Different forms of Schrodinger wave equation

i) Laplacian Operator:

Let us take ψ as common from the terms of differentiation from given equation.

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E-P)\psi = 0$$

$$\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)\psi + \frac{8\pi^2 m}{h^2}(E-P)\psi = 0$$

$$\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} = \nabla^2$$

Now

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

∇^2 is laplacian operator and spoken as del square. It is a differential operator.

ii) <u>Hamiltonian operator</u> :

As we know that

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

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

$$\nabla^2 \psi - \frac{8\pi^2 m}{h^2} P\psi = -\frac{8\pi^2 m}{h^2} E\psi$$

Now multiply both sides with

$$-\frac{h^2}{8\pi^2 m}$$

$$-\frac{h^2}{8\pi^2 m} \times \nabla^2 \psi - \frac{8\pi^2 m}{h^2} P\psi \times -\frac{h^2}{8\pi^2 m} =$$

$$-\frac{8\pi^2 m}{h^2} E\psi \times -\frac{h^2}{8\pi^2 m}$$

$$-\frac{h^2}{8\pi^2 m} \times \nabla^2 \psi \cdot P\psi = E\psi$$

$$\left(-\frac{h^2}{8\pi^2 m} \times \nabla^2 + P\right)\psi = E\psi$$

$$H = \left(\frac{-h^2}{8\pi^2 m} \times \nabla^2 + P\right)\psi$$

$$H = \left(-\frac{h^2}{8\pi^2 m} \times \nabla^2 + P\right)$$

putting this equation in above equation

$$H\psi = E\psi$$

H is Hamiltonian operator.

$H\psi = E\psi$ is the simplest form of schordinger wave equation.

If we want to convert this equation in ~~the~~ a form, for calculating the energy of the molecules then,

multiply equation $E\psi = H\psi$ with ψ.

$$\psi E \psi = \psi H \psi$$

ψ on the left side of 'H' is multiplying with 'H' and ψ on R.H.S is being operated by H so both ψ should remain at their places.

$$E\psi^2 = \psi H \psi$$

$$E = \frac{\psi H \psi}{\psi^2}$$

integrate the numinator and denominator

$$E = \frac{\int \psi H \psi \, d\tau}{\int \psi^2 \, d\tau}$$

Physical Significance of ψ and ψ^2

→ ψ is the Symbol used for amplitude of the wave

$$\psi^2 \propto I$$

Square of the amplitude of the wave at any point is proportional to the intensity of the wave.

So,

greater the intensity of a wavefunction at particular point, greater the probability of locating the eletron at that point

→ ψ^2 can also be interpreted as proportional to <u>eletron</u> <u>density</u>.

Motion of Particle in One Dimensional box

This is one of the best application of schrodinger wave equation and is simplest way to apply the equation.

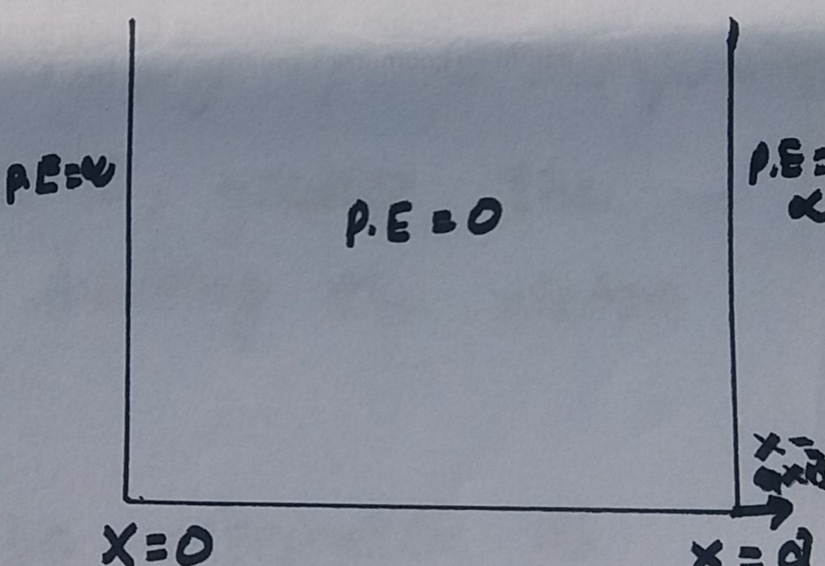
Consider a partide say an eletron of mass 'm' moving in a one dimensional box of width 'a' along x-axis as shown in diagram.

Boundaries of the box are

$x = 0$

and $x = a$

height of the walls at $x = 0$ and $x = a$ are infinite.



P.E inside the box are zero, so eletron can move without any restriction inside the box.

Anyhow P.E at walls and outside the box are infinity.

Particle is fully confined within the box and cannot escape.

