One Dimension Infinite Square Well Potential

dimensional box. Inside the box the particle is free but experiences a sudden large force directed towards the origin as it reaches the points $x = \pm a$. Therefore, the potential energy for this problem is,

$$V(x) = \begin{cases} 0 & |x| < a \\ \infty & |x| > a \end{cases} \tag{7.1}$$

The potential is shown in Figure 7.1.

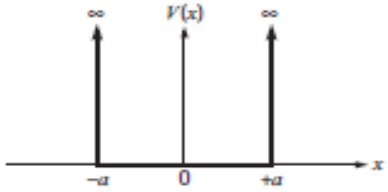

Figure 7.1 The one-dimensional infinite square well potential.

In order to find the eigenfunctions and energy eigenvalues for this system, we have to solve the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{7.2}$$

Since the potential energy is infinite at $x = \pm a$, the probability of finding the particle outside the well is zero. Therefore the wave function $\psi(x)$ must vanish for $|x| > a$. Further, since the wave function must be continuous, it must vanish at the walls:

$$\psi(x) = 0 \qquad \text{at} \qquad x = \pm a \tag{7.3}$$

For $|x| < a$, the Schrödinger equation (7.2) reduces to

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

or

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0; \quad k^2 = \frac{2mE}{\hbar^2} \tag{7.4}$$

The general solution[†] of this equation is

$$\psi(x) = A \sin kx + B \cos kx \tag{7.5}$$

Applying the boundary condition (7.3), we obtain at $x = a$,

$$A \sin ka + B \cos ka = 0$$

and at $x = -a$,

$$-A \sin ka + B \cos ka = 0$$

These equations give

$$A \sin ka = 0, \quad B \cos ka = 0 \tag{7.6}$$

[†] The general solution can also be written in the complex form: $\psi = A\exp(ikx) + B\exp(-ikx)$. However, in the present problem it is more convenient to use the real form (7.5).

Now we cannot allow both A and B to be zero because this would give the physically uninteresting trivial solution $\psi(x) = 0$ for all x. Also, we cannot make both $\sin ka$ and $\cos ka$ zero for a given value of k. Hence, there are *two* possible classes of solutions:

For the *first* class,

$$A = 0 \qquad \text{and} \qquad \cos ka = 0$$

and for the *second* class,

$$B = 0 \qquad \text{and} \qquad \sin ka = 0$$

These conditions are satisfied if

$$ka = \frac{n\pi}{2} \tag{7.7}$$

where n is an *odd* integer for the first class and an *even* integer for the second class. Thus, the eigenfunctions for the two classes are, respectively,

$$\boxed{\psi_n(x) = B\cos\frac{n\pi x}{2a}, \quad n = 1,3,5,\ldots}$$

and

$$\boxed{\psi_n(x) = A\sin\frac{n\pi x}{2a}, \quad n = 2,4,6,\ldots}$$

In order to normalize the eigenfunctions, we apply the condition

$$\int_{-a}^{a} \psi_n^*(x)\ \psi_n(x)dx = 1$$

This gives

$$A^2\int_{-a}^{a}\sin^2\frac{n\pi x}{2a}dx = B^2\int_{-a}^{a}\cos^2\frac{n\pi x}{2a}dx = 1$$

Solving these integrals we obtain

$$\boxed{A = B = 1/\sqrt{a}} \tag{7.8}$$

Thus, the **normalized eigenfunctions** for the two classes are, respectively,

$$\boxed{\psi_n(x) = \frac{1}{\sqrt{a}}\cos\frac{n\pi x}{2a}, \quad n = 1,3,5,\ldots} \tag{7.9}$$

and

$$\boxed{\psi_n(x) = \frac{1}{\sqrt{a}}\sin\frac{n\pi x}{2a}, \quad n = 2,4,6,\ldots} \tag{7.10}$$

It may be noted that it is unnecessary to consider negative values of n because the resulting solutions will not be linearly independent of those corresponding to positive values of n.

From (7.7), the only allowed values of k are

$$k_n = \frac{n\pi}{2a}, \qquad n = 1,2,3,\ldots \tag{7.11}$$

Using (7.4) and (7.11) the **energy eigenvalues** for both the classes are given by

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{8ma^2}, \quad n = 1,2,3,\ldots} \tag{7.12}$$

Thus, the energy is *quantized*. The integer n is called a *quantum number*. There is an *infinite* sequence of *discrete energy levels*. There is only one eigenfunction for each level, so the energy levels are *nondegenerate*.

