

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 others¹. 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

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

with the consequent terminology that the wave function is usually referred to as a ‘probability amplitude’. What this interpretation means in a practical sense can be arrived at in a number of ways, the conventional manner making use of the notion of an ‘ensemble of identically prepared systems’. By this we mean that take a vast number of identical copies of the same system, in our case a very simple system, consisting on just one particle, and put them all through exactly the same experimental procedures, so that they all end up in exactly the same physical state. An example would be the two slit experiment in which every electron is prepared with the same momentum and energy. The collection of identical copies of the same system all prepared in the same fashion is known as an ensemble. We then in effect assume that, at time t after the start

¹The 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.

of the preparation procedure, the state of each particle will be given by the same wave function $\Psi(x, t)$, though it is common practice (and a point of contention) in quantum mechanics to say that the wave function describes the whole ensemble, not each one of its members. We will however usually refer to the wave function as if it is associated with a single system, 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 prepared in exactly the same fashion, and we measure the position of the particle. If the particle were described by classical physics, we would have to say that for each copy of the experiment we would get exactly the same result, and if we did not get the same answer every time, then we would presume that this is because we did not carry out our experiment as well as we might have: some error has crept in because of some flaw in the experimental apparatus, or in the measurement process. For instance, in the two slit experiment where the bullets struck the observation screen at random because the machine gun fired off the bullets in an erratic fashion. But the situation is not the same quantum mechanically – invariably we will find that we get different results for the measurement of position in spite of the fact that each run of the experiment is supposedly identical to every other run. Moreover the results vary in an entirely random fashion from one measurement to the next, as evidenced in the two slit experiment with electrons. This randomness cannot be removed by refining the experiment – it is built into the very nature of things. But the randomness is not without some kind of order – the manner in which the measured values of position are scattered is determined by the wave function $\Psi(x, t)$, i.e. the scatter of values is quantified by the probability distribution given by $P(x, t) = |\Psi(x, t)|^2$.

This probability function does not, by itself, give the chances of a particle being observed at a particular position. But what can be obtained from it is the probability of a particle being observed to be positioned in a range x to $x + \delta x$, this probability being given by the product $P(x, t)\delta x$. So to properly understand what $P(x, t)$ is telling us, we have to first suppose that the range of x values are divided into regions of width δx . Now when we measure the position of the particle in each run of the experiment, what we take note of is the interval δx in which each particle is observed. If we do the experiment N times, we can count up the number of particles for which the value of x lies in the range $(x, x + \delta x)$. Call this number $\delta N(x)$. The fraction of particles that are observed to lie in this range will then be

$$\frac{\delta N(x)}{N}. \quad (5.1)$$

Our intuitive understanding of probability then tells us that this ratio gives us, approximately, the probability of observing the particle in this region $(x, x + \delta x)$. So if N is made a very large number, we would then expect that

$$\frac{\delta N(x)}{N} \approx P(x, t)\delta x \quad \text{or} \quad \frac{\delta N(x)}{N\delta x} \approx P(x, t) \quad (5.2)$$

where the approximate equality will become more exact as the number of particles becomes larger.

Ex 5.1 An electron placed in the region $x > 0$ adjacent to the surface of liquid helium is attracted to the surface by its oppositely charged ‘image’ inside the surface. However, the electron cannot penetrate the surface (it is an infinitely high potential barrier). The wave function for the electron, in its lowest energy state, can be shown to be given by

$$\begin{aligned} \Psi(x, t) &= 2a_0^{-1/2}(x/a_0) e^{-x/a_0} e^{-i\omega t} & x > 0 \\ &= 0 & x < 0. \end{aligned}$$

where a_0 is a constant determined by the mass and charge of the particle and by the dielectric properties of the helium, and is ≈ 7.6 nm. The energy of the electron is given by $E = \hbar\omega$.

