Unit V – Wave Mechanics

Q.1 Write **three forms** of **Heisenberg's Uncertainty principle** and **give** any **two examples** of its application.

It is ***impossible to measure precisely*** *and* ***simultaneously*** *both the* ***pair of*** *certain* ***canonical conjugate variables*** *that describe the behavior of an atomic system.*

The product can never be smaller than the number of the order of ħ/2 (ħ = h/2π), ***h (Planck's constant)=*** *6.6 X 10^{-34} J-sec*

1. ΔP. ΔX ≥ ħ/2 or change in **momentum x Displacement** ≥ ħ/2
2. ΔE. Δt ≥ ħ/2 or change in **Energy x** change in **time** ≥ ħ/2
3. ΔJ. Δϕ ≥ ħ/2 or change in **Angular momentum x** Change in **Angle** ≥ ħ/2

Applications: *1. Non existence of electron in nucleus (or electron cannot be found in nucleus)*

2. *Finite width of spectral lines.*

3. *The radius of Bohr's first Orbit.*

4. The binding energy of an electron in an atom

5. Zero point energy of a Harmonic Oscillator.

Q.2 Derive the Schrödinger's Time independent (TI) and Time dependent (TD) wave equations.

Schrödinger wave equations [(Time independent-**TI** and Time dependent-**TD**) enable us to establish the De-Broglie wave function (ψ) of a wave associated with a moving particle.

(Time independent-TI)

The general differential equation of motion is given by $\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=\frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2}$ where ψ is function of x, y, z and t. v is velocity of the particle in medium.

$$or\ \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi=\frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2}$$

$$\text{since } \nabla(\text{Del Operator})=\left(i\frac{\partial}{\partial x}+j\frac{\partial}{\partial y}+k\frac{\partial}{\partial z}\right)$$

$$therefore\ \nabla^2(\text{Laplacian Operator})=\nabla.\nabla=\left(i\frac{\partial}{\partial x}+j\frac{\partial}{\partial y}+k\frac{\partial}{\partial z}\right).\left(i\frac{\partial}{\partial x}+j\frac{\partial}{\partial y}+k\frac{\partial}{\partial z}\right)\Rightarrow\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$$

$$or\ \nabla^2\psi=\frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2}\quad \dots\dots[1]$$

Let the solution of above differential equation be $\psi=\psi_0 e^{-i\omega t}$

Double differentiating it *w.r.t.* t

$$\frac{\partial\psi}{\partial t}=-i\omega\,\psi_0 e^{-i\omega t}$$

$$\frac{\partial\psi}{\partial t^2}=i^2\omega^2\psi$$

$$\frac{\partial \boldsymbol{\psi}}{\partial \boldsymbol{t}^2} = -\boldsymbol{\omega}^2\boldsymbol{\psi} \qquad \ldots \ldots [2]$$

Substituting [2] into [1] gives us

$$\nabla^2\psi = -\frac{\omega^2}{v^2}\,\psi$$

$$\nabla^2\psi + \frac{\omega^2}{v^2}\,\psi = 0$$

$$\boxed{\begin{array}{l} \omega = 2\pi\mathbf{v} \; where \; \mathbf{v} \; is \; frequency \; of \; wave \\ v = \mathbf{v}\lambda \; where \;\; v \; is \; velocity \; if \; wave \end{array}}$$

$$\nabla^2\psi + \frac{4\pi^2\mathbf{v}^2}{v^2}\,\psi \;= 0$$

$$\nabla^2\psi + \frac{4\pi^2\cancel{\mathbf{v}^2}}{\cancel{\mathbf{v}^2}\lambda^2}\,\psi \;= 0 \quad \ldots \ldots [3]$$

According to **De-Broglie hypothesis,** a wave is associated of wavelength λ with any moving particle. The relation is λ =h/p (where h = Planck's constant (6.6X10^{-34} joule-sec) and p = momentum of moving particle with velocity v (p = mv). If we introduce **λ = h/p** into [3] then wave function equation ψ become the **wave function(** $\boldsymbol{\psi}$) **of a De-Broglie wave** associated with moving particle.

$$\nabla^2\psi + \frac{4\pi^2 p^2}{h^2}\,\psi \;= 0 \qquad\qquad [momentum\;(p) = mv]$$

$$\nabla^2\psi + \frac{4\pi^2 m^2 v^2}{h^2}\,\psi \;= 0 \qquad\qquad [since\;\hbar = \frac{h}{2\pi}\; therfore\; \hbar^2 = \frac{h^2}{4\pi^2}]$$

$$\nabla^2\psi + \frac{m^2v^2}{\left(\frac{h^2}{4\pi^2}\right)}\,\psi \;= 0 \Longrightarrow \boldsymbol{\nabla^2\psi + \frac{m^2v^2}{\hbar^2}\,\psi \;= 0} \quad \ldots \ldots [4]$$

Since total energy of particle is $\boldsymbol{E = \frac{1}{2}mv^2 + V}$

$$or\;\frac{1}{2}mv^2 = 2(E - V)$$

$$mv^2 = 2(E - V)$$

$$\boldsymbol{m^2v^2 = 2m(E - V)} \ldots \ldots [5]$$

Substituting equation [5] into [4] we get

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

This equation is known as Schrödinger's time-independent (TI) equation because the time derivative ($\frac{\partial\psi}{\partial t^2}$) in equation [1] was eliminated by substituting its value from equation [2].

