Chapter 13

Solving Schrödinger's Wave Equation - (1)

Topics

Qualitative Solutions of the Schrödinger Equation. The Finite Depth Potential Well. Quantum Mechanical Tunnelling.

In this chapter we investigate solutions of Schrödinger's wave equation and apply these to a number of problems. In many cases we shall only find approximate solutions, since, in all but a few simple cases, the general exact solutions of Schrödinger's equation are highly non-trivial. We will develop a semi-quantitative approach, which involves simple calculation and quantitative sketching. For the important case of the harmonic oscillator, we will go one stage further and find a solution to the differential equation.

Another important aspect of this chapter is that it enables us to understand more clearly the physical meaning of second-order differential equations which are *omnipresent throughout physics*, for the simple reason that we need to know how physical quantities vary in space and time, as well as all the other spaces we work in.

13.1 Qualitative Solution of the Schrödinger Equation

In this section we develop approximate techniques for 'solving' Schrödinger's wave equation. We consider only one-dimensional problems initially although the techniques can mostly be extended to higher dimensions.

In chapter 12 we introduced the wave function as a means of deriving a probability density, in the sense that the probability of finding a particle in the range x to $x + \mathrm{d}x$ is

$$p(x)\,\mathrm{d}x = |\psi|^2\,\mathrm{d}x = \psi\psi^*\,\mathrm{d}x. \tag{13.1}$$

The wave function is normalised so that

$$\int_{-\infty}^{\infty} \psi\psi^*\mathrm{d}x = 1. \tag{13.2}$$

Let us now consider in a little more detail the boundary conditions that the wave function must satisfy. We have already met these in passing when we considered the infinitely deep square-well potential in Chapter 12. First of all, we note that, since the wave function must be normalisable, the function must tend to zero as $x \to \pm\infty$. We start with the time independent one-dimensional Schrödinger's equation in the form:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi = E\psi. \tag{13.3}$$

Re-arranging, we find

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

Integrating once from $-\infty$ to some general position x,

$$\frac{\mathrm{d}\psi}{\mathrm{d}x} = -\frac{2m}{\hbar^2}\int_{-\infty}^{x}(E - V)\psi\,\mathrm{d}x \tag{13.4}$$

Thus, even if there are discontinuities in $(E - V)$, for example, potential steps such as the walls of our square well, the integral (13.4) changes continuously (see Figure 13.1). Further, since $\mathrm{d}\psi/\mathrm{d}x$ is continuous, taking the next integral to find ψ, ψ must also be continuous.

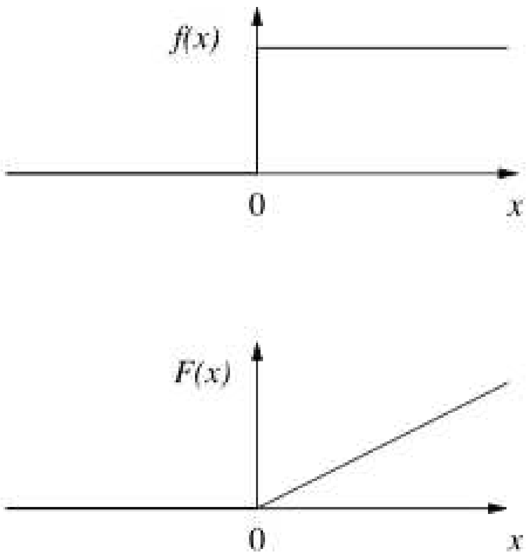


Figure 13.1 Integrating over a step: $F(x) = \int f(x)\,\mathrm{d}x$. Although $f(x)$ is discontinuous, $F(x) = \int f(x)\,\mathrm{d}x$ is continuous.

Hence, the three essential conditions for acceptable solutions of the wave equation are:

- ψ falls to zero as $x \to \pm\infty$
- $\dfrac{d\psi}{dx}$ is continuous
- ψ is continuous

Conditions on ψ

- ψ falls to zero as $x \to \pm\infty$
- $\dfrac{d\psi}{dx}$ is continuous
- ψ is continuous

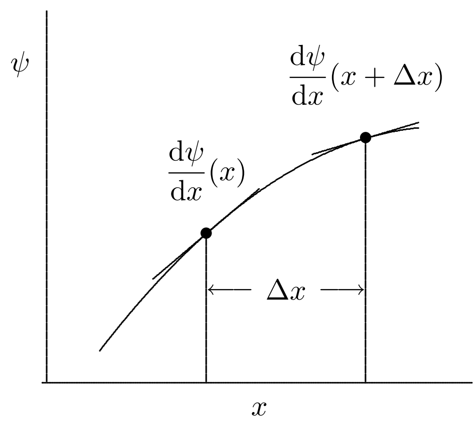
Schrödinger's equation also gives us directly important information about the shape of the wave function. $d^2\psi/dx^2 = d/dx(d\psi/dx)$ describes the rate of change of the *gradient* of ψ, in other words, it describes the *change of gradient* of the wave function with x, that is,

$$\frac{d}{dx}\left(\frac{d\psi}{dx}\right) = -\frac{2m}{\hbar^2}[E - V(x)]\psi \qquad (13.5)$$

