2 Quantum Mechanics

SYLLABUS

Quantum Mechanics - Schrodinger's equation (Time dependent and time independent equations), Physical significance of wave function Ψ, Operators, Expectation values of a dynamical quantities, Ehrenfest's theorem, Eigen value and Eigen functions, Particle in a box, Application to free particle in a one and three dimension.

SCHRÖDINGER'S EQUATION

Q. 1. Derive Schrodinger's time dependent equation for matter waves.

Ans: **Schrodinger's time dependent wave equation:**

A plane wave moving in the positive-x direction is represented in the exponential form as

$$y = A.e^{-i(\omega t - kx)} \qquad \text{.........(1)}$$

Where, $\omega = 2\pi\nu$ (ν is frequency of the wave)

$k = 2\pi / \lambda$ (λ is wavelength of the wave)

Let E be the total energy and p be the momentum of the particle.

$$\therefore \; E = h\nu = \frac{h}{2\pi} \times 2\pi\nu = \hbar\omega \Rightarrow \omega = \frac{E}{\hbar} \text{ and}$$

$$p = \frac{h}{\lambda} = \frac{h}{2\pi} \times \frac{2\pi}{\lambda} = \hbar k \Rightarrow k = \frac{p}{\hbar}$$

Therefore equation (1) becomes

$$y = A.e^{-i\left(\frac{E}{\hbar}t - \frac{p}{\hbar}x\right)}$$

$$= A.e^{-\frac{i}{\hbar}(Et - px)} \qquad \text{.........(2)}$$

In quantum mechanics the wave function ψ denotes the amplitude of matter wave corresponds to the wave variable y of plane wave. For this reason we assume that the wave function ø for a particle moving freely in the +ve X- direction is specified by

$$\psi = A.e^{-\frac{i}{\hbar}(E.t-p.x)} \qquad \text{..........(3)}$$

Equation (3) represents matter wave for a free particle of total energy E and momentum p.

Differentiating equation (3) twice with respect to x, we get

$$\frac{\partial\psi}{\partial x} = A\left(-\frac{i}{\hbar}\right)(-p).\left[e^{-\frac{i}{\hbar}(E.t-px)}\right] = \frac{i}{\hbar}.p\psi$$

$$\therefore \quad \frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial x}\frac{\partial\psi}{\partial x} = \frac{\partial}{\partial x}\left(\frac{ip\psi}{\hbar}\right) = \frac{i^2p^2}{\hbar^2}\psi = -\frac{p^2}{\hbar^2}\psi$$

Therefore $p^2\psi = -\hbar^2\frac{\partial^2\psi}{\partial x^2}$ ....(4)

Differentiating equation (3) with respect to t, we get

$$\frac{\partial\psi}{\partial t} = A\left(-\frac{i}{\hbar}\right)E.\left[e^{-\frac{i}{\hbar}(E.t-px)}\right] = \frac{i}{\hbar}.E\psi$$

Therefore $E\psi = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t}$ ....(5)

For a particle of mass m, moving with a velocity v piloted by the wave function ø, the total energy in a non-relativistic case is given by

$$E = K.E. + P.E.$$

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

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

Multiplying both the sides by Ψ, we get

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

i.e. $$\left(\frac{p^2}{2m}\right)\psi + V\psi = E\psi \qquad \text{..........(6)}$$

Substituting the values of $p^2\psi$ from (4) and $E\psi$ from (5), we have

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}\right) + V\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad \text{..........(7)}$$

This is Schrodinger's one dimensional time dependent equation for matter waves.

In three dimensions, ø is a function of x, y, z & t. Therefore, for three dimensions it converts to following equation.

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right] + V\psi = i\hbar\frac{\partial\psi}{\partial t}$$

or $$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad \text{..........(8)}$$

This is Schrodinger's three dimensional time dependent equation for matter waves.

Note: For free particle potential energy, V = 0.

Q. 2. Derive Schrodinger's time independent equation.

or

Obtain Schrodinger's time independent equation for a non-relativistic free particle.

Ans: **Schrodinger's time independent wave equation:**

When the potential energy V of a particle does not depends explicitly on time and P.E. vary with the position of the particle only. *In such situations, the wave function* $\psi(x,t)$ *can be written as the product of two separate functions* $\psi(x)$ *a function only of x and f(t) a function only of t.*

$$\therefore \quad \psi(x,t) = \psi(x).f(t)$$

Hence the one dimensional wave function ø of an unrestricted particle may be written in the form –

$$\psi = A.e^{-\frac{i}{\hbar}(E.t-p.x)}$$

$$= A.e^{\frac{i}{\hbar}p.x}.e^{-\frac{i}{\hbar}E.t}$$

$$\therefore \quad \psi = \psi_0 . e^{-\frac{i}{\hbar}E.t} \qquad \text{..........(1)}$$