It can be easily shown that the eigenfunctions $\psi_m(x)$ and $\psi_n(x)$ corresponding to different eigenvalues are orthogonal:

$$\int_{-a}^{a} \psi_m^*(x)\,\psi_n(x)\,dx = 0, \quad m \neq n$$

Combining orthogonality and normalization, we have the *orthonormality* condition:

$$\int_{-a}^{a} \psi_m^*(x)\,\psi_n(x)\,dx = \delta mn \tag{7.13}$$

The first four energy levels, eigenfunctions and position probability densities are shown in Figures 7.2, 7.3 and 7.4, respectively.

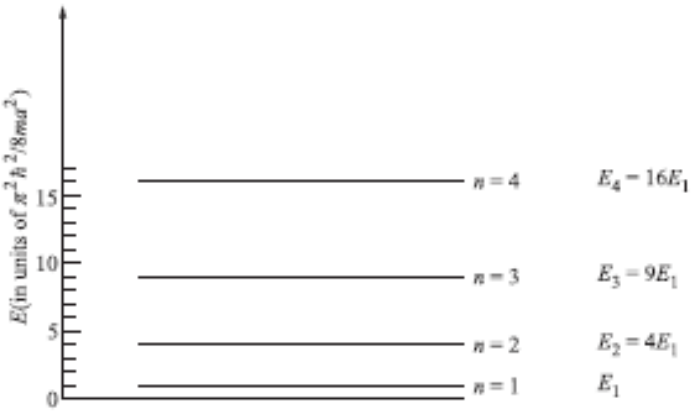

Figure 7.2 Energy-level diagram.

Connection with the De Broglie Hypothesis

It is interesting to note the connection between the eigenfunctions of the infinite square well and the de Broglie hypothesis. The de Broglie wavelength for the nth quantum state is

$$\lambda_n = \frac{2\pi}{k_n} = \frac{2}{n}(2a)$$

This gives

$$2a = \frac{n}{2}\lambda_n$$

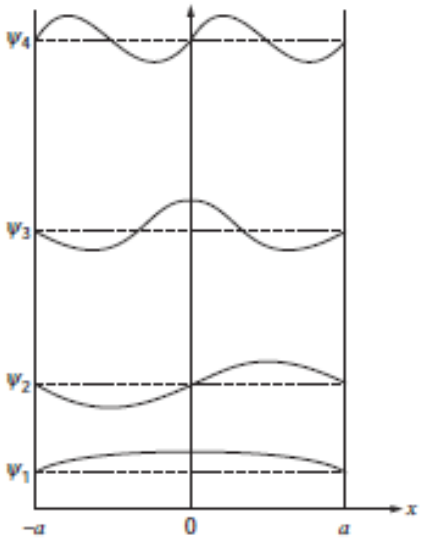

Figure 7.3 Wave functions.

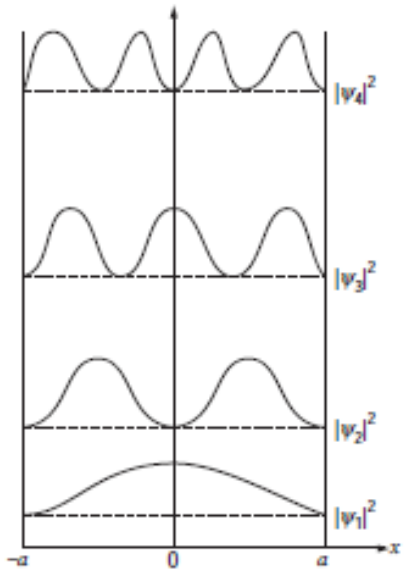

Figure 7.4 Probability densities.

This shows that *the* nth *quantum state is obtained when* $n/2$ *de Broglie wavelengths can fit into the box.*

Also note that the nth eigenfunction has $(n-1)$ nodes within the box. This follows from (7.9) and (7.10).

Zero-point Energy

It is important to note that the lowest possible energy, also called the *zero-point energy*, is not zero. This fact is in agreement with the *uncertainty principle*. By trapping the particle in a limited region, we acquire information about its position. Therefore, its momentum cannot be known with complete precision. This prevents any possibility of the particle being at rest. Hence the lowest energy cannot be zero.

The position uncertainty is roughly given by $\Delta x \approx a$. Therefore the minimum momentum uncertainty is $\Delta p \approx \hbar/a$. This leads to a minimum kinetic energy of order $\hbar^2/ma^2$. Equation (7.12) tells us that this agrees, qualitatively, with the value of E_1.