(Time-dependent-TD):

To find the time dependent-equation (TD) from time-independent (TI) [i.e. $\boldsymbol{\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\,\psi \;= 0}$, we substitute the value of Eψ again into time independent-equation. The value Eψ is obtained from first time derivative of solution of ψ (i.e. $\psi = \psi_0 e^{-i\omega t}$).

Differentiating it *w.r.t.* t

$$\frac{\partial\psi}{\partial t} = -i\omega\, \psi_0 e^{-i\omega t} \qquad \begin{bmatrix} since\ \omega = 2\pi\nu\ and\ E = h\nu \\ therfore\ \omega = 2\pi\frac{E}{h} \end{bmatrix}$$

$$\frac{\partial\psi}{\partial t} = -\frac{i^2}{i}\frac{2\pi E}{h}\psi$$

$$\frac{\partial\psi}{\partial t} = -\frac{}{i}\frac{E}{\left(\frac{h}{2\pi}\right)}\psi$$

$$\frac{\partial\psi}{\partial t} = \frac{E}{i}\frac{\boldsymbol{\psi}}{\hbar} \quad \left[since\ \hbar = \frac{h}{2\pi}\right]$$

$$\boldsymbol{E\psi = i\hbar\frac{\partial\psi}{\partial t}} \qquad \dots\dots[\mathbf{1}]$$

Here **E** equivalent to $\boldsymbol{i\hbar\frac{\partial}{\partial t}}$**.** Therefore, $\boldsymbol{i\hbar\frac{\partial}{\partial t}}$ is known as energy operator.

The same value of Eψ can also be found out from Schrödinger’s time-independent (TI) equation as

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

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

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

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

$$E\psi = \left(-\nabla^2\frac{\hbar^2}{2m} + V\right)\psi \quad \dots\dots[2]$$

Here the quantity $\left(-\nabla^2\frac{\hbar^2}{2m} + V\right)$is known as **Hamiltonian operator (H).** It can be total energy operator for conservative force field and for non-conservative force field it is not the total energy operator.

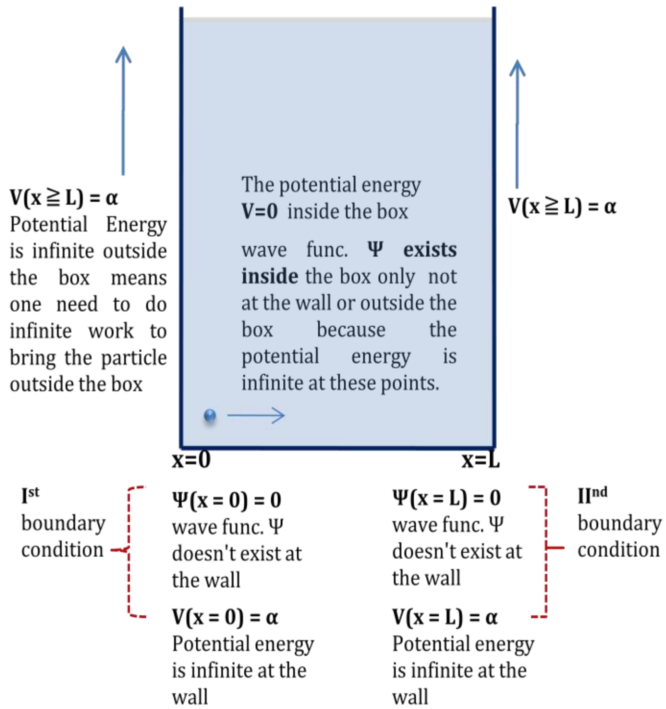
The equation [1] and [2] can be written as $E\psi = i\hbar\frac{\partial\psi}{\partial t} = \left(-\nabla^2\frac{\hbar^2}{2m} + V\right)\psi$ or

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

This equation is known as Schrödinger’s time-dependent (TD) equation.

Q.3 Establish the wave function ψ of a particle confined in 1-D (one dimensional) box of infinite potential barrier height.

Q. Discuss the Application of Schrödinger wave equation or Establish the wave function ψ of a **Particle confined in 1-D (one dimensional) box of infinite potential barrier height.**



Since the TI Schrodinger equation:

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

The wave function (ψ) exist only inside the box where V=0. Therefore the above expression reduces to

$$\nabla^2\psi + \frac{2m}{\hbar^2}E\psi \; = 0 \qquad \dots \dots [1]$$

$$Let\,\frac{2mE}{\hbar^2} \; = k^2 \qquad \dots \dots [2]$$

$$\nabla^2\psi + k^2\psi \; = 0$$

Let the solution of above differential equation be

$$\psi_n = \boldsymbol{A}\sin kx + \boldsymbol{B}\cos kx \qquad \dots \dots [3]$$ Here values of A and B is to be determined.

