Chapter 6

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.

The Schrödinger equation has two 'forms', one in which time explicitly appears, and so describes how the wave function of a particle will evolve in time. In general, the wave function behaves like a wave, and so the equation is often referred to as the time dependent Schrödinger wave equation. The other is the equation in which the time dependence has been 'removed' and hence is known as the time independent Schrödinger equation and is found to describe, amongst other things, what the allowed energies are of the particle. These are not two separate, independent equations – the time independent equation can be derived readily from the time dependent equation (except if the potential is time dependent, a development we will not be discussing here). In the following we will describe how the first, time dependent equation can be 'derived', and in then how the second follows from the first.

6.1 Derivation of the Schrödinger Wave Equation

6.1.1 The Time Dependent Schrödinger Wave Equation

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

$$\Psi(x,t) = Ae^{i(kx-\omega t)} \tag{6.1}$$

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

$$\frac{\partial^2\Psi}{\partial x^2} = -k^2\Psi \tag{6.2}$$

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

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = \frac{p^2}{2m}\Psi. \tag{6.3}$$

Similarly

$$\frac{\partial\Psi}{\partial t} = -i\omega\Psi \tag{6.4}$$

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

$$i\hbar\frac{\partial\Psi}{\partial t} = \hbar\omega\psi = E\Psi. \tag{6.5}$$

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

$$E\Psi = \frac{p^2}{2m}\Psi + V(x)\Psi \tag{6.6}$$

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. (6.3) and Eq. (6.5) still apply in this case then we have

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\Psi = i\hbar\frac{\partial\psi}{\partial t} \tag{6.7}$$

which is the famous time dependent Schrödinger wave equation. It is setting up and solving this equation, then analyzing the physical contents of its solutions that form the basis of that branch of quantum mechanics known as wave mechanics.

Even though this equation does not look like the familiar wave equation that describes, for instance, waves on a stretched string, it is nevertheless referred to as a 'wave equation' as it can have solutions that represent waves propagating through space. We have seen an example of this: the harmonic wave function for a free particle of energy E and momentum p, i.e.

$$\Psi(x,t) = Ae^{-i(px-Et)/\hbar} \tag{6.8}$$

is a solution of this equation with, as appropriate for a free particle, $V(x) = 0$. But this equation can have distinctly non-wave like solutions whose form depends, amongst other things, on the nature of the potential $V(x)$ experienced by the particle.

In general, the solutions to the time dependent Schrödinger equation will describe the *dynamical* behaviour of the particle, in some sense similar to the way that Newton's equation $F = ma$ describes the dynamics of a particle in classical physics. However, there is an important difference. By solving Newton's equation we can determine the position of a particle as a function of time, whereas by solving Schrödinger's equation, what we get is a wave function $\Psi(x,t)$ which tells us (after we square the wave function) how the *probability* of finding the particle in some region in space varies as a function of time.

It is possible to proceed from here look at ways and means of solving the full, time dependent Schrödinger equation in all its glory, and look for the physical meaning of the solutions that are found. However this route, in a sense, bypasses much important physics contained in the Schrödinger equation which we can get at by asking much simpler questions. Perhaps the most important 'simpler question' to ask is this: what is the wave function for a particle of a given energy E? Curiously enough, to answer this question requires 'extracting' the time dependence from the time dependent Schrödinger equation. To see how this is done, and its consequences, we will turn our attention to the closely related time independent version of this equation.

6.1.2 The Time Independent Schrödinger Equation

We have seen what the wave function looks like for a free particle of energy E – one or the other of the harmonic wave functions – and we have seen what it looks like for the particle in an infinitely deep potential well – see Section 5.3 – though we did not obtain that result by solving the Schrödinger equation. But in both cases, the time dependence entered into the wave function via a complex exponential factor $\exp[-iEt/\hbar]$. This suggests that to 'extract' this time dependence we guess a solution to the Schrödinger wave equation of the form

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \tag{6.9}$$

i.e. where the space and the time dependence of the complete wave function are contained in separate factors[1]. The idea now is to see if this guess enables us to derive an equation for $\psi(x)$, the spatial part of the wave function.

If we substitute this trial solution into the Schrödinger wave equation, and make use of the meaning of partial derivatives, we get:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}e^{-iEt/\hbar} + V(x)\psi(x)e^{-iEt/\hbar} = i\hbar.-iE/\hbar e^{-iEt/\hbar}\psi(x) = E\psi(x)e^{-iEt/\hbar}. \tag{6.10}$$

We now see that the factor $\exp[-iEt/\hbar]$ cancels from both sides of the equation, giving us

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{6.11}$$

If we rearrange the terms, we end up with

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \big(E - V(x)\big)\psi(x) = 0 \tag{6.12}$$

which is the time independent Schrödinger equation. We note here that the quantity E, which we have identified as the energy of the particle, is a free parameter in this equation. In other words, at no stage has any restriction been placed on the possible values for E. Thus, if we want to determine the wave function for a particle with some specific value of E that is moving in the presence of a potential $V(x)$, all we have to do is to insert this value of E into the equation with the appropriate $V(x)$, and solve for the corresponding wave function. In doing so, we find, perhaps not surprisingly, that for different choices of E we get different solutions for $\psi(x)$. We can emphasize this fact by writing $\psi_E(x)$ as the solution associated with a particular value of E. But it turns out that it is not all quite as simple as this. To be physically acceptable, the wave function $\psi_E(x)$ must satisfy two conditions, one of which we have seen before namely that the wave function must be normalizable (see Eq. (5.3)), and a second, that the wave function and its derivative must be continuous. Together, these two requirements, the first founded in the probability interpretation of the wave function, the second in more esoteric mathematical necessities which we will not go into here and usually only encountered in somewhat artificial problems, lead to a rather remarkable property of physical systems described by this equation that has enormous physical significance: the quantization of energy.

[1] A solution of this form can be shown to arise by the method of 'the separation of variables', a well known mathematical technique used to solve equations of the form of the Schrödinger equation.

