

Chapter 7

The Schroedinger Equation in One Dimension

In classical mechanics the state of motion of a particle is specified by the particle's position and velocity. In quantum mechanics the state of motion of a particle is given by the wave function. The goal is to predict how the state of motion will evolve as time goes by. This is what the equation of motion does. The classical equation of motion is Newton's second law $\mathbf{F} = m\mathbf{a}$. In quantum mechanics the equation of motion is the time-dependent Schroedinger equation. If we know a particles wave function at $t = 0$, the time-dependent Schroedinger equation determines the wave function at any other time.

The states of interest are the ones where the system has a definite total energy. In these cases, the wave function is a standing wave. When the time-dependent Schroedinger equation is applied to these standing waves, it reduces to the simpler time-independent Schroedinger equation. We will use the time-independent Schroedinger equation to find the wave function of the standing waves and the corresponding energies. So when we say "Schroedinger equation", we will mean the time-independent Schroedinger equation.

Even though the world is 3 dimensional, let's start by considering the the simple problem of a particle confined to move in just one dimension. For example, imagine an electron moving along a very narrow wire.

Classical Standing Waves

Let's review what we know about classical standing waves in 1D. Think of waves on a string where the string's displacement is described by $y(x, t)$. Or we might consider a sound wave with a pressure variation $p(x, t)$. For an EM wave, the wave function of the electric field would be $\vec{E}(x, t)$. We'll consider waves on a string for concreteness, but this will apply to all kinds of 1D waves, so we'll use the general notation $\Psi(x, t)$ to represent the wave function.

Let us consider first 2 sinusoidal traveling waves, one moving to the right,

$$\Psi_1(x, t) = B \sin(kx - \omega t) \tag{1}$$

and the other moving to the left with the same amplitude

$$\Psi_2(x, t) = B \sin(kx + \omega t) \tag{2}$$

The superposition principle guarantees that the sum of these two waves is itself a possible wave motion:

$$\Psi(x, t) = \Psi_1(x, t) + \Psi_2(x, t) = B[\sin(kx - \omega t) + \sin(kx + \omega t)] \tag{3}$$

Using the trigonometric identity

$$\sin a + \sin b = 2 \sin \left(\frac{a + b}{2} \right) \cos \left(\frac{a - b}{2} \right) \tag{4}$$

we can rewrite Eq. (3)

$$\Psi(x, t) = 2B \sin kx \cos \omega t \tag{5}$$

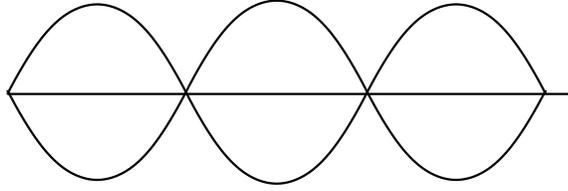


Figure 1: Standing Wave with Nodes

or if we set $2B = A$

$$\Psi(x, t) = A \sin kx \cos \omega t \quad (6)$$

The resulting wave is not traveling. It's a stationary standing wave as shown in Figure 1 (see also Figures 7.1 and 7.2). It has fixed points which don't move. These are called **nodes** of the wave function and they occur where $\sin kx = 0$ and hence $\Psi(x, t)$ is always zero. At any other point the string simply oscillates up and down. By superposing 2 traveling waves, we have formed a **standing wave**.

Now consider a string clamped between 2 fixed points separated by a distance a . What are the possible standing waves that can fit on the string? The distance between 2 adjacent nodes is $\lambda/2$, so the distance between any pair of nodes is an integer multiple of this, $n\lambda/2$. A standing wave fits on a string provided $n\lambda/2 = a$, i.e.,

$$\lambda = \frac{2a}{n} \quad \text{where } n = 1, 2, 3, \dots \quad (7)$$

Note that the possible wavelengths of a standing wave on a string of length a are quantized with the allowed values being $2a$ divided by any positive integer. The quantization of wavelengths arises from the requirement that the wave function must always be zero at the two fixed ends of the string. This is an example of a **boundary condition**. It is the boundary conditions that lead to quantization for both classical and quantum waves.

Standing Waves in Quantum Mechanics: Stationary States

Look at the classical standing wave:

$$\Psi(x, t) = A \sin kx \cos \omega t \quad (8)$$

It is a product of one function of x (namely, $A \sin kx$) and one function of t (namely, $\cos \omega t$). So we could rewrite Eq. (8) as a product of a function of space and a function of time:

$$\Psi(x, t) = \psi(x) \cos \omega t \quad (9)$$

where the capital letter Ψ represents the full wave function $\Psi(x, t)$ and the lower case letter ψ is for its spatial part $\psi(x)$. $\psi(x)$ gives the full wave function $\Psi(x, t)$ at time $t = 0$ (since $\cos \omega t = 1$ when $t = 0$).

In our particular example (a wave on a uniform string) the spatial function $\psi(x)$ was a sine function

$$\psi(x) = A \sin kx \quad (10)$$

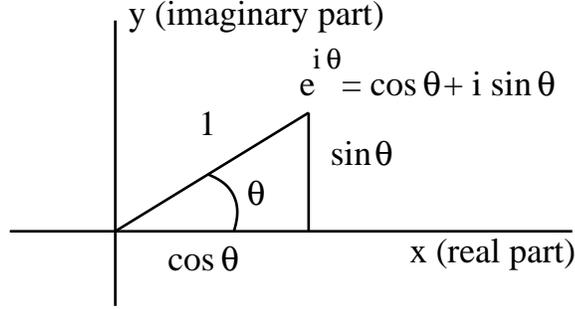


Figure 2: Complex number in the complex plane represented with polar angle θ .

but in more complicated problems, $\psi(x)$ can be a more complicated function of x . Even in these more complicated problems, the time dependence is still sinusoidal. It could be a sine or a cosine; the difference being just the choice in the origin of the time. The general sinusoidal standing wave is a combination of both:

$$\Psi(x, t) = \psi(x)(a \cos \omega t + b \sin \omega t) \quad (11)$$

Different choices for the ratio of the coefficients a and b correspond to different choices of the origin of time. For a classical wave, the function $\Psi(x, t)$ is a real number, and the coefficients a and b in (11) are always real. In quantum mechanics, on the other hand, the wave function can be a complex number, and for quantum standing waves it usually is complex. Specifically, the time-dependent part of the wave function (11) is given by

$$\cos \omega t - i \sin \omega t \quad (12)$$

That is, the standing waves of a quantum particle have the form

$$\Psi(x, t) = \psi(x)(\cos \omega t - i \sin \omega t) \quad (13)$$

We can simplify this using Euler's formula (see Figure 2)

$$\cos \theta + i \sin \theta = e^{i\theta} \quad (14)$$

The complex number $e^{i\theta}$ lies on a circle of radius 1, with polar angle θ . Notice that since $\cos(-\theta) = \cos \theta$ and $\sin(-\theta) = -\sin(\theta)$,

$$\cos \theta - i \sin \theta = e^{-i\theta} \quad (15)$$

we can write the general standing wave of a quantum system as

$$\Psi(x, t) = \psi(x)e^{-i\omega t} \quad (16)$$

Since this function has a definite angular frequency, ω , it has a definite energy $E = \hbar\omega$. Conversely, any quantum system that has a definite energy has a wave function of the form (16).

