~~Schroedinger wave equation~~ →

Wave function → Amplitude of matter wave is described by wave function, represented by ψ. It consist of real and Imaginary part,

$$\psi = A + iB$$

Conjugate $\psi^* = A - iB$

and $\psi^* \psi = |\psi|^2 = A^2 + B^2 \quad [i^2 = 1]$

$|\psi|^2$ at a particular place at a particular time is propotional to the probability of finding the particle. Therefore at that time,

$$\text{Probability density} = |\psi|^2 = \psi^* \psi$$

Physical significance → In Schroedinger wave equation for a particle the wave function $\psi(\vec{r}, t)$ give the behaviour of the particle at a given position $\vec{r}$ and a given time t, It's magni is large in regions where the probability of finding the particle is high and its magnitude is small where the probability of finding the particle is low.

→ The square root $[\psi(x, y, z, t)]^2$ of wave function is called Modulus of ψ, It is also positive quantity and called the probability amplitude of the particle.

→ The wave function $\psi(x\, y\, z)$ itself have no physical significance but the Square of absolute value $|\psi|^2 = \psi^* \psi$ interpreted as probability density and ψ is probability amplitude

→ **Limitation** → ① ψ must be finite every where.
② It must be single value.
③ It must be continuous and hence a continuous first derivative every where from Schroedinger equation, we know $\frac{\partial^2 \psi}{\partial x^2}$ must we finite every where This is possible only when $\frac{\partial \psi}{\partial x}$ and ψ is continuous across a boundary.

Normalisation and orthogonality of wave function (ψ)

The probability of finding the particle over the entire region of space will obviously be equal to unity. Since the probability of finding the particle over a small volume τ is $|\psi(r,t)|^2 d\tau$, so the particle can easily get the probability over the whole space by integrating the probability distribution $|\psi(r,t)|^2$ for whole space,

$$\int |\psi(r,t)|^2 = 1 \quad \text{or} \quad \int \psi(r,t)\, \psi^*(r,t)\, d\tau = 1 \quad -(1)$$

The wave function that satisfy this condition are known as normalised wave function.

→ Any wave function may be normalised by multiplying or dividing it by a constant. Let the wave function is formed by multiplying it by a constant, so,

$$\psi_1 = \frac{1}{\sqrt{N}}\psi \quad \text{and} \quad \psi_1^* = \frac{1}{\sqrt{N}}\psi^*$$

Then $\int \psi_1 \psi_1^* \, d\tau = \frac{1}{N}\int \psi_1 \psi_1^* \, d\tau = 1$ or $N = \int \psi_1 \psi_1^* \, d\tau$

ψ_1 is called Normalised wave function an $\frac{1}{\sqrt{N}}$ is Normalisation factor, since $\frac{1}{\sqrt{N}}$ is constant and also does not depend on space co-ordinate (x, y, z) and ψ is a solution of the wave equation, it follow $\frac{\psi}{\sqrt{N}}$ will also be a satisfactory solution of the wave equation i.e. it will discribe the same physical system.

→ If ψ_i and ψ_j are two different wave function, both are satisfactory solution of Schrodinger equation for a given system then if $\int \psi_i^* \psi_j \, d\tau = \int \psi_j^* \psi_i \, d\tau = 0$ for $i \neq j$

Then function are said to be orthogonal.

Schroedinger wave equation →

For explaining the motion of a matter particle it is compulsory that the wave function associated with the particle at all position and times, for this a differential equation required this equation should have first order time derivatives and second order space derivatives of wave function. This equation which satisfied by $\psi(x, t)$ is known as Schroedinger wave equation. Schroedinger equation is fundamental equation of wave mechanics similar to Newton's second law of motion in classical mechanics. It is differential equation of the de broglie waves associated with particle and discribes the motion of particles.

Time Independent →

Let us consider that ψ for a particle moving freely in the $+x$ direction, $\psi = A \sin \omega t = A \sin 2\pi\nu t$ ①

eq ① differentiating w.r to t two times

$$\frac{\partial \psi}{\partial t} = 2\pi\nu A \cos 2\pi\nu t \quad —②, \quad \frac{\partial^2 \psi}{\partial t^2} = -4\pi^2\nu^2 A \sin 2\pi\nu t = -4\pi^2\nu^2\psi \quad —③$$

we know differential equation of wave motion

$$\nabla^2\psi = \frac{1}{u^2}\frac{\partial^2\psi}{\partial t^2} \quad —④ \qquad \nabla^2 u^2\psi = \frac{\partial^2\psi}{\partial t^2} \quad ⑤$$