The Quantization of Energy

At first thought it might seem to be perfectly acceptable to insert any value of E into the time independent Schrödinger equation and solve it for $\psi_E(x)$. But in doing so we must remain aware of one further requirement of a wave function which comes from its probability interpretation: to be physically acceptable a wave function must satisfy the normalization condition, Eq. (5.3)

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

for all time t. For the particular trial solution introduced above, Eq. (6.9):

$$\Psi(x,t) = \psi_E(x)e^{-iEt/\hbar} \tag{6.13}$$

the requirement that the normalization condition must hold gives, on substituting for $\Psi(x,t)$, the result[2]

$$\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 \, dx = \int_{-\infty}^{+\infty} |\psi_E(x)|^2 \, dx = 1. \tag{6.14}$$

Since this integral must be finite, (unity in fact), we *must* have $\psi_E(x) \to 0$ as $x \to \pm\infty$ in order for the integral to have any hope of converging to a finite value. The importance of this with regard to solving the time dependent Schrödinger equation is that we must check whether or not a solution $\psi_E(x)$ obtained for some chosen value of E satisfies the normalization condition. If it does, then this is a physically acceptable solution, if it does not, then that solution *and the corresponding value of the energy* are not physically acceptable. The particular case of considerable physical significance is if the potential $V(x)$ is attractive, such as would be found with an electron caught by the attractive Coulomb force of an atomic nucleus, or a particle bound by a simple harmonic potential (a mass on a spring), or, as we have seen in Section 5.3, a particle trapped in an infinite potential well. In all such cases, we find that except for certain discrete values of the energy, the wave function $\psi_E(x)$ does not vanish, or even worse, diverges, as $x \to \pm\infty$. In other words, it is only for these discrete values of the energy E that we get physically acceptable wave functions $\psi_E(x)$, or to put it more bluntly, the particle can never be observed to have any energy other than these particular values, for which reason these energies are often referred to as the 'allowed' energies of the particle. This pairing off of allowed energy and normalizable wave function is referred to mathematically as $\psi_E(x)$ being an eigenfunction of the Schrödinger equation, and E the associated energy eigenvalue, a terminology that acquires more meaning when quantum mechanics is looked at from a more advanced standpoint.

So we have the amazing result that the probability interpretation of the wave function forces us to conclude that the allowed energies of a particle moving in a potential $V(x)$ are restricted to certain discrete values, these values determined by the nature of the potential. This is the phenomenon known as the quantization of energy, a result of quantum mechanics which has enormous significance for determining the structure of atoms, or, to go even further, the properties of matter overall. We have already seen an example of this quantization of energy in our earlier discussion of a particle in an infintely deep potential

[2] Note that the time dependence has cancelled out because

$$|\Psi(x,t)|^2 = |\psi_E(x)e^{-iEt/\hbar}|^2 = |\psi_E(x)|^2|e^{-iEt/\hbar}|^2 = |\psi_E(x)|^2$$

since, for any complex number of the form $\exp(i\phi)$, we have $|\exp(i\phi)|^2 = 1$.

well, though we did not derive the results by solving the Schrödinger equation itself. We will consider how this is done shortly.

The requirement that $\psi(x) \rightarrow 0$ as $x \rightarrow \pm\infty$ is an example of a *boundary condition*. Energy quantization is, mathematically speaking, the result of a combined effort: that $\psi(x)$ be a solution to the time independent Schrödinger equation, and that the solution satisfy these boundary conditions. But both the boundary condition and the Schrödinger equation are derived from, and hence rooted in, the nature of the physical world: we have here an example of the unexpected relevance of purely mathematical ideas in formulating a physical theory.

Continuity Conditions There is one additional proviso, which was already mentioned briefly above, that has to be applied in some cases. If the potential should be discontinuous in some way, e.g. becoming infinite, as we have seen in the infinite potential well example, or having a finite discontinuity as we will see later in the case of the finite potential well, it is possible for the Schrödinger equation to have solutions that themselves are discontinuous. But discontinuous potentials do not occur in nature (this would imply an infinite force), and as we know that for continuous potentials we always get continuous wave functions, we then place the extra conditions that the wave function *and* its spatial derivative also must be continuous[3]. We shall see how this extra condition is implemented when we look at the finite potential well later.

Bound States and Scattering States But what about wave functions such as the harmonic wave function $\Psi(x,t) = A\exp[i(kx - \omega t)]$? These wave functions represent a particle having a definite energy $E = \hbar\omega$ and so would seem to be legitimate and necessary wave functions within the quantum theory. But the problem here, as has been pointed out before in Chapter 5, is that $\Psi(x,t)$ does *not* vanish as $x \rightarrow \pm\infty$, so the normalization condition, Eq. (6.14) cannot be satisfied. So what is going on here? The answer lies in the fact that there are two kinds of wave functions, those that apply for particles trapped by an attractive potential into what is known as a bound state, and those that apply for particles that are free to travel to infinity (and beyond), otherwise known as scattering states. A particle trapped in an infinitely deep potential well is an example of the former: the particle is confined to move within a restricted region of space. An electron trapped by the attractive potential due to a positively charged atomic nucleus is also an example – the electron rarely moves a distance more than $\sim$10 nm from the nucleus. A nucleon trapped within a nucleus by attractive nuclear forces is yet another. In all these cases, the probability of finding the particle at infinity is zero. In other words, the wave function for the particle satisfies the boundary condition that it vanish at infinity. So we see that it is when a particle is trapped, or confined to a limited region of space by an attractive potential $V(x)$ (or $V(\mathbf{r})$ in three dimensions), we obtain wave functions that satisfy the above boundary condition, and hand in hand with this, we find that their energies are quantized. But if it should be the case that the particle is free to move as far as it likes in space, in other words, if it is not bound by any attractive potential, (or even repelled by a repulsive potential) then we find that the wave function need not vanish at infinity, and nor is its energy quantized. The problem of how to reconcile this with the normalization condition, and the probability interpretation of the wave function, is a delicate mathematical issue which we cannot hope to address here, but it can be done. Suffice to say that provided the wave function does not diverge at infinity (in

[3]The one exception is when the discontinuity is infinite, as in the case of the infinite potential well. In that case, only the wave function is reguired to be continuous.

other words it remains finite, though not zero) we can give a physical meaning of such states as being an idealized mathematical limiting case which, while it does not satisfy the normalization condition, can still be dealt with in, provided some care is taken with the physical interpretation, in much the same way as the bound state wave functions.