An experiment is conducted with the aim of measuring the distance of the electron from the surface. Suppose that the position x can be measured to an accuracy of $\pm a_0/4$. We can then divide the x axis into intervals of length $\delta x = a_0/2$, and record the number of times that the electron is found in the ranges $(0, a_0/2)$, $(a_0/2, a_0)$, $(a_0, 3a_0/2)$, \dots , $(4.5a_0, 4.74a_0)$. The experiment is repeated 300 times, yielding the results in the adjacent table. This raw data can be plotted as a histogram:

$\frac{x}{a_0}$	no. of detections $\delta N(x)$ in interval $(x, x + \delta x)$
0	28
0.5	69
1.0	76
1.5	58
2.0	32
2.5	17
3.0	11
3.5	6
4.0	2
4.5	1

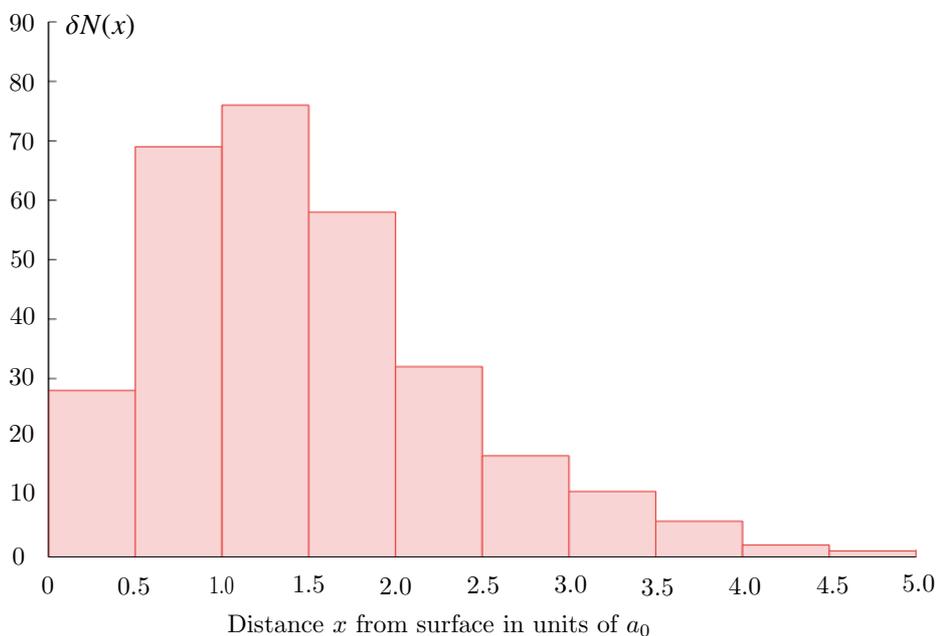


Figure 5.1: Histogram of raw data plotted vertically is the number $\delta N(x)$ of electrons measured to be in the range $(x, x + \delta x)$.

which tells us that there is a preference for the electron to be found at a distance of between a and $1.5a$ from the surface.

To relate this to the probability distribution provided by the quantum theory, we can set $\delta x = 0.5a$, and construct a histogram of the values of $\delta N(x)/N\delta x$ which, as we can see from Eq. (5.2), should approximate to $P(x, t) = |\Psi(x, t)|^2$ where

$$P(x, t) = \left| 2a_0^{-1/2}(x/a_0) e^{-x/a_0} e^{-i\omega t} \right|^2 = 4(x^2/a_0^3) e^{-2x/a_0} \quad (5.3)$$

