Schroedinger Time Dependent Wave Equation

A particle can behave as a wave only under motion. So, it should be accelarated 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.

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

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

$$E = V + \frac{p^2}{2m} \quad [\because p = mv]$$

$$E\psi = V\psi + \frac{p^2}{2m}\psi \longrightarrow (1)$$

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

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

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

$$\psi(x, y, z, t) = Ae^{-i\omega(t - x/v)} \longrightarrow (2)$$

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

$\therefore$ Equation ② becomes

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

we know $E = h\nu$ or $\nu = \frac{E}{h}$ $\longrightarrow$ ④

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

Substituting equations ④ and ⑤ in equation ③ we get

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

If p is the momentum of the particle, then the de-Broglie wavelength is given by

$$\lambda = \frac{h}{mv} = \frac{h}{p} \longrightarrow ⑦$$

Substituting equation ⑦ in ⑥ we get

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

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

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

$$\psi(x, y, z, t) = A e^{-i/\hbar (Et - px)} \longrightarrow ⑧$$

Differentiating equation ⑧ partially w.r.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 $\psi(x,y,z,t) = Ae^{\frac{-i}{\hbar}(Et-px)}$ and $i^2=-1$ we can write

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

$$p^2\psi = -\hbar^2\frac{\partial^2\psi}{\partial x^2} \longrightarrow (9)$$

Differentiating equation (8) partially with respect to 't'.

we get
$$\frac{\partial\psi}{\partial t} = Ae^{\frac{-i}{\hbar}(Et-px)}\left[\frac{-iE}{\hbar}\right]$$

(or) $$\frac{\hbar}{-i}\frac{\partial\psi}{\partial t} = \psi(x,y,z,t)\,E$$

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

(or) $$E\psi = i\hbar\frac{\partial\psi}{\partial t} \longrightarrow (10)$$

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

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

$$i\hbar\frac{\partial}{\partial t}\psi = \left[V - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right]\psi \longrightarrow (11)$$

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

$$i\hbar \frac{\partial \psi}{\partial t} = \left[v - \frac{\hbar^2}{2m} \nabla^2 \right] \psi \longrightarrow (12)$$

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

$$E\psi = H\psi \longrightarrow (13)$$

where E is the energy operator given by

$$E = i\hbar \frac{\partial}{\partial t} \text{ and}$$

H is called Hamiltonian operator given by

$$H = V - \frac{\hbar^2}{2m} \nabla^2$$

Schroodinger 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 schroodinger time dependent wave equation the wave function 'ψ' depends on time, but in schroodinger time independent wave function ψ doesnot depend on time and hence it has many applications.

we know that time dependent wave function

$$\psi(x, y, z, t) = A e^{\frac{-i}{\hbar}(Et - px)}$$

Splitting the RHS of this equation into two parts

viz ① Time dependent factor

② Time independent factor. we get

$$\psi(x, y, z, t) = A e^{-\frac{iEt}{\hbar}} \cdot e^{\frac{ipx}{\hbar}}$$

(or) $$\psi(x, y, z, t) = A \psi e^{\frac{iEt}{\hbar}} \longrightarrow ①$$

where ψ represents the time independent wave function

ie $$\psi = e^{\frac{ipx}{\hbar}}$$

Differentiating equation ① partially with respect to t

we get $$\frac{\partial \psi}{\partial t} = A \psi e^{\frac{-iEt}{\hbar}} \left[\frac{-iE}{\hbar}\right] \longrightarrow ②$$

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

we know the schroedinger time dependent wave equation

is $i\hbar \frac{\partial \Psi}{\partial t} = V\Psi - \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} \longrightarrow (4)$

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 $i\hbar A\psi e^{\frac{-iEt}{\hbar}} \left[\frac{-iE}{\hbar}\right] = VA\psi e^{\frac{-iEt}{\hbar}} - \frac{\hbar^2}{2m} A e^{\frac{-iEt}{\hbar}} \cdot \frac{d^2\psi}{dx^2}$

(or) $i\hbar \left[\frac{-iE}{\hbar}\right]\psi = V\psi - \frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}$

$$-(i)^2 E\psi = V\psi - \frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}$$

$$E\psi - V\psi = \frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2}$$

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

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

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E-V]\psi = 0 \longrightarrow (5)$$

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

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

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

Free particle.

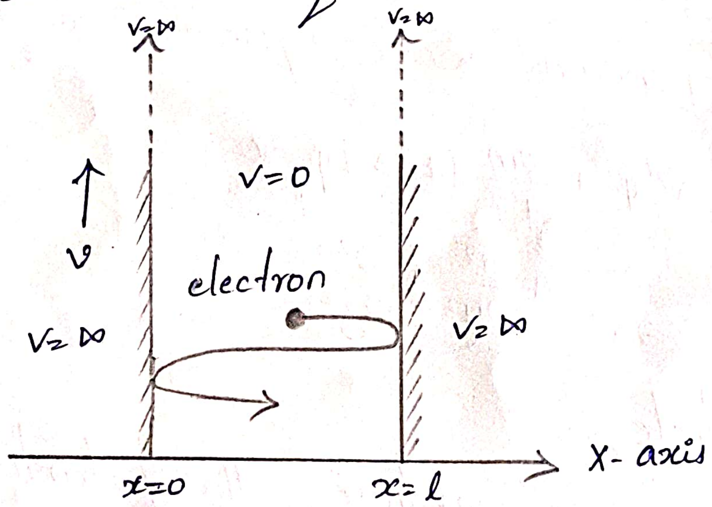
For a free particle, the potential energy $V=0$

$\therefore$ Schroodinger time independent wave equation becomes $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0$ [for one dimension]

$$\nabla^2\psi + \frac{2m}{\hbar^2}E\psi = 0 \text{ [for three dimension]}$$

Particle Enclosed in a One Dimensional (1D) Infinite Potential well (or) Box.