In order to illustrate how the time independent Schrödinger equation can be solved in practice, and some of the characteristics of its solutions, we will here briefly reconsider the infinitely deep potential well problem, already solved by making use of general properties of the wave function, in Section 5.3. We will then move on to looking at other simple applications.

6.2 Solving the Time Independent Schrödinger Equation

6.2.1 The Infinite Potential Well Revisited

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 $x > L$. The potential experienced by the particle is then:

$$V(x) = 0 \qquad 0 < x < L \tag{6.15}$$

$$= \infty \qquad x \geq L; \quad x \leq 0 \tag{6.16}$$

In the regions for which the potential is infinite, the wave function will be zero, for exactly the same reasons that it was set to zero in Section 5.3, that is, there is zero probability of the particle being found in these regions. Thus, we must impose the boundary conditions

$$\psi(0) = \psi(L) = 0. \tag{6.17}$$

Meanwhile, in the region $0 < x < L$, the potential vanishes, so the time independent Schrödinger equation becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x). \tag{6.18}$$

To solve this, we define a quantity k by

$$k = \sqrt{\frac{2mE}{\hbar^2}} \tag{6.19}$$

so that Eq. (6.18) can be written

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \tag{6.20}$$

whose general solution is

$$\psi(x) = A\sin(kx) + B\cos(kx). \tag{6.21}$$

It is now that we impose the boundary conditions, Eq. (6.17), to give, first at $x = 0$:

$$\psi(0) = B = 0 \tag{6.22}$$

so that the solution is now

$$\psi(x) = A\sin(kx). \tag{6.23}$$

Next, applying the boundary condition at $x = L$ gives

$$\psi(L) = A\sin(kL) = 0 \tag{6.24}$$

which tells us that either $A = 0$, in which case $\psi(x) = 0$, which is not a useful solution (it says that there is no partilce in the well at all!) or else $\sin(kL) = 0$, which gives an equation for k:

$$kL = n\pi, \quad n = 0, \pm 1, \pm 2, \ldots. \tag{6.25}$$

We exclude the $n = 0$ possibility as that would give us, once again $\psi(x) = 0$, and we exclude the negative values of n as the will merely reproduce the same set of solutions (except with opposite sign[4]) as the positive values. Thus we have

$$k_n = n\pi/L, \quad n = 1, 2, \ldots \tag{6.26}$$

where we have introduced a subscript n. This leads to, on using Eq. (6.19),

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2mL^2}, \quad n = 1, 2, \ldots \tag{6.27}$$

as before in Section 5.3. Thus we se that the boundary conditions, Eq. (6.17), have the effect of restricting the values of the energy of the particle to those given by Eq. (6.27). The associated wave functions will be as in Section 5.3, that is we apply the normalization condition to determine A (up to an inessential phase factor) which finally gives

$$\begin{aligned} \psi_n(x) &= \sqrt{\frac{2}{L}}\sin(n\pi x/L) \quad && 0 < x < L \\ &= 0 && x < 0, \quad x > L. \end{aligned} \tag{6.28}$$

6.2.2 The Finite Potential Well

The infinite potential well is a valuable model since, with the minimum amount of fuss, it shows immediately the way that energy quantization as potentials do not occur in nature. However, for electrons trapped in a block of metal, or gas molecules contained in a bottle, this model serves to describe very accurately the quantum character of such systems. In such cases the potential experienced by an electron as it approaches the edges of a block of metal, or as experienced by a gas molecule as it approaches the walls of its container are effectively infinite as far as these particles are concerned, at least if the particles have sufficently low kinetic energy compared to the height of these potential barriers.

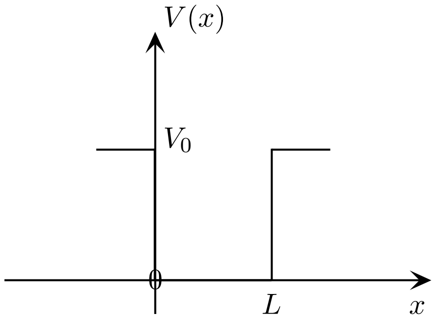

Figure 6.1: Finite potential well.

But, of course, any potential well is of finite depth, and if a particle in such a well has an energy comparable to the height of the potential barriers that define the well, there is the prospect of the particle escaping from the well. This is true both classically and quantum mechanically, though, as you might expect, the behaviour in the quantum mechanical case is not necessarily consistent with our classical physics based expectations. Thus we now proceed to look at the quantum properties of a particle in a finite potential well.

[4]The sign has no effect on probabilities as we always square the wave function.

In this case, the potential will be of the form

$$V(x) = 0 \qquad 0 < x < L \tag{6.29}$$
$$= V \qquad x \geq L \quad x \leq 0 \tag{6.30}$$

i.e. we have 'lowered' the infinite barriers to a finite value V. We now want to solve the time independent Schrödinger equation for this potential.

To do this, we recognize that the problem can be split up into three parts: $x \leq 0$ where the potential is V, $0 < x < L$ where the potential is zero and $x \geq 0$ where the potential is once again V. Therefore, to find the wave function for a particle of energy E, we have to solve three equations, one for each of the regions:

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + (E - V)\psi(x) = 0 \quad x \leq 0 \tag{6.31}$$
$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + E\psi(x) = 0 \quad 0 < x < L \tag{6.32}$$
$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + (E - V)\psi(x) = 0 \quad x \geq L. \tag{6.33}$$

The solutions to these equations take different forms depending on whether $E < V$ or $E > V$. We shall consider the two cases separately.

