# Schrödinger wave equation:-



Schrödinger time-independent with respect to space in cartesian co-ordinate is given by

$$\boxed{\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0} \dashrightarrow ①$$

Where, $\psi$ = wave-function of the system.
$m$ = mass of the particle
$h$ = planck's constant
$E$ = total energy
$V$ = potential energy

Equation ① can be expressed as

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

where $\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$ and is called Laplacian operator.

The above equation is time-independent and depends only on stationary state only.

Now, multiplying equation ② by $-\frac{h^2}{8\pi^2 m}$, we get

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

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

$$\Rightarrow \boxed{\hat{H}\psi=E\psi} \dashrightarrow ③$$

Where, $\hat{H}$ = Hamiltonian operator $=-\frac{h^2}{8\pi^2 m}\cdot\nabla^2+V$

Here, $\psi$ is an eigen function of hamiltonian operator and $E$ which is total energy represents the eigen value.

Now, $\hat{H}=-\frac{h^2}{8\pi^2 m}\cdot\nabla^2+V$

$$=\hat{KE}+\hat{PE}$$

Hence, Hamiltonian operator represents total energy of the system.

## Schrödinger time-dependent equation:-

$$\boxed{\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t} \quad \text{where } \hbar = h/2\pi}$$

## Interpretation of $\psi$ and $\psi^2$:-

$\psi$ is the amplitude function and depends on the co-ordinates of the system.

$\psi^2$ at any point is the probability of finding the particle at that point at a given time.

If $\psi$ represents the wave-function of a particle at some point $x$, the probability of finding the particle at point $x$ is $\psi^2$ or $\psi\psi^*$ ($\psi^*$ = complex conjugate of $\psi$). Then probability of finding the particle between $x$ and $x+dx$ is $\psi^2 dx$ or $\psi\psi^* dx$ where $dx$ = volume element. Thus, total probability of finding the particle is $\boxed{\int\psi^2 dx = 1}$ or $\boxed{\int\psi\psi^* dx = 1}$

The wave-function $\psi$ may be real or imaginary but probability is always real. Thus, the wave function $\psi$ or $\psi^*$ do not have any physical significance but $\psi\psi^*$ or $\psi^2$ has.

## Condition for $\psi$ to be acceptable or well-behaved function:-

(i) $\psi$ must be single valued.
(ii) $\psi$ must be finite
(iii) $\psi$ and its first derivative must be continuous
(iv) $\psi$ must be zero at infinity.
(v) $\int\psi^2 dx$ must be finite where $dx$ = volume element.

Only those functions which satisfy the above conditions are called eigen functions and the energy correspond to these eigen functions are called eigen values.

An acceptable solution of Schrödinger wave eqn exist only for discrete value of energy, i.e., eigen value. This implies that particle must possess only certain amount of energies. This is quantization of energy.

## Normalized and orthogonal wave function:-

Let us consider $\psi$ is an acceptable wave function so $N\psi$ is also acceptable solution.

Now, probability of finding the particle is

$$\int (N\psi)(N\psi^*)\,dx = 1$$

$$\Rightarrow N^2 \int \psi\psi^*\,dx = 1$$ Here $N$ = normalization constant.

If $\psi_1, \psi_2$ are two eigen function, then condition of normalization.

$$\boxed{\int \psi_1\psi_1^*\,dx = 1} ; \boxed{\int \psi_2\psi_2^*\,dx = 1}$$

If they are orthogonal, then $\int \psi_1\psi_2\,dx = 0$

$$\int \psi_1\psi_2^*\,dx = 0$$

$$\int \psi_1^*\psi_2\,dx = 0$$

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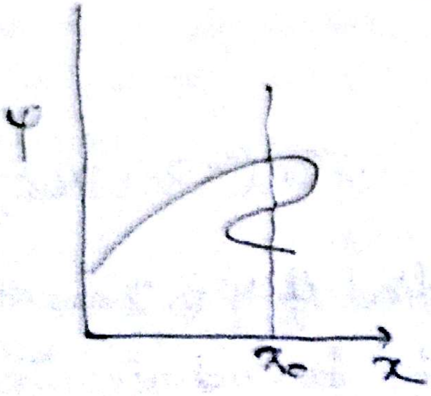
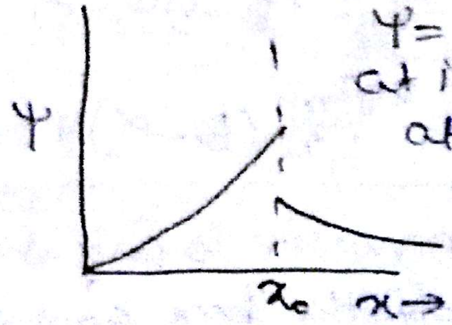
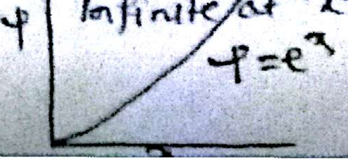