The probability density associated with a quantum wave function $\Psi(x, t)$ is the absolute value squared, $|\Psi(x, t)|^2$.

$$|\Psi(x, t)|^2 = |\psi(x)|^2 |e^{-i\omega t}|^2 = |\psi(x)|^2 \quad (17)$$

Thus, for a quantum standing wave, the probability density is independent of time. For a quantum standing wave, the distribution of matter is time independent or stationary. This is why it's called a **stationary state**. These are states of definite energy. Because their charge distribution is static, atoms in stationary states do not radiate.

The interesting part of the wave function $\Psi(x, t)$ is its spatial part $\psi(x)$. We will see that a large part of quantum mechanics is devoted to finding the possible spatial functions $\psi(x)$ and their corresponding energies. Our principal tool in finding these will be the time-independent Schroedinger equation.

The Particle in a Rigid Box

Consider a particle that is confined to some finite interval on the x axis, and moves freely inside that interval. This is a one-dimensional rigid box, and is often called the infinite square well. An example would be an electron inside a length of very thin conducting wire. The electron would move freely back and forth inside the wire, but could not escape from it.

Consider a quantum particle of mass m moving in a 1D rigid box of length a , with no forces acting on it inside the box between $x = 0$ and $x = a$. So the potential $U = 0$ inside the box. Therefore, the particle's total energy is just its kinetic energy. In quantum mechanics, we write the kinetic energy as $p^2/2m$, rather than $\frac{1}{2}mv^2$, because of the de Broglie relation, $\lambda = h/p$. (This will make more sense later.) So we write the energy as

$$E = K = \frac{p^2}{2m} \quad (18)$$

States of definite energy are standing waves that have the form

$$\Psi(x, t) = \psi(x)e^{-i\omega t} \quad (19)$$

By analogy with waves on a string, one might guess that the spatial function would have the form

$$\psi(x) = A \sin kx + B \cos kx \quad (20)$$

for $0 \leq x \leq a$.

Since it is impossible for the particle to escape from the box, the wave function must be zero outside; that is $\psi(x) = 0$ when $x < 0$ and when $x > a$. If we assume that $\psi(x)$ is continuous, then it must also vanish at $x = 0$ and $x = a$:

$$\psi(0) = \psi(a) = 0 \quad (21)$$

These boundary conditions are identical to those for a classical wave on a string clamped at $x = 0$ and $x = a$.

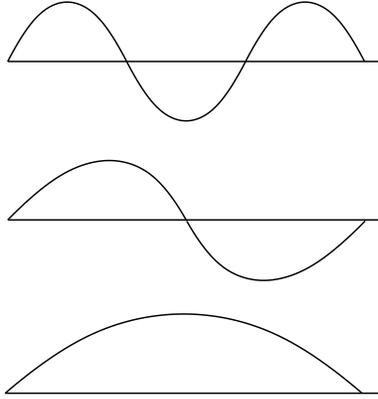


Figure 3: Wave functions in a rigid box for lowest 3 energy levels.

From (20) $\psi(0) = B = 0$ which leaves

$$\psi(x) = A \sin kx \quad (22)$$

The boundary condition $\psi(a) = 0$ requires that

$$A \sin ka = 0 \quad (23)$$

which implies that

$$ka = \pi, \text{ or } 2\pi, \text{ or } 3\pi, \dots \quad (24)$$

or

$$k = \frac{n\pi}{a} \quad n = 1, 2, 3, \dots \quad (25)$$

So the only standing waves that satisfy the boundary conditions (21) have the form $\psi(x) = A \sin kx$ with k given by (25). In terms of the wavelength, this condition implies that

$$\lambda = \frac{2\pi}{k} = \frac{2a}{n} \quad n = 1, 2, 3, \dots \quad (26)$$

which is precisely the condition for standing waves on a string. In both cases the quantization of wavelengths arose from the boundary condition that the wave function must be zero at $x = 0$ and $x = a$. The wave functions in Figure 3 (see also Fig. 7.5) look like standing waves on a string.

The important point is that quantization of the wavelength λ implies quantization of the momentum, and hence also of the energy. Substituting (26) into the de Broglie relation $p = h/\lambda$, we find that

$$p = \frac{nh}{2a} = \frac{n\pi\hbar}{a} \quad n = 1, 2, 3, \dots \quad (27)$$

Plugging this into $E = p^2/2m$ yields

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2ma^2} \quad n = 1, 2, 3, \dots \quad (28)$$

The **ground state energy** is obtained for $n = 1$:

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2} \quad (29)$$

This is consistent with the lower bound derived from the Heisenberg uncertainty principle for a particle confined in a region of length a :

$$E \geq \frac{\hbar^2}{2ma^2} \quad (30)$$

The actual minimum energy (29) is larger than the lower bound (30) by a factor of $\pi^2 \approx 10$. In terms of the ground state energy E_1 , the energy of the n th level (28) is

$$E_n = n^2 E_1 \quad n = 1, 2, 3, \dots \quad (31)$$

Note that the energy levels are farther and farther apart as n increases and that E_n increases without limit as $n \rightarrow \infty$. The number of nodes of the wave functions increases steadily with energy; this is what one should expect since more nodes mean shorter wavelength (larger curvature of ψ) and hence larger momentum and kinetic energy. You can see this from

$$\begin{aligned} p &= \frac{h}{\lambda} \\ E &= \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} \end{aligned}$$

The complete wave function $\Psi(x, t)$ for any of our standing waves has the form

$$\Psi(x, t) = \psi(x)e^{-i\omega t} = A \sin(kx)e^{-i\omega t} \quad (32)$$

Using the identity

$$\sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i} \quad (33)$$

we can write

$$\Psi(x, t) = \frac{A}{2i} \left(e^{i(kx-\omega t)} - e^{-i(kx+\omega t)} \right) \quad (34)$$

Thus, our quantum standing wave (just like the classical standing wave) can be expressed as the sum of two traveling waves, one moving to the right and one moving to the left. The right-moving wave represents a particle with momentum $\hbar k$ directed to the right, and the left-moving wave represents a particle with momentum $\hbar k$ but directed to the

left. So a particle in a stationary state has momentum with magnitude $\hbar k$ but is an equal superposition of momenta in either direction. This corresponds to the result that on average a classical particle is equally likely to be moving in either direction as it bounces back and forth inside a rigid box.