$E < V$

First define

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{and} \quad \alpha = \sqrt{\frac{2m(V - E)}{\hbar^2}}. \tag{6.34}$$

Note that, as $V > E$, α will be a real number, as it is square root of a positive number. We can now write these equations as

$$\frac{d^2\psi(x)}{dx^2} - \alpha^2\psi(x) = 0 \quad x \leq 0 \tag{6.35}$$
$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \quad 0 < x < L \tag{6.36}$$
$$\frac{d^2\psi(x)}{dx^2} - \alpha^2\psi(x) = 0 \quad x \geq L. \tag{6.37}$$

Now consider the first of these equations, which will have as its solution

$$\psi(x) = Ae^{-\alpha x} + Be^{+\alpha x} \tag{6.38}$$

where A and B are unknown constants. It is at this point that we can make use of our boundary condition, namely that $\psi(x) \to 0$ as $x \to \pm\infty$. In particular, since the solution we are currently looking at applies for $x < 0$, we should look at what this solution does for $x \to -\infty$. What it does is diverge, because of the term $A\exp(-\alpha x)$. So, in order to guarantee that our solution have the correct boundary condition for $x \to -\infty$, we must have $A = 0$. Thus, we conclude that

$$\psi(x) = Be^{\alpha x} \quad x \leq 0. \tag{6.39}$$

We can apply the same kind of argument when solving Eq. (6.37) for $x \geq L$. In that case, the solution is

$$\psi(x) = Ce^{-\alpha x} + De^{\alpha x} \tag{6.40}$$

but now we want to make certain that this solution goes to zero as $x \to \infty$. To guarantee this, we must have $D = 0$, so we conclude that

$$\psi(x) = Ce^{-\alpha x} \quad x \geq L. \tag{6.41}$$

Finally, at least for this part of the argument, we look at the region $0 < x < L$. The solution of Eq. (6.36) for this region will be

$$\psi(x) = P\cos(kx) + Q\sin(kx) \quad 0 < x < L \tag{6.42}$$

but now we have no diverging exponentials, so we have to use other means to determine the unknown coefficients P and Q.

At this point we note that we still have four unknown constants B, P, Q, and C. To determine these we note that the three contributions to $\psi(x)$ do not necessarily join together smoothly at $x = 0$ and $x = L$. This awkward state of affairs has its origins in the fact that the potential is discontinuous at $x = 0$ and $x = L$ which meant that we had to solve three separate equations for the three different regions. But these three separate solutions cannot be independent of one another, i.e. there must be a relationship between the unknown constants, so there must be other conditions that enable us to specify these constants. The extra conditions that we impose, as discussed in Section 6.1.2, are that the wave function has to be a continuous function, i.e. the three solutions:

$$\begin{aligned}
\psi(x) &= Be^{\alpha x} && x \leq 0 && (6.43)\\
&= P\cos(kx) + Q\sin(kx) && 0 < x < L && (6.44)\\
&= Ce^{-\alpha x} && x \geq L. && (6.45)
\end{aligned}$$

should all 'join up' smoothly at $x = 0$ and $x = L$. This means that the first two solutions and their slopes (i.e. their first derivatives) must be the same at $x = 0$, while the second and third solutions and their derivatives must be the same at $x = L$. Applying this requirement at $x = 0$ gives:

$$B = P \tag{6.46}$$

$$\alpha B = kQ \tag{6.47}$$

and then at $x = L$:

$$P\cos(kL) + Q\sin(kL) = Ce^{-\alpha L} \tag{6.48}$$

$$-kP\sin(kL) + kQ\cos(kL) = -\alpha Ce^{-\alpha L}. \tag{6.49}$$

If we eliminate B and C from these two sets of equations we get, in matrix form:

$$\begin{pmatrix} \alpha & -k \\ \alpha\cos(kL) - k\sin(kL) & \alpha\sin(kL) + k\cos(kL) \end{pmatrix} \begin{pmatrix} P \\ Q \end{pmatrix} = 0 \tag{6.50}$$

and in order that we get a non-trivial solution to this pair of homogeneous equations, the determinant of the coefficients must vanish:

$$\begin{vmatrix} \alpha & -k \\ \alpha\cos(kL) - k\sin(kL) & \alpha\sin(kL) + k\cos(kL) \end{vmatrix} = 0 \tag{6.51}$$

which becomes, after expanding the determinant and rearranging terms:

$$\tan(kL) = \frac{2\alpha k}{k^2 - \alpha^2}. \tag{6.52}$$

Solving this equation for k will give the allowed values of k for the particle in this finite potential well, and hence, using Eq. (6.34) in the form

$$E = \frac{\hbar^2 k^2}{2m} \tag{6.53}$$

we can determine the allowed values of energy for this particle. What we find is that these allowed energies are finite in number, in contrast to the infinite potential well, but to show this we must solve this equation. This is made difficult to do analytically by the fact that this is a transcendental equation – it has no solutions in terms of familiar functions. However, it is possible to get an idea of what its solutions look like either numerically, or graphically. The latter has some advantages as it allows us to see how the mathematics conspires to produce the quantized energy levels. We can first of all simplify the mathematics a little by writing Eq. (6.52) in the form

$$\tan(kL) = \frac{2(\alpha/k)}{1-(\alpha/k)^2} \tag{6.54}$$

which, by comparison with the two trigonometric formulae

$$\tan 2\theta = \frac{2\tan\theta}{1-\tan^2\theta}$$
$$\tan 2\theta = \frac{2\cot(-\theta)}{1-\cot^2(-\theta)}$$

we see that Eq. (6.52) is equivalent to the two conditions

$$\tan(\tfrac{1}{2}kL) = \frac{\alpha}{k} \tag{6.55}$$
$$\cot(-\tfrac{1}{2}kL) = -\cot(\tfrac{1}{2}kL) = \frac{\alpha}{k}. \tag{6.56}$$