Here, $\psi_0 = A.e^{\frac{i}{\hbar}p.x}$. That is, ø is the product of position dependent function ψ_0 and a time dependent function ψ_0 and a time dependent function $.e^{-.\frac{i}{\hbar}.E.t}$,

Differentiating equation (1) twice with respect to x, we get

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial^2\psi_0}{\partial x^2}.e^{-.\frac{i}{\hbar}.E.t} \qquad \text{..........(2)}$$

Differentiating equation (2) with respect to t, we get

$$\frac{\partial\psi}{\partial t} = -.\frac{i}{\hbar}E.\psi_0.e^{-.\frac{i}{\hbar}.E.t} \qquad \text{..........(3)}$$

Schrodinger's one dimensional time dependent equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}\right) + V\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad \text{..........(4)}$$

put $\left(\frac{\partial^2\psi}{\partial x^2}\right)$ from equation (2) and $\frac{\partial\psi}{\partial t}$ from equation (3), we get

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi_0}{\partial x^2}.e^{-.\frac{i}{\hbar}E.t}\right) + V\psi_0.e^{-.\frac{i}{\hbar}E.t} = i\hbar\left[-.\frac{i}{\hbar}E.\psi_0.e^{-.\frac{i}{\hbar}E.t}\right]$$

Dividing both the sides by common exponential factor, we get

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi_0}{\partial x^2}\right) + V\psi_0 = E\psi_0$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi_0}{\partial x^2}\right) + (E - V)\psi_0 = 0$$

or $\left(\frac{\partial^2\psi_0}{\partial x^2}\right) + \frac{2m}{\hbar^2}(E - V)\psi_0 = 0$

Further, ψ_0 is a function of x only, hence usually it is written in the form

$$\left(\frac{\partial^2\psi}{\partial x^2}\right)+\frac{2m}{\hbar^2}(E-V)\psi=0 \qquad \text{..........(5)}$$

Equation (5) is the time independent (steady-state) Schrodinger's equation in one dimension.

Three dimensional time independent equation-

For motion of particle in three dimensions, ø is a function of x,y,z. In such a case *the time independent form of Schrodinger's equation is given by*

$$\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+\frac{2m}{\hbar^2}(E-V)\psi=0 \text{ or}$$

$$\nabla^2\psi+\frac{2m}{\hbar^2}(E-V)\psi=0 \qquad \text{..........(6)}$$

Equation (6) is the time independent (steady-state) Schrodinger's equation in three dimensions.

Q. 3. Why the Schrodinger's equations do not valid for relativistic particles?

Ans: Schrodinger's equations are not valid for relativistic particles because in deriving these equations we use classical (non-relativistic) expression for total energy $E = (p^2/2m) + V$. We also take the momentum of the particle as non-relativistic and equal to mv. The K.E. is taken as $½.mv^2$, which is also a non-relativistic expression.

PHYSICAL SIGNIFICANCE OF ψ

Q. 4. What is wave function ψ? Give the physical significance of wave function ψ and $|\Psi|^2$.

Ans: **Wave function ψ :** The wave function ø is a function of space variable (x, y, z) and time t and it can give nearly complete information about the state of a physical system at a particular time in accordance with the rules of quantum mechanics.

Physical significance of wave function ψ and $|\Psi|^2$:

The wave function ø has no physical existence because it can be complex. Also it cannot be taken as the probability at (r, t) because the probability is real and nonnegative. However the value of wave function ψ associated with a moving particle at a particular point x, y, z in space at the time t is related to the likelihood of finding the particle there at that time.

The product of wave function ø and its complex conjugate Ψ^* is interpreted as the position probability density P(r,t).

$$P(r,t) = \psi^*(r,t).\psi(r,t) = |\psi(r,t)|^2 \quad ....(1)$$

According to this view $\Psi^*\Psi = |\psi|^2$ represents probability density of the particle in the state Ψ.

The probability of finding the particle in a volume element dV = dx.dy.dz surrounding the point r(x, y, z) at time t is expressed as

$$P(r,t).dV = \psi^*(r,t).\psi(r,t).dV = |\psi(r,t)|^2 .dV$$

It is large in magnitude where the particle is likely to be located and small elsewhere. When $|\psi(r,\ t)|^2\ dV$ *is integrated over the entire space one should get the total probability, which is unity.*

Therefore,

$$\text{Total probability} = \int_{-\infty}^{+\infty} |\psi(r,t)|^2\ dV = 1 \ \text{(i.e. 100\% presence)} \quad ....(2)$$

Any wave function satisfying the above equation is said to be normalized.

