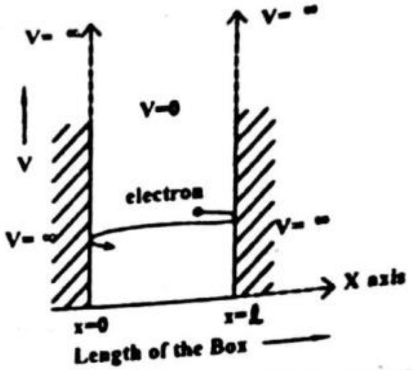
APPLICATION OF SCHRODINGER WAVE EQUATION TO A PARTICLE (ELECTRON) ENCLOSED IN A 1 DIMENSIONAL POTENTIAL BOX

Let us consider a particle (electron) of mass 'm' moving along x-axis, enclosed in a one dimensional potential box as shown in Fig. 4.8.

Since the walls are of infinite potential the particle does not penetrate out from the box.

Also, the particle is confined between the length 'l' of the box and has *elastic collisions* with the walls. *Therefore, the potential energy of the electron inside the box is constant and can be taken as zero for simplicity.*



The interactive animation of this concept can be viewed in the CD.

Fig. 4.8

∴ *We can say that* ***Outside the box*** *and* ***on the wall of the box****, the potential energy V of the electron is ∞.*

Inside the box *the potential energy (V) of the electron is zero.*

In other words we can write the ***boundary conditions*** as

$$\boxed{V(x) = 0 \text{ when } 0 < x < l}$$

$$\boxed{V(x) = \infty \text{ when } 0 \geq x \geq l}$$

Since the particle cannot exist outside the box the wave function $\psi = 0$ when $0 \geq x \geq l$.

To find the wave function of the particle within the box of length 'l', let us consider the schroedinger one dimensional time independent wave equation (i.e.,)

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V]\,\psi = 0$$

Since the potential energy inside the box is zero [(i.e) $V = 0$], the particle has kinetic energy alone and thus it is named as a free particle (or) free electron.

∴ For a *free particle (electron)*, the Schroedinger wave equation is given by

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\,\psi = 0$$

(or)
$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad \ldots (1)$$

where $k^2 = \frac{2mE}{\hbar^2}$ ... (2)

Equation (1) is a second order differential equation, therefore, it should have olution with two arbitrary constants.

∴ The solution for equation (1) is given by

$$\boxed{\psi(x) = A \sin kx + B \cos kx} \qquad \ldots (3)$$

here A and B are called as arbitrary constants, which can be found by applying e boundary conditions.

(i.e.,) $V(x) = \infty$ when $x = 0$ and $x = l$

Boundary condition (i) at $x = 0$, potential energy $V = \infty$, ∴ There is no ance for finding the particle at the walls of the box, ∴ $\psi(x) = 0$

∴ Equation (3) becomes

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

$$0 = 0 + B(1)$$

$$\therefore \mathbf{B = 0}$$

Boundary condition (ii) at $x = l$, potential energy $V = \infty$, ∴ There is no ce for finding the particle at the walls of the box, ∴ $\psi(x) = 0$

∴ Equation (3) becomes

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

Since $B = 0$ (from 1st Boundary condition), we have

$$0 = A \sin kl$$

Since $A \neq 0$; $\sin kl = 0$

We know $\sin n\pi = 0$

Comparing these two equations, we can write $kl = n\pi$

where n is an integer.

$$\text{(or)} \quad k = \frac{n\pi}{l} \qquad \ldots (4)$$

Substituting the value of B and k in equation (3) we can write the wave function associated with the free electron confined in a one dimensional box as

$$\boxed{\psi_n(x) = A \sin \frac{n\pi x}{l}} \qquad \ldots(5)$$

Energy of the particle (Electron)

We know from equation (2)

$$k^2 = \frac{2mE}{\hbar^2}$$

$$= \frac{2mE}{(h^2/4\pi^2)} \qquad \left[\because \hbar^2 = \frac{h^2}{4\pi^2} \right]$$

$$\text{(or)} \quad k^2 = \frac{8\pi^2 mE}{h^2} \qquad \ldots (6)$$

Squaring equation (4) we get

$$k^2 = \frac{n^2\pi^2}{l^2} \qquad \ldots (7)$$

Equating equation (6) and equation (7), we can write

$$\frac{8\pi^2 mE}{h^2} = \frac{n^2\pi^2}{l^2}$$

$$\boxed{\therefore \textit{ Energy of the particle (electron) } E_n = \frac{n^2h^2}{8ml^2}} \qquad \ldots(8)$$

∴ From equations (8) and (5) we can say that, for each value of 'n', there is an energy level and the corresponding wave function.