This is illustrated in the following figure

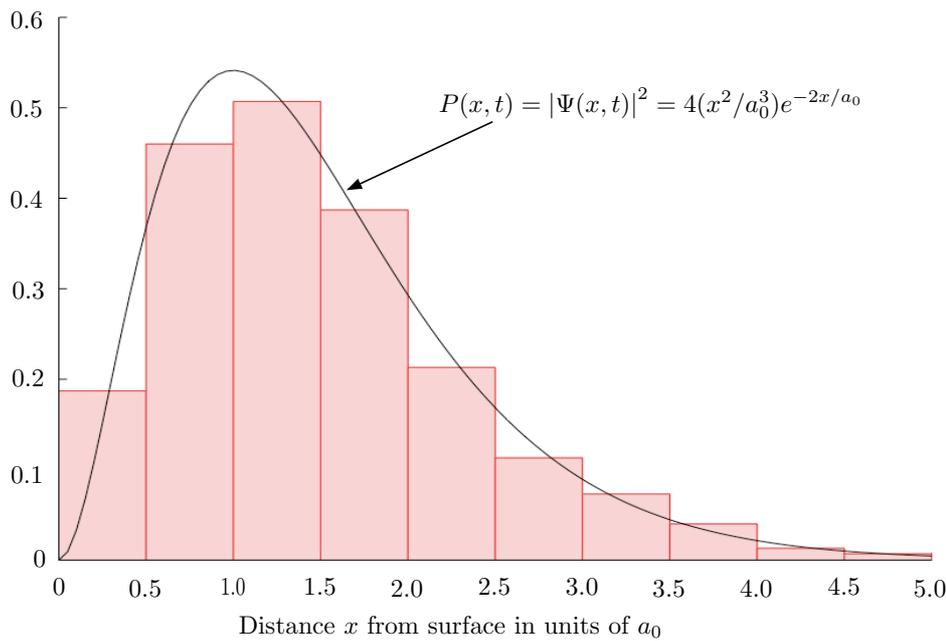


Figure 5.2: Histogram of $\delta N(x)/(N\delta x)$ and of the probability distribution $P(x, t)$ to which it approximates.

If many more measurements were made, and the interval δx was made smaller and smaller, the expectation is that the tops of the histogram would form a smooth curve that would better approximate to the form of $P(x, t)$ predicted by quantum mechanics.

5.1.1 Normalization

The probability interpretation of the wave function has an immediate consequence of profound significance. The probability interpretation given above tells us the probability of finding the particle in a small interval δx . We can calculate the probability of finding the particle in a finite range by dividing this range into segments of size δx and simply adding together the contributions from each such segment. In the limit that δx is made infinitesimally small, this amounts to evaluating an integral. To put it more precisely, the probability of finding the particle in a finite range $a < x < b$, will be given by the integral

$$\int_a^b |\Psi(x, t)|^2 dx \quad (5.4)$$

From this it immediately follows that the probability of finding the particle somewhere in the range $-\infty < x < \infty$ must be unity. After all, the particle is guaranteed to be found somewhere. Mathematically, this can be stated as

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1. \quad (5.5)$$

A wave function that satisfies this condition is said to be ‘normalized 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

$$\Psi(x, t) = A \sin(kx - \omega t), \quad A \cos(kx - \omega t), \quad Ae^{i(kx - \omega t)}, \quad \dots, \quad (5.6)$$

does not satisfy the normalization condition Eq. (5.5) – 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.

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 make use again of the notion of an ‘ensemble of identically prepared systems’ to build up a record of the number of particles $\delta N(x)$ for which the value of x lies in the range $(x, x + \delta x)$.

The fraction of particles that are observed to lie in this range will then be

$$\frac{\delta N(x)}{N} \quad (5.7)$$

We can then calculate the mean or average value of all these results, call it $\bar{x}(t)$, in the usual way:

$$\bar{x}(t) = \sum_{\text{All } \delta x} x \frac{\delta N(x)}{N}. \quad (5.8)$$

This mean will be an approximation to the mean value that would be found if the experiment were repeated an infinite number of times and in the limit in which $\delta x \rightarrow 0$. This latter mean value will be written as $\langle x \rangle$, and is given by the integral:

$$\langle x(t) \rangle = \int_{-\infty}^{+\infty} x P(x, t) dx = \int_{-\infty}^{+\infty} x |\Psi(x, t)|^2 dx \quad (5.9)$$

This average value is usually referred to as the expectation value of x .