Note: *The process of integration over all possible locations to give unity is called normalization.*

Q. 5. What are the conditions for the wave function to be well behaved?

Ans: The wave function ø must satisfy the following conditions.

i) ψ must be *finite* for all values of x, y, z.

ii) ψ must be *single valued* i.e. for each set of values of x, y and z, ψ must have one value only.

iii) ψ must be *continuous* in all regions except in those regions where the P.E.V(x, y, z) = ∞

iv) The partial derivatives of Ψ, i.e. $\frac{\partial\psi}{\partial x}, \frac{\partial\psi}{\partial y}, \frac{\partial\psi}{\partial z}$ must also be continuous. *The wave function* ψ *satisfying all the above conditions is called well behaved wave function.*

Q. 6. What is normalization of a wave function? Prove that normalization is independent of time.

Ans: **Normalisation** : If we consider a small element of volume dv defined by the coordinates (x, x + dx); (y, y + dy); and (z, z + dz) then, the probability of finding the particle existing within this element of volume dv is given by

$$P(dv) = \psi^* \psi.dv = \psi^* \psi.dx.dy.dz$$

The probability of finding the particle in a finite volume v is given by

$$P(dv) = \iiint_v \psi^* \psi.dx.dy.dz$$

The particle must always be somewhere in space so that extending the integral over all space, the probability becomes a certainty i.e. it equals *unity*.

$$\therefore \quad P(dv) = \iiint_{\text{All spae}} \psi^* \psi.dx.dy.dz = 1$$

The process of integration over all possible locations to give unity is called rmalization.

As ψ and ψ^* are functions of x only and are independent of time, the probability of locating a system in the region $-\infty$ to $+\infty$ continues to be one for all times i.e. normalization is preserved in time or is independent of time.

Q. 7. Normalise the one dimensional wave function given by

$$\boldsymbol{\psi(x) = A \sin\left(\frac{n_x \pi}{L}\right).x \quad 0 < x < L}$$

$$\boldsymbol{\psi = 0, \text{ outside}}$$

Ans: The wave function is said to be normalized if it satisfies the condition

$$\int_{-\infty}^{+\infty} \psi * \psi.dx = 1$$

The given wave function ψ exists in the region 0 < x < L

$$\therefore \quad \int_0^L A^2 \sin^2\left(\frac{n_x \pi}{L}\right).x.dx = 1$$

But $\cos 2\theta = 1 - 2\sin^2\theta$. Therefore $\sin^2\theta = (1 - \cos 2\theta)/2$

$$\therefore \quad A^2\int_0^L\left(\frac{1-\cos 2n_x\pi x/L}{2}\right).x.dx = 1 \Rightarrow A^2\frac{L}{2} = 1.\text{gives}.A = \sqrt{\frac{2}{L}}$$

Hence, the normalized wave functions of the particle are given by

$$\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n_x\pi}{L}\right).x \quad \text{......}\textbf{(Ans)}$$

OPERATORS

Q. 8. What are the postulates of quantum mechanics?

Ans: The mathematical formulation of quantum mechanics is based on linear operators.

Postulates of quantum mechanics:

i) *There is a state vector (or wave function) associated with every physical state of the system which contains the entire description.* i.e. the information of a system is contained in the wave function ø of the system.

ii) *For every physical observable (dynamical variable) there is corresponding linear Hermitian operator.*

The most important operators of wave mechanics are

Variable	Symbol	Quantum mechanical operator
Position	x, y, z	Multiplication by x / y / z resp.
Linear momentum	Px, Py, Pz	$\hat{P}_x = \frac{\hbar}{i}.\frac{\partial}{\partial x};\ \hat{P}_y = \frac{\hbar}{i}.\frac{\partial}{\partial y};\ \hat{P}_z = \frac{\hbar}{i}.\frac{\partial}{\partial z}$
Potential energy	V	Multiplication by V
Energy	E	$\hat{E} = i\hbar.\frac{\partial}{\partial t}$
Hamiltonian	H	$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$

iii) *The only possible values that can be obtained from the measurement of the observable of a system* (*whose operator is* $\hat{A}$) *are the eigen values* A_n *of the equation.* Thus

$$\hat{A}\psi_n = A_n.\psi_n$$

iv) *The expectation value of a variable x of a system in the state ø is given by* $<x> = \dfrac{\int \psi^* \hat{x} \psi . d\vec{r}}{\int \psi^* \psi . d\vec{r}}$ ....(1)

These are the postulates of the quantum mechanics.

Q. 9. Explain the observable and operator.

Ans: **Observable:** *A quantity obtained by the process of observation or measurement on a physical system is called an observable.* An observable is the result of actual measurement.

Operator: *An operator is a mathematical rule or prescription.* Mathematical operations in algebra and calculus like addition, subtraction, multiplication, division, finding square root, differentiation or integration are represented by characteristic symbols like $+, -, \times, \div, \sqrt{\ }, \dfrac{\partial}{\partial x}, \dfrac{d}{dt} .\text{and}. \int f.dx$ can be considered as operators.

