $\psi_n(x)$  with the allowed energy  $E_n$ . The wave function  $\psi_n(x)$  is known as an energy eigenfunction and the associated energy is known as the energy eigenvalue. This terminology has its origins in the more general formulation of quantum mechanics in terms of state vectors and operators that we will be considering in later Chapters.

### Probability Distributions

The probability distributions corresponding to the wave functions obtained above are

$$\begin{aligned}
 P_n(x) &= |\Psi(x, t)|^2 = \frac{2}{L} \sin^2(n\pi x/L) & 0 < x < L \\
 &= 0 & x < 0, \quad x > L
 \end{aligned}
 \tag{5.30}$$

which are all independent of time, i.e. these are analogous to the stationary states of the hydrogen atom introduced by Bohr – states whose properties do not change in time. The nomenclature stationary state is retained in modern quantum mechanics for such states. We can plot  $P_n(x)$  as a function of  $x$  for various values of  $n$  to see what we can learn about the properties of the particle in the well (see Fig. (5.1)). We note that  $P_n$  is not uniform across the well. In fact, there are regions where it is very unlikely to observe the particle, whereas elsewhere the chances are maximized. If  $n$  becomes very large (see Fig. (5.1)(d)), the probability oscillates very rapidly, averaging out to be  $1/L$ , so that the particle is equally likely to be found anywhere in the well. This is what would be found classically if the particle were simply bouncing back and forth between the walls of the well, and observations were made at random times, i.e. the chances of finding the particle in a region of size  $\delta x$  will be  $\delta x/L$ .

The expectation value of the position of the particle can be calculated directly from the above expressions for the probability distributions, using the general result Eq. (5.7). The integral is straightforward, and gives

$$\langle x \rangle = \frac{2}{L} \int_0^L x \sin^2(n\pi x/L) = \frac{1}{2}L
 \tag{5.31}$$

i.e. the expectation value is in the middle of the well. Note that this does not necessarily correspond to where the probability is a maximum. In fact, for, say  $n = 2$ , the particle is most likely to be found in the vicinity of  $x = L/4$  and  $x = 3L/4$ .

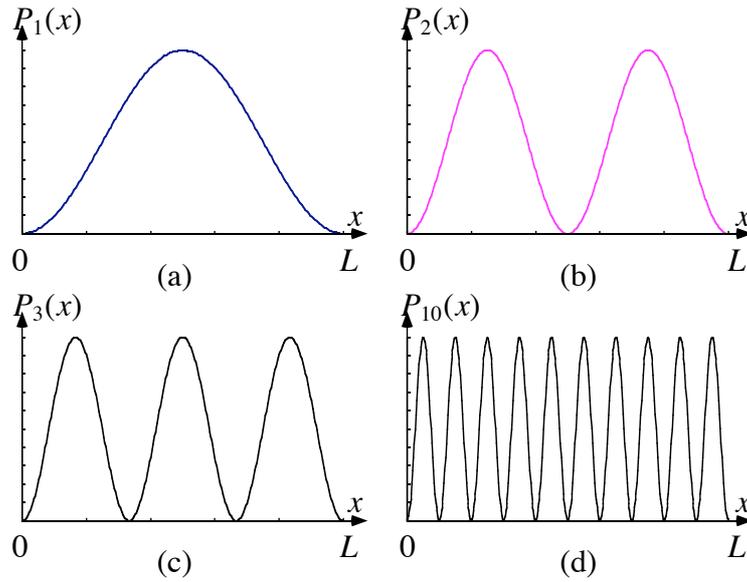


Figure 5.1: Plots of the probability distributions  $P_n(x)$  for a particle in an infinite potential well of width  $L$  for (a)  $n = 1$ , (b)  $n = 2$ , (c)  $n = 3$  and (d)  $n = 10$ . The rapid oscillations on (d) imply that the probability averages out to be constant across the width of the well.

From the wave functions  $\Psi_n(x, t)$ , using the definition Eq. (5.7) to calculate  $\langle x^2 \rangle$  and  $\langle x \rangle$ , it is also possible to calculate the uncertainty in the position of the particle. Since the probability distributions  $P_n(x)$  is symmetric about  $x = L/2$ , it is to be expected that  $\langle x \rangle = L/2$ . This can be readily confirmed by calculating the integral

$$\langle x \rangle = \int_0^L P_n(x) dx = \frac{2}{L} \int_0^L x \sin^2(n\pi x/L) dx = \frac{1}{2}L. \quad (5.32)$$

The other expectation value  $\langle x^2 \rangle$  is given by

$$\langle x^2 \rangle = \frac{2}{L} \int_0^L x^2 \sin^2(n\pi x/L) dx = L^2 \frac{2n^2\pi^2 - 3}{6n^2\pi^2}. \quad (5.33)$$