7.2 THREE-DIMENSIONAL INFINITE SQUARE WELL

The discussions of section 7.1 and problem 7.3 can be easily generalized to the case of a particle in a **three-dimensional box**. This problem is more closely related to actual physical systems.

Let us consider a particle of mass m constrained to move in a rectangular box shown in Figure 7.5. The origin O is at one corner of the box and the lengths of the box along x –, y – and z – axes are a, b and c, respectively. Inside the box the potential energy is zero and outside it is infinite.

The time-independent Schrödinger equation inside the box is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x, y, z) = E\psi(x, y, z)$$

or
$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{2mE}{\hbar^2}\psi = 0 \qquad (7.23)$$

which is to be solved subject to the condition that $\psi(x, y, z) = 0$ at the walls of the box.

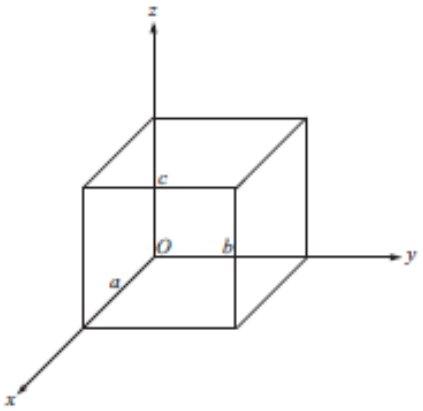

Figure 7.5 Three-dimensional box.

This partial differential equation can be solved by the technique of separation of variables. We assume that the function $\psi(x, y, z)$ can be written as a product of three functions each of which depends on only one of the coordinates:

$$\psi(x, y, z) = X(x)\ Y(y)\ Z(z) \tag{7.24}$$

Substituting into Equation (7.23) and dividing by XYZ, we get

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} + \frac{2mE}{\hbar^2} = 0 \tag{7.25}$$

Note that each term of this equation is a function of only one of the independent variables x, y, z and the last term is a constant. Therefore, this equation can be valid only if each term is a constant. We write

$$\frac{1}{X}\frac{d^2X}{dx^2} = -k_x^2 \tag{7.26}$$

$$\frac{1}{Y}\frac{d^2Y}{dy^2} = -k_y^2 \tag{7.27}$$

$$\frac{1}{Z}\frac{d^2Z}{dz^2} = -k_z^2 \tag{7.28}$$

where k_x, k_y, k_z are constants. Equation (7.25) reduces to

$$k_x^2 + k_y^2 + k_z^2 = \frac{2mE}{\hbar^2} \tag{7.29}$$

Each of the three Equations (7.26), (7.27) and (7.28) depends on only one of the variables and, therefore, can be solved easily. Equation (7.26) can be rewritten as

$$\frac{d^2X}{dx^2} + k_x^2 X = 0 \tag{7.30}$$

The general solution of this equation is

$$X(x) = A \sin k_x x + B \cos k_x x$$

The boundary condition $X(0) = 0$ makes $B = 0$. The boundary condition $X(a) = 0$ gives

$$k_x a = n_x \pi$$

or
$$k_x = \frac{n_x \pi}{a}, \qquad n_x = 1, 2, 3\ldots \tag{7.31}$$

Thus the normalized solution to (7.30) is

$$X(x) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a}, \qquad n_x = 1, 2, 3\ldots \tag{7.32}$$

Similarly, for $Y(y)$ and $Z(z)$ we have,

$$k_y = \frac{n_y \pi}{b}, \qquad n_y = 1, 2, 3,\ldots \tag{7.33}$$

$$Y(y) = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b}, \qquad n_y = 1, 2, 3,\ldots \tag{7.34}$$

$$k_z = \frac{n_z \pi}{c}, \qquad n_z = 1, 2, 3,\ldots \tag{7.35}$$

$$Z(z) = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c}, \quad n_z = 1, 2, 3,\ldots \tag{7.36}$$

Combining (7.32), (7.34) and (7.36), we obtain the **normalized eigenfunctions:**

$$\boxed{\psi_{n_x,n_y,n_z}(x,y,z) = \left(\frac{8}{abc}\right)^{1/2} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c}} \tag{7.37}$$

where n_x, n_y, n_z = 1,2,3...

Now, substituting (7.31), (7.33) and (7.35) into (7.29) and rearranging, we get the expression for the **energy** E as

$$\boxed{E_{n_x,n_y,n_z} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)} \tag{7.38}$$

Note that there are three quantum numbers that are necessary to describe each quantum state. This is a general property of all three-dimensional systems. For the ground state $n_x = n_y = n_z = 1$. However, the set of quantum numbers which defines the first and the higher states depends on the relative magnitudes of a, b, and c.