Ex 5.2 Using the data from the previous example, we can calculate the average value of the distance of the electron from the surface of the liquid helium using the formula of Eq. (5.8). Thus we have

$$\begin{aligned} \langle x \rangle \approx \bar{x} &= 0 \times \frac{28}{300} + 0.5a_0 \times \frac{69}{300} + a_0 \times \frac{76}{300} + 1.5a_0 \times \frac{58}{300} + 2a_0 \times \frac{32}{300} \\ &+ 2.5a_0 \times \frac{17}{300} + 3a_0 \times \frac{11}{300} + 3.5a_0 \times \frac{6}{300} + 4a_0 \times \frac{2}{300} + 4.5a_0 \times \frac{1}{300} \\ &= 1.235a_0. \end{aligned}$$

This can be compared with the result that follows for the expectation value calculated from the wave function for the particle:

$$\langle x \rangle = \int_{-\infty}^{+\infty} x |\Psi(x, t)|^2 dx = \frac{4}{a_0^3} \int_0^{\infty} x^3 e^{-2x/a_0} dx = \frac{4.6a_0^4}{2^4 a_0^4} = 1.5a_0.$$

Similarly, expectation values of functions of x can be derived. For $f(x)$, we have

$$\langle f(x) \rangle = \int_{-\infty}^{+\infty} f(x) |\Psi(x, t)|^2 dx. \quad (5.10)$$

In particular, we have

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 |\Psi(x, t)|^2 dx. \quad (5.11)$$

We can use this to define the uncertainty in the position of the particle. The uncertainty is a measure of how widely the results of the measurement of the position of the electron are spread around the mean value. As is the case in the analysis of statistical data, this is done in terms of the usual statistical quantity, the standard deviation, written Δx . This quantity is determined in terms of the average value of the *squares* of the distance of each value x from the average value of the data – if we did not square these differences, the final average would be zero, a useless result. For a sample obtained by N measurements of the position of the particle, it is obtained by the following formula:

$$(\Delta x)^2 \approx \sum_{\text{All } \delta x} (x - \bar{x})^2 \frac{\delta N(x)}{N} \quad (5.12)$$

where \bar{x} is the average value obtained from the data. The uncertainty is then found by taking the square root of this average.

In the limit of an infinite number of measurements, the uncertainty can be written

$$(\Delta x)^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2. \quad (5.13)$$

It is the uncertainty defined in this way that appears in the standard form for the Heisenberg uncertainty relation.

Ex 5.3 Once again, using the data given above for an electron close to the surface of liquid helium, we can calculate the uncertainty in the position of the electron from this surface. Using $\bar{x} = 1.235a_0$ we have

$$\begin{aligned} (\Delta x)^2 &\approx (0 - 1.235)^2 a_0^2 \times \frac{28}{300} + (0.5 - 1.235)^2 a_0^2 \times \frac{69}{300} \\ &\quad + (1 - 1.235)^2 a_0^2 \times \frac{76}{300} + (1.5 - 1.235)^2 a_0^2 \times \frac{58}{300} \\ &\quad + (2 - 1.235)^2 a_0^2 \times \frac{32}{300} + (2.5 - 1.235)^2 a_0^2 \times \frac{17}{300} \\ &\quad + (3 - 1.235)^2 a_0^2 \times \frac{11}{300} + (3.5 - 1.235)^2 a_0^2 \times \frac{6}{300} \\ &\quad + (4 - 1.235)^2 a_0^2 \times \frac{2}{300} + (4.5 - 1.235)^2 a_0^2 \times \frac{1}{300} \\ &= 0.751 a_0^2 \end{aligned}$$

so that $\Delta x \approx 0.866a_0$. This can be compared to the uncertainty as calculated from the wave function itself. This will be given by

$$(\Delta x)^2 = \langle x^2 \rangle - 2.25a_0^2$$

where we have used the previously calculated value for $\langle x \rangle = 1.5a_0$. What is required is