The Time-Independent Schroedinger Equation

Our discussion of the particle in a rigid box required some guessing as to the form of the spatial wave function $\psi(x)$. We want to take the guesswork out of finding $\psi(x)$. So we need an equation to determine $\psi(x)$. This is what the time-independent Schroedinger equation does. Like all basic laws of physics, the Schroedinger equation cannot be derived. However, we can try to motivate it.

Almost all laws of physics can be expressed as differential equations. For example, Newton's second law:

$$m \frac{d^2 x}{dt^2} = \sum F \quad (35)$$

Another example is the equation of motion for classical waves which is a differential equation. We expect the equation that determines the possible standing waves of a quantum system to be a differential equation. Since we already know the form of the wave functions for a particle in a box, we can try to spot a simple differential equation that they satisfy and that we can generalize to more complicated systems.

$$\begin{aligned} \psi(x) &= A \sin kx \\ \frac{d\psi}{dx} &= kA \cos kx \\ \frac{d^2\psi}{dx^2} &= -k^2 A \sin kx \\ \frac{d^2\psi}{dx^2} &= -k^2 \psi \end{aligned} \quad (36)$$

We can rewrite k^2 in (36) in terms of the particle's kinetic energy K . Using $p = \hbar k$, we have

$$K = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad (37)$$

$$k^2 = \frac{2mK}{\hbar^2} \quad (38)$$

$$\frac{d^2\psi}{dx^2} = -\frac{2mK}{\hbar^2} \psi \quad (39)$$

Since the kinetic energy K is the difference between the total energy E and the potential energy $U(x)$, we can replace K in (39) by

$$K = E - U(x) \quad (40)$$

to get

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2} [U(x) - E] \psi \quad (41)$$

This differential equation is called the **Schroedinger equation**, or more precisely, the **time-independent Schroedinger equation**, in honor of the Austrian physicist, Erwin Schroedinger, who first published it in 1926. There is no way to prove that this equation is correct. But its predictions agree with experiment. Schroedinger himself showed that it correctly predicts the energy levels of the hydrogen atom. The Schroedinger equation is the basis of nonrelativistic quantum mechanics.

Here is the general procedure for using the equation. Given a system whose stationary states and energies we want to know, we must first find the potential energy function $U(x)$. For example, a particle in a harmonic oscillator potential (a spring potential) has potential energy

$$U(x) = \frac{1}{2}kx^2 \quad (42)$$

Another example is an electron in a hydrogen atom:

$$U(x) = -\frac{ke^2}{r} \quad (43)$$

In most cases, it turns out that for many values of the energy E , the Schroedinger equation has no solutions, i.e., no acceptable solutions satisfying the particular conditions of the problem. This leads to the quantization of the energy. As a result, only certain values of the energy are allowed and these are called eigenvalues. Associated with each eigenvalue is a stationary wave function called an eigenfunction.

An acceptable solution must satisfy certain conditions. First $\psi(x)$ may have to satisfy boundary conditions, e.g., $\psi(x)$ must vanish at the walls of a perfectly rigid box with infinitely high walls ($U = \infty$). Another condition is that $\psi(x)$ must always be continuous, and in most problems, its first derivative must also be continuous. An acceptable solution of the Schroedinger equation must satisfy all the conditions appropriate to the problem at hand.

Note that quantum mechanics focuses primarily on potential energies, whereas Newtonian mechanics focuses on forces.

The Rigid Box Again

As a first application of the Schroedinger equation, we use it to rederive the allowed energies of a particle in a rigid box and check that we get the same answers as before. We start by identifying the potential energy function $U(x)$. Inside the box the potential energy is zero, and outside the box it is infinite. Thus

$$U(x) = \begin{cases} 0 & \text{for } 0 \leq x \leq a \\ \infty & \text{for } x < 0 \text{ and } x > a \end{cases} \quad (44)$$

This potential energy function is often described as an infinitely deep square well because a graph of $U(x)$ looks like a well with infinitely high sides and square corners (see Figure 4).

Since $U(x) = \infty$ outside the box, the particle can never be found there, so $\psi(x)$ must be zero outside the box, i.e., when $x < 0$ and when $x > a$. The continuity of $\psi(x)$ requires

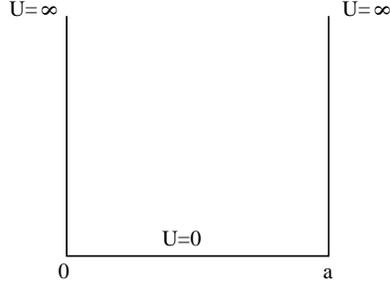


Figure 4: Rigid box potential.

that

$$\psi(0) = \psi(a) = 0 \quad (45)$$

Inside the box, where $U(x) = 0$, the Schroedinger equation reduces to

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi \quad \text{for } 0 \leq x \leq a \quad (46)$$

Introducing the shorthand notation:

$$\psi' = \frac{d\psi}{dx} \quad \text{and} \quad \psi'' = \frac{d^2\psi}{dx^2} \quad (47)$$

yields

$$\psi''(x) = -\frac{2mE}{\hbar^2}\psi(x) \quad (48)$$

Show that no solutions have negative energy: If $E < 0$, the coefficient $-2mE/\hbar^2$ on the right side of (48) would be positive and we could call it α^2 , where

$$\alpha = \frac{\sqrt{-2mE}}{\hbar} \quad (49)$$

So Eq. (48) becomes

$$\psi''(x) = \alpha^2\psi(x) \quad (50)$$

This is a second order differential equation which has the solutions $\exp(\alpha x)$ and $\exp(-\alpha x)$ or any combination of these:

$$\psi(x) = Ae^{\alpha x} + Be^{-\alpha x} \quad (51)$$

where A and B are any constants, real or complex. Eq. (51) is the most general solution of Eq. (50), i.e., every solution of Eq. (50) has the form of Eq. (51). Here are some facts about second order differential equations: These equations always have 2 independent solutions, e.g., $\psi_1(x)$ and $\psi_2(x)$, such that a linear combination

$$\psi(x) = A\psi_1(x) + B\psi_2(x) \quad (52)$$

is also a solution for any constants A and B . In addition, given 2 independent solutions, $\psi_1(x)$ and $\psi_2(x)$, every solution can be expressed as a linear combination of the form (52). So, if by any means, we can spot 2 independent solutions, we are assured that every solution is a linear combination of these two.

Having 2 arbitrary constants, A and B , comes from the following consideration. The differential equation has a second derivative $\psi''(x)$. To find $\psi(x)$, one has to effectively do 2 integrations which produces 2 constants of integration. The 2 arbitrary constants correspond to these 2 constants of integration.