Let us consider the simplest case of a **cubical box**. Then $a = b = c$ and the **energy eigenvalues** become

$$\boxed{E_{n_x,n_y,n_z} = \frac{\pi^2 \hbar^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2)} \tag{7.39}$$

Finite Square Well (Fist Type)

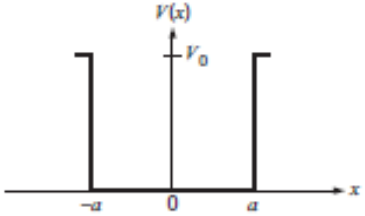

Figure 7.6 Finite square well (first type).

The square well potential shown in Figure 7.6 is given by

$$V(x) = \begin{cases} 0 & |x| < a \\ V_0 & |x| > a \end{cases} \tag{7.42}$$

Consider a particle of mass m moving in this potential with energy E. We shall consider the case when $E < V_0$. The particle is then confined in a *bound state*. In the other case, when $E > V_0$ the particle is unconfined. This situation is relevant in the scattering of a particle by a potential. Such problems will be discussed in the next chapter.

Inside the well the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi, \qquad |x| < a$$

or

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0, \qquad k^2 = \frac{2mE}{\hbar^2} \tag{7.43}$$

The general solution of this equation is

$$\psi(x) = A \sin kx + B \cos kx \tag{7.44}$$

Outside the well the equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V_0\psi = E\psi, \qquad |x| > a$$

or

$$\frac{d^2\psi}{dx^2} - K^2\psi = 0, \quad K^2 = \frac{2m(V_0 - E)}{\hbar^2} \tag{7.45}$$

Since $V_0 > E$, the quantity K^2 is positive. Therefore, the general solution of this equation is

$$\psi(x) = Ce^{-Kx} + De^{Kx} \tag{7.46}$$

Now, the wave function should not become infinite as $x \to \pm\infty$. Therefore, we must take $C = 0$ for $x < -a$ and $D = 0$ for $x > a$. So, the wave function can be written as

$$\psi(x) = \begin{cases} De^{Kx} & x < -a \\ A \sin kx + B \cos kx & -a < x < a \\ Ce^{-Kx} & x > a \end{cases} \tag{7.47}$$

The requirement that $\psi(x)$ and $d\psi/dx$ be continuous at $x = -a$ gives

$$-A \sin ka + B \cos ka = De^{-Ka} \tag{7.48}$$

and

$$kA \cos ka + kB \sin ka = KDe^{-Ka} \tag{7.49}$$

Similarly, the continuity of $\psi(x)$ and $d\psi/dx$ at $x = a$ gives

$$A \sin ka + B \cos ka = Ce^{-Ka} \tag{7.50}$$

and

$$kA \cos ka - kB \sin ka = -KCe^{-Ka} \tag{7.51}$$

Equations (7.48) and (7.50) give

$$2A \sin ka = (C - D)\, e^{-Ka} \tag{7.52}$$

$$2B \cos ka = (C + D)\, e^{-Ka} \tag{7.53}$$

Equations (7.49) and (7.51) give

$$2kA \cos ka = -K(C - D)\, e^{-Ka} \tag{7.54}$$

$$2kB \sin ka = K(C + D)\, e^{-Ka} \tag{7.55}$$

Equations (7.52) and (7.54) yield

$$k \cot ka = -K \tag{7.56}$$

unless $A = 0$ and $C = D$. Similarly, Equations (7.53) and (7.55) yield

$$k \tan ka = K \tag{7.57}$$

unless $B = 0$ and $C = -D$.

Eliminating K from (7.56) and (7.57) leads to $\tan^2 ka = -1$ which is not possible because both k and a are real. Therefore, these two equations cannot be valid simultaneously. Thus, we have two classes of solutions:

For the *first class*

$$A = 0,\ C = D \quad \text{and} \quad k \tan ka = K \tag{7.58}$$

and for the *second class*

$$B = 0,\ C = -D \quad \text{and} \quad k \cot ka = -K \tag{7.59}$$

Eigenfunctions

The *eigenfunctions* of the *first class* are given by

$$\psi(x) = \begin{cases} Ce^{Kx} & x < -a \\ B \cos kx & -a < x < a \\ Ce^{-Kx} & x > a \end{cases} \tag{7.60}$$