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 |\Psi(x, t)|^2 dx = \frac{4}{a_0^3} \int_0^{\infty} x^4 e^{-2x/a_0} dx = \frac{4}{a_0^3} \frac{24a_0^5}{2^5} = 3a_0^2$$

and hence

$$\Delta x = \sqrt{3a_0^2 - 2.25a_0^2} = 0.866a_0.$$

The question now arises as to how the wave function can be obtained for a particle, or indeed, for a system of particles. The most general way is by solving the Schrödinger equation, but before we consider this general approach, 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

$$\Psi(0, t) = \Psi(L, t) = 0. \quad (5.14)$$

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

$$E = \frac{p^2}{2m}. \quad (5.15)$$

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

$$k = \pm \frac{\sqrt{2mE}}{\hbar} \quad (5.16)$$

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

$$\omega = E/\hbar. \quad (5.17)$$

In the region $0 < x < L$ the particle is free, so the wave function must be of the form Eq. (5.6), 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. (5.14) must be satisfied and secondly, we note that the wave function must be normalized to unity, Eq. (5.5). 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. (5.16) 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

$$\Psi(x, t) = Ae^{i(kx-\omega t)} + Be^{-i(kx-\omega t)} + Ce^{i(kx+\omega t)} + De^{-i(kx+\omega t)} \quad (5.18)$$

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

$$\begin{aligned} \Psi(0, t) &= Ae^{-i\omega t} + Be^{i\omega t} + Ce^{i\omega t} + De^{-i\omega t} \\ &= (A + D)e^{-i\omega t} + (B + C)e^{i\omega t} \\ &= 0. \end{aligned} \quad (5.19)$$

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

$$\begin{aligned} \Psi(x, t) &= Ae^{i(kx-\omega t)} + Be^{-i(kx-\omega t)} - Be^{i(kx+\omega t)} - Ae^{-i(kx+\omega t)} \\ &= A(e^{ikx} - e^{-ikx})e^{-i\omega t} - B(e^{ikx} - e^{-ikx})e^{i\omega t} \\ &= 2i \sin(kx)(Ae^{-i\omega t} - Be^{i\omega t}). \end{aligned} \quad (5.20)$$

Now check for normalization:

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 4|Ae^{-i\omega t} - Be^{i\omega t}|^2 \int_0^L \sin^2(kx) dx \quad (5.21)$$

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

$$\begin{aligned} |Ae^{-i\omega t} - Be^{i\omega t}|^2 &= (Ae^{-i\omega t} - Be^{-i\omega t})(A^*e^{i\omega t} - B^*e^{-i\omega t}) \\ &= AA^* + BB^* - AB^*e^{-2i\omega t} - A^*Be^{2i\omega t} \end{aligned} \quad (5.22)$$

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

$$\Psi(x, t) = 2iA \sin(kx)e^{-i\omega t}. \quad (5.23)$$

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

$$\sin(kL) = 0 \quad (5.24)$$

and hence

$$kL = n\pi \quad n \text{ an integer} \quad (5.25)$$

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

$$k_n = \frac{n\pi}{L}. \quad (5.26)$$

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

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\pi^2 n^2 \hbar^2}{2mL^2} = \hbar\omega_n \quad (5.27)$$

i.e. the energy is ‘quantized’.

Using these values of k in the normalization condition leads to

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 4|A|^2 \int_0^L \sin^2(k_n x) = 2|A|^2 L \quad (5.28)$$

so that by making the choice

$$A = \sqrt{\frac{1}{2L}} e^{i\phi} \quad (5.29)$$

where ϕ 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 ϕ , 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

$$A = -i \sqrt{\frac{1}{2L}}. \quad (5.30)$$

The wave function therefore becomes

$$\begin{aligned} \Psi_n(x, t) &= \sqrt{\frac{2}{L}} \sin(n\pi x/L) e^{-i\omega_n t} & 0 < x < L \\ &= 0 & x < 0, \quad x > L. \end{aligned} \quad (5.31)$$

with associated energies

$$E_n = \frac{\pi^2 n^2 \hbar^2}{2mL^2} \quad n = 1, 2, 3, \dots \quad (5.32)$$

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 ≥ 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

$$\Psi_n(x, t) = \psi_n(x) e^{-iE_n t/\hbar} \quad (5.33)$$

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. (5.32). 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.