The aim here is to plot the left and right hand sides of these two expressions as a function of k (well, actually as a function of $\frac{1}{2}kL$), but before we can do that we need to take account of the fact that the quantity α is given in terms of E by $\sqrt{2m(V-E)/\hbar^2}$, and hence, since $E = \hbar^2k^2/2m$, we have

$$\frac{\alpha}{k} = \sqrt{\frac{V-E}{E}} = \sqrt{\left(\frac{k_0}{k}\right)^2 - 1}$$

where

$$k_0 = \sqrt{\frac{2mV}{\hbar^2}}. \tag{6.57}$$

As we will be plotting as a function of $\frac{1}{2}kL$, it is useful to rewrite the above expression for α/k as

$$\frac{\alpha}{k} = f(\tfrac{1}{2}kL) = \sqrt{\left(\tfrac{1}{2}k_0L/\tfrac{1}{2}kL\right)^2 - 1}. \tag{6.58}$$

Thus we have

$$\tan(\tfrac{1}{2}kL) = f(\tfrac{1}{2}kL) \quad \text{and} \quad -\cot(\tfrac{1}{2}kL) = f(\tfrac{1}{2}kL). \tag{6.59}$$

We can now plot $\tan(\frac{1}{2}kL)$, $-\cot(\frac{1}{2}kL)$ and $f(\frac{1}{2}kL)$ as functions of $\frac{1}{2}kL$ for various values for k_0. The points of intersection of the curve $f(\frac{1}{2}kL)$ with the tan and cot curves will then give the kL values for an allowed energy level of the particle in this potential.

This is illustrated in Fig. (6.2) where four such plots are given for different values of V. The important feature of these curves is that the number of points of intersection is finite, i.e. there are only a finite number of values of k that solve Eq. (6.52). Correspondingly, there will only be a finite number of allowed values of E for the particle, and there will always be at least one allowed value.

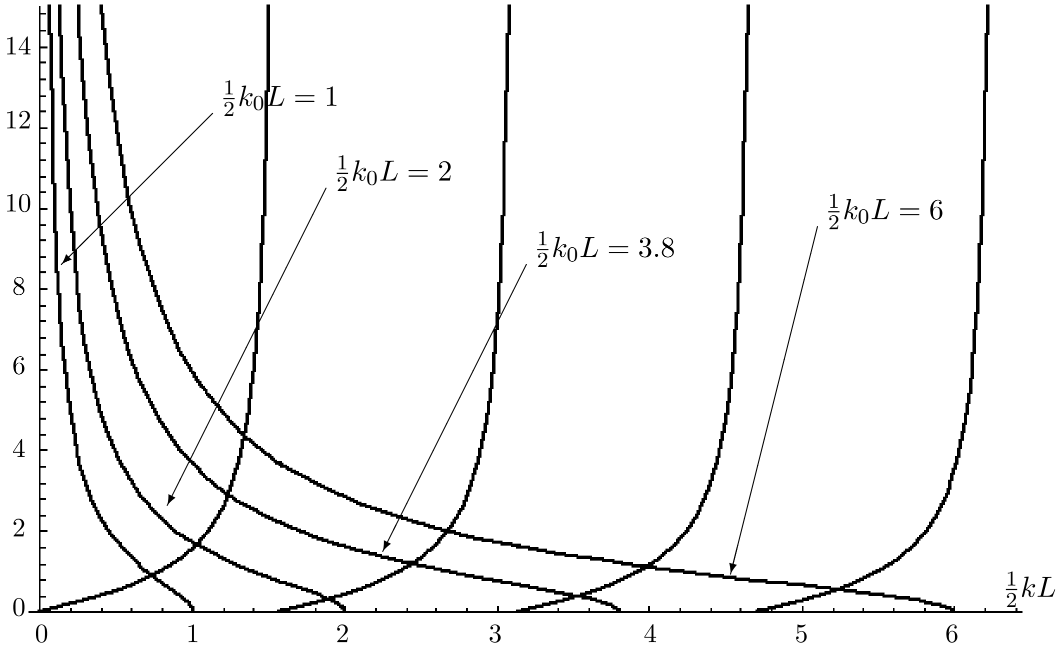

Figure 6.2: Graph to determine bound states of a finite well potential. The points of intersection are solutions to Eq. (6.52). The plots are for increasing values of V, starting with V lowest such that $\frac{1}{2}k_0L = 1$, for which there is only one bound state, slightly higher at $\frac{1}{2}k_0L = 2$, for which there are two bound states, slightly higher again for $\frac{1}{2}k_0L = 3.8$ where there are three bound states, and highest of all, $\frac{1}{2}k_0L = 6$ for which there is four bound states.

To determine the corresponding wave functions is a straightforward but complicated task. The first step is to show, by using Eq. (6.52) and the equations for B, C, P and Q that

$$C = e^{\alpha L}B \tag{6.60}$$

from which readily follows the solution

$$\begin{aligned}
\psi(x) &= Be^{\alpha x} && x \leq 0 && (6.61)\\
&= B\big(\cos kx + \frac{\alpha}{k}\sin kx\big) && 0 < x < L && (6.62)\\
&= Be^{-\alpha(x-L)} && x \geq L. && (6.63)
\end{aligned}$$

The constant B is determined by the requirement that $\psi(x)$ be normalized, i.e. that

$$\int_{-\infty}^{+\infty} |\psi(x)|^2\, dx = 1. \tag{6.64}$$

which becomes:

$$|B|^2\left[\int_{-\infty}^{0} e^{-2\alpha x}\, dx + \int_0^L \big(\cos kx + \frac{\alpha}{k}\sin kx\big)^2 dx + \int_L^{+\infty} e^{-2\alpha(x-L)}\, dx\right] = 1. \tag{6.65}$$

After a somewhat tedious calculation that makes liberal use of Eq. (6.52), the result found is that

$$B = \frac{k}{k_0}\sqrt{\frac{\alpha}{\frac{1}{2}\alpha L + 1}}. \tag{6.66}$$

The task of determining the wave functions is then that of determining the allowed values of k from the graphical solution, or numerically, and then substituting those vaules into the above expressions for the wave function. The wave functions found a similar in appearance to the infinte well wave functions, with the big difference that they are non-zero outside the well. This is true even if the particle has the lowest allowed energy, i.e. there is a non-zero probability of finding the particle outside the well. This probability can be readily calculated, being just

$$P_{outside} = |B|^2\left[\int_{-\infty}^{0} e^{-2\alpha x}\,dx + \int_{L}^{+\infty} e^{-2\alpha(x-L)}\,dx\right] = \alpha^{-1}|B|^2 \tag{6.67}$$