Consequently, the uncertainty in position is

$$(\Delta x)^2 = L^2 \frac{n^2\pi^2 - 3}{n^2\pi^2} - \frac{L^2}{4} = L^2 \frac{n^2\pi^2 - 6}{12n^2\pi^2}. \quad (5.34)$$

### Orthonormality

An important feature of the wave functions derived above follows from considering the following integral:

$$\int_{-\infty}^{+\infty} \psi_m^*(x) \psi_n(x) dx = \frac{2}{L} \int_0^L \sin(m\pi x/L) \sin(n\pi x/L) dx = \delta_{mn} \quad (5.35)$$

where  $\delta_{mn}$  is known as the Kronecker delta, and has the property that

$$\begin{aligned} \delta_{mn} &= 1 & m &= n \\ &= 0 & m &\neq n \end{aligned} \quad (5.36)$$

Thus, if  $m = n$ , the integral is unity, as it should be as this is just the normalization condition that was imposed earlier on the wave functions. However, if  $m \neq n$ , then the integral vanishes. The two wave functions are then said to be orthogonal, a condition somewhat analogous to two vectors being orthogonal. The functions  $\psi_n$  for all  $n = 1, 2, 3, \dots$  are then said to be *orthonormal*. The property of orthonormality of eigenfunctions is found to be a general property of the states of quantum systems that will be further explored in later Chapters.

### Linear Superpositions

We found earlier that if we combine together wave functions of different wavelength and frequency, corresponding to different particle momenta and energies, we produce something that had an acceptable physical meaning – a wave packet. What we will do now is combine together – but in this case only two – different wave functions and see what meaning can be given to the result obtained. Thus, we will consider the following linear combination, or linear superposition, of two wave functions:

$$\begin{aligned}\Psi(x, t) &= \frac{1}{\sqrt{2}}[\Psi_1(x, t) + \Psi_2(x, t)] \\ &= \frac{1}{\sqrt{L}}[\sin(\pi x/L)e^{-i\omega_1 t} + \sin(2\pi x/L)e^{-i\omega_2 t}] \quad 0 < x < L \\ &= 0 \quad x < 0 \text{ and } x > L.\end{aligned}\quad (5.37)$$

The factor  $1/\sqrt{2}$  guarantees that the wave function is normalized to unity, as can be seen by calculating the normalization integral Eq. (5.1) for the wave function defined in Eq. (5.37).

How are we to interpret this wave function? Superficially, it is seen to be made up of two wave functions associated with the particle having energies  $E_1$  and  $E_2$ . These wave functions contribute equally to the total wave function  $\Psi(x, t)$  in the sense that they both have the same amplitude, so it is tempting to believe that if we were to measure the energy of the particle rather than its position, we would get either result  $E_1$  and  $E_2$  with equal probability of  $\frac{1}{2}$ . This interpretation in fact turns out to be the case as we will see later. But the fact that the particle does not have a definite energy has important consequences as can be seen by considering the probability distribution for the position of the particle.

This probability distribution is

$$\begin{aligned}P(x, t) &= |\Psi(x, t)|^2 \\ &= \frac{1}{L}[\sin^2(\pi x/L) + \sin^2(2\pi x/L) + 2\sin(\pi x/L)\sin(2\pi x/L)\cos(\Delta\omega t)]\end{aligned}\quad (5.38)$$

where  $\Delta\omega = (E_2 - E_1)/\hbar$ . This is obviously a time dependent probability distribution, in contrast to what was found for the eigenfunctions  $\Psi_n(x, t)$ . In other words, if the wave function is made up of contributions of different energies, the particle is not in a stationary state.

In Fig. (5.2), this probability distribution is plotted at three times. At  $t = 0$ , the probability distribution is

$$P(x, 0) = \frac{1}{L}(\sin(\pi x/L) + \sin(2\pi x/L))^2 \quad (5.39)$$

which results in the distribution being peaked on the left hand side of the well. At the time  $t = \pi/2\Delta\omega$ , the time dependent term vanishes and the distribution is

$$P(x, \pi/2\Delta\omega) = \frac{1}{L}(\sin^2(\pi x/L) + \sin^2(2\pi x/L)). \quad (5.40)$$

Finally, at time  $t = \pi/\Delta\omega$ , the distribution is

$$P(x, \pi/\Delta\omega) = \frac{1}{L}(\sin(\pi x/L) - \sin(2\pi x/L))^2 \quad (5.41)$$

which gives a peak on the right hand side of the well. Thus, the maximum probability swings from the left to the right hand side of the well (and back again), *but without the maximum moving through the centre of the well*. This is counterintuitive: the maximum would be expected to also move back and forth between the walls, mirroring the expected classical behaviour of the particle bouncing back and forth between the walls.