To find the values of constants, we apply I[st] **boundary condition** (i.e. ψ(x=0) = 0 means ψ doesn't exist at x=0 or at the wall)

$$0 = \boldsymbol{A}\sin k.0 + \boldsymbol{B}\cos k.0$$
$$\boldsymbol{or\;B} = 0$$

Substituting it in eq. [3] we get

$\psi_n = \boldsymbol{A} \sin kx \;\ldots\ldots [4]$

Now, to find the value of constant A, we apply **IInd boundary condition** (i.e. ψ(x=L) = 0 means ψ… … [4] doesn't exist at x=L or at the wall). Subs. x=L and ψ =0 in eq. [4],

$0 = \boldsymbol{A} \sin kL$, we find that A≠0 then Sin kL =0

$\sin kL = 0$

$kL = \pm n\pi$

$$k = \frac{n\pi}{L} \qquad or\ k^2 = \frac{n^2\pi^2}{L^2} \;\ldots\ldots [5]$$

Since eq. [2] = [5] therefore, $k^2 = \frac{n^2\pi^2}{L^2} = \frac{2mE}{\hbar^2}$

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} \to \frac{n^2\pi^2h^2}{4.\pi^2.2mL^2} \to \frac{n^2\cancel{\pi^2}h^2}{4.\cancel{\pi^2}.2mL^2} \to \frac{n^2h^2}{8mL^2}$$

$$\boldsymbol{E = \frac{n^2h^2}{8mL^2}}$$

Since ***n*** is an integer or a variable value in above expression and other parameter are constants therefore, we infer that energy of a particle in 1D box is quantized or has fixed values.

$$E_n = \frac{n^2h^2}{8mL^2} \to E_1 = \frac{1^2h^2}{8mL^2} = \frac{h^2}{8mL^2} \to \boldsymbol{E_1}$$

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

$$\boldsymbol{E_3} = \frac{3^2h^2}{8mL^2} \to \boldsymbol{9E_1}$$

As we found above that on applying the IInd boundary condition we won't be able to determine the value of constant A, therefore we use a mathematical tool called **normalization condition**.

$\int_{-\infty}^{+\infty} \psi_n.\psi_n{}^* \, dx = 1, here\ \psi_n{}^*\ is\ complex\ conjugate\ of\ function\ \psi_n$. Therefore, $\int_{-\infty}^{+\infty} |\psi_n|^2 \, dx = 1$

It is to mention that $|\psi_n|^2$ represents the probability density of finding the particle in length L.

Since $\psi_n = \boldsymbol{A} \sin kx$ eq. [4] therefore,

$$\int_{-\infty}^{+\infty} |\psi_n|^2 \, dx = \int_0^L |\psi_n|^2 \, dx = A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx \ = 1$$

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

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

$$\frac{A^2}{2}L = 1 \ \ or\ \boldsymbol{A} = \sqrt{\frac{2}{L}} = \boldsymbol{1}$$

$$\boldsymbol{\psi_n = \sqrt{\frac{2}{L}} \sin kx}$$

This is the required wave function of particle confined in 1D box of infinite potential barrier height.

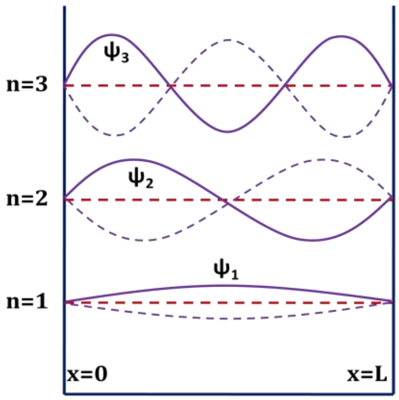


Fig1 represents the waveforms at n=1,n=2 and n=3

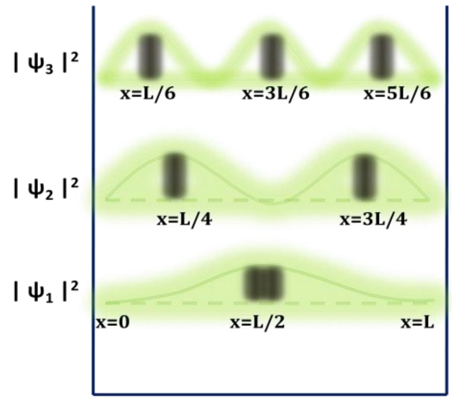
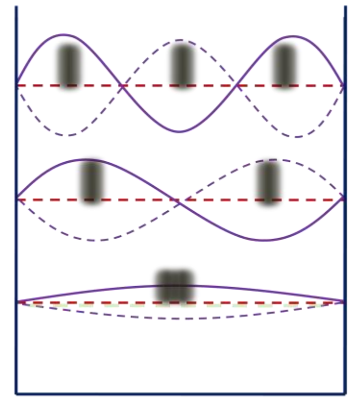


Fig2 Black shaded portion represents the probability density of finding the particle in length L



combined figure showing waveform and position of finding the particle (black shaded portion)

Try numerical **on Energy** $E_n = \frac{n^2h^2}{8mL^2}$ **and wave function the particle confined in 1D box** $\psi_n = \sqrt{\frac{L}{2}}\sin kx.$