Since $e^{\alpha x}$ and $e^{-\alpha x}$ are independent solutions of (50), it follows that the most general solution is (51). The next question is whether any of these solutions could satisfy the required boundary conditions (45), and the answer is 'no'. To see this, note that $\psi(0) = 0$ implies that

$$A + B = 0 \quad (53)$$

while $\psi(a) = 0$ implies that

$$Ae^{\alpha a} + Be^{-\alpha a} = 0 \quad (54)$$

The only way to satisfy these 2 conditions is $A = B = 0$. So if $E < 0$, then the only solution of the Schroedinger equation is $\psi = 0$. So if $E < 0$, then there can be no standing waves and so negative values of the energy E are not allowed. A similar argument gives the same conclusion for $E = 0$.

Solutions for positive energy: With $E > 0$, the coefficient $-2mE/\hbar^2$ on the right hand side of (48) is negative and can be called $-k^2$ where

$$k = \frac{\sqrt{2mE}}{\hbar} \quad (55)$$

Then the Schroedinger equation reads

$$\psi''(x) = -k^2\psi(x) \quad (56)$$

The solutions are $\sin kx$ and $\cos kx$. The general solution has the form

$$\psi(x) = A \sin kx + B \cos kx \quad (57)$$

This is exactly the form of the wave function that we assumed earlier, but now we have derived it from the Schroedinger equation. You can plug (57) into the Schroedinger equation (56) to show that it is a solution of the Schroedinger equation. Everything now proceeds as before. The boundary condition $\psi(0) = 0$ requires that $B = 0$ in (57). The boundary condition $\psi(a) = 0$ can be satisfied without setting A to zero by requiring $\sin ka = 0$ which leads to

$$k = \frac{n\pi}{a} \quad (58)$$

Plugging this into $p = \hbar k$ and $E = p^2/2m = (\hbar^2 k^2)/2m$ yields

$$E = \frac{\hbar^2 k^2}{2m} = n^2 \frac{\pi^2 \hbar^2}{2ma^2} \quad (59)$$

as before.

We have one loose end to take care of. What determines A in wave function?

$$\psi(x) = A \sin \frac{n\pi x}{a} \quad (60)$$

To answer this, recall that $|\psi(x)|^2$ is the probability P of finding the particle between x and $x + dx$:

$$P(\text{between } x \text{ and } x + dx) = |\psi(x)|^2 dx \quad (61)$$

Since the total probability of finding the particle anywhere must be 1, it follows that

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1 \quad (62)$$

This relation is called the **normalization condition** and a wave function that satisfies it is said to be **normalized**. It is the condition (62) that fixes the value of the constant A , which is called the **normalization constant**.

In the case of the rigid box, $\psi(x)$ is zero outside the box. So we can write

$$\int_0^a |\psi(x)|^2 dx = 1 \quad (63)$$

or

$$A^2 \int_0^a \sin^2 \left(\frac{n\pi x}{a} \right) dx = 1 \quad (64)$$

The integral is $a/2$, so we obtain

$$\frac{A^2 a}{2} = 1 \quad (65)$$

so

$$A = \sqrt{\frac{2}{a}} \quad (66)$$

So the normalized wave functions for a particle in a rigid box is

$$\psi(x) = \sqrt{\frac{2}{a}} \sin \left(\frac{n\pi x}{a} \right) \quad (67)$$

Example 7.2 Consider a particle in the ground state of a rigid box of length a . (a) Find the probability density $|\psi|^2$. (b) Where is the particle most likely to be found? (c) What is the probability of finding a particle in the interval between $x = 0.50a$ and $x = 0.51a$? (skip (d)) (e) What would be the average result if the position of a particle in the ground state were measured many times?

Solution:

(a) The probability density is just $|\psi(x)|^2$, where $\psi(x)$ is given by (67) with $n = 1$. Therefore it is

$$|\psi(x)|^2 = \frac{2}{a} \sin^2 \left(\frac{\pi x}{a} \right) \quad (68)$$

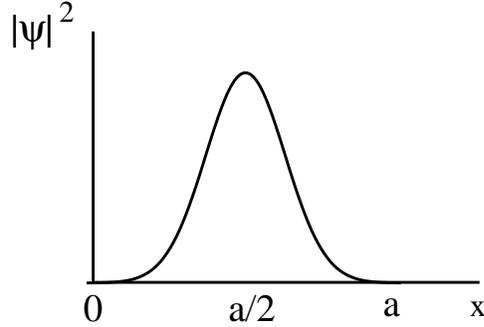


Figure 5: Probability density of a particle in the ground state of a rigid box.

which is sketched in Figure 5 (see also Fig. 7.6).

(b) The most probable value, x_{mp} , is the value of x for which $|\psi(x)|^2$ is a maximum. From Figure 7.6, this is seen to be

$$x_{mp} = a/2 \quad (69)$$

(c) The probability of finding the particle in any small interval from x to $x + \Delta x$ is given by (61) as

$$P(\text{between } x \text{ and } x + \Delta x) \approx |\psi(x)|^2 \Delta x \quad (70)$$

Thus,

$$P(0.50a \leq x \leq 0.51a) \approx |\psi(x = 0.50a)|^2 \Delta x = \frac{2}{a} \sin^2\left(\frac{\pi}{2}\right) \times 0.01a = 0.02 = 2\% \quad (71)$$

(e) The average result if we measure the position many times (always with the particle in the same state) is

$$\langle x \rangle = \int_0^a x |\psi(x)|^2 dx \quad (72)$$

The average value $\langle x \rangle$ is called the **expectation value** of x . It is the average value expected after many measurements. For the ground state

$$\langle x \rangle = \frac{2}{a} \int_0^a x \sin^2\left(\frac{\pi x}{a}\right) dx \quad (73)$$

$$= \frac{a}{2} \quad (74)$$

For the ground state of a particle in a box, the most probable position x_{mp} and the mean position $\langle x \rangle$ are the same, but this is not always the case as we shall see.

Expectation Values

In Example 7.2 we introduced the notation of the expectation value $\langle x \rangle$ of x . This is not the value of x expected in any one measurement; rather it is the average value

expected if we repeat the measurement many times (always with the system in the same state).

A quantity x can take various values with different probabilities. x could be a continuous or a discrete variable. Let us first consider the discrete case: Suppose the possible results of the measurement are $x_1, x_2, \dots, x_i, \dots$ and that these results occur with probabilities $P_1, P_2, \dots, P_i, \dots$. If a large number N of statistically independent measurements are made, the number of measurements resulting in the value x_i will be $n_i = P_i \cdot N$, i.e., $P_i = n_i/N$ is the fraction of the measurements that yield the value x_i . The average value of x is the sum of all the results of all the measurements divided by the total number N . Since n_i of the measurements produce the value x_i , this sum of all the measurements is $\sum_i n_i x_i$, and the average value is

$$\langle x \rangle = \frac{1}{N} \sum_i n_i x_i \quad (75)$$

$$= \sum_i \frac{n_i}{N} x_i \quad (76)$$

$$= \sum_i P_i x_i \quad (77)$$

If x is a continuous variable, the probability P_i is replaced with a probability increment $p(x)dx$, where $p(x)$ is the probability density. For example, if x is the position of a quantum particle, $p(x)dx = |\psi(x)|^2 dx$. Then we get

$$\langle x \rangle = \sum_i P_i x_i \quad \rightarrow \quad \langle x \rangle = \int x p(x) dx \quad (78)$$

More generally, if we measure x^2 or x^3 or any function $f(x)$, we can repeat the same argument, simply replacing x with $f(x)$, and conclude that

$$\langle f(x) \rangle = \int f(x) p(x) dx \quad (79)$$

Example 7.3

Answer the same questions as in Example 7.2 but for the first excited state of the rigid box.