***Ex.*:** If A is an operator represented as $\hat{A}$ and stands for the operation $\dfrac{\partial}{\partial x}$, then

$$\hat{A}x^4 = \frac{\partial}{\partial x}\left(x^4\right) = 4x^3$$

Q. 10. What is a linear operator? Show that the following operators are linear.

1) $\dfrac{\mathbf{xp + px}}{\mathbf{2}}$ **2)** $(\mathbf{p^2 x - xp^2})$ **3)** $\dfrac{\mathbf{d}}{\mathbf{dx}}$

Ans: **Linear Operator:** An operator $\hat{P}$ is said to be linear if it satisfies the following conditions

$$\hat{P}(u + v) = \hat{P}u + \hat{P}v \text{ and}$$

$$\hat{P}(\alpha . u) = \alpha . \hat{P}u$$

where u and v are arbitrary functions and α is an arbitrary constant.

1) $$\frac{xp + px}{2}(u + v) = \frac{1}{2}\left[x\frac{\hbar}{i}.\frac{\partial}{\partial x}.(u + v) + \frac{\hbar}{i}\frac{\partial}{\partial x}x.(u + v)\right]$$

$$= \frac{1}{2}\left[x\frac{\hbar}{i}.\frac{\partial u}{\partial x} + x\frac{\hbar}{i}.\frac{\partial v}{\partial x} + \frac{\hbar}{i}\frac{\partial xu}{\partial x} + \frac{\hbar}{i}\frac{\partial xv}{\partial x}\right]$$

which follows the conditions $\hat{P}(u+v) = \hat{P}u + \hat{P}v$ and $\hat{P}(\alpha.u) = \alpha.\hat{P}u$. Hence operator $\frac{xp+px}{2}$ is linear.

ii) $(p^2x - xp^2)(u+v) = -\hbar^2 \frac{\partial^2}{\partial x^2}[x.(u+v)] + x\hbar^2 \frac{\partial^2}{\partial x^2}[(u+v)]$

$$= -\hbar^2 \frac{\partial^2 xu}{\partial x^2} - \hbar^2 \frac{\partial^2 xv}{\partial x^2} + x\hbar^2 \frac{\partial^2 u}{\partial x^2} + x\hbar^2 \frac{\partial^2 v}{\partial x^2}$$

which follows the conditions $\hat{P}(u+v) = \hat{P}u + \hat{P}v$ and $\hat{P}(\alpha.u) = \alpha.\hat{P}u$. Hence operator) $p^2x -$ xp)^2 is linear.

iii) $\hat{x}(u+v) = xu + xv$ which follows the conditions $\hat{P}(u+v) = \hat{P}u + \hat{P}v$ and $\hat{P}(\alpha.u) = \alpha.\hat{P}u.$ Hence operator x is linear.

iv) $\frac{d}{dx}(u+v) = \frac{d}{dx}u + \frac{d}{dx}v$ which follows the conditions $\hat{P}(u+v) = \hat{P}u + \hat{P}v$ and $\hat{P}(\alpha.u) = \alpha.\hat{P}u.$ Hence operator $\frac{d}{dx}$ is linear.

Q. 11. What is a Hermitian operator? Give its properties.

Ans: **Hermitian Operator :** *An operator $\hat{p}$ associated with dynamical variable is said to be Hermitian if its average value in any state ψ is real.*

Thus for u and v are two acceptable normalized wave functions, defined over a certain range of configuration space V, then operator $\hat{p}$ associated with a dynamical variable is **Hermitian** (self-adjoint or real) if

$$\int_{-\infty}^{+\infty} u^* \hat{P} v \, dV = \int_{-\infty}^{+\infty} \hat{P}^* u^* \, v \, dV$$

Properties of Hermitian operator:

1) *Hermitian operators have real eigen values.*
2) *Two eigen functions of Hermitian operators belonging to different eigen values are orthogonal.*
3) *If two Hermitian operators commute then their product is also Hermitian operator.*

Note: Every Schrodinger operator associated with areal dynamical variable is Hermitian.

Q. 12. Show that momentum operator $\hat{P}_x = \frac{\hbar}{i}.\frac{\partial}{\partial x}$ is Hermitian operator.

Ans: Momentum Operator $\hat{P}_x = \frac{\hbar}{i}.\frac{\partial}{\partial x}$

Complex conjugate of $\hat{P}$ is $\hat{P}^* = -\frac{\hbar}{i}\frac{\partial}{\partial x}$

If p is Hermitian operator its expectation value <p> in any state ψ must be real i.e.

$$\langle \hat{p} \rangle = \int_{-\infty}^{+\infty} \psi^* \frac{\hbar}{i}\frac{\partial \psi}{\partial x} dx \text{ must be real} \qquad ....(1)$$

Integrating (1) by parts, we get

$$\langle \hat{p} \rangle = \frac{\hbar}{i}\left[\psi^*\psi\right]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \frac{\hbar}{i}\frac{\partial \psi^*}{\partial x}\psi.dx$$

$$= \int_{-\infty}^{+\infty} \psi \left(\frac{\hbar}{i}\frac{\partial \psi}{\partial x}\right)^* dx = \langle \hat{p} \rangle^* \qquad ....(2)$$

It is obvious from (1) and (2) that $<\hat{p}>$ is equal to its complex conjugate. In other words $<\hat{p}>$ is real. Hence the momentum operator $\hat{P}_x = \frac{\hbar}{i}.\frac{\partial}{\partial x}$ is Hermitian.