Comparing eq ③ and ⑤, $\nabla^2 u^2 \psi = -4\pi^2\nu^2\psi$

or $\nabla^2 u^2\psi + 4\pi^2\nu^2\psi = 0$ — ⑥

→

$$\nabla^2 u^2 \psi + 4\pi^2 \frac{u^2}{\lambda^2}\psi = 0 \quad [\because \nu = \frac{u}{\lambda}] \Rightarrow \nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi = 0 \quad \text{--- (7)}$$

$$\nabla^2\psi + 4\pi^2 \frac{m^2 v^2}{h^2}\psi = 0 \quad [\because \lambda = \frac{h}{mv}] \quad \text{--- (8)}$$

and $E = K.E + P.E \Rightarrow E = \frac{1}{2}mv^2 + V \Rightarrow 2(E - V) = mv^2$

$$2m[E-V] = m^2 v^2 \quad \text{--- (9)}$$

The from eq (8) and (9)

$$\nabla^2\psi + \frac{4\pi^2[2m(E-V)]\psi}{h^2} = 0$$

$$\nabla^2\psi + \frac{8\pi^2 m(E-V)\psi}{h^2} = 0$$

$$\nabla^2\psi + \frac{8\pi^2 m(E-V)\psi}{4\pi^2 \hbar^2} = 0 \quad [\because h = 2\pi\hbar]$$

$$\boxed{\nabla^2\psi + \frac{2m(E-V)\psi}{\hbar^2} = 0} \quad \text{--- (10)}$$

This is Time Independent Schroedinger equation.

Time dependent Schroedinger equation →

we know $E\psi = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = i\hbar\frac{\partial\psi}{\partial t}$ — (11)

Putting this value in eq (10)

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left(i\hbar\frac{\partial\psi}{\partial t} - V\psi\right) = 0$$

$$\frac{\hbar^2}{2m}\nabla^2\psi + i\hbar\frac{\partial\psi}{\partial t} - V\psi = 0 \quad \text{or} \quad i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi$$

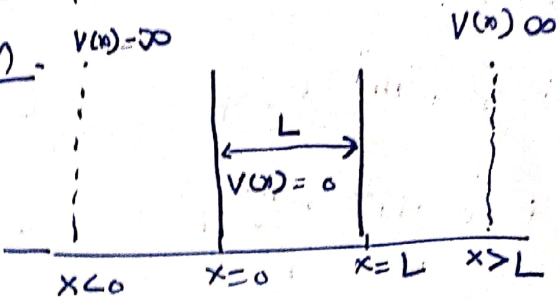
$$\text{or} \quad i\hbar\frac{\partial\psi}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\psi \quad \text{--- (12)}$$

$$\boxed{E\psi = H\psi} \quad \text{--- (13)}$$

Here $\left[-\frac{\hbar^2}{2m}\nabla^2 + V\right] = H$ is Hamiltonian operator, E and H both energy operator but H depend only space co-ordinate and E depend on time co-ordinate.

Application of Schroedinger equation.

Particle in 1-D Potential Box:...



Let a particle is restricted to move in 1-D with a certain region from $x=0$ to $x=L$. For this situation we consider that there are impenitrable walls of infinite hight at $x=0$ and $x=L$, so when ever the particle reaches at these walls, it is reflected back into the well. The potential function $V(x)$ can be defined as

$$V = \infty \quad \text{for } x \leq 0 \text{ and } x \geq L$$

$$V = 0 \quad \text{fo } 0 \leq x \leq L$$

[boundary condition]

The particle can not exist out side the box, so its wave funct ψ is 0 for $x \leq 0$ and $x \geq L$.

with in the ~~well for~~ box the Schroeding equation becomes

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

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \quad \text{—} (1) \qquad \text{Here } \alpha = \sqrt{\frac{2mE}{\hbar^2}}$$

The general solution of this equation is

$$\psi = A\sin\alpha x + B\cos\alpha x \quad (2)$$

Using Boundary Condition

$\psi = 0$ at $x=0 \Rightarrow 0 = A\sin 0 + B\cos 0$ or $B = 0$ (3)

$\psi = 0$ at $x=L \Rightarrow$ using both boundary condition

$$0 = A\sin\alpha L, \quad A \neq 0 \quad \text{—} (4)$$

$$\sin\alpha L = 0 \quad \text{or} \quad \sin\alpha L = \sin n\pi \quad \text{or} \quad \alpha = \frac{n\pi}{L} \quad (5)$$

So
wave function $\boxed{\psi_n(x) = A \sin \frac{n\pi x}{L}}$ — ⑥ where $n = 1, 2, 3 \ldots$

Energy level, since $\alpha = \frac{n\pi}{L} = \sqrt{\frac{2mE}{\hbar^2}}$ from eq ①

$$\frac{n^2\pi^2}{L^2} = \frac{2mE}{\hbar^2} \quad \text{or} \quad E = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2\pi^2 h^2}{4\pi^2 \cdot 2mL^2}$$

$$\boxed{E_n = \frac{n^2 h^2}{8mL^2}} \text{ — ⑦ [where } n = 1, 2, 3 \ldots] \quad [\because \hbar = \frac{h}{2\pi}]$$