Solution:

The wave function is given by (67) with $n = 2$, so

$$|\psi(x)|^2 = \frac{2}{a} \sin^2 \left(\frac{2\pi x}{a} \right) \quad (80)$$

This is plotted in Figure 6 (see also Fig. 7.7) and shows a double peaked function symmetric about $x = 1/2$. The 2 maxima are at

$$x_{mp} = \frac{a}{4} \quad \text{and} \quad \frac{3a}{4} \quad (81)$$

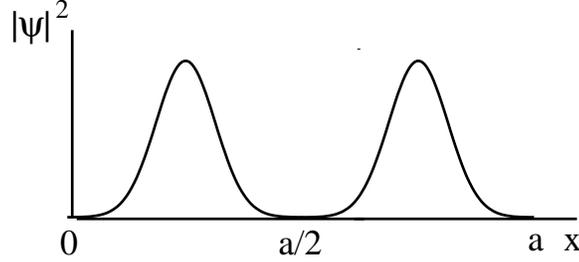


Figure 6: Probability density for a particle in the first excited state of a rigid box.

The expectation value $\langle x \rangle$ is

$$\langle x \rangle = \frac{a}{2} \quad (82)$$

Probability of finding a particle between $0.50 \leq x \leq 0.51$ is

$$P(0.50 \leq x \leq 0.51) \approx |\psi(0.50a)|^2 \Delta x = 0 \quad (83)$$

since $\psi(0.50a) = 0$. Notice that although $x = a/2$ is the average value of x , the probability of finding the particle in the immediate neighborhood of $x = a/2$ is zero.

The Free Particle ($U = 0$)

The energy of the particle can have any positive value $E \geq 0$, i.e., the energy of a free particle is not quantized, and its allowed values are the same as those of a classical free particle.

Since $U = 0$, the Schrodinger equation becomes

$$\psi''(x) = -\left(\frac{2mE}{\hbar^2}\right) \psi(x) \quad (84)$$

This is like a particle in a rigid box but with the walls infinitely far apart so that

$$-\infty < x < \infty \quad (85)$$

Negative Energies: First let us show that no states have $E < 0$. If $E < 0$, the coefficient $-2mE/\hbar^2$ in (84) is positive and we can write

$$\psi''(x) = \alpha^2 \psi(x) \quad (86)$$

where $\alpha = \sqrt{-2mE/\hbar}$. The solutions are $\exp(\alpha x)$ and $\exp(-\alpha x)$ or a linear combination of both:

$$\psi(x) = Ae^{\alpha x} + Be^{-\alpha x} \quad (87)$$

As $x \rightarrow \infty$, $\exp(\alpha x)$ blows up which is not physically reasonable. It makes $\psi(x)$ impossible to normalize. So we must have $A = 0$. Similarly, as $x \rightarrow -\infty$, $\exp(-\alpha x)$ blows up and so $B = 0$, leaving $\psi(x) \equiv 0$. So there are no acceptable states with $E < 0$.

An acceptable wave function $\psi(x)$ must not blow up as $x \rightarrow \pm\infty$. This is another example of a boundary condition, since the points $x = \pm\infty$ are the boundaries of the system.

Nonnegative Energies: Now consider $E \geq 0$. The Schroedinger equation becomes

$$\psi''(x) = -\left(\frac{2mE}{\hbar^2}\right)\psi(x) = -k^2\psi(x) \quad (88)$$

where

$$k = \frac{\sqrt{2mE}}{\hbar} \quad (89)$$

As before, the general solution is

$$\psi(x) = A \sin kx + B \cos kx \quad (90)$$

Note that neither $\sin kx$ nor $\cos kx$ blow up as $x \rightarrow \pm\infty$. For any value of k , the function (90) is an acceptable solution for any value of A and B . Since we can have any value of k , the allowed energies are continuous and are in the range $0 \leq E < \infty$. So the energy of a free particle is not quantized. Only when the particle is confined in some way is its energy quantized.

The positive energy wave functions are right and left moving waves. To see this, use

$$\sin kx = \frac{e^{ikx} - e^{-ikx}}{2i} \quad \text{and} \quad \cos kx = \frac{e^{ikx} + e^{-ikx}}{2} \quad (91)$$

to rewrite $\psi(x)$ as

$$\psi(x) = Ce^{ikx} + De^{-ikx} \quad (92)$$

where C and D are arbitrary constants. The full, time-dependent wave function $\Psi(x, t)$ for the spatial wave function in (92) is

$$\Psi(x, t) = \psi(x)e^{-i\omega t} = Ce^{i(kx-\omega t)} + De^{-i(kx-\omega t)} \quad (93)$$

This is a superposition of 2 traveling waves, one moving to the right (first term with coefficient C) and the other moving to the left (second term with coefficient D). This means that if both C and D are nonzero, the wave function is a superposition of both momenta, going in the right and left directions.

The Nonrigid Box

Recall that for a rigid box

$$U(x) = \begin{cases} 0 & \text{for } 0 \leq x \leq a \\ \infty & \text{for } x < 0 \text{ and } x > a \end{cases} \quad (94)$$

Here we consider a potential $U < \infty$ for $x < 0$ and $x > a$. This means a finite amount of energy is needed to remove a particle from the box.

$$U(x) = \begin{cases} 0 & \text{for } 0 \leq x \leq a \\ U_0 & \text{for } x < 0 \text{ and } x > a \end{cases} \quad (95)$$



Figure 7: Square well potential.

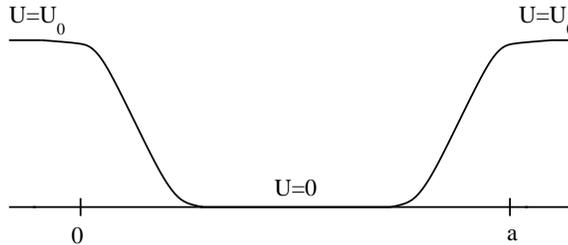


Figure 8: Rounded well potential.