EXPECTATION VALUES

Q. 13. Discuss expectation values of dynamical variables.

Ans: **Expectation value :** The expectation value represents the arithmetic mean over a large number of a simultaneous measurements in identical state (ψ).

The expectation value of a variable x of a system in the state ψ is given by

$$< x > = \frac{\int \psi^* \hat{x} \psi.d\tau}{\int \psi^* \psi.d\tau} \qquad ....(1)$$

<x> is called expectation value.

If the wave function ø is normalized, then $\int \psi^* \psi d\tau = 1$. Hence,

The expectation value of a dynamical variable x for normalized wave function is given by

$$< x >= \int \psi^* x\psi.d\tau \qquad ....(2)$$

Ex.: 1) Expectation value of position coordinate x-

$$< x >= \int \psi^* x\psi.dx$$

2) Expectation value of component of momentum p_x along x-

$$< p_x >= \int \psi^* \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\psi.dx$$

3) Expectation value of momentum -

$$< p >= \int \psi^* \left(\frac{\hbar}{i}\nabla\right)\psi.dx$$

4) Expectation value of Energy-

$$< E >= \int \psi^* \left(i\hbar\frac{\partial}{\partial t}\right)\psi.d\tau$$

EHRENFEST'S THEOREM

Q. 14. State and prove Ehrenfest's theorem.***

Ans: **Ehrenfest's theorem** : *It states that the average motion of a wave packet agrees with the motion of the corresponding classical particle.*

Hence, the classical laws (Newton's laws) may be expressed as

$$m.\frac{dr}{dt} = p \qquad ....(1)$$

and $$\frac{dp}{dt} = -\text{grad}\, V \qquad ....(2)$$

or In terms of components,

$$m.\frac{dx}{dt} = p_x \qquad m.\frac{dy}{dt} = p_y \qquad m.\frac{dz}{dt} = p_Z \qquad ....(A)$$

and $$\frac{dp_X}{dt} = -\frac{\partial V}{\partial x}; \quad \frac{dp_y}{dt} = -\frac{\partial V}{\partial y}; \quad \frac{dp_z}{dt} = -\frac{\partial V}{\partial z} \qquad ....(B)$$

Where, p = linear momentum of a particle and V, the P.E. of particle of mass m.

Proof:

In quantum theory it is not possible to define the derivative of x, y, z, p_x, p_y and p_z in the classical sense. The approximate values of derivatives found by considering the time rate of change of average values of x, y, z, p_x, p_y and p_z.

A) Thus x component of velocity may be defined as the time rate of change of expectation value of x i.e.

$$\frac{d}{dt} < x >= \frac{d}{dt}\int \psi^* x\psi .d\tau$$

$$= \int \psi^* x \frac{\partial \psi}{\partial t}.d\tau + \int \frac{\partial \psi^*}{\partial t}.x.\psi.d\tau \qquad ....(3)$$

Time dependent Schrodinger's equation is

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi \qquad ....(4)$$

Complex conjugate time dependent Schrodinger's equation is

$$-i\hbar \frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^* \qquad ....(5)$$

Substituting values of $\frac{\partial \psi}{\partial t}$ and $\frac{\partial \psi^*}{\partial t}$ from (4) and (5) in equation (3), we get

$$\frac{d}{dt} < x >= \int \psi^* x.\left\{\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi\right)\right\}d\tau + \int\left\{-\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^*\right)\right\}.x.\psi.d\tau$$

$$= -\frac{\hbar}{2im}\int [\psi^* x.(\nabla^2\psi) - (\nabla^2\psi^*).x.\psi].d\tau$$

$$\frac{d}{dt} < x >= -\frac{\hbar}{2im}\int \psi^* x(\nabla^2\psi).d\tau + \frac{\hbar}{2im}\int (\nabla^2\psi^*).x.\psi.d\tau \qquad ....(6)$$

In the above equation the second integral can be integrated by parts, i.e.

$$\int_V (\nabla^2\psi^*).x.\psi.d\tau = \int_A (x.\psi.\text{grad}\psi).dA - \int_V \nabla\psi^*\,\text{grad}(x\psi).d\tau$$

$$= \int_A (x.\psi.\text{grad}\psi^*)_n.dA - \int_V \text{grad}\psi^* \cdot \nabla(x\psi).d\tau \qquad \text{..........(7)}$$

Here the integral of the normal component of $(x\psi.\text{grad}\,\Psi^*)$ over the infinite bounding surface A is zero because the wave-packet vanishes at great distances.