Let us consider a particle (electron) of mass 'm' moving along x-axis, enclosed in a one-dimensional (1D) infinite potential well as shown in the figure. Since the walls are of infinite potential, the particle doesnot penetrate out from the well.



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

∴ we can say that outside the well and on the wall of the well, the potential energy V of the electron is ∞.

Inside the well the potential energy (v) of the electron is zero. In other words we can write the boundary conditions as

$V(x) = 0$ when $0 < x < l$

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

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

To find the wave function of the particle within the well of length 'l', let us consider the schroedinger one dimensional time independent wave equation (ie)

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

Since the potential energy inside the well 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

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

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

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

Equation ① is a second order differential equ[ation]
therefore it should have solution with two arbitrary constants.

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

$$\psi(x) = A\sin kx + B\cos kx \longrightarrow ③$$

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

ie $V(x) = \infty$ 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 well $\therefore \psi(x) = 0$

$\therefore$ Equation ③ becomes

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

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

$$\therefore B = 0$$

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

$\therefore$ 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.

(or) $k = \frac{n\pi}{l} \longrightarrow (4)$

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 well as

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

Energy of the particle (Electron)

we know from equation (2)

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

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

$$k^2 = \frac{8\pi^2 mE}{h^2} \longrightarrow (6)$$

Squaring equation (4) we get

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

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

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

$\therefore$ Energy of the particle $E_n = \frac{n^2h^2}{8ml^2} \longrightarrow (8)$

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

Similarly we can get the other energy values.

when n=2 we get $E_2 = \frac{4h^2}{8ml^2} \Rightarrow 4E_1$

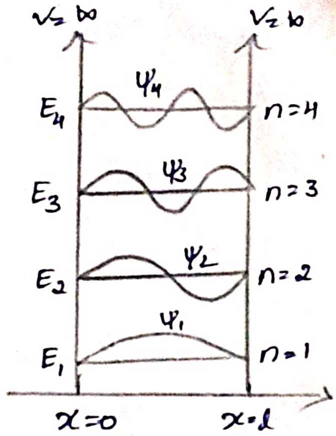
when n=3 we get $E_3 = \frac{9h^2}{8ml^2} \Rightarrow 9E_1$

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

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

$$E_n = n^2E_1 \longrightarrow (9)$$

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 is as shown in figure. Thus we have discrete energy values.

Normalisation of the wave function.

Normalisation: It is the process by which the probability (P) of finding the particle inside the well can be done. we know that the total probability (P) is equal to 1 means, then there is a particle inside the well.

$\therefore$ For a one dimensional potential well of length 'l',

the probability $P = \int_0^l |\psi|^2 dx = 1 \longrightarrow$ (10)

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

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

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

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

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

$$A^2\left[\frac{l}{2}-\frac{1}{2}\,\frac{\sin 2n\pi}{2n\pi/l}\right]=1 \longrightarrow (11')$$

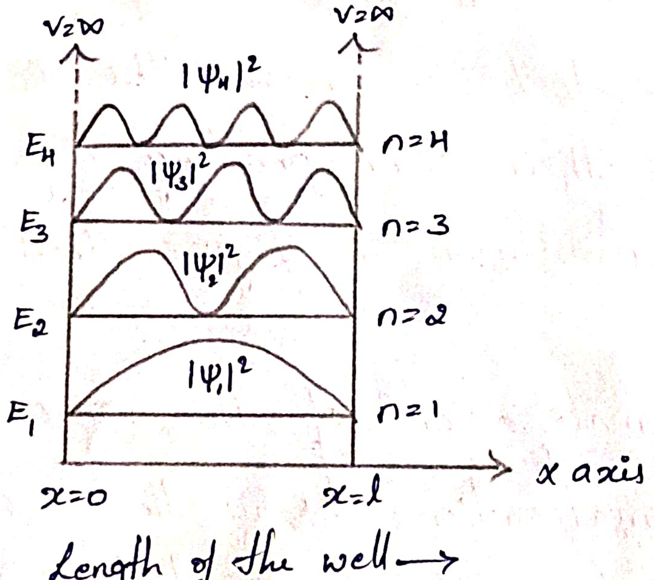
we know $\sin n\pi = 0$ $\therefore$ $\sin 2n\pi$ is also $= 0$

$\therefore$ Equation (11) can be written as

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

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

$$A=\sqrt{2/l}$$



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

The normalised wave function can be written as

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

The normalised wave function and their energy values are shown in the figure.