Your book calls this a nonrigid box, but it is often called a finite square well. A sketch of such a well is shown in Figure 7 (see also Fig 7.8). $U(x)$ changes abruptly at $x = 0$ and $x = a$. For a rounded well the potential energy $U(x)$ changes continuously. We will assume that the rounded well has $U(x) = U_0$ for $x < 0$ and $x > a$ as shown in Figure 8 (see also Fig. 7.8c). The properties of both the finite square well and the rounded well are similar. No states with $E < 0$ are allowed. The particle can escape from the well if $E > U_0$. In this case ($E > U_0$), the wave functions are quite similar to those for a free particle and the energies are not quantized.

Our main interest is in the bound states whose energies lie in the interval $0 < E < U_0$. A classical particle in the finite square well with $0 < E < U_0$ would simply bounce back and forth indefinitely between the points $x = 0$ and $x = a$. For the rounded well, the classical turning points at $x = b$ and $x = c$ are determined by the condition $E = U(x)$. See Figure 9 (see also Figure 7.9).

Now consider the Schoedinger equation:

$$\psi''(x) = \frac{2m}{\hbar^2}[U(x) - E]\psi(x) \quad (96)$$

We want values of E in the range $0 < E < U_0$ that correspond to physically acceptable solutions. There are 2 important regions of x : those where $[U(x) - E] > 0$ and those where $[U(x) - E] < 0$. The boundaries of those regions are given by the classical turning points $x = b$ and $x = c$. The regions where $[U(x) - E] > 0$ are classically forbidden regions since a classical particle cannot penetrate there because it does not have have

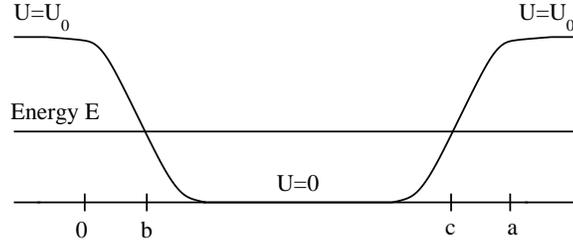


Figure 9: Rounded well potential with classical turning points at b and c .

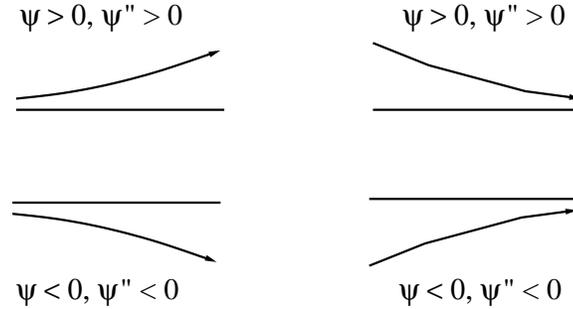


Figure 10: Wave function curves away from axis if ψ and ψ'' are both positive or both negative.

enough energy. The $[U(x) - E] < 0$ region lies in the interval $b < x < c$ and is the classically allowed region. The wave function is quite different in these 2 regions.

Wave Functions Outside the Well ($U(x) > E$)

In the region where $[U(x) - E] > 0$, the Schroedinger equation has the form

$$\psi''(x) = (\text{positive function}) \times \psi(x) \quad (97)$$

where “positive function” is $(2m/\hbar^2)[U(x) - E]$. Whether $\psi(x)$ is positive (above the x-axis) or negative (below the x-axis), it is concave away from the x-axis as shown in Figure 10 (see also Fig. 7.11). To see this, recall that the curvature of $\psi(x)$ is given by the second derivative $\psi''(x)$.

If we look at the math, then we can define α by

$$\frac{2m}{\hbar^2} [U_0 - E] = +\alpha^2 \quad (98)$$

and write the Schroedinger equation as

$$\psi''(x) = +\alpha^2 \psi(x) \quad (99)$$

As we have seen, the solution has the form

$$\psi(x) = Ae^{\alpha x} + Be^{-\alpha x} \quad (100)$$

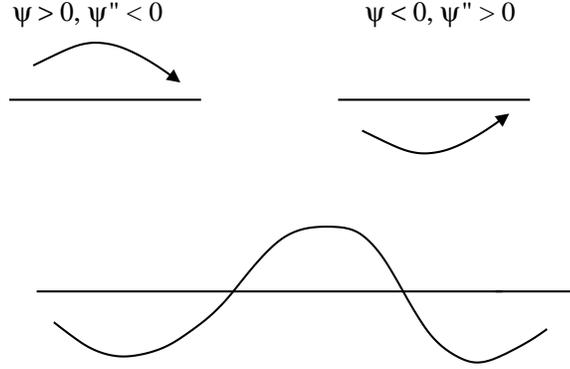


Figure 11: Wave function curves toward from axis if ψ and ψ'' have opposite signs. In this case the wave function oscillates.

Left of the well ($x < 0$), as $x \rightarrow \infty$, the exponential $e^{-\alpha x}$ blows up and is physically unacceptable. So $B = 0$ for $x < 0$.

To the right of the well, in the region $x > a$, the general solution has the same form:

$$\psi(x) = Ce^{\alpha x} + De^{-\alpha x} \quad (101)$$

$C = 0$ is required to prevent $\psi(x)$ from diverging as $x \rightarrow \infty$. Thus, in the classically forbidden regions, the wave functions decay exponentially as $x \rightarrow \pm\infty$.

Wave Functions Within the Well ($U(x) < E$)

In the region $b < x < c$ where ($U(x) < E$), the Schroedinger equation has the form

$$\psi''(x) = (\text{negative function}) \times \psi(x) \quad (102)$$

In this case $\psi(x)$ is concave toward the axis and tends to oscillate. See Figure 11 (see also Fig. 7.12 in the book).

In (102) the “negative function” is $(2m/\hbar^2)[U(x) - E]$. If this negative function has a large magnitude, then the curvature is large and $\psi(x)$ curves and oscillates rapidly. Conversely, when the negative function is small, $\psi(x)$ bends gradually and oscillates slowly. This makes sense physically. Since $[U(x) - E]$ is just the negative of the kinetic energy, large kinetic energy means short wavelengths and rapid oscillations. Small kinetic energy means long wavelengths and slow oscillations.

For a finite square well where $U_0 = 0$ within the well, we can define the constant k by

$$-\frac{2m}{\hbar^2}E = -k^2 \quad (103)$$

and the Schroedinger equation becomes

$$\psi''(x) = -k^2\psi(x) \quad (104)$$

The most general solution is

$$\psi(x) = F \sin kx + G \cos kx \quad (105)$$

Solving for the allowed energies is rather messy. It involves starting with the general solutions and using the conditions that $\psi(x)$ and $\psi'(x)$ must be continuous at the edges of the well to solve for the coefficients A , D , F , and G (we already know $B = C = 0$). There is no simple analytic solution to this problem and you have to use a computer to obtain a numerical solution.

