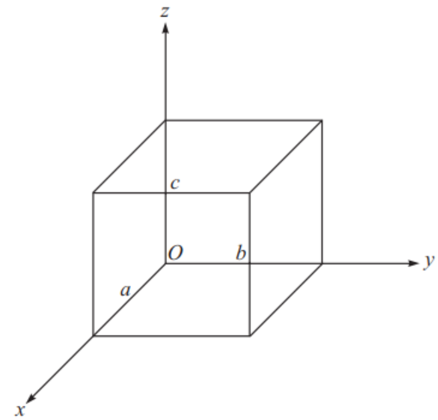
4.3 Three-Dimensional Infinite Square Well



Let us consider a particle of mass *m* constrained to move in a rectangular box,

- The origin *O* is at one corner of the box.
- 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

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{2mE}{\hbar^2}\psi = 0 \qquad \ldots(4.25)$$

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

$$\psi(x, y, z) = X(x)Y(y)Z(z) \qquad \ldots(4.26)$$

Substituting into Equation (4.25) and dividing by *XYZ*, we get

$$\frac{1}{X}\frac{d^2X}{dx^2}+\frac{1}{Y}\frac{d^2Y}{dy^2}+\frac{1}{Z}\frac{d^2Z}{dz^2}+\frac{2mE}{\hbar^2} = 0 \qquad \ldots(4.27)$$

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

$$\frac{1}{X}\frac{d^2X}{dx^2} = -k_x^2 \qquad \text{...(4.28)}$$

$$\frac{1}{Y}\frac{d^2Y}{dy^2} = -k_y^2 \qquad \text{...(4.29)}$$

$$\frac{1}{Z}\frac{d^2Z}{dz^2} = -k_z^2 \qquad \text{...(4.30)}$$

Where k_x, k_y, k_z are constants. Equation (4.27) reduces to,

$$k_x^2 + k_y^2 + k_z^2 = \frac{2mE}{\hbar^2} \qquad \text{...(4.31)}$$

Each of the three Equations (4.28), (4.29), and (4.30) depends on only one of the variables and, therefore, can be solved easily.

Equation (4.28) can be rewritten as,

$$\frac{d^2X}{dx^2} + k_x^2X = 0 \qquad \text{...(4.32)}$$

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

$$k_x a = n_x \pi$$

$$k_x = \frac{n_x \pi}{a}, \qquad n_x = 1, 2, 3\ldots \qquad \text{...(4.33)}$$

Thus the normalized solution to (4.32) is,

$$X(x) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a}, \qquad n_x = 1, 2, 3\ldots \qquad \text{...(4.34)}$$

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

$$k_y = \frac{n_y \pi}{b}, \qquad n_y = 1, 2, 3,\ldots \qquad \text{...(4.35)}$$

$$Y(y) = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b}, \qquad n_y = 1, 2, 3,\ldots \qquad \text{...(4.36)}$$

$$k_z = \frac{n_z \pi}{c}, \qquad n_z = 1,\ 2,\ 3, \ldots \qquad \ldots(4.37)$$

$$Z(z) = \sqrt{\frac{2}{c}}\ \sin\frac{n_z \pi z}{c}, \quad n_z = 1,\ 2,\ 3, \ldots \qquad \ldots(4.38)$$

Combining (4.34), (4.36) and (4.38), we obtain the **normalized eigenfunctions**:

$$\boxed{\psi_{n_x,n_y,n_z}(x,y,z) = \left(\frac{8}{abc}\right)^{1/2} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b} \sin\frac{n_z \pi z}{c}} \qquad \ldots(4.39)$$

Where $n_x, n_y, n_z = 1,2,3 \ldots$

Now, substituting (4.33), (4.35), and (4.37) into (4.31) and rearranging, we get the expression for the energy E as

$$\boxed{E_{n_x,n_y,n_z} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)} \qquad \ldots(4.40)$$

Note that three quantum numbers 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,

$$\boxed{E_{n_x,n_y,n_z} = \frac{\pi^2 \hbar^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2)} \qquad \ldots(4.41)$$

The corresponding **eigenfunctions** are,

$$\boxed{\psi_{n_x,n_y,n_z}(x,y,z) = \left(\frac{8}{a^3}\right)^{1/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right)} \qquad \ldots(4.42)$$

Taking $n_x = n_y = n_z = 1$, the ground state energy is

$$E_{1,1,1} = \frac{3\pi^2\hbar^2}{2ma^2} \qquad \ldots(4.43)$$

This state is *nondegenerate.*

The next higher energy:

n_x	n_y	n_z	E		n_x	n_y	n_z	E		n_x	n_y	n_z	E		n_x	n_y	n_z	E
1	1	1	$3E_0$		2	1	1	$6E_0$		2	1	2	$9E_0$		3	1	1	$11E_0$
2	2	2	$12E_0$		1	2	1	$6E_0$		1	2	2	$9E_0$		1	3	1	$11E_0$
					1	1	2	$6E_0$		2	2	1	$9E_0$		1	1	3	$11E_0$

This shows that :

- most of the higher states are degenerate.
- The degeneracy occurs because the energy depends on the quantum numbers n_x, n_y and n_z only through the combination $n^2 = n_x^2 + n_y^2 + n_z^2$,
- the same value of n can be obtained for different sets of values of n_x, n_y and n_z.

Problem: In the problem of cubical potential box with rigid walls, $n_x^2 + n_y^2 + n_z^2 = 14$, Write down:

1- Schrödinger equation for the particle inside the box.

2- The possible values of: a- n_x, n_y, n_z. b- E_{n_x,n_y,n_y}, c- ψ_{n_x,n_y,n_y} d-degree of degeneracy.