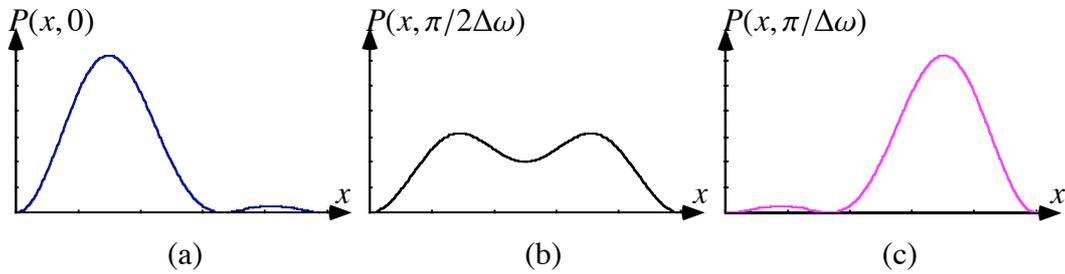


Figure 5.2: Plots of the time dependent probability distributions  $P(x, t) = (\Psi_1(x, t) + \Psi_2(x, t))/\sqrt{2}$  for a particle in an infinite potential well. The times are (a)  $t = 0$ , (b)  $t = \pi/2\Delta\omega$  and (c)  $t = \pi/\Delta\omega$  where  $\hbar\Delta\omega = E_2 - E_1$ .

As a final illustration, we can find the total probability of finding the particle on the left hand half of the well, i.e. in the region  $0 < x < L/2$ :

$$P_L = \int_0^{L/2} P(x, t) dx = \frac{1}{2} + \pi^{-1} \cos(\Delta\omega t) \quad (5.42)$$

while the corresponding result for the right hand side is

$$P_R = \frac{1}{2} - \pi^{-1} \cos(\Delta\omega t) \quad (5.43)$$

which perhaps better illustrates the ‘see-sawing’ of the probability from one side to the other with a frequency of  $2\pi\Delta\omega$ . What can be learned from this example is that if the wave function is made up of two contributions of different energy, then the properties of the system do not stay constant in time, i.e. the system is no longer in a stationary state. Once again, the example of a particle in a well illustrates a generic feature of quantum systems, namely that if they do not have a definite energy, then the properties of the system change in time.

### Probability Distribution for Momentum

A final point to be considered here is that of determining what the momentum is of the particle in the well. We cannot do this in an entirely correct fashion at this stage, but for the purposes of further illustrating that the wave function contains more than just information on the position of the particle, we will use a slightly less rigorous argument to arrive at essentially correct conclusions. If we return to the eigenfunctions  $\Psi_n(x, t)$ , we see that they can be written in the form

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \frac{e^{i(k_n x - \omega_n t)} - e^{-i(k_n x + \omega_n t)}}{2i} \quad (5.44)$$

i.e. a linear combination of two counterpropagating waves, one associated with the particle having momentum  $p_n = \hbar k_n$ , the other with the particle having momentum  $p_n = -\hbar k_n$ . These two contributions enter the above expression with equal weight, by which is meant that the magnitude of the coefficients of each of the exponentials is the same. It therefore seems reasonable to suspect that the particle has an equal chance of being observed to have momenta  $p_n = \pm \hbar k_n$  when the wave function of the particle is  $\Psi_n(x, t)$ . This conjecture is consistent with what we would suppose is going on classically – the particle would be bouncing back and forth between the walls, simply reversing the direction of its momentum on each bounce. It should be pointed out that this is the argument alluded to above which is not entirely correct. The momentum actually has a probability distribution which is peaked at the values we have obtained here. The point can still be taken that information on other than the position of the particle is to be found in the wave function.

Accepting this, we can then say that the particle has a chance of  $\frac{1}{2}$  of being observed to have momentum  $\hbar k_n$  and a chance of  $\frac{1}{2}$  of being observed to have momentum  $-\hbar k_n$ , at least if the wave function is  $\Psi_n(x, t)$ . On this basis, we can calculate the expectation value of the momentum, that is

$$\langle p \rangle = \frac{1}{2} \hbar k_n + \frac{1}{2} (-\hbar k_n) = 0 \quad (5.45)$$

and the expectation value of the momentum squared:

$$\langle p^2 \rangle = \frac{1}{2} (\hbar k_n)^2 + \frac{1}{2} (-\hbar k_n)^2 = \hbar^2 k_n^2. \quad (5.46)$$

Both these results are, in fact, exact. The uncertainty in the momentum,  $\Delta p$ , follows from

$$(\Delta p)^2 = \langle p^2 \rangle - \langle p \rangle^2 = \hbar^2 k_n^2 = \hbar^2 (n\pi/L)^2. \quad (5.47)$$