Searching for Allowed Energies

Acceptable solutions come from matching the solutions from various regions so that the wave functions and their slopes are continuous at the boundaries between the regions. We do not want $\psi(x)$ to diverge as $x \rightarrow \pm\infty$. For example, $\psi(x) = Ae^{\alpha x}$ is well behaved for $x < 0$ but blows up as $x \rightarrow \infty$. Go through Figures 7.13 to 7.16 for the rounded well.

Acceptable solutions for the finite square well are compared to those for the infinite square well in Figure 7.17. The ground state of the infinite square well fits exactly half an oscillation while that of the finite well fits somewhat less than half an oscillation. The second function (first excited state) has one complete oscillation in the infinite well while the finite well has just less than one oscillation. The wave function leaks a little outside the finite well. More wiggles mean higher kinetic energy, or more curvature means higher energy. Just look at the term with the second derivative with respect to x in the Schrodinger equation to see this. So the energy of each level of the finite square well is slightly lower than that of the corresponding level in the infinite well.

Notice that the ground-state wave function for any finite well has no nodes. A node is where the wave function goes to zero. The second level (first excited state) has one node. The n th level has $n - 1$ nodes. More nodes correspond to higher energies since higher energy corresponds to a wave function that oscillates more quickly.

Note that the wave functions of the finite well are nonzero outside the well in the classically forbidden region. The particle is bound inside or close to the potential well. Unlike a classical particle, there is a definite nonzero probability of finding the particle in the classically forbidden regions. The ability of the quantum wave function to penetrate into classically forbidden regions has important consequences like tunneling.

For the finite well, when E reaches U_0 , there are no more bound states and the particle is no longer confined. The number of bound states depends on the well depth U_0 and width a , but is always finite.

The Simple Harmonic Oscillator (SHO)

Familiar classical examples of a harmonic oscillator are a mass suspended from an ideal spring and a pendulum oscillating with a small amplitude. If a particle is displaced from its stable equilibrium position, x_0 , there is a restoring force pushing it back toward its equilibrium position:

$$F(x) = -k(x - x_0) \quad (106)$$

So a particle slightly displaced from equilibrium will oscillate harmonically about its equilibrium position. A microscopic example of a quantum harmonic oscillator is the

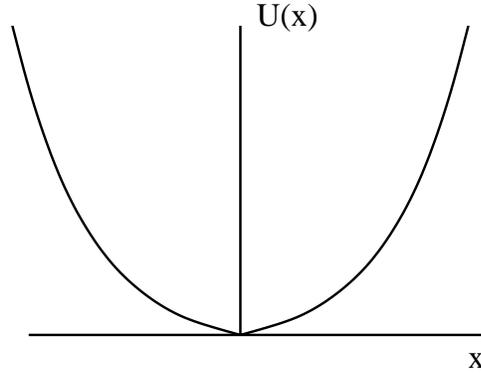


Figure 12: Harmonic oscillator potential.

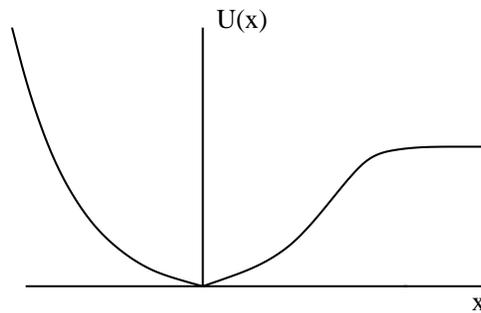


Figure 13: Potential of a diatomic molecule is parabolic at the bottom. So for small displacements, it acts like a harmonic oscillator.

motion of an atom inside a solid crystal about its lattice site. Another example is in a diatomic molecule where 2 atoms can vibrate harmonically, getting closer and farther from one another.

In quantum mechanics, we work, not with forces F , but with the potential energy U :

$$U(x) = - \int_{x_0}^x F(x) dx = \frac{1}{2} k(x - x_0)^2 \quad (107)$$

if we take U to be zero at x_0 . $U(x)$ is a parabola with its minimum at $x = x_0$ as shown in the Figure 12. Usually this is only valid for small displacements from x_0 . For large x , $U(x)$ may not be a parabola. An example is shown in Figure 13 (see also Figure 7.18). Small displacements from equilibrium are very common, and that is why the harmonic oscillator is so important.

Let us start with a review of the classical harmonic oscillator or spring. Consider a mass m on a spring with spring constant k . Let the equilibrium position $x_0 = 0$. The force is $F = -kx$. $F = ma$ gives

$$ma = -kx \quad (108)$$

The natural angular frequency is

$$\omega_c = \sqrt{\frac{k}{m}} \quad (109)$$

Then we can write

$$\frac{d^2x}{dt^2} = -\omega_c^2 x \quad (110)$$

which has the general solution

$$x = a \sin \omega_c t + b \cos \omega_c t \quad (111)$$

Let the initial conditions be $x = 0$ at $t = 0$. Then

$$x = a \sin \omega_c t \quad (112)$$

a is the amplitude of the oscillations, and the particle oscillates between $x = a$ and $x = -a$. $x = \pm a$ are the classical turning points. When the particle is at $x = a$, all of its energy is potential energy:

$$E = \frac{1}{2}ka^2 \quad (113)$$

or

$$a = \sqrt{\frac{2E}{k}} \quad (114)$$

The classical amplitude a increases with increasing energy E .

To find the allowed energies of the quantum harmonic oscillator, we must solve the Schroedinger equation with $U(x)$ given by

$$U(x) = \frac{1}{2}kx^2 \quad (115)$$

Only special values of E produce a solution that satisfies the boundary conditions, i.e., decays exponentially as $x \rightarrow -\infty$ and $x \rightarrow \infty$. Thus, the allowed energies are quantized. Since the potential energy $U(x)$ increases to infinity as $x \rightarrow \pm\infty$, the particle is confined for all energies, and we would expect to find infinitely many allowed energies. The solution of the Schroedinger equation for the simple harmonic oscillator is quite complicated and will not be given here. However, the allowed energies have a very simple form and are given by

$$E = \frac{1}{2}\hbar\sqrt{\frac{k}{m}}, \frac{3}{2}\hbar\sqrt{\frac{k}{m}}, \frac{5}{2}\hbar\sqrt{\frac{k}{m}}, \dots \quad (116)$$

or

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega_c \quad n = 0, 1, 2, \dots \quad (117)$$

Notice that the energy levels of the harmonic oscillator are all equally spaced.