$\psi$ = not acceptable as it is multivalued at $x_0$

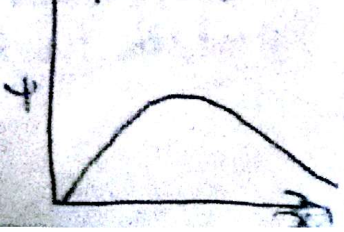



$\psi$ = not acceptable as it is discontinuous at $x_0$

$\psi$ = not acceptable as it is infinite at $x = \infty$

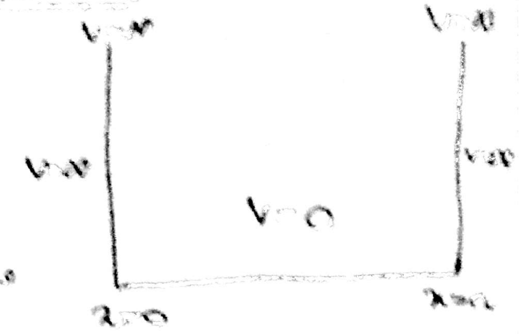



$\psi$ = acceptable



## Particle in a ~~two~~ one Dimensional box:

Let us consider a particle (say electron) of mass 'm' is subjected to move in a box in the x-direction from $x=0$ to $x=a$. Thus, the length of the box becomes a. The height of the ~~box~~ ~~walls~~ walls at $x=0$ and $x=a$ is infinite.




particle in a one dimensional rectangular box

Inside the box the potential energy (V) of the particle is considered to be zero, so that the particle can move freely within the box.

At $x \leq 0$ and $x \geq a$, the potential energy is considered to be infinity, so that particle is fully confined within the box and it cannot escape from the box by crossing the walls of infinite height.

Now, Schrödinger wave equation at the walls and outside the box ($x \geq a$ $x \leq 0$) is

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

$$\Rightarrow \boxed{\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-\infty)\psi = 0} \quad \text{---> (1)} \quad (x \geq a, x \leq 0)$$

The above equation is only satisfied if $\psi$ is zero at all points outside the box and at the boundaries. In other words, there is no existence of the particle

Inside the box, the schrödinger equation.

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

$$\Rightarrow \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-0)\psi = 0 \quad [V=0 \text{ inside the box}]$$

$$\Rightarrow \boxed{\frac{d^2\psi}{dx^2} + \frac{8\pi^2 mE}{h^2}\psi = 0} \dashrightarrow (2)$$

Let, the solution of the equation (2) is

$$\psi = A\sin bx + B\cos bx \dashrightarrow (3)$$

where, A, B and b are arbitary Constants.

Now, $\frac{d\psi}{dx} = b.A\cos bx - bB\sin bx$

$$\Rightarrow \frac{d^2\psi}{dx^2} = -b^2[A\sin bx + B\cos bx]$$

$$= -b^2\psi$$

$$\Rightarrow \boxed{\frac{d^2\psi}{dx^2} + b^2\psi = 0} \dashrightarrow (4)$$

Comparing equation (2) and (4), we get,

$$\boxed{b^2 = \frac{8\pi^2 mE}{h^2}} \dashrightarrow (5)$$

Now, boundary condition applied to find out the Constants.

<u>Case-I</u> :- at $x=0$, $\psi=0$

Hence, eq$^n$ (3) becomes

$$0 = A\sin(b\cdot 0) + B\cos(b\cdot 0)$$

$$\Rightarrow \boxed{B=0}$$

Hence, equation (3) becomes $\boxed{\psi = A\sin bx} \dashrightarrow (6)$

~~Now~~ <u>Case-II</u> :- at $x=a$, $\psi=0$.

Therefore, $0 = A\sin(ba)$.

Now, $A \neq 0$. If $A=0$, then $\psi=0$ for any value of $x$, which means particle does not exist within the box.

Hence, $\sin(ba) = 0 = \sin(n\pi)$ where $n = 0, 1, 2, 3, \ldots$

$$\Rightarrow ba = n\pi$$

$$\Rightarrow \boxed{b = \frac{n\pi}{a}}$$

Hence, the Schrödinger wave-equation

$$\boxed{\psi_n = A \cdot \sin\left(\frac{n\pi x}{a}\right)} \dashrightarrow (7)$$

Here, $n = 0$ is not permitted. If $n = 0$, the $\psi$ becomes zero everywhere within the box. Hence $n = 0$ is not acceptable.

Now, substituting value of $b = \frac{n\pi}{a}$ in equation (5), we get

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

$$\Rightarrow \boxed{E_n = \frac{n^2h^2}{8ma^2}} \dashrightarrow (8)$$

This is the energy expression for a particle in a 1D box of length. $n$ is called the quantum no.