6.2.3 Scattering from a Potential Barrier

The above examples are of *bound states*, i.e. wherein the particles are confined to a limited region of space by some kind of attractive or confining potential. However, not all potentials are attractive (e.g. two like charges repel), and in any case, even when there is an attractive potential acting (two opposite charges attracting), it is possible that the particle can be 'free' in the sense that it is not confined to a limited region of space. A simple example of this, classically, is that of a comet orbiting around the sun. It is possible for the comet to follow an orbit in which it initially moves towards the sun, then around the sun, and then heads off into deep space, never to return. This is an example of an unbound orbit, in contrast to the orbits of comets that return repeatedly, though sometimes very infrequently, such as Halley's comet. Of course, the orbiting planets are also in bound states.

A comet behaving in the way just described – coming in from infinity and then ultimately heading off to infinity after bending around the sun – is an example of what is known as a scattering process. In this case, the potential is attractive, so we have the possibility of both scattering occurring, as well as the comet being confined to a closed orbit – a bound state. If the potential was repulsive, then only scattering would occur.

The same distinction applies in quantum mechanics. It is possible for the particle to confined to a limited region in space, in which case the wave function must satisfy the boundary condition that

$$\psi(x) \to 0 \qquad \text{as} \qquad x \to \pm\infty.$$

As we have seen, this boundary condition is enough to yield the quantization of energy. However, in the quantum analogue of scattering, it turns out that energy is not quantized. This in part can be linked to the fact that the wave function that describes the scattering of a particle of a given energy does not decrease as $x \to \pm\infty$, so that the very thing that leads to the quantization of energy for a bound particle does not apply here.

This raises the question of what to do about the quantization condition, i.e. that

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

If the wave function does not go to zero as $x \to \pm\infty$, then it is not possible for the wave function to satisfy this normalization condition – the integral will always diverge.

So how are we to maintain the claim that the wave function must have a probability interpretation if one of the principal requirements, the normalization condition, does not hold true? Strictly speaking, a wave function that cannot be normalized to unity is not physically permitted (because it is inconsistent with the probability interpretation of the wave function). Nevertheless, it is possible to retain, and work with, such wave functions, provided a little care is taken. The answer lies in interpreting the wave function so that $|\Psi(x,t)|^2 \propto$ particle flux[5], though we will not be developing this idea to any extent here.

To illustrate the sort of behaviour that we find with particle scattering, we will consider a simple, but important case, which is that of a particle scattered by a potential barrier. This is sufficient to show the sort of things that can happen that agree with our classical intuition, but it also enables us to see that there occurs new kinds of phenomena that have no explanation within classical physics.

Thus, we will investigate the scattering problem of a particle of energy E interacting with a potential $V(x)$ given by:

$$\begin{aligned} V(x) =& 0 \quad x < 0 \\ V(x) =& V_0 \quad x > 0. \end{aligned} \tag{6.68}$$

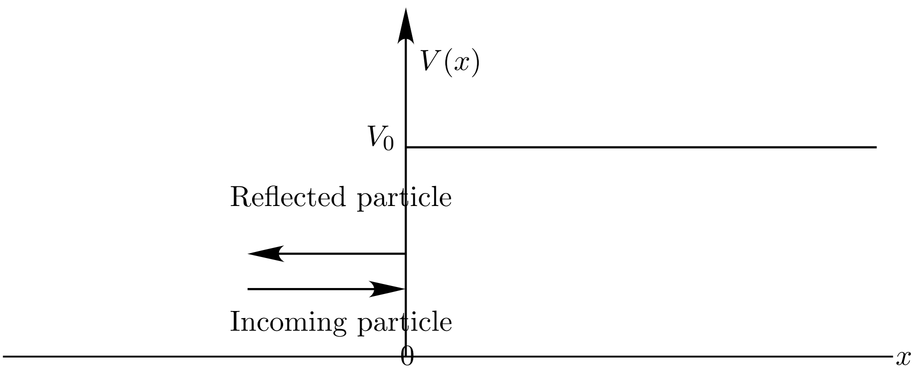

Figure 6.3: Potential barrier with particle of energy $E < V_0$ incident from the left. Classically, the particle will be reflected from the barrier.

In Fig. (6.3) is illustrated what we would expect to happen if a classical particle of energy $E < V_0$ were incident on the barrier: it would simply bounce back as it has insufficient energy to cross over to $x > 0$. Quantum mechanically we find that the situation is not so simple.

Given that the potential is as given above, the Schrödinger equation comes in two parts:

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} &= E\psi \quad x < 0 \\ -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V_0\psi &= E\psi \quad x > 0 \end{aligned} \tag{6.69}$$

where E is, once again, the total energy of the particle.

[5]In more advanced treatments, it is found that the usual probability interpretation does, in fact, continue to apply, though the particle is described not by a wave function corresponding to a definite energy, but rather by a wave packet, though then the particle does not have a definite energy.

We can rewrite these equations in the following way:

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \quad x < 0$$
$$\frac{d^2\psi}{dx^2} - \frac{2m}{\hbar^2}\Big(V_0 - E\Big)\psi = 0 \quad x > 0 \tag{6.70}$$

If we put

$$k = \frac{\sqrt{2mE}}{\hbar} \tag{6.71}$$

then the first equation becomes

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad x < 0$$

which has the general solution

$$\psi = Ae^{ikx} + Be^{-ikx} \tag{6.72}$$

where A and B are unknown constants. We can get an idea of what this solution means if we reintroduce the time dependence (with $\omega = E/\hbar$):

$$\begin{aligned} \Psi(x,t) =& \psi(x)e^{-iEt/\hbar} &=& \quad \psi(x)e^{-i\omega t} \\ =& Ae^{i(kx-\omega t)} &+& \quad Be^{-i(kx+\omega t)} \\ =& \text{wave travel-} &+& \quad \text{wave travel-} \\ & \text{ling to right} && \quad \text{ling to left} \end{aligned} \tag{6.73}$$

i.e. this solution represents a wave associated with the particle heading towards the barrier and a reflected wave associated with the particle heading away from the barrier. Later we will see that these two waves have the same amplitude, implying that the particle is perfectly reflected at the barrier.