So equation (7) becomes

$$\int_V (\nabla^2\psi^*).x\psi.d\tau = -\int_V \text{grad}.\psi^* \bullet \nabla(x\psi)d\tau$$

Integrating above equation by parts in which the surface integral again vanishes, we get

$$\int (\nabla^2\psi^*).x\psi.d\tau = \int \psi^*\nabla^2(x\psi)d\tau$$

Using equation (9), equation (6) can be written as

$$\frac{d}{dt}<x> = -\frac{\hbar}{2im}\int \psi^* x(\nabla^2\psi).d\tau + \frac{\hbar}{2im}\int \psi^*\nabla^2(x\psi).d\tau$$

$$= -\frac{\hbar}{2im}\int \psi^*[x(\nabla^2\psi). - \nabla^2(x\psi)].d\tau$$

$$= -\frac{\hbar}{im}\int \psi^*\frac{\partial\psi}{\partial x}.d\tau$$

$$\because \quad x\nabla^2\psi - \nabla^2(x\psi) = -2\frac{\partial\psi}{\partial x}$$

$$= \frac{1}{m}\int \psi^*\left(-i\hbar\frac{\partial\psi}{\partial x}\right).d\tau$$

i.e. $\dfrac{d}{dt}<x> = \dfrac{1}{m}<p_x>$

Similarly, $\dfrac{d}{dt}<y> = \dfrac{1}{m}<p_y>$ and $\dfrac{d}{dt}<z> = \dfrac{1}{m}<p_z>$

Combining all components,

$$\frac{d}{dt}<r> = \frac{1}{m}<p> \qquad \text{..........(8)}$$

B) The time rate of change of change of x component of momentum is given by

$$\frac{d}{dt}<p_x> = \frac{d}{dt}\int \psi^*\left(-i\hbar\frac{\partial\psi}{\partial x}\right).d\tau$$

$$= -i\hbar\left[\int \psi^*\frac{\partial}{\partial x}\frac{\partial\psi}{\partial t}.d\tau + \int \frac{\partial\psi^*}{\partial t}.\frac{\partial\psi}{\partial x}..d\tau\right] \qquad \text{..........(9)}$$

$$= -\int \psi^* \frac{\partial}{\partial x}\left(i\hbar \frac{\partial \psi}{\partial t}\right) d\tau + \int \left(-i\hbar \frac{\partial \psi^*}{\partial t}\right) \frac{\partial \psi}{\partial x} . d\tau$$

Using Schrodinger time dependent equation and its complex congugate

$$= -\int \psi^* \frac{\partial}{\partial x}\left(-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi\right) d\tau + \int \left(-\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi\right) \frac{\partial \psi}{\partial x} . d\tau \qquad \text{..........(10)}$$

$$= -\int \psi^* \left[\frac{\partial}{\partial x}(V\psi) - V\frac{\partial \psi}{\partial x}\right] . d\tau$$

i.e. $\frac{d}{dt} < p_x > = -\int \psi^* \frac{\partial V}{\partial x} . d\tau = - < \frac{\partial V}{\partial x} >$

Similarly, $\frac{d}{dt} < p_y > = - < \frac{\partial V}{\partial y} >$ and

$$\frac{d}{dt} < p_z > = - < \frac{\partial V}{\partial z} >$$

Combining all components,

$$\frac{d}{dt} < p > = < -\nabla V >$$

Equation (8) and (11)are analogous to the classical equations of motion:

$$m.\frac{dr}{dt} = p \text{ and } \frac{dp}{dt} = -\text{grad } V$$

This proves Ehernfest's theorem.

EIGEN VALUE AND EIGEN FUNCTIONS

Q. 15. What is an eigen function and eigen value?

Ans: **Eigen function**: A function f is called an eigen function of the operator $\hat{A}$ if when the operator $\hat{A}$ operates on the function f, we get the same function multiplied by a constant C i.e.

$$\hat{A}f = Cf \qquad \text{..........(1)}$$

The constant C is called the eigen value of the operator $\hat{A}$.

Equation (1) is known as **eigen value equation .**

Note: Eigen value means proper or characteristic value and Eigen function means proper or characteristic function.

Q. 16. The operator for Z-component of angular momentum is $\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$, determine whether or not sin(mö) is its eigen function.

Ans: Eigen value equation is

$$\hat{A}f = Cf \vdots \qquad \text{..........(1)}$$

Here $f = \sin(m\phi)$ and operator $\hat{L}_Z = -i\hbar\frac{\partial}{\partial\varphi}$

$$\therefore\ \hat{A}f = \hat{L}_Z \sin(m\varphi) = -i\hbar\frac{\partial}{\partial\phi}\sin(m\phi) = -i\hbar.m.\cos(m\phi)$$

As $\hat{L}_Z \sin(m\phi) \neq \text{a cons tan t} \times \sin(m\phi)$

Hence, sin $\sin(m\varphi)$ is not an eigen function of angular momentum $\hat{L}_Z = -i\hbar\frac{\partial}{\partial\varphi}$

PARTICLE IN A BOX

Q. 17. What is a free particle? Write its potential.

Ans: A free particle is one for which no force of any kind is acting upon it and hence it has constant P.E. which can be assumed to be zero. Thus the total energy of a free particle is all the kinetic.