Thus we can say that, each value of E_n is known as ***Eigen value*** *and the corresponding value of ψ_n is called as* ***Eigen function***.

Energy levels of an electron

For various values of 'n' we get various energy values of the electron. ***The lowest energy value (or) ground state energy value*** can be got by substituting $n = 1$ in equation (8)

$\therefore$ When $n = 1$ we get $E_1 = \frac{h^2}{8ml^2}$

Similarly we can get the other energy values

(i.e.,) When $n = 2$ we get $E_2 = \frac{4h^2}{8ml^2} \Rightarrow 4E_1$

When $n = 3$ we get $E_3 = \frac{9h^2}{8ml^2} \Rightarrow 9E_1$

When $n = 4$ we get $E_4 = \frac{16\,h^2}{8\,ml^2} \Rightarrow 16\,E_1$

$\therefore$ In general we can write the energy eigen function as

$$\boxed{E_n = n^2 E_1} \qquad \text{...(9)}$$

*It is found from the energy levels E_1, E_2, E_3 etc the energy levels of an electron are **Discrete.***

This is the great success which is achieved in quantum mechanics than classical mechanics, in which the energy levels are found to be continuous.

The various energy eigen values and their corresponding eigen functions of an electron enclosed in a one dimensional box is as shown in Fig. 4.9. Thus we have discrete energy values.

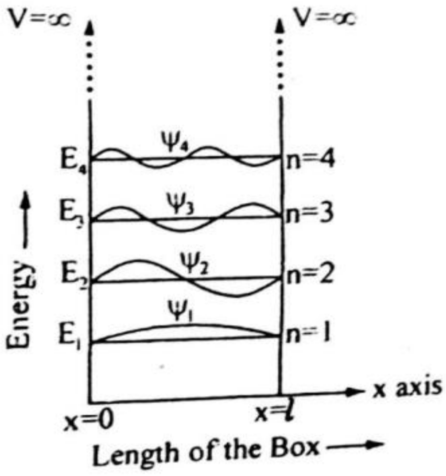


Fig. 4.9

Note: The number of nodes and antinodes in the wave with respect to the quantum number can be got from a general formula (i.e.,) if we have n is the number of antinodes then $(n + 1)$ number of nodes will be there.

For example if $n = 3$ then ψ_3 has 3 antinodes and 4 nodes

(at $x = 0$, $x = \frac{l}{3}$, $x = \frac{2l}{3}$ and $x = l$)

Normalisation of the wave function

Normalisation: It is the process by which the probability (P) of finding the particle (electron) inside the box can be done.

We know that the total probability (P) is equal to 1 means then there is a particle inside the box.

∴ For a one dimensional potential box of length 'l', the probability

$$P = \int_0^l |\psi|^2 \, dx = 1 \quad \left(\begin{array}{l} \text{Since the particle is present inside the well between the} \\ \text{length 0 to '}l\text{' the limits are chosen between 0 to } l \end{array} \right) \quad (10)$$

Substituting equation (5) in equation (10), we get

$$P = \int_0^l A^2 \sin^2 \frac{n\pi x}{l} \, dx = 1$$

$$\text{(or)} \quad A^2 \int_0^l \left[\frac{1 - \cos 2n\pi x/l}{2} \right] dx = 1$$

$$A^2 \left[\frac{x}{2} - \frac{1}{2} \frac{\sin 2n\pi x/l}{2n\pi/l} \right]_0^l = 1$$

$$A^2 \left[\frac{l}{2} - \frac{1}{2} \frac{\sin 2n\pi l/l}{2n\pi/l} \right] = 1$$

$$A^2 \left[\frac{l}{2} - \frac{1}{2} \frac{\sin 2n\pi}{2n\pi/l} \right] = 1 \quad \text{...(11)}$$

