ł.11 SCHROEDINGER TIME DEPENDENT WAVE EQUATION

Schroedinger describes the wave nature of a particle in mathematical form nd is known as ***Schroedinger wave equation***. There are two types of wave quations, *viz*

(i) Time dependent wave equation.

(ii) Time independent wave equation.

TIME DEPENDANT WAVE EQUATION:

A particle can behave as a wave only under motion. So, it should be accelerated by a potential field. Therefore, the total energy (E) of the particle is equal to the sum of its potential energy (V) and kinetic energy.

$$\therefore \quad E = V + \frac{1}{2} m v^2$$

$$\text{(or)} \quad E = V + \frac{1}{2} \frac{m^2 v^2}{m}$$

$$\text{(or)} \quad E = V + \frac{p^2}{2m} \qquad [\because \quad p = mv]$$

$$\text{(or)} \quad E\Psi = V\Psi + \frac{p^2}{2m}\Psi \qquad \text{... (1)}$$

According to classical mechanics, if 'x' is the position of the particle moving with the velocity 'v', then the displacement of the particle at any time 't' is given by

$$y = A\, e^{-i\omega (t - x/v)}$$

where ω is the Angular frequency of the particle.

Similarly, in Quantum Mechanics the wave function $\Psi (x, y, z, t)$ represents the position (x, y, z) of a moving particle at any time 't' and is given by

$$\Psi (x, y, z, t) = A\, e^{-i\omega (t - x/v)} \qquad \text{... (2)}$$

We know angular frequency $\omega = 2\pi\nu$

$\therefore$ Equation (2) becomes

$$\Psi (x, y, z, t) = A\, e^{-2\pi i \left(\nu t - \frac{\nu x}{v} \right)} \qquad \text{... (3)}$$

We know $E = h\nu$ (or) $\nu = \frac{E}{h}$ ... (4)

Also, if 'v' is the velocity of the particle behaving as a wave, then the frequency $\nu = \frac{v}{\lambda}$ (or) $\frac{\nu}{v} = \frac{1}{\lambda}$ ... (5)

Substituting equations (4) and (5) in equation (3), we get,

$$\Psi (x, y, z, t) = A\, e^{-2\pi i \left(\frac{E}{h} t - \frac{x}{\lambda} \right)} \qquad \text{... (6)}$$

If 'p' is the momentum of the particle, then the de-Broglie wavelength is given by $\lambda = \frac{h}{mv} = \frac{h}{p}$ ... (7)

Substituting equation (7) in (6) we get

$$\Psi(x, y, z, t) = A\, e^{-2\pi i\left(\frac{Et}{h} - \frac{px}{h}\right)}$$

$$\text{(or)}\quad \Psi(x, y, z, t) = A\, e^{-\frac{2\pi i}{h}(Et - px)}$$

Since $\hbar = \frac{h}{2\pi}$, **we can write**

$$\boxed{\Psi(x, y, z, t) = A\, e^{-\frac{i}{\hbar}(Et - px)}} \quad ...(8)$$

Differentiating equation (8) partially with respect to 'x' we get

$$\frac{\partial \Psi}{\partial x} = A e^{\frac{-i}{\hbar}(Et - px)}\left(\frac{ip}{\hbar}\right)$$

Differentiating once again partially with respect to 'x' we get

$$\frac{\partial^2 \Psi}{\partial x^2} = A e^{\frac{-i}{\hbar}(Et - px)}\left(\frac{i^2 p^2}{\hbar^2}\right)$$

Since $\Psi(x, y, z, t) = A e^{\frac{-i}{\hbar}(Et - px)}$ and $i^2 = -1$, we can write

$$\frac{\partial^2 \Psi}{\partial x^2} = \Psi(x, y, z, t) \cdot \left(\frac{-p^2}{\hbar^2}\right)$$

(or)

$$\boxed{p^2 \Psi = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2}} \quad ...(9)$$

Differentiating equation (8) partially with respect to 't', we get

$$\frac{\partial \Psi}{\partial t} = A e^{\frac{-i}{\hbar}(Et - px)}\left(\frac{-iE}{\hbar}\right)$$

$$\text{(or)}\quad \frac{\hbar}{-i}\frac{\partial \Psi}{\partial t} = \Psi(x, y, z, t)\, E \qquad \left[\because\ \Psi(x, y, z, t) = A\, e^{-\frac{i}{\hbar}(Et - px)}\right]$$

or

$$\boxed{E\Psi = i\hbar \frac{\partial \Psi}{\partial t}} \quad ...(10)$$

Substituting equations (9) and (10) in equation (1), we get,

$$i\hbar \frac{\partial\Psi}{\partial t} = V\Psi - \frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}$$

(or)

$$\frac{i\hbar\partial}{\partial t}\Psi = \left[V - \frac{\hbar^2}{2m}\frac{\partial}{\partial x^2} \right]\Psi \qquad \text{...(11)}$$

Equation (11) represents the ***one dimensional*** *(along 'x' direction)* ***Schroedinger time dependent equation***. It is called time dependent wave equation, because here the wave function $\Psi(x, y, z, t)$ depends both on position (x, y, z) and time (t).

