2.22 PARTICLE IN A THREE-DIMENSIONAL BOX

We have seen that a particle moving freely in a one-dimensional box (potential energy $V = 0$) serves as a very convenient model for several types of atomic and molecular systems. Calculations, though approximate, agree fairly well with observed results. Electronic motions in atoms and molecules, are, however, three-dimensional and a three-dimensional box model should be more appropriate. Though electron motions in atoms and molecules are complicated due to some other factors, let us see how far results of quantum-mechanical treatment of a single particle moving in a three-dimensional box are of interest.

Let us consider a particle of mass "m" moving in a three-dimensional rectangular box having sides *a*, *b*, and *c* along x, y and z-axis as shown in Fig.2.16. The potential energy of the particle moving inside the box will be zero. The remainder of space outside the box will have infinite potential energy. The potential energy at the boundaries of the rigid walls will also be zero in order to avoid discontinuity of the wave function, i.e.

$$V(x, y, z) = 0,$$

for $0 < x < a$, $0 < y < b$ and $0 < z < c$

$$V(x, y, z) = \infty \text{ elsewhere}$$

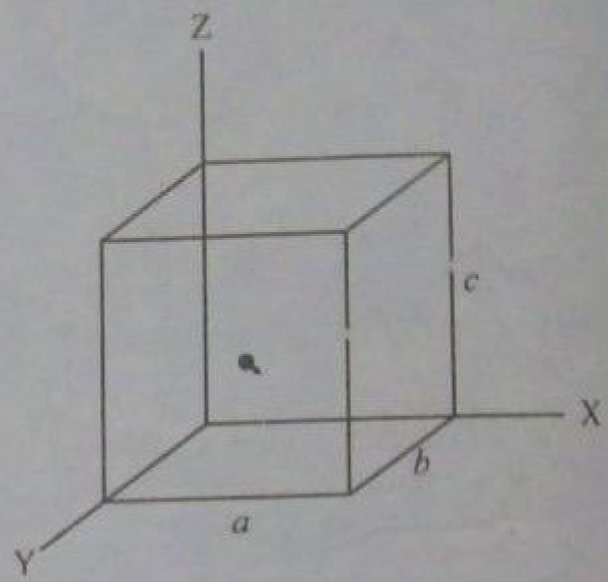

Fig.2.16 Particle in a three-dimensional box

The Schrodinger wave equation for such a particle moving within the box is given by

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} E\Psi = 0 \qquad (2.69)$$

or $$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi + \frac{8\pi^2 m}{h^2} E\Psi = 0$$

or $$\nabla^2\Psi + \frac{8\pi^2 m}{h^2} E\Psi = 0 \qquad (2.70)$$

This is second-order partial differential equation where the wave function Ψ is a function of coordinates (x, y, z) and ∇^2 (del squared) is a Laplacian operator. It is initially assumed that the wave function $\Psi(x, y, z)$ is a product of these function, each depending on just one coordinate, i.e.,

$$\Psi(x, y, z) = X_{(x)} Y_{(y)} Z_{(z)} \qquad (2.71)$$

Since $\frac{\partial^2}{\partial x^2}$ has no effect on $Y_{(y)}$ and $Z_{(z)}$ and similarly $\frac{\partial^2}{\partial y^2}$ has no effect on $X_{(x)}$ and $Z_{(z)}$ etc. the differential equations for each wave function may be written as

$$\frac{\partial^2\Psi}{\partial x^2} = YZ\frac{d^2X}{dx^2} \qquad (a)$$

$$\frac{\partial^2\Psi}{\partial y^2} = XZ\frac{d^2Y}{\partial y^2} \qquad \text{(b)}$$

and $$\frac{\partial^2\Psi}{\partial z^2} = XY\frac{d^2Z}{dz^2} \qquad \text{(c)}$$

Substituting the values from (a), (b) and (c), into equation (2.69), we get

$$YZ\frac{d^2X}{\partial x^2} + XZ\frac{d^2Y}{dy^2} + XY\frac{d^2Z}{dz^2} + \frac{8\pi^2 m}{h^2}EXYZ = 0$$

or $$YZ\frac{d^2X}{dx^2} + XZ\frac{d^2Y}{dy^2} + XY\frac{d^2Z}{\partial z^2} = -\frac{8\pi^2 m}{h^2}EXYZ$$

Divide the above equation by XYZ, we get

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} = -\frac{8\pi^2 m}{h^2}E \qquad (2.72)$$

It is apparent that each term on the L.H.S. of equation (2.72) is a function of only one variable and sum of these terms is equal to a constant quantity $\left(-\frac{8\pi^2 m E}{h^2}\right)$. For example, if x is varied and y and z are held constant, then second and third terms will be zero. Since the sum of these terms is a constant quantity, such a situation can exist only if the first term is equal to a constant quantity. Let this quantity or constant be $\left(-\frac{8\pi^2 m}{h^2}E_X\right)$. Similarly, the second and third terms must also be constant. This converts the partial differential equation (2.72) into these ordinary differential equations.