We can combine this with the result Eq. (5.34) for the uncertainty in the position to give

$$(\Delta x)^2 (\Delta p)^2 = L^2 \frac{n^2 \pi^2 - 6}{12 n^2 \pi^2} \hbar^2 (n\pi/L)^2 = \frac{\hbar^2}{4} \left( \frac{n^2 \pi^2 - 6}{3} \right). \quad (5.48)$$

Since the term  $(n^2 \pi^2 - 6)/3$  is always bigger than unity (at the smallest, when  $n = 1$ , it is 1.29), we have

$$(\Delta x)^2 (\Delta p)^2 \geq \frac{\hbar^2}{4} \quad (5.49)$$

or, in other words

$$\Delta x \Delta p \geq \frac{1}{2} \hbar \quad (5.50)$$

in agreement with the Heisenberg uncertainty principle, Eq. (3.14).

## 5.4 The Schrödinger Wave Equation

So far, we have made a lot of progress concerning the properties of, and interpretation of the wave function, but as yet we have had very little to say about how the wave function may be derived in a general situation, that is to say, we do not have on hand a ‘wave equation’ for the wave function. There is no true derivation of this equation, but its form can be motivated by physical and mathematical arguments at a wide variety of levels of sophistication. Here, we will offer a simple derivation based on what we have learned so far about the wave function.

In the discussion of the particle in an infinite potential well, it was observed that the wave function of a particle of fixed energy  $E$  could most naturally be written as a linear combination of wave functions of the form

$$\Psi(x, t) = Ae^{i(kx - \omega t)} \quad (5.51)$$

representing a wave travelling in the positive  $x$  direction, and a corresponding wave travelling in the opposite direction, so giving rise to a standing wave, this being necessary in order to satisfy the boundary conditions. This corresponds intuitively to our classical notion of a particle bouncing back and forth between the walls of the potential well, which suggests that we adopt the wave function above as being the appropriate wave function for a *free* particle of momentum  $p = \hbar k$  and energy  $E = \hbar\omega$ . With this in mind, we can then note that

$$\frac{\partial^2 \Psi}{\partial x^2} = -k^2 \Psi \quad (5.52)$$

which can be written, using  $E = p^2/2m = \hbar^2 k^2/2m$ :

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = \frac{p^2}{2m} \Psi. \quad (5.53)$$

Similarly

$$\frac{\partial \Psi}{\partial t} = -i\omega \Psi \quad (5.54)$$

which can be written, using  $E = \hbar\omega$ :

$$i\hbar \frac{\partial \Psi}{\partial t} = \hbar\omega \Psi = E\Psi. \quad (5.55)$$

We now generalize this to the situation in which there is both a kinetic energy and a potential energy present, then  $E = p^2/2m + V(x)$  so that

$$E\Psi = \frac{p^2}{2m} \Psi + V(x)\Psi \quad (5.56)$$

where  $\Psi$  is now the wave function of a particle moving in the presence of a potential  $V(x)$ . But if we assume that the results Eq. (5.53) and Eq. (5.55) still apply in this case then we have

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\Psi = i\hbar \frac{\partial \psi}{\partial t} \quad (5.57)$$

which is the famous Schrödinger wave equation. We will not be much concerned with solving this equation here, but it is worthwhile to point out that it is the basic equation of that branch of quantum mechanics known as wave mechanics.

## 5.5 Is the Wave Function all that is Needed?

So far, we have been concerned almost entirely with the quantum mechanics associated with the motion of particles through space, which may give rise to the mistaken notion that all of quantum mechanics revolves around the idea of the wave function. However, this is far from the case. There is no objective reality that can be attached to the wave function – it is just one of many ways that the quantum nature of matter can be expressed. It is useful for many kinds of problems, but entirely inappropriate for others, and a singular focus on the wave function can give the impression that the wave function *is* the heart of quantum mechanics. But the quantum mechanical nature of matter makes itself known in ways that have little to do with waves and wave functions. Correspondingly, the mathematical theory of quantum mechanics is much more than just the mathematics of waves.

But what are the other aspects of quantum mechanics that need more than wave mechanics? For one thing, it can be shown there is no such thing as a wave function for a photon. There are many physical processes in which the physically observable quantity is not where a particle is, or how fast it is moving, but rather how many particles there are of a certain kind – an important consideration as particles can be created or destroyed in a random way. The whole subject of the quantum theory of fields is expressed in the language of particle numbers. But one of the most important examples of a circumstance in which wave mechanics falls short is in describing the intrinsic spin of elementary particles. In the following Chapter, attention will be focussed on the example of particle spin and the Stern-Gerlach experiment as being a way of illustrating some of the general principles of quantum mechanics.