Now, to find out. A, we use the condition (normalization condition).

$$\int_0^a \psi^2 dx = 1$$

$$\Rightarrow \int_0^a \left(A \sin\frac{n\pi x}{a}\right)^2 dx = 1$$

$$\Rightarrow A^2 \cdot \int_0^a \sin^2 \frac{n\pi x}{a} \, dx = 1$$

$$\Rightarrow A^2 \cdot \frac{a}{2} = 1$$

$$\Rightarrow \boxed{A = \sqrt{2/a}}$$

Hence, the Complete wave-function for particle in 1D box is (7)

$$\boxed{\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}} \quad \boxed{E_n = \frac{n^2h^2}{8ma^2}}$$

Zero-point Energy:- In particle in a 1D box, the potential energy is considered zero. Thus, minimum energy is purely a Kinetic energy of the particle within the box which is obtained for $n=1$.

$$\boxed{E_1 = E_{zero-point} = \frac{h^2}{8ma^2}}$$

The existence of zero-point energy which is non-zero indicates that even at 0K, the particle is not at rest. Hence, the position of the particle cannot be precisely determined. Thus, the momentum of the particle cannot also be determined precisely. Therefore, the existence of zero-point energy is in conformity with the Heisenberg's ~~unct~~ uncertainty principle.

## Characteristic features of $\psi_n$, $\psi_n^2$, $E_n$ for particle in 1D box:-

(a) $E = \frac{n^2h^2}{8ma^2} = \frac{1}{2}mu^2$ [since $V=0$]

$$= \frac{p^2}{2m}$$

$$\therefore \frac{n^2h^2}{8ma^2} = \frac{h^2}{\lambda^2}\frac{1}{2m} \quad \left[\lambda = \frac{h}{p}\right]$$

$$\Rightarrow \boxed{a = \frac{n\lambda}{2}}$$

Hence length of the box must be an integral multiple of half-wavelength.

(ii) Verification of uncertainty principle:-

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

$$\therefore \frac{n^2h^2}{8ma^2} = \frac{p^2}{2m}$$

$$\Rightarrow p = \frac{nh}{2a}$$

$$\therefore \Delta p = p_{(n+1)} - p_n$$

$$= (n+1)\cdot\frac{h}{2a} - \frac{nh}{2a}$$

$$= \frac{h}{2a}$$

Let, $\boxed{\Delta x = a}$

$$\therefore \boxed{\Delta p \cdot \Delta x = \frac{h}{2a}\cdot a = \frac{h}{2}}$$

(iii) Internal nodal points:- At which wave function is zero i.e, no particle exists at the nodal points.

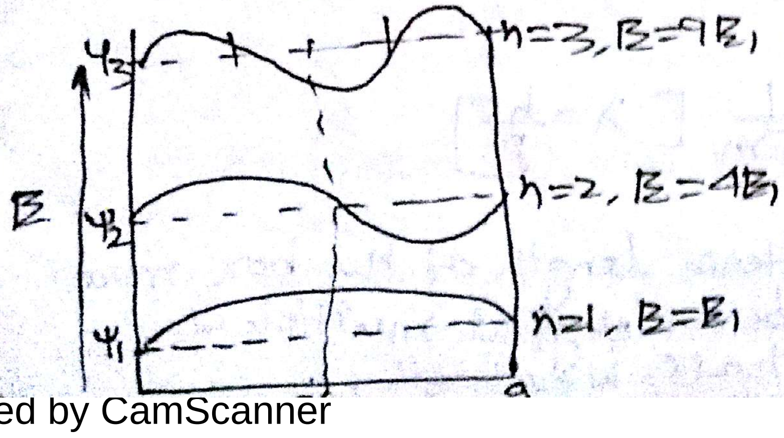
For a particular value of $n$, there are $(n-1)$ internal nodal points.

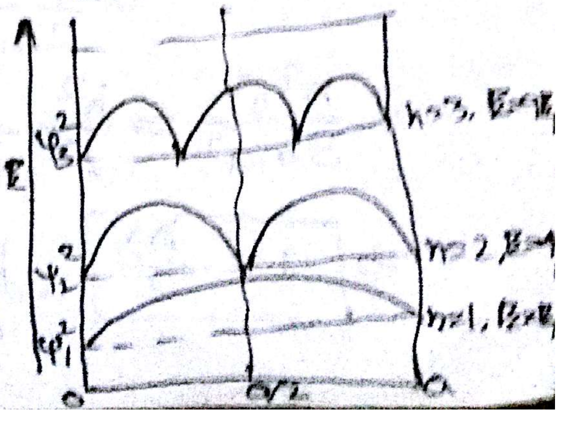
For $n=1$, no. of nodal point $= 0$

$n=2$, " " " " $= 1$ at $x = a/2$

$n=3$ " " " " $= 2$ at $x = a/3, 2a/3$

$n=4$ " " " " $= 3$.



* Energy difference between two successive energy level is given by

$$\Delta E = E_{n+1} - E_n = \frac{(n+1)^2 h^2}{8ma^2} - \frac{n^2 h^2}{8ma^2}$$

$$= \frac{(2n+1).\, h^2}{8ma^2}$$

Hence, $\Delta E$ decreases as the ~~energy~~ length of the box increases. $\Delta E$ also decreases as the mass of the particle increases. $\Delta E$ increases with the increase in the value of $n$.

⊛ With the increase of $n$, the no. of nodes increases, also the energy of the system increases.