The *eigenfunctions* of the *second class* are given by

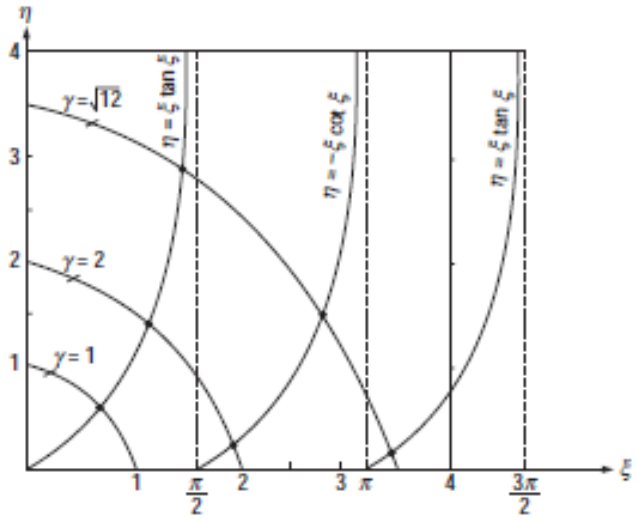

Figure 7.7 Graphical determination of the energy levels for a square well potential.

In the limiting case of infinite square well, $V_0 \to \infty$. In that case $\eta \to \infty$. The roots of Equations (7.62) and (7.63) will then be

$$\xi = \frac{n\pi}{2}, \qquad n = 1, 2, \ldots$$

Since $\xi = ka = (2mE/\hbar^2)^{1/2}\, a$, we get

$$\frac{2mEa^2}{\hbar^2} = \frac{n^2\pi^2}{4}$$

or

$$E = \frac{n^2\pi^2\hbar^2}{8ma^2}$$

which is same as the earlier result (7.13). Further, $K \to \infty$ when $V_0 \to \infty$. Therefore, the eigenfunctions (7.60) and (7.61) will vanish for $|x| > a$ as is the case for the infinte square well (section 7.1).

7.4 ONE-DIMENSIONAL FINITE SQUARE WELL (SECOND TYPE)

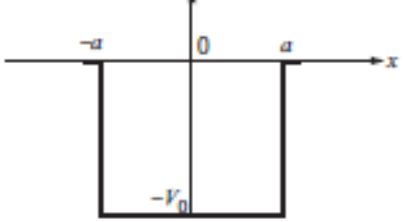

Figure 7.8 Finite square well (second type).

We shall discuss the case $E < 0$ which gives rise to bound states. Inside the well the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - V_0\psi = E\psi = -|E|\psi, \quad |x| < a$$

or
$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0, \quad \alpha^2 = \frac{2m(V_0 - |E|)}{\hbar^2} \tag{7.66}$$

Here $|E| = -E$ is the binding energy of the particle in the well. Since $V_0 > |E|$, the quantity α^2 is positive. Therefore, the general solution of this equation is

$$\psi(x) = A \sin \alpha x + B \cos \alpha x \tag{7.67}$$

Outside the well the equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi = -|E|\psi, \quad |x| > a$$

or
$$\frac{d^2\psi}{dx^2} - \beta^2\psi = 0, \quad \beta^2 = \frac{2m|E|}{\hbar^2} \tag{7.68}$$

The general solution of this equation is

$$\psi(x) = Ce^{-\beta x} + De^{\beta x} \tag{7.69}$$

Now, the wave function should not become infinite as $x \to \pm\infty$. Therefore, we must take $C = 0$ for $x < -a$ and $D = 0$ for $x > a$. So the wave function can be written as

$$\psi(x) = \begin{cases} De^{\beta x} & x < -a \\ A \sin \alpha x + B \cos \alpha x & -a < x < a \\ Ce^{-\beta x} & x > a \end{cases} \tag{7.70}$$

Imposing the requirements that $\psi(x)$ and $d\psi/dx$ be continuous at $x = \pm a$ and carrying out the same manipulations as in the previous section, we obtain two classes of solutions.

The eigenfunctions of the *first class* are given by

$$\psi(x) = \begin{cases} Ce^{\beta x} & x < -a \\ B\cos \alpha x & -a < x < a \\ Ce^{-\beta x} & x > a \end{cases} \tag{7.71}$$

The eigenfunctions of the *second class* are given by

$$\psi(x) = \begin{cases} Ce^{\beta x} & x < -a \\ A\sin \alpha x & -a < x < a \\ -Ce^{-\beta x} & x > a \end{cases} \tag{7.72}$$

The energy levels can be found by solving the equations

$$\xi \tan \xi = \eta$$
$$\xi \cot \xi = -\eta$$

where $\xi = \alpha a$ and $\eta = \beta a$. These equations can be solved to obtain the energy levels following the same procedure as in the previous section.