In the region $x > 0$, we write

$$\alpha = \sqrt{2m(V_0 - E)}/\hbar > 0 \tag{6.74}$$

so that the Schrödinger equation becomes

$$\frac{d^2\psi}{dx^2} - \alpha^2\psi = 0 \quad x > 0 \tag{6.75}$$

which has the solution

$$\psi = Ce^{-\alpha x} + De^{\alpha x} \tag{6.76}$$

where C and D are also unknown constants.

The problem here is that the $\exp(\alpha x)$ solution grows exponentially with x, and we do not want wave functions that become infinite: it would essentially mean that the particle is forever to be found at $x = \infty$, which does not make physical sense. So we must put $D = 0$. Thus, if we put together our two solutions for $x < 0$ and $x > 0$, we have

$$\begin{aligned} \psi =& Ae^{ikx} + Be^{-ikx} \quad x < 0 \\ =& Ce^{-\alpha x} \quad x > 0. \end{aligned} \tag{6.77}$$

If we reintroduce the time dependent factor, we get

$$\Psi(x,t) = \psi(x)e^{-i\omega t} = Ce^{-\alpha x}e^{-i\omega t} \tag{6.78}$$

which is *not* a travelling wave at all. It is a stationary wave that simply diminishes in amplitude for increasing x.

We still need to determine the constants A, B, and C. To do this we note that for arbitrary choice of these coefficients, the wave function will be discontinuous at $x = 0$. For reasons connected with the requirement that probability interpretation of the wave function continue to make physical sense, we will require that the wave function *and* its first derivative both be continuous[6] at $x = 0$.

These conditions yield the two equations

$$\begin{aligned} C =& A + B \\ -\alpha C =& ik(A - B) \end{aligned} \tag{6.79}$$

which can be solved to give

$$\begin{aligned} B =& \frac{ik + a}{ik - a} A \\ C =& \frac{2ik}{ik - \alpha} A \end{aligned} \tag{6.80}$$

and hence

$$\begin{aligned} \psi(x) =& Ae^{ikx} + \frac{ik + a}{ik - a} Ae^{-ikx} \quad x < 0 \\ =& \frac{2ik}{ik - \alpha} Ae^{-\alpha x} \quad x < 0. \end{aligned} \tag{6.81}$$

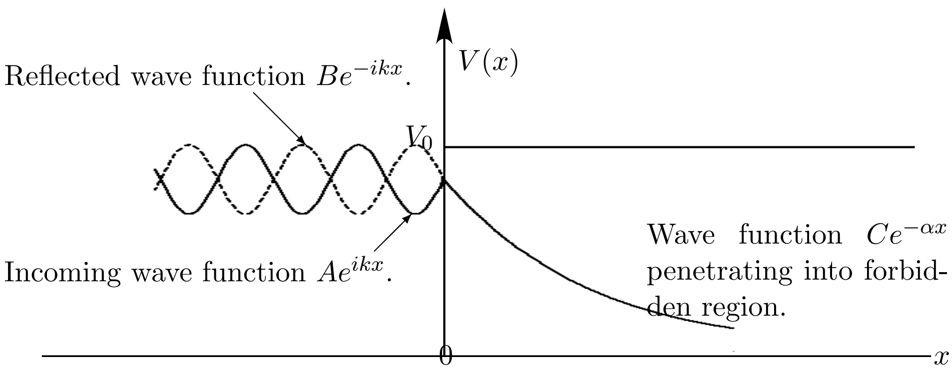

Figure 6.4: Potential barrier with wave function of particle of energy $E < V_0$ incident from the left (solid curve) and reflected wave function (dotted curve) of particle bouncing off barrier. In the clasically 'forbidden' region of $x > 0$ there is a decaying wave function. Note that the complex wave functions have been represented by their real parts.

Having obtained the mathematical solution, what we need to do is provide a physical interpretation of the result.

[6]To properly justify these conditions requires introducing the notion of 'probability flux', that is the rate of flow of probability carried by the wave function. The flux must be such that the point $x = 0$, where the potential is discontinuous, does not act as a 'source' or 'sink' of probability. What this means, as is shown later, is that we end up with $|A| = |B|$, i.e. the amplitude of the wave arriving at the barrier is the same as the amplitude of the wave reflected at the barrier. If they were different, it would mean that there is more probability flowing into the barrier than is flowing out (or vice versa) which does not make physical sense.

First we note that we cannot impose the normalization condition as the wave function does not decrease to zero as $x \to -\infty$. But, in keeping with comments made above, we can still learn something from this solution about the behaviour of the particle.

Secondly, we note that the incident and reflected waves have the same 'intensity'

$$\begin{aligned}\text{Incident intensity} =& |A|^2\\ \text{Reflected intensity} =& |A|^2\left|\frac{ik+\alpha}{ik-\alpha}\right|^2 = |A|^2\end{aligned} \tag{6.82}$$

and hence they have the same amplitude. This suggests that the incident de Broglie wave is totally reflected, i.e. that the particle merely travels towards the barrier where it 'bounces off', as would be expected classically. However, if we look at the wave function for $x > 0$ we find that

$$\begin{aligned}|\psi(x)|^2 \propto& \left|\frac{2ik}{ik-\alpha}\right|^2 e^{-2\alpha x}\\ =& \frac{4k^2}{\alpha^2+k^2}e^{-2\alpha x}\end{aligned} \tag{6.83}$$

which is an exponentially decreasing probability.

This last result tells us that there is a non-zero probability of finding the particle in the region $x > 0$ where, classically, the particle has no chance of ever reaching. The distance that the particle can penetrate into this 'forbidden' region is given roughly by $1/2\alpha$ which, for a subatomic particle can be a few nanometers, while for a macroscopic particle, this distance is immeasurably small.

