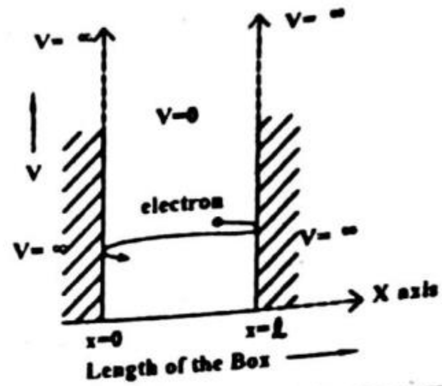
APPLICATION OF SCHRODINGER WAVE EQUATION TO A PARTICLE (ELECTRON) ENCLOSED IN A 1 DIMENSIONAL POTENTIAL BOX

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

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

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

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.

$\therefore$ 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)

$$\frac{d^2\psi}{dx^2} + k^2\,\psi = 0 \qquad \text{... (1)}$$

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

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

$\therefore$ The solution for equation (1) is given by

$$\boldsymbol{\psi(x) = A \sin kx + B \cos kx} \qquad \text{... (3)}$$

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

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

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

$\therefore$ Equation (3) becomes

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

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

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

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

$\therefore$ 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.

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

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

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

Energy of the particle (Electron)

We know from equation (2)

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

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

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

Squaring equation (4) we get

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

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

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

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

$\therefore$ 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 $E_1 = \dfrac{h^2}{8ml^2}$

Similarly we can get the other energy values

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

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

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

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

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

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.

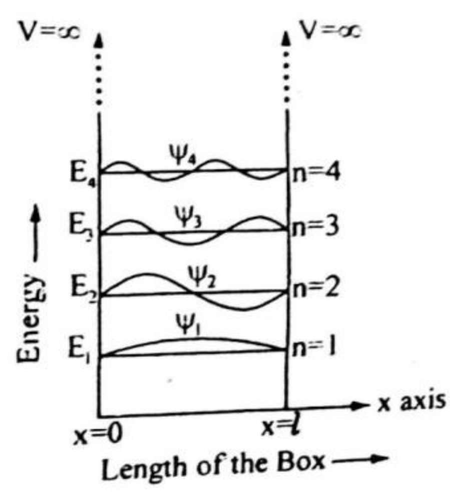


Fig. 4.9

$$\therefore \quad \hat{H} = -\frac{h^2}{8\pi^2 m}\left[\frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \qquad ...(6.18)$$

The Schrodinger equation, $\hat{H}\,\psi = E\,\psi$ becomes

$$-\frac{h^2}{8\pi^2 mr^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right] = E\,\psi \qquad ...(6.19)$$

or, on simplification,

$$\frac{\partial^2\psi}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\cdot\frac{\partial\psi}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{8\pi^2 mr^2}{h^2}E\,\psi = 0 \qquad ...(6.20)$$

where the wave function ψ is $\psi(\theta, \varphi)$.

6.2.1.2 Separation of Variables

The partial differential Schrodinger Equation (6.20) can be solved by separating the variables. For this, suppose that the function $\psi(\theta, \varphi)$ is a product of two functions $P(\theta)$ and $F(\varphi)$, each being a function of a single variable only, *i.e.*,

$$\psi(\theta, \varphi) = P(\theta)\,F(\varphi) \qquad ...(6.21)$$

Differentiating partially with respect to θ, we get

$$\frac{\partial\psi}{\partial\theta} = F(\varphi)\frac{dP}{d\theta}, \quad \frac{\partial^2\psi}{\partial\theta^2} = F(\varphi)\frac{d^2P}{d\theta^2}$$

and with respect to φ, we get

$$\frac{\partial\psi}{\partial\varphi} = P(\theta)\frac{dF}{d\varphi}, \quad \frac{\partial^2\psi}{\partial\varphi^2} = P(\theta)\frac{\partial^2F}{\partial\varphi^2}$$

Substituting these relations into Equation (6.20)

$$F\cdot\frac{d^2P}{d\theta^2} + \frac{\cos\theta}{\sin\theta}\cdot F\cdot\frac{dP}{d\theta} + \frac{1}{\sin^2\theta}P\frac{d^2F}{d\varphi^2} + \frac{8\pi^2 mr^2}{h^2}EPF = 0$$

Multiplying through by $\frac{\sin^2\theta}{PF}$,

$$\frac{\sin^2\theta}{P}\cdot\frac{d^2P}{d\theta^2} + \cos\theta\cdot\sin\theta\cdot\frac{1}{P}\cdot\frac{dP}{d\theta} + \frac{1}{F}\cdot\frac{d^2F}{d\varphi^2} + \frac{8\pi^2 mr^2}{h^2}\sin^2\theta\,E = 0$$

where P and F stand for $P(\theta)$ and $F(\varphi)$ respectively.

or

$$\frac{\sin^2\theta}{P}\cdot\frac{d^2P}{d\theta^2} + \cos\theta\,.\,\sin\theta\cdot\frac{1}{P}\cdot\frac{dP}{d\theta} + \frac{8\pi^2 mr^2}{h^2}\sin^2\theta\,E = -\frac{1}{F}\cdot\frac{d^2F}{d\varphi^2} \qquad ...(6.22)$$

Now the left hand side (l.h.s.) of Equation (6.22) depends on θ only while the right hand side (r.h.s.) depends on φ only. If φ is maintained constant while θ varies, the r.h.s. will remain constant. Since l.h.s. = r.h.s., the l.h.s. will also remain equal to the same constant even though θ varies. The same argument applies to the situation when θ is kept constant and φ varies. Both sides of Equation (6.22) are, therefore, equal to the same constant. Let the constant be denoted by M^2 for convenience. Thus, Equation (6.22) splits into the following two ordinary differential equations:

$$-\frac{1}{F}\cdot\frac{d^2 F}{d\varphi^2} = M^2 \qquad ...(6.23)$$

and, after multiplying Equation (6.22) by $P/\sin^2\theta$,

$$\frac{d^2 P}{d\theta^2} + \frac{\cos\theta}{\sin\theta}\cdot\frac{dP}{d\theta} + \beta\cdot P = \frac{M^2 P}{\sin^2\theta} \qquad ...(6.24)$$

where $$\beta = \frac{8\pi^2 mr^2}{h^2} E \qquad ...(6.25)$$