We note some important consequences:

- To find the stationary 'wave-like' solutions of the equation, we require $E - V(x)$ to be positive. Otherwise, the wavefunction decays exponentially, if $V(x) > E$. We therefore see that (13.5) tells us that the *change* in gradient is always negative when moving from x to $x + \Delta x$. In other words, the function is always *concave* with respect to the x-axis (Figure 13.2). Furthermore, the rate of change of the gradient of ψ is given by the magnitude of $E - V(x)$. Hence, the lowest energy state has the minimum value of $E - V(x)$ and the wave function has the least curvature.

Figure 13.2. Illustrating the form of solution of Schrödinger's wave equation.



- In regions in which V is a constant, Schrödinger's equation reduces to

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

Adopting a trial solution $\psi = A\exp(ikx)$,

$$\frac{d^2\psi}{dx^2} = -k^2\psi \quad \text{and so} \quad k^2 = \frac{2m}{\hbar^2}(E - V)$$

or

$$k = \pm\frac{1}{\hbar}\left[2m(E - V)\right]^{1/2} \qquad (13.6)$$

- This result has an important physical interpretation. $(E - V)$ is the *kinetic energy* and therefore the greater the kinetic energy the greater the wave number and the shorter the wavelength.
- Although (13.6) is strictly correct only in regions in which V is a constant, we can use it approximately in regions in which V is changing to help us work out what the wave function looks like. We will give some examples in what follows.

13.2 The Finite Depth Potential Well

We now apply the discussion of section 13.1 to the problem of a potential well of finite depth. The potential function $V(x)$ is illustrated in Figure 13.3 and has the form:

$$V(x) = \begin{cases} V_0 & x < 0, \\ 0 & 0 \leq x \leq L, \\ V_0 & x > L. \end{cases}$$

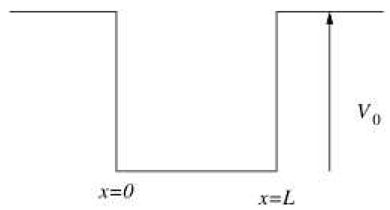


Figure 13.3. The finite depth potential well

Unlike the potential well we met in Chapter 12 the potential containing the particle is no longer infinite. The full solution of this problem is surprisingly tough mathematically, but the main physical results can be obtained using physical arguments.

First, we need to find the form of the wave function for the lowest energy state. Then, we will investigate how the ground-state energy differs from that of an infinitely deep potential well. We will answer these questions qualitatively. We will also assume that the potential well is sufficiently deep that the particle is confined within the well in the classical sense – we say that we seek a *bound state solution*, corresponding physically to the case when $E < V_0$.

We first consider the region with $x > L$. Classically a particle with total energy $E < V_0$ cannot enter these regions. As the particle approaches the wall, it would feel an infinite force for a vanishingly short time and be reflected. Quantum mechanically the solution is very different. The region $x > L$ is a

Remember $f = -\dfrac{\mathrm{d}V}{\mathrm{d}x}$

region of constant potential and so we can apply (13.6):

$$\begin{aligned} k &= \frac{1}{\hbar}\left[2m(E-V_0)\right]^{1/2}, \\ &= i\frac{1}{\hbar}\left[2m(V_0-E)\right]^{1/2}, \\ &= i\alpha, \end{aligned}$$

where α is a real number. What is the meaning of an imaginary wavenumber? Inserting the result into our trial solution, we find

$$\psi = A\exp(ikx) = A\exp(-\alpha x) \tag{13.7}$$

This result is perfectly sensible. It states that the wave function falls off exponentially in the classically forbidden region. The requirement that the wave function falls to zero at infinity is satisfied, but more important, since $|\psi|^2$ is non-zero for $x > L$, there is a finite probability of finding the particle in the classically forbidden region. We call a wave which falls off exponentially in this way an *evanescent wave* and, although we have met this in the context of quantum mechanics, classical examples of evanescent waves also exist. These include the incidence of electromagnetic waves upon a material of large, but finite, conductivity, viscous waves in a fluid, and so on.

Similar behaviour must exist for $x < 0$, but in this case the wave function must fall to zero at $-\infty$. This boundary condition is matched by taking the negative root of (13.6) so that $k = -i\alpha$ and $\psi = B\exp(\alpha x)$ for $x < 0$.

We can now sketch the lowest energy state, the ground state, of the finite potential well. To do so we shall use the following ideas, which we have already discussed.