The way to interpret this result is along the following lines. If we imagine that a particle is fired at the barrier, and we are waiting a short distance on the far side of the barrier in the forbidden region with a 'catcher's mitt' poised to grab the particle then we find that *either* the particle hits the barrier and bounces off with the same energy as it arrived with, but with the opposite momentum – it never lands in the mitt, *or* it lands in the mitt and we catch it – it does not bounce off in the opposite direction. The chances of the latter occurring are generally very tiny, but it occurs often enough in microscopic systems that it is a phenomenon that is exploited, particularly in solid state devices. Typically this is done, not with a single barrier, but with a barrier of finite width, in which case the particle can penetrate through the barrier and reappear on the far side, in a process known as quantum tunnelling.

6.3 Expectation Value of Momentum

We can make use of Schrödinger's equation to obtain an alternative expression for the expectation value of momentum given earlier in Eq. (5.13). This expression is

$$\langle p\rangle = m\langle v(t)\rangle = m\int_{-\infty}^{+\infty} x\left[\frac{\partial\Psi^*(x,t)}{\partial t}\Psi(x,t) + \Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial t}\right]dx. \tag{6.84}$$

We note that the appearance of time derivatives in this expression. If we multiply both sides by $i\hbar$ and make use of Schrödinger's equation, we can substitute for these time derivatives to give

$$i\hbar\langle p\rangle = m\int_{-\infty}^{+\infty} x\left[\left\{\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*(x,t)}{\partial x^2} - V(x)\Psi^*(x,t)\right\}\Psi(x,t)\right. \tag{6.85}$$

$$\left. + \Psi^*(x,t)\left\{-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t)\right\}\right]dx. \tag{6.86}$$

The terms involving the potential cancel. The common factor $\hbar^2/2m$ can be moved outside the integral, while both sides of the equation can be divided through by $i\hbar$, yielding a slightly less complicated experssion for $\langle p\rangle$:

$$\langle p\rangle = -\tfrac{1}{2}i\hbar\int_{-\infty}^{+\infty} x\left[\frac{\partial^2\Psi^*(x,t)}{\partial x^2}\Psi(x,t) - \Psi^*(x,t)\frac{\partial^2\Psi(x,t)}{\partial x^2}\right]dx. \tag{6.87}$$

Integrating both terms in the integrand by parts then gives

$$\begin{aligned}\langle p\rangle =&\tfrac{1}{2}i\hbar\int_{-\infty}^{+\infty}\left[\frac{\partial\Psi^*(x,t)}{\partial x}\frac{\partial x\Psi(x,t)}{\partial x} - \frac{\partial x\Psi^*(x,t)}{\partial x}\frac{\partial\Psi(x,t)}{\partial x}\right]dx\\ &+\tfrac{1}{2}i\hbar\left[\frac{\partial\Psi^*(x,t)}{\partial x}\Psi(x,t) - \Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x}\right]_{-\infty}^{+\infty}\end{aligned} \tag{6.88}$$

As the wave function vanishes for $x\to\pm\infty$, the final term here will vanish. Carrying out the derivatives in the integrand then gives

$$\langle p\rangle = \tfrac{1}{2}i\hbar\int_{-\infty}^{+\infty}\left[\frac{\partial\Psi^*(x,t)}{\partial x}\Psi(x,t) - \Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x}\right]dx \tag{6.89}$$

Integrating the first term only by parts once again then gives

$$\langle p\rangle = -i\hbar\int_{-\infty}^{+\infty}\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x}dx + \tfrac{1}{2}i\hbar\Psi^*(x,t)\Psi(x,t)\Big|_{-\infty}^{+\infty}. \tag{6.90}$$

Once again, the last term here will vanish as the wave function itself vanishes for $x\to\pm\infty$ and we are left with

$$\langle p\rangle = -i\hbar\int_{-\infty}^{+\infty}\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x}dx. \tag{6.91}$$

This is a particularly significant result as it shows that the expectation value of momentum can be determined directly from the wave function – i.e. information on the momentum of the particle is contained within the wave function, along with information on the position of the particle. This calculation suggests making the identification

$$p\to -i\hbar\frac{\partial}{\partial x} \tag{6.92}$$

which further suggests that we can make the replacement

$$p^n\to\Big(-i\hbar\frac{\partial}{\partial x}\Big)^n \tag{6.93}$$

so that, for instance

$$\langle p^2\rangle = -\hbar^2\int_{-\infty}^{+\infty}\Psi^*(x,t)\frac{\partial^2\Psi(x,t}{\partial x^2}dx \tag{6.94}$$

and hence the expectation value of the kinetic energy of the particle is

$$\langle K\rangle = \frac{\langle p^2\rangle}{2m} = -\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty}\Psi^*(x,t)\frac{\partial^2\Psi(x,t}{\partial x^2}dx. \tag{6.95}$$

We can check this idea by turning to the classical formula for the total energy of a particle

$$\frac{p^2}{2m} + V(x) = E. \tag{6.96}$$

If we multiply this equation by $\Psi(x,t) = \psi(x)\exp(-iEt/\hbar)$ and make the replacement given in Eq. (6.94) we end up with

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{6.97}$$

which is just the time independent Schrödinger equation. So there is some truth in the ad hoc procedure outlined above.

This association of the physical quantity p with the derivative i.e. is an example of a physical observable, in this case momentum, being represented by a differential operator. This correspondence between physical observables and operators is to be found throughout quantum mechanics. In the simplest case of position, the operator corresponding to position x is itself just x, so there is no subtlties in this case, but as we have just seen this simple state of affairs changes substantially for other observables. Thus, for instance, the observable quantity K, the kinetic energy, is represented by the differential operator

$$K \to \widehat{K} = -\hbar^2\frac{\partial^2}{\partial x^2}. \tag{6.98}$$

while the operator associated with the position of the particle is $\hat{x}$ with

$$x \to \widehat{x} = x. \tag{6.99}$$

In this last case, the identification is trivial.

Updated: 23rd May 2005 at 11:13am.