We know $\sin n\pi = 0$ ∴ $\sin 2n\pi$ is also $= 0$

∴ Equation (11) can be written as

$$\frac{A^2 l}{2} = 1$$

(or) $$A^2 = \frac{2}{l}$$

(or) $$A = \sqrt{\frac{2}{l}}$$

Substituting the value of 'A' in equation (5),

The normalised wave function can be written as

$$\boxed{\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}}$$

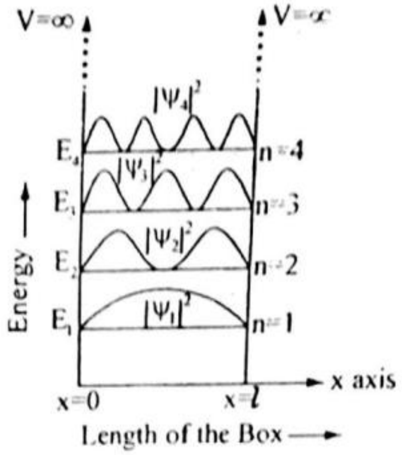


Fig. 4.10

The normalised wave function and their energy values are as shown in fig. 4.10.

THREE DIMENSIONAL POTENTIAL BOX

The solution of one-dimensional potential box can be extended for a three dimensional potential box. In a three dimensional potential box, the particle (electron) can move in any direction in space. Therefore instead of one quantum number 'n', we have to use three quantum number n_x, n_y and n_z corresponding the three co-ordinate axis (ie) x, y and z respectively.

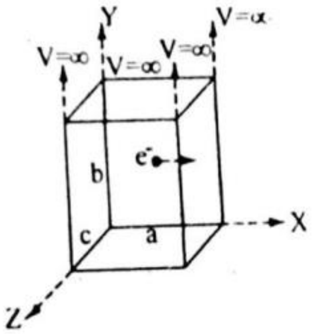


Fig. 4.11

∴ If a, b, c are the length of the box as shown in Fig. 4.11 along x, y and z axis, then the

The energy of the particle $= E_x + E_y + E_z$

$$\text{(i.e.,)}\ E_{n_x, n_y, n_z} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

If $a = b = c$ (i.e.,) for a ***cubical box.***

Energy Eigen value is $\boxed{E_{n_x n_y n_z} = \frac{h^2}{8ma^2}[n_x^2 + n_y^2 + n_z^2]}$ ...(1)

The corresponding normalized wave function of an electron in a cubical box can be written as

$$\psi_{n_x n_y n_z} = \sqrt{\frac{2}{a} \times \frac{2}{a} \times \frac{2}{a}} \cdot \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{a} \sin\frac{n_z \pi z}{a}$$

$$\therefore \quad \boxed{\psi_{n_x n_y n_z} = \sqrt{\frac{8}{a^3}} \cdot \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{a} \sin\frac{n_z \pi z}{a}} \quad \text{... (2)}$$

From equations (1) and (2) we can note that, several combinations of the three quantum numbers (n_x, n_y and n_z) leads to different energy eigen values and eigen functions.

Example

If a state has quantum numbers $n_x = 1\ n_y = 1\ n_z = 2$

$$\text{Then, } n_x^2 + n_y^2 + n_z^2 = 6$$

Similarly for $n_x = 1$; $n_y = 2$; $n_z = 1$ combination and $n_x = 2\ n_y = 1\ n_z = 1$ combination we have $n_x^2 + n_y^2 + n_z^2 = 6$

$$\boxed{\therefore \quad E_{112} = E_{121} = E_{211} = \frac{6h^2}{8ma^2}} \quad \text{... (3)}$$

The corresponding wave functions can be written as

$$\psi_{112} = \sqrt{\frac{8}{a^3}} \sin\frac{\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{2\pi z}{a}$$

$$\psi_{121} = \sqrt{\frac{8}{a^3}} \sin\frac{\pi x}{a} \sin\frac{2\pi y}{a} \sin\frac{\pi z}{a}$$

$$\psi_{211} = \sqrt{\frac{8}{a^3}} \sin\frac{2\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{\pi z}{a} \qquad (4)$$