- The wave function falls off exponentially in the classically forbidden regions.
- The ground state has the lowest energy E and therefore the wave function has the smallest curvature in the region $0 \leq x \leq L$. This means that the waves must have the largest allowable wavelength. This is very similar to

the requirements for the infinitely deep well, except that now the wave function does *not* go to zero at the walls. Instead this part of the wave function must join smoothly onto the exponentially decaying part of the solution.

- Taking these considerations together and remembering that both ψ and $\mathrm{d}\psi/\mathrm{d}x$ must be continuous functions through the walls of the potential well, we see that we must obtain a function similar to a harmonic wave in the region $0 \leq x \leq L$ with wavelength such that $\lambda > 2L$. A sketch of the wave function for such a ground state is shown in the top diagram of Figure 13.4.

- For the infinitely deep potential well we showed that $\lambda_\infty = 2L$ and, since the wavelength is now greater than this case, the energy of the ground state of the finite depth potential well must be *less* than the energy of an infinitely deep well of the same width,

$$E < \frac{\hbar^2 k_\infty^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2}$$

Once again, the ground state energy is not equal to zero – there is a zero-point energy, as we found for the infinitely deep potential well. The physical reasons for this are the same as discussed earlier. This type of argument is extremely useful. We obtain an understanding of the form of the wave function and can say something important about the energy of the state.

We can extend the argument to higher energy states. Remember that, for the infinitely deep well, each successively higher energy level had an extra node in the wave function. We expect exactly the same behaviour in this case, and so the first energy level above the ground state – *the first excited state* – must have one node. We can again use symmetry arguments to understand the form of the wave function. The potential is symmetrical about the point $x = L/2$ and therefore we expect on physical grounds that the probability of finding our particle should also be symmetric about this point as is

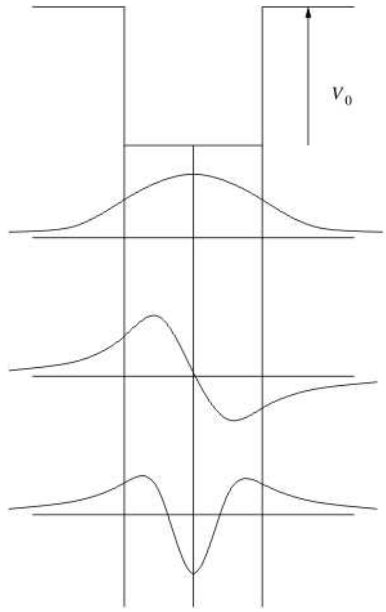


Figure 13.4. A sketch of the ground state wave function in the finite depth potential well

clearly true for the ground state. Now the first excited state $|\psi|^2$ must be symmetric about $x = L/2$, but this can be achieved if ψ is either *symmetric* or *anti-symmetric*. By the latter, we mean that the function changes sign about the point $x = L/2$. To meet these symmetry requirements with one node means that the node must be at $x = L/2$. The sketch solution is shown in the second diagram from the top of Figure 13.4.

The second excited state has two nodes and so the wave function can be *symmetric* about the point $x = L/2$ (see bottom diagram of Figure 13.4), while the third has three nodes and the wave function is *antisymmetric* about $x = L/2$ and so on. This feature of alternating between symmetric and anti-symmetric solutions is a common feature of any potential which is symmetric about a point.

We can extend these arguments to any form of potential to obtain an intuitive grasp of the form of the wave function and also obtain some constraints upon the energy of the states. We will consider further examples below.

13.3 Quantum Mechanical Tunnelling

Consider the finite rectangular potential barrier shown in Figure 13.5

$$V(x) = \begin{cases} \infty & x < 0, \\ 0 & 0 \leq x \leq L_1, \\ V_0 & L_1 < x < L_2, \\ 0 & x \geq L_2. \end{cases}$$

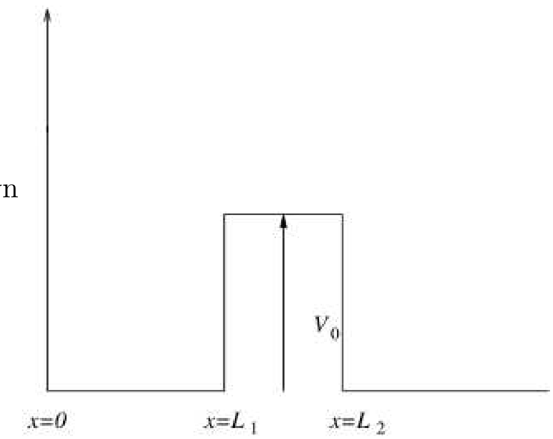


Figure 13.5. A finite rectangular potential barrier

We first need to find the bound states of this system in the interval $0 \leq x \leq L_1$ for particles with $E < V_0$. We apply the arguments just developed to obtain a semi-quantitative solution to this problem.