It is free from any force, hence its potential = zero.

APPLICATION TO FREE PARTICLE IN A ONE DIMENSION

Q. 18. Solve the Schrodinger wave equation for a free particle in a one dimensional rigid potential box to obtain energy eigen values and eigen functions.

Ans: Suppose a particle is restricted to move freely inside a box in one dimension between two points at x = 0 & x = L i.e. 0<= x <= L. The walls of the box are rigid, hard and elastic.

A particle confined to a box of widh L.

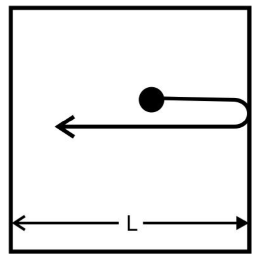

Fig. 1.1

The potential energy V of the particle is infinite on both the sides of the box while V inside the box is constant and assumed to be zero as shown in figure below.

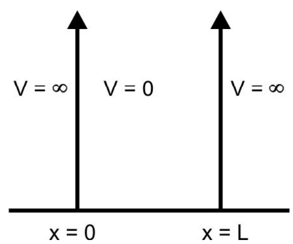

Fig. 1.2

Boundary conditions:

$V = 0$ for $0 < x < L$ and

$V = \infty$ for $x \le 0$ and $x \ge L$

Schrodinger's one dimensional time independent equation gives

$$\left(\frac{d^2\psi}{dx^2}\right) + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad \text{..........(1)}$$

For a free particle inside the box, V = 0. Hence within the box, Schrodinger's equation becomes

$$\left(\frac{d^2\psi}{dx^2}\right) + \frac{2m}{\hbar^2}E\psi = 0 \qquad \text{..........(2)}$$

Putting, $\frac{2m}{\hbar^2}E = {k_x}^2$ the equation (2) becomes

$$\left(\frac{d^2\psi}{dx^2}\right) + {k_x}^2\psi = 0$$

The general solution of this differential equation can be written as

$$\psi = A\sin K_x.x + B\cos K_x.x \qquad \text{..........(3)}$$

where A and B are arbitrary constants. To find the values of A and B we apply the boundary conditions. For continuity of the wave function at the boundary, we have

$$\psi = 0 \text{ when } x = 0 \;\&\; x = L, \text{both}$$

Using boundary condition

$\psi = 0$ when $x = 0$, we get from equation (3)

$$B = 0$$

Therefore equation (3) now becomes

$$\psi = A\sin K_x.x \qquad \text{..........(4)}$$

Using boundary condition $\psi = 0$ when $x = L$, we get from equation (4)

$$0 = A\sin K_x.L$$

$$\therefore\ k_x.L = n_x\pi \text{ where } n = 1, 2, 3, ...$$

$$\therefore\ k_x = \frac{n_x\pi}{L} \qquad \text{..........(5)}$$

$$\therefore\ k_x^{\,2} = \frac{n_x^{\,2}\pi^2}{L^2}$$

But, $\dfrac{2m}{\hbar^2}E = k_x^{\,2}$

Equating both the equations, $\dfrac{2mE}{\hbar^2} = \dfrac{n_x^{\,2}\pi^2}{L^2}$

$$\therefore\ E_n = \left(\frac{\hbar^2\pi^2}{2mL^2}\right).n_x^{\,2} \qquad \text{where } n_x = 1,2,3,\ldots\ldots \qquad \text{..........(6)}$$

For each value of n_x, there is corresponding energy value. Thus the particle inside the box can have the discrete energy values given by equation (6). Also note that the particle cannot have zero energy.

The particle in a box: Wave functions-

Put $k_x = \dfrac{n_x\pi}{L}$ From equation (5) to equation (4), we get the wave functions

$$\psi = A\sin K_x.x = A\sin\left(\frac{n_x\pi}{L}\right).x$$

The particle is somewhere inside the box. Hence for a normalized wave function

$$\int_0^L \psi^* \psi.dx = 1$$

$$\therefore \int_0^L A^2 \sin^2\left(\frac{n_x\pi}{L}\right).x.dx = 1$$

But, $A^2\int_0^L\left(\frac{1-\cos 2n_x\pi x/L}{2}\right).x.dx = 1 \Rightarrow A^2\frac{L}{2} = 1.\text{gives}.A = \sqrt{\frac{2}{L}}$

Hence, the normalized wave functions of the particle are given by-

$$\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n_x\pi}{L}\right).x \qquad \text{..........(7)}$$

and are plotted in the figure below.