Similarly, the ***3-dimensional Schroedinger time dependent wave equation*** can be written as

$$i\hbar \frac{\partial\Psi}{\partial t} = \left[V - \frac{\hbar^2}{2m}\nabla^2 \right]\Psi \qquad \text{... (12)}$$

where, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Equation (12) can also be written as

$$E\Psi = H\Psi \qquad \text{...(13)}$$

where E is the ***energy operator*** given by $E = i\hbar\frac{\partial}{\partial t}$ and

H is called ***Hamiltonian Operator,*** given by $H = V - \frac{\hbar^2}{2m}\nabla^2$

4.12 SCHROEDINGER TIME INDEPENDENT WAVE EQUATION

It is convenient to use the time independent wave equation rather than using time dependent wave equation, because of the following reason.

In Schroedinger time dependent wave equation the wave function 'Ψ' depends on time, but in Schroedinger time independent wave function ψ does not depend on time and hence it has many applications.

We know that time dependent wave function

$$\Psi(x, y, z, t) = Ae^{-\frac{i}{\hbar}(Et - px)}$$

Splitting the RHS of this equation into two parts, *viz.*, (i) Time dependent factor and (ii) Time independent factor, we get

$$\text{(i.e.,)} \quad \Psi' (x, y, z, t) = A\, e^{-\frac{iEt}{\hbar}} \cdot e^{\frac{ipx}{\hbar}}$$

$$\text{(or)} \quad \Psi' (x, y, z, t) = A\, \psi\, e^{-\frac{iEt}{\hbar}} \quad \ldots (1)$$

where ψ *represents the time independent wave function* (i.e.,) $\psi = e^{\frac{ipx}{\hbar}}$

Differentiating equation (1) partially with respect to 't' we get

$$\frac{\partial \Psi'}{\partial t} = A\, \psi\, e^{-\frac{iEt}{\hbar}} \left(\frac{-iE}{\hbar} \right) \quad \ldots (2)$$

Differentiating equation (1) partially with respect to 'x' we get,

$$\frac{\partial \Psi'}{\partial x} = A\, e^{\frac{-iEt}{\hbar}}\, \frac{\partial \psi}{\partial x}$$

Differentiating once again partially with respect to 'x' we get

$$\frac{\partial^2 \Psi'}{\partial x^2} = A\, e^{\frac{-iEt}{\hbar}}\, \frac{\partial^2 \psi}{\partial x^2} \quad \ldots (3)$$

We know the Schroedinger time dependent wave equation (one dimensional) is

$$i\hbar \frac{\partial \Psi'}{\partial t} = V\Psi' - \frac{\hbar^2}{2m} \frac{\partial^2 \Psi'}{\partial x^2} \quad \ldots (4)$$

We can get the Schroedinger time dependent wave equation, just by substituting equations (1), (2) and (3), which has relation between the time dependent wave function (Ψ') and time independent wave function (ψ), in equation (4).

$\therefore$ Substituting equations (1), (2) and (3) in equation (4) we get

$$i\hbar\, A\, \psi\, e^{\frac{-iEt}{\hbar}} \left(\frac{-iE}{\hbar} \right) = VA\, \psi\, e^{\frac{-iEt}{\hbar}} - \frac{\hbar^2}{2m} A\, e^{\frac{-iEt}{\hbar}} \cdot \frac{\partial^2 \psi}{\partial x^2}$$

$$\text{(or)} \quad i\hbar \left(\frac{-iE}{\hbar} \right) \psi = V\psi - \frac{\hbar^2}{2m} \cdot \frac{\partial^2 \psi}{\partial x^2}$$

$$\text{(or)} \quad -(i)^2 E\psi = V\psi - \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}$$

$$\text{(or)} \quad E\psi - V\psi = \frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}$$

$$\text{(or)} \quad \frac{\partial^2\psi}{\partial x^2} = \frac{-2m}{\hbar^2}[E\,\psi - V\psi]$$

$$\text{(or)} \quad \frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}[E\,\psi - V\psi] = 0$$

(or)

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\,\psi = 0 \quad \text{... (5)}$$

Equation (5) represents the ***one dimensional*** *(x- direction) Schroedinger time independent wave equation, because, in this equation the wave funtion* ψ *is independent of time. Similarly the* ***three dimensional Schroedinger time independent wave equation*** *can be written as*

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\,\psi = 0$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Reference:
1.Introduction to Quantum Chemistry by R.K.Prasad.
2. Engineering Physics by Senthil Kumar