Now, let us apply the schrodinger wave equation

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E-P)\psi = 0$$

Particle is moving in one dimension and P.E inside the box is zero so above equation become

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E)\psi = 0 \quad \text{—— i}$$

for a given state of system, the energy 'E' is constant which is one of postulates of quantum mechanics

So,

$$\frac{8\pi^2 m}{h^2}E = K^2 \quad \text{—— ii}$$

putting eq-ii in eq-i

$$\frac{d^2\psi}{dx^2} + K^2\psi = 0 \quad \text{--- iii}$$

This is the second order differential equation has the following solution.

$$\psi = A\sin(Kx) + B\cos(Kx) \quad \text{--- iv}$$

In order to determine the value of constant 'K' let's apply the boundary conditions in equation — iv

i) when $x = 0$ $\quad \psi = 0$

It means that selection of equation-iv as a solution of equ- iii is correct.

$$\psi = A\sin(Kx) + B\cos(Kx)$$

$$0 = A\sin(K\times 0) + B\cos(K\times 0)$$

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

$$0 = 0 + B\times 1$$

$$B = 0$$

Putting that condition $B = 0$ in equ — iv we get

$$\psi = A\sin(Kx) \quad \text{—— v}$$

ii) Second boundary condition

$x = a \qquad \psi = 0$

$$0 = A\sin(K\times a) + B\cos(K\times a)$$

putting $B = 0$ in above equation

$$0 = A \sin(k \times a) + 0 \cos(k \times a)$$

$$0 = A \sin(k \times a)$$

if two things are multiplying and the answer is zero it means one term is zero

and

$A \neq 0$ because when

$A = 0$ then $\psi = 0$

which is not possible

$$\Rightarrow \sin(k \times a) = 0 \quad \text{—— a}$$

we know that

$$\sin(n\pi) = 0 \quad \text{—— b}$$

by comparing 'a' and 'b'

$$Ka = n\pi$$

$$K = \frac{n\pi}{a}$$

Putting the value of 'K' in equation — v

$$\psi = A\sin(Kx)$$

$$\psi = A\sin\left(\frac{n\pi x}{a}\right)$$

n = quantum number

if $n = 0$ then $\psi = 0$ everywhere in the box which is not possible

So $n = 0$ not acceptable

and acceptable value for

$n = 1, 2, 3 \ldots$

we know that

$$K^2 = \frac{8\pi^2 m E}{h^2} \quad \text{——— C}$$

and $K = \frac{n\pi}{a}$

$$K^2 = \frac{n^2\pi^2}{a^2} \quad \text{——— D}$$

rearrange the equ – C and then putting the value of equ – D in equ – C

$$E = \frac{h^2 k^2}{8\pi^2 m}$$

$$E = \frac{h^2}{8\pi^2 m}\left(\frac{n^2\pi^2}{a^2}\right)$$

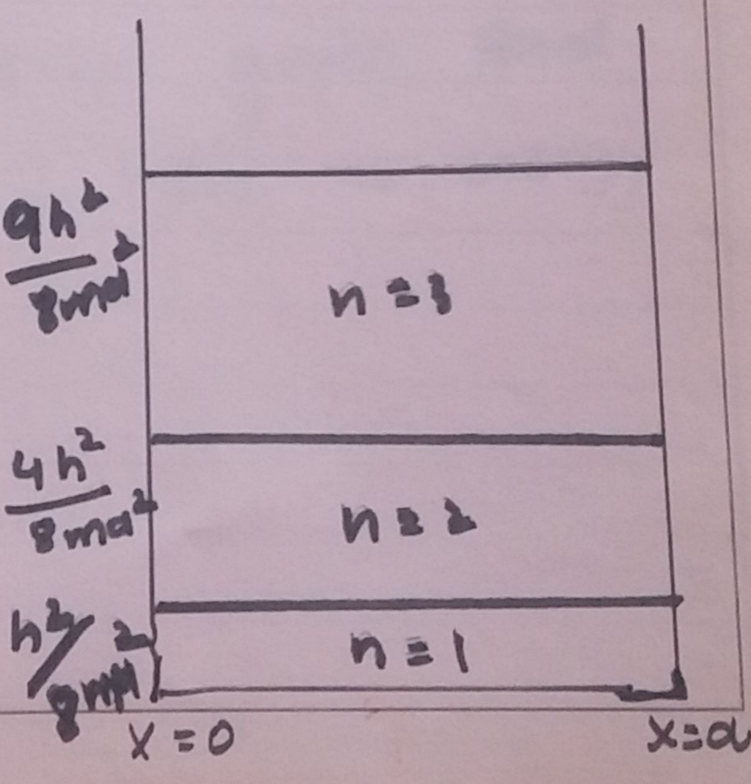
$$E = \frac{n^2 h^2}{8md^2} \quad \text{— vi}$$

eqn - vi gives the energies of the moving eletrons in one dimensional box.

$$E \propto \frac{1}{m}$$

$$E \propto \frac{1}{d}$$

'a is the width of the box'



Greater the mass of the particle moving in one dimensional box, smaller the energy associated with the particle and smaller the energy gap.

⇒ If proton is moving in a box it means that energy levels are 1836 times lower and gapes are smaller.

⇒ Greater the width of the box, smaller the energy gaps and macroscopic boxes have no energy levels.