$$\frac{1}{X}\cdot\frac{d^2X}{dx^2} = -\frac{8\pi^2 m}{h^2}E_X \qquad (2.73(a))$$

$$\frac{1}{Y}\cdot\frac{d^2Y}{dy^2} = -\frac{8\pi^2 m}{h^2}E_Y \qquad (2.73(b))$$

$$\frac{1}{Z}\cdot\frac{d^2Z}{dz^2} = -\frac{8\pi^2 m}{h^2}E_Z \qquad (2.73(c))$$

Equation (2.73,a b, and c) can be rearranged to give

$$\frac{d^2X}{dx^2} + \frac{8\pi^2 m}{h^2}E_x X = 0 \qquad (2.74(a))$$

$$\frac{d^2Y}{dy^2} + \frac{8\pi^2 m^2}{h^2}E_y Y = 0 \qquad (2.74(b))$$

$$\frac{d^2Z}{dz^2} + \frac{8\pi^2 m}{h^2} E_z Z = 0 \qquad (2.74(c))$$

It is clear from these equations that

$$E = E_x + E_y + E_z \qquad (2.75)$$

Each of the equations (2.74a-c) is the same as the equation for one-dimensional box. Therefore, the solution of these equations may be written as

$$X = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right) \qquad (2.76\text{-a})$$

$$Y = \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi y}{b}\right) \qquad (2.76\text{-b})$$

$$Z = \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi z}{c}\right) \qquad (2.76\text{-c})$$

and

$$E_x = \frac{n_x^2 h^2}{8ma^2} \qquad (2.76\text{-a})$$

$$E_y = \frac{n_y^2 h^2}{8mb^2} \qquad (2.77\text{-b})$$

$$E_z = \frac{n_z^2 h^2}{8mc^2} \qquad (2.77\text{-c})$$

where n_x, n_y an n_z are integers, excluding zero. Thus, three is a quantum number for each coordinate. The total kinetic energy of particle from equations (2.77 a-c) is given by

$$E = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad (2.78)$$

The complete wave function for the particle is given by

$$\Psi = X_{(x)}, Y_{(y)}, Z_{(z)}$$

$$\Psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right) \cdot \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi y}{b}\right) \cdot \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi z}{c}\right)$$

$$\Psi = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \cdot \sin\left(\frac{n_y \pi y}{b}\right) \cdot \sin\left(\frac{n_z \pi z}{c}\right)$$

or

$$\Psi = \sqrt{\frac{8}{v}} \cdot \sin\left(\frac{n_x \pi x}{a}\right) \cdot \sin\left(\frac{n_y \pi y}{b}\right) \cdot \left(\frac{n_z \pi z}{c}\right)$$

or $\Psi = \sqrt{\frac{8}{v}} \cdot \sin\left(\frac{n_x \pi x}{a}\right) \cdot \left(\frac{n_y \pi y}{b}\right) \cdot \sin\left(\frac{n_z \pi z}{c}\right)$ (2.79)

The lowest (ground state) energy (E_1) corresponds to $n_x = n_y = n_z = 1$. This is also known as zero point energy. The properties of the wave functions will be same as that in one-dimensional box problem, except for nodes (in the latter) and degeneracy (in the former). Here the factor $\sqrt{\frac{8}{v}}$ is the normalization of factor or constant.

The results of particle in a three-dimensional box are of interest mainly with regard to the following points:

(i) Unlike the classical predictions, the probability of finding the particle is not constant, but is a function of x, y and z-coordinates.

(ii) The probability of finding the particle in a particular portion of the box depends upon the energy of the particle.

(iii) Only certain energy levels, related to n are allowed, others are not allowed. The lowest kinetic energy is given when $n_x = n_y = n_z = 1$

$$E_{111} = \frac{3h^2}{8ma^2}$$

Example 2.13

Determine the lowest kinetic energy of a particle in a three-dimensional box of dimensions 0.1×10^{-15} m, 1.5×10^{-15} m and 2.0×10^{-15} m.

Solution

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

In lowest state, $n_x = n_y = n_z = 1$

$$E = \frac{(6.626 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31}}\left[\frac{1}{(0.1 \times 10^{-15})^2} + \frac{1}{(1.5 \times 10^{-15})^2} + \frac{1}{(2.0 \times 10^{-15})^2}\right]$$

$$= \frac{(6.626 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31}} \times \frac{1}{10^{-30}}\left[\frac{1}{(0.1)^2} + \frac{1}{(1.5)^2} + \frac{1}{(2.0)^2}\right]$$

$$= 6.067 \times 10^{-8}\ J$$