The functional form of the wave functions are in Table 7.1 of the textbook. You can plug these wave functions into the Schroedinger equation to verify that they are indeed

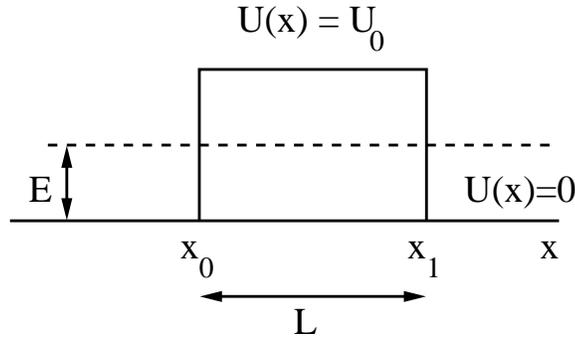


Figure 14: The potential for a tunnel barrier.

solutions. Their form is plotted in Figure 7.19. They are similar to those of the finite square well. The lowest wave function has no nodes, the next (first excited state) has one node, etc. Wave functions with higher energy spread out farther from $x = 0$ just as the classical turning points $x = \pm a = \pm\sqrt{2E/k}$ (from Eq. (114)) move farther out when E increases. Finally, note that the ground state ($n = 0$) has a zero-point energy of $\hbar\omega_c/2$ as required by the uncertainty principle.

An example of the simple harmonic oscillator is vibrational modes of the diatomic molecule. The molecular potential energy $U(r)$ in Figure 7.20 deviates from the parabolic shape of the SHO at higher energies. Therefore, the higher energy levels depart from the uniform spacing for the SHO. Photons are emitted when molecules make transitions between different vibrational levels. For example, the H_2 molecule emits infrared photons of frequency 1.2×10^{14} Hz when it drops from one vibrational level to the next. This radiation is used by astronomers to locate clouds of H_2 molecules in our galaxy.

Tunneling

Quantum mechanically, particles can go through walls. Consider a particle whose potential energy has a “barrier.” In classical mechanics such barriers are impenetrable. In quantum mechanics the particle can “tunnel” through the barrier and emerge on the other side. This **barrier penetration**, or **tunneling**, has remarkable consequences in several natural phenomena such as radioactive decay and the scanning tunneling microscope. Another example is electrons going through a gap or insulating oxide layer between two metal conductors.

A simple example of a barrier is shown in Figure 14 (see also Figure 7.21). An electron moves along an x -axis consisting of two identical conducting wires separated by a small gap between x_0 to x_1 . The gap forms a barrier of thickness $L = x_1 - x_0$ between the two wires. Inside either wire the potential energy is a constant, which we can take to be zero ($U = 0$), but in the barrier it has a higher value $U_0 > 0$. We are interested in the case where the particle’s energy is less than the barrier height, $0 < E < U_0$. A classical particle is excluded from the barrier since with $E < U_0$, its kinetic energy between x_0 and x_1 would be negative which is impossible in classical mechanics. A classical particle

would be reflected from the barrier.

Now let us see what would happen quantum mechanically. Consider first a barrier whose length L is infinite as shown in Figure 7.22. The potential energy is a step function. It is like a square well with just the right wall of the well. Suppose the step occurs at $x = x_0$. To the left of x_0 , the kinetic energy $K = (E - U)$ of a particle is positive and $\psi(x)$ is an oscillating sinusoidal wave. To the right of x_0 , $(E - U)$ is negative and $\psi(x)$ is a decreasing exponential with the form

$$\psi(x) = Be^{-\alpha x} \quad (118)$$

where (see Eq. (98))

$$\alpha = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}} \quad (119)$$

The quantum particle has a nonzero probability of being found in the classically forbidden region where $E - U$ is negative.

In the case of the infinitely long barrier, $\psi(x)$ goes steadily to zero as x increases. But if the barrier has a finite length, there is a finite probability that the particle can be found on the other side of the barrier. Suppose the barrier extends from x_0 to x_1 . The situation is shown in Figure 7.23. $\psi(x)$ is sinusoidal (with amplitude A_L) to the left of x_0 , and decays exponentially within the barrier ($x_0 < x < x_1$). The barrier stops at x_1 , and $(E - U) > 0$ for $x > x_1$. Therefore, before $\psi(x)$ has decayed to zero, it starts oscillating again with amplitude A_R to the right of the barrier.

The probability that the particle with $E < U_0$ will tunnel through the barrier and emerge on the other side is

$$P \approx e^{-2\alpha L} \quad (120)$$

To see where this comes from, consider

$$\begin{aligned} \psi(L) &\sim e^{-\alpha L} \\ P &= |\psi|^2 \sim e^{-2\alpha L} \end{aligned}$$

where α is given by Eq. (119).

The probability that a quantum particle will tunnel through the classically impenetrable barrier depends on α and L , the thickness of the barrier. In many applications the product αL is very large and the probability (120) is therefore very small. Nevertheless, if the particle keeps trying and keeps bumping against the barrier, it will eventually pass through it.

A modern application of quantum tunneling is the scanning tunneling microscope (STM). A tiny tip is placed a little ways above the conducting surface of the sample and electrons are fired at the surface from the tip. This stream of electrons is an electric current. By measuring the current, we can obtain information about the topography of the surface.

Example 7.5

Consider two identical conducting wires, lying on the x axis and separated by an air gap of thickness $L = 1$ nm, i.e., a few atomic diameters). An electron that is moving inside either conductor has $U = 0$, but in the gap $U_0 > 0$. Thus the gap is the barrier in Figure 7.21. The electron approaches the barrier from the left with energy E such that $U_0 - E = 1$ eV, i.e., the electron's energy is 1 eV below the top of the barrier. What is the probability that the electron will emerge on the other side of the barrier? How different would this be if the barrier were twice as wide?

Answer: The required probability is given by Eq. (120) with

$$\begin{aligned} \alpha &= \frac{\sqrt{2m(U_0 - E)}}{\hbar} \\ &= \frac{\sqrt{2mc^2(U_0 - E)}}{\hbar c} \\ &\approx \frac{\sqrt{2 \times (5 \times 10^5 \text{ eV}) \times (1 \text{ eV})}}{197 \text{ eV} \cdot \text{nm}} \\ &\approx 5.1 \text{ nm} \end{aligned}$$

Thus $\alpha L = 5.1$ and the transmission probability is $P = e^{-2\alpha L} = e^{-10.2} = 3.7 \times 10^{-5}$ or about 0.004%. This probability is not large, but if we shoot enough electrons at the barrier, some are bound to get through. If we double L , this will give a transmission probability

$$P' = e^{-4\alpha L} = e^{-20.4} = 1.4 \times 10^{-9} \quad (121)$$

This is a dramatically smaller result. This is worse than your chance of winning the lottery. This illustrates the extreme sensitivity of the transmission probability to the width of the gap. So in STM, small changes in separation between the tip and the surface would produce big changes in tunneling current. These changes would come from the hills and valleys or bumps in the surface. In fact, the tunneling current of the STM is held constant by having the tip stay at a constant distance from the surface through a feedback mechanism, and the changing position of the tip gives us the topography of the surface. See Chapter 14 for more information on how an STM works.