Some illustrative plots of the wave functions are presented in Fig. 5.3

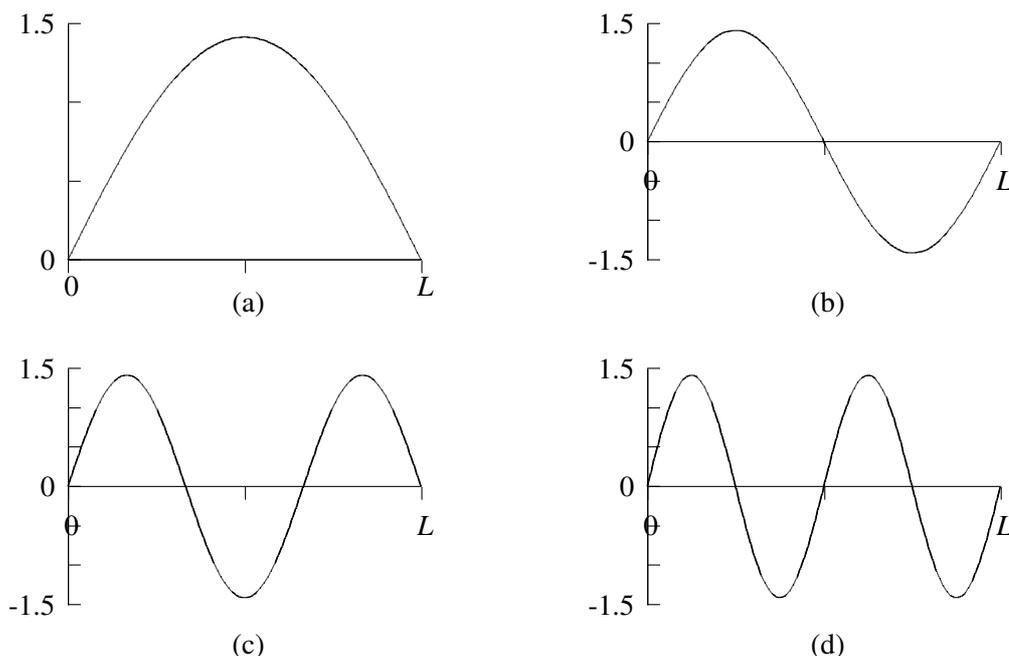


Figure 5.3: Plots of infinite potential well wave function $\psi_n(x)$ for (a) $n = 1$, (b) $n = 2$, (c) $n = 3$, and (d) $n = 4$.

Probability Distributions

The probability distributions corresponding to the wave functions obtained above are

$$\begin{aligned}
 P_n(x) &= |\Psi(x, t)|^2 = \frac{2}{L} \sin^2(n\pi x/L) & 0 < x < L \\
 &= 0 & x < 0, \quad x > L
 \end{aligned}
 \tag{5.34}$$

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. (5.4)). 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. (5.4)(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 δx 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. (5.10). The integral is straightforward, and gives

$$\langle x \rangle = \frac{2}{L} \int_0^L x \sin^2(n\pi x/L) dx = \frac{1}{2}L \quad (5.35)$$

i.e. the expectation value is in the middle of the well. Since the probability distributions $P_n(x)$ is symmetric about $x = L/2$, this result is as expected. 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 $x = 3L/4$.