- In the regions in which $V = 0$, from (13.5) there are *harmonic-like* solutions with

  $$k = \sqrt{2mE}/\hbar.$$

  By 'harmonic-like', we mean that they are not quite complete sine or cosine functions because they 'leak' into the 'forbidden' region $L_1 < x < L_2$, as discussed in the last section.

- In the classically forbidden region, $L_1 < x < L_2$, the wave functions are *evanescent-like* functions with

$$\alpha = \sqrt{2m(V_0 - E)}/\hbar.$$

  Again, the solution is not perfectly exponential decay since we need to ensure continuity with the wave functions on either side of the barrier.

- The wave function must be zero at $x = 0$ and the whole solution must join smoothly across the boundaries at $x = L_1$ and $x = L_2$.

This solution is sketched in Figure 13.6. Something quite remarkable has happened. We have simply applied the rules we developed earlier and have found a surprising, but very important, result. Classically, if the particle were in the region $0 \le x \le L_1$, it would be trapped there forever since it could not pass through the barrier.

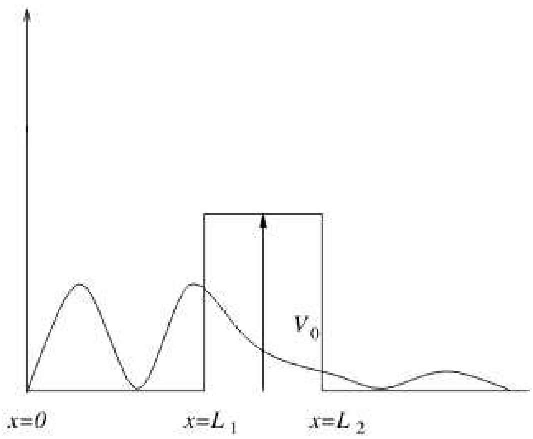


Figure 13.6. The probability distribution $\psi\psi^*$ in the presence of a potential barrier. Note that the wave function exists outside the region in which the classical particle would be confined.

In seeking a solution of the Schrödinger equation, however, we have shown that it is possible for the wave function to have a non-zero solution for $x > L_2$ and hence for there to be a probability of finding the particle in this region. The question is 'Does the wave function have non-zero amplitude at $x > L_2$?' The answer to this question is 'Yes'. Consider the solution in the region $L_1 < x < L_2$; the fastest the wave function can fall off in this region is as $\exp(-\alpha x)$, but it cannot fall to zero in the finite distance $L_2 - L_1$. The wave function must be non-zero at $x = L_1$ to join on smoothly to the solution inside the well and therefore the wave function must be non-zero for $x > L_2$.

This is the phenomenon known as *quantum mechnical tunnelling.* According to quantum mechanics, there is a finite probability of finding a particle outside a potential well in which, classically, it would be trapped. If we compare the amplitude of the wave function across the potential barrier, we see that it has decreased by $\exp[-\alpha(L_2 - L_1)]$. Hence, the probability of finding the particle just outside, compared to just inside, the barrier is the square of this ratio, $\exp[-2\alpha(L_2 - L_1)]$.

According to the precepts developed so far, the wave function describes the probability of finding a particle in the interval x to $x + \mathrm{d}x$. Alternatively, if there are many particles trapped in the potential well, we can think of the wave function as describing the density of particles at different locations in the x-direction. Furthermore, we can think of a stream of particles incident from the left upon the barrier shown in Figure 13.7. We can now apply the ideas we have just developed to this problem. Even if the particle energy is less than the barrier height $E < V_0$, a few particles can still pass through the barrier by quantum mechanical tunnelling. The fraction of the particles incident on the barrier which are transmitted is $|\psi(x > L)|^2/|\psi(x < 0)|^2$. But this ratio follows from our approximate analysis given above, resulting in a transmission coefficient, T:

This analogy is correct if the particles are non-interacting.

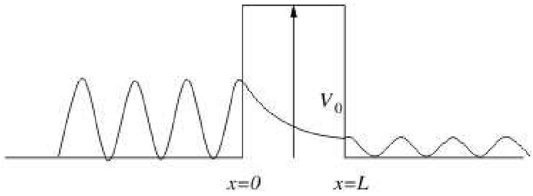


Figure 13.7. Tunnelling of particles as they approach a barrier

$$T = \frac{|\psi(x > L)|^2}{|\psi(x < 0)|^2} \approx \exp[-2\alpha(L_2 - L_1)] \qquad (13.8)$$

$$= \exp[-2\sqrt{2m(V_0 - E)}(L_2 - L_1)/\hbar] \qquad (13.9)$$

In the next chapter, we will apply these ideas to a variety of important physical processes which pervade much of modern physics and other sciences.