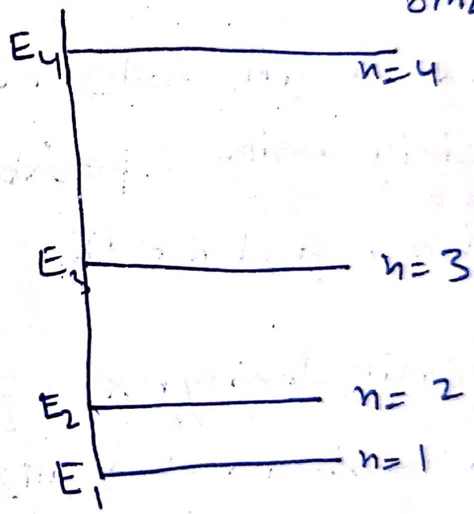
This eq gives the allowed value of energy or the eigen values for the particle.
Lowest allowed value of energy at $n=1$ is $E_1 = \frac{h^2}{8mL^2}$ — ⑧
from ⑦ and ⑧ $E_n = n^2 E_1$ — ⑨

So $E_2 = \frac{4h^2}{8mL^2} = 4E_1$

$E_3 = \frac{9h^2}{8mL^2} = 9E_1$

$E_4 = \frac{16h^2}{8mL^2} = 16E_1$

⋮



These are called excited energy level
→ Separation between nth and $(n+1)$th energy level

$$(n+1)^2 E_1 - n^2 E_1 = (2n+1)E_1 = (2n+1)\frac{h^2}{8mL^2} \quad ⑩$$

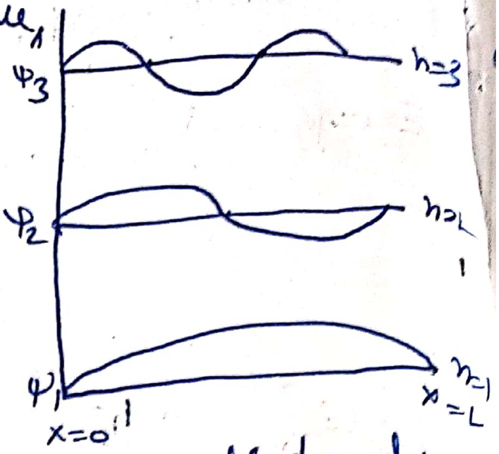
which indicate that energy level are not equally spaced but the separation between energy level increases with increase in value of n.

wave function or Eigen function →
The constant A in eq ⑥ can be found from the condition of normalisation. Since the probability of finding the particle

with in the region $0 < x < L$ is unity we have,

$$\int_0^L \psi_n(x)\,\psi_n^*(x)\,dx = 1 \quad \text{or,} \quad A^2\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx = 1$$

$$A^2\left|\frac{L}{2}\right| = 1 \quad \text{so } A = \sqrt{\frac{2}{L}}$$



Hence normalised wave function becomes

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \quad \text{—— (11)}$$

- The point where wave function has zero value is called nodes.
- Nodes for wave function ψ_1 – Two nodes, at $x=0$ and $x=L$
- " " " " ψ_2 – Three " at $x=0$, $x=\frac{L}{2}$ and $x=L$
- " " " " ψ_3 – Four " at $x=0$, $x=\frac{L}{3}$, $x=\frac{2L}{3}$ and $x=L$

So there are $(n+1)$ nodes in wave function ψ_n.

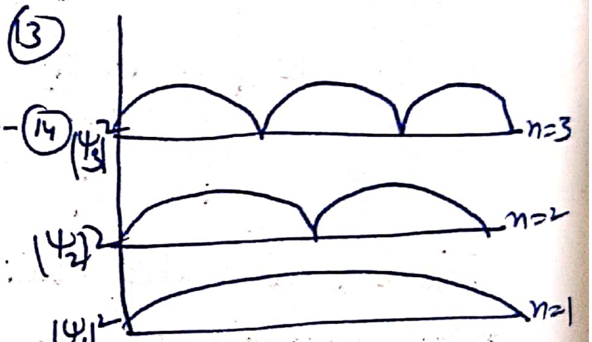
→ Probability density – Probability of finding the particle between the position x and $x+dx$,

$$P(x)\,dx = |\psi_n|^2 dx = \frac{2}{L}\sin^2\frac{n\pi x}{L}\,dx \quad \text{—— (12)}$$

Probability density, $P(x) = \frac{2}{L}\sin^2\frac{n\pi x}{L}$ -- (13)

It is maximum when $\frac{n\pi x}{L} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}$ ---- (14)

or $\quad x = \frac{L}{2n}, \frac{3L}{2n}, \frac{5L}{2n}$ --- (15)



for $n=1$ (Lowest energy state), $x=\frac{L}{2}$ i.e. the particle is most likely to be in the middle of the box (because $|\psi_1|^2$ is maximum there). For $n=2$ next energy state $x=\frac{L}{4}$ and $\frac{3L}{4}$, the particle is most likely to be at $\frac{L}{4}$ and $\frac{3L}{4}$ and never found in middle because $|\psi_2|^2$ is zero in middle for $n=3$, the most likely position of particle are, $x=\frac{L}{6}, \frac{3L}{6}, \frac{5L}{6}$ --