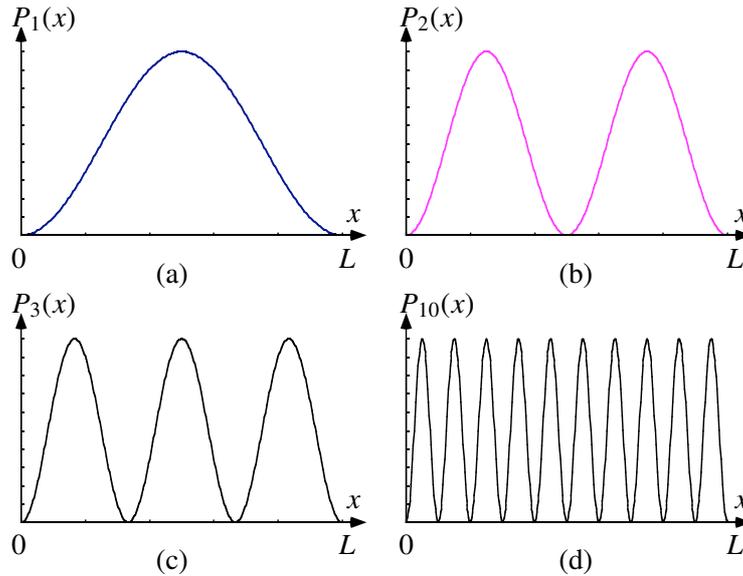


Figure 5.4: Plots of the probability distributions $P_n(x)$ for a particle in an infinite potential well of width L for (a) $n = 1$, (b) $n = 2$, (c) $n = 3$ and (d) $n = 10$. The rapid oscillations on (d) imply that the probability is averages out to be constant across the width of the well.

From the wave functions $\Psi_n(x, t)$, using the definition Eq. (5.10) to calculate $\langle x^2 \rangle$ and $\langle x \rangle$, it is also possible to calculate the uncertainty in the position of the particle. We have already seen that $\langle x \rangle = L/2$, while the other expectation value $\langle x^2 \rangle$ is given by

$$\langle x^2 \rangle = \frac{2}{L} \int_0^L x^2 \sin^2(n\pi x/L) dx = L^2 \frac{2n^2\pi^2 - 3}{6n^2\pi^2}. \quad (5.36)$$

Consequently, the uncertainty in position is

$$(\Delta x)^2 = L^2 \frac{n^2\pi^2 - 3}{n^2\pi^2} - \frac{L^2}{4} = L^2 \frac{n^2\pi^2 - 6}{12n^2\pi^2}. \quad (5.37)$$

Orthonormality

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

$$\int_{-\infty}^{+\infty} \psi_m^*(x) \psi_n(x) dx = \frac{2}{L} \int_0^L \sin(m\pi x/L) \sin(n\pi x/L) dx = \delta_{mn} \quad (5.38)$$

where δ_{mn} is known as the Kronecker delta, and has the property that

$$\begin{aligned}\delta_{mn} &= 1 & m = n \\ &= 0 & m \neq n\end{aligned}\quad (5.39)$$

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 ψ_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:

$$\begin{aligned}\Psi(x, t) &= \frac{1}{\sqrt{2}}[\Psi_1(x, t) + \Psi_2(x, t)] \\ &= \frac{1}{\sqrt{L}}[\sin(\pi x/L)e^{-i\omega_1 t} + \sin(2\pi x/L)e^{-i\omega_2 t}] & 0 < x < L \\ &= 0 & x < 0 \text{ and } x > L.\end{aligned}\quad (5.40)$$

The factor $1/\sqrt{2}$ guarantees that the wave function is normalized to unity, as can be seen by calculating the normalization integral Eq. (5.5) for the wave function defined in Eq. (5.40).

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

$$\begin{aligned}P(x, t) &= |\Psi(x, t)|^2 \\ &= \frac{1}{L}[\sin^2(\pi x/L) + \sin^2(2\pi x/L) + 2\sin(\pi x/L)\sin(2\pi x/L)\cos(\Delta\omega t)]\end{aligned}\quad (5.41)$$

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

$$P(x, 0) = \frac{1}{L}(\sin(\pi x/L) + \sin(2\pi x/L))^2\quad (5.42)$$

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

$$P(x, \pi/2\Delta\omega) = \frac{1}{L}(\sin^2(\pi x/L) + \sin^2(2\pi x/L)). \quad (5.43)$$

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

$$P(x, \pi/\Delta\omega) = \frac{1}{L}(\sin(\pi x/L) - \sin(2\pi x/L))^2 \quad (5.44)$$

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.

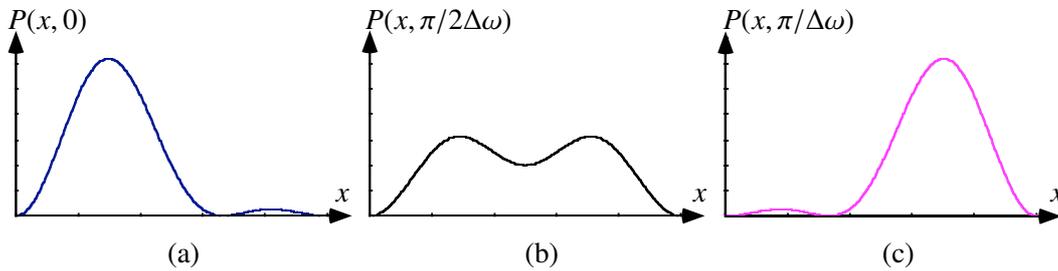


Figure 5.5: Plots of the time dependent probability distributions $P(x, t) = (\Psi_1(x, t) + \Psi_2(x, t))/\sqrt{2}$ for a particle in an infinite potential well. The times are (a) $t = 0$, (b) $t = \pi/2\Delta\omega$ and (c) $t = \pi/\Delta\omega$ where $\hbar\Delta\omega = E_2 - E_1$.

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 $0 < x < L/2$:

$$P_L = \int_0^{L/2} P(x, t) dx = \frac{1}{2} + \pi^{-1} \cos(\Delta\omega t) \quad (5.45)$$

while the corresponding result for the right hand side is

$$P_R = \frac{1}{2} - \pi^{-1} \cos(\Delta\omega t) \quad (5.46)$$

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

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \frac{e^{i(k_n x - \omega_n t)} - e^{-i(k_n x + \omega_n t)}}{2i} \quad (5.47)$$

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

$$\langle p \rangle = \frac{1}{2} \hbar k_n + \frac{1}{2} (-\hbar k_n) = 0 \quad (5.48)$$

and the expectation value of the momentum squared:

$$\langle p^2 \rangle = \frac{1}{2} (\hbar k_n)^2 + \frac{1}{2} (-\hbar k_n)^2 = \hbar^2 k_n^2. \quad (5.49)$$

Both these results are, in fact, exact. The uncertainty in the momentum, Δp , follows from

$$(\Delta p)^2 = \langle p^2 \rangle - \langle p \rangle^2 = \hbar^2 k_n^2 = \hbar^2 (n\pi/L)^2. \quad (5.50)$$

We can combine this with the result Eq. (5.37) for the uncertainty in the position to give

$$(\Delta x)^2 (\Delta p)^2 = L^2 \frac{n^2 \pi^2 - 6}{12 n^2 \pi^2} \hbar^2 (n\pi/L)^2 = \frac{\hbar^2}{4} \left(\frac{n^2 \pi^2 - 6}{3} \right). \quad (5.51)$$

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

$$(\Delta x)^2 (\Delta p)^2 \geq \frac{\hbar^2}{4} \quad (5.52)$$

or, in other words

$$\Delta x \Delta p \geq \frac{1}{2} \hbar \quad (5.53)$$

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

$$\Psi(x, t) = Ae^{i(kx - \omega t)} \quad (5.54)$$

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

$$\frac{\partial^2 \Psi}{\partial x^2} = -k^2 \Psi \quad (5.55)$$

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

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = \frac{p^2}{2m} \Psi. \quad (5.56)$$

Similarly

$$\frac{\partial \Psi}{\partial t} = -i\omega \Psi \quad (5.57)$$

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

$$i\hbar \frac{\partial \Psi}{\partial t} = \hbar\omega \Psi = E\Psi. \quad (5.58)$$

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

$$E\Psi = \frac{p^2}{2m} \Psi + V(x)\Psi \quad (5.59)$$

where Ψ 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. (5.56) and Eq. (5.58) still apply in this case then we have

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\Psi = i\hbar \frac{\partial \psi}{\partial t} \quad (5.60)$$

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.