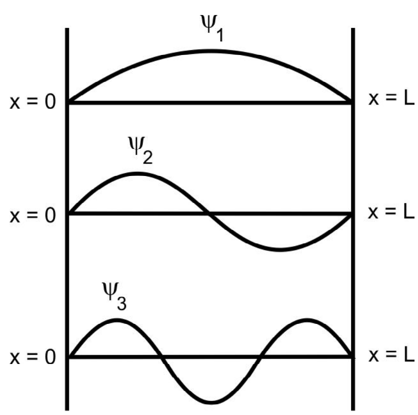

Fig. 2.3

We know, Probability density $P_n = \psi_n{}^* \psi_n = |\psi_n|^2$

$$= \frac{2}{L}\sin^2\left(\frac{n_x\pi}{L}\right).x \qquad \text{..........(8)}$$

and are plotted in the figure below

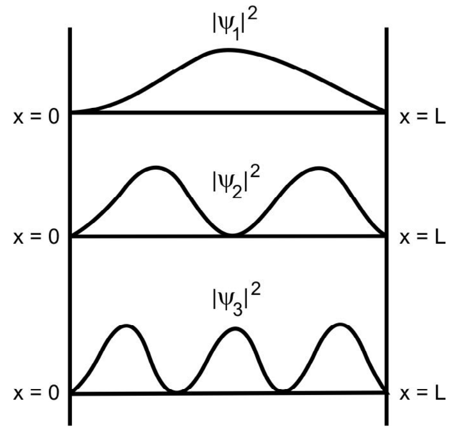

Fig. 2.4

It is clear that the probability of locating the particle at x = 0 and x = L i.e. near the walls is always zero.

Note: A node is the position of minimum displacement and an anti-node is the position of maximum displacement.

APPLICATION TO FREE PARTICLE IN A THREE DIMENSION

Q. 19. Solve the Schrodinger wave equation for a free particle in a rectangular potential box. Obtain energy eigen values and eigen functions.

or

Write Schrodinger's equation for a particle in a rectangular rigid box and solve it. Find the eigen values of momentum and energy.

Ans. Suppose a particle is restricted to move freely inside a rectangular box of sides L_x, L_y and L_z. The walls of the box are rigid, hard and elastic.

The potential energy V of the particle is infinite outside the box while V inside the box is constant and assumed to be zero as shown in figure below.

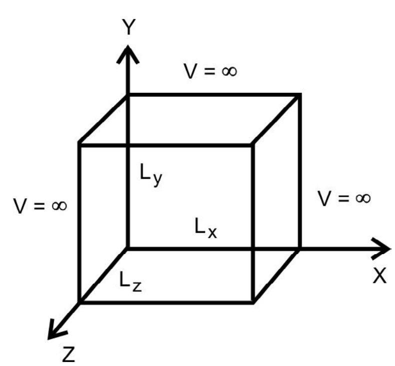

Fig. 2.5

Boundary conditions:

V = 0 inside the box and

$V = \infty$ outside the box

Schrodinger's three dimensional time independent equation gives

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \quad \text{..........(1)}$$

For a free particle inside the box, V = 0. Hence within the box, Schrodinger's equation becomes

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

$$\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + \frac{2m}{\hbar^2}E\psi = 0 \quad \text{..........(2)}$$

Now, ψ is a function of x, y, z co-ordinates. We can therefore put

$$\Psi(x, y, z) = \Psi_x, \Psi_y, \Psi_z \quad \text{..........(3)}$$

Using equation (3) in equation (2), we get

$$\left(\frac{\partial^2}{\partial x^2}(\psi_x.\psi_y.\psi_z) + \frac{\partial^2}{\partial y^2}(\psi_x.\psi_y.\psi_z) + \frac{\partial^2}{\partial z^2}(\psi_x.\psi_y.\psi_z)\right) + \frac{2m}{\hbar^2}E(\psi_x.\psi_y.\psi_z) = 0$$

$$\left(\frac{\partial^2\psi_x}{\partial x^2}.(\psi_y.\psi_z) + \frac{\partial^2\psi_y}{\partial y^2}.(\psi_x.\psi_z) + \frac{\partial^2\psi_z}{\partial z^2}.(\psi_x.\psi_y)\right) + \frac{2m}{\hbar^2}E(\psi_x.\psi_y.\psi_z) = 0$$

Dividing this equation by $\Psi_x\Psi_y\Psi_z$

$$\left(\frac{1}{\psi_x}.\frac{\partial^2\psi_x}{\partial x^2} + \frac{1}{\psi_y}.\frac{\partial^2\psi_y}{\partial y^2} + \frac{1}{\psi_z}.\frac{\partial^2\psi_z}{\partial z^2}\right) + \frac{2m}{\hbar^2}E = 0$$

$$\therefore \quad \frac{1}{\psi_x}\frac{\partial^2\psi_x}{\partial x^2} = -\frac{1}{\psi_y}\frac{\partial^2\psi_y}{\partial y^2} - \frac{1}{\psi_z}\frac{\partial^2\psi_z}{\partial z^2} - \frac{2mE}{\hbar^2} \quad \text{..........(4)}$$

Put $\frac{1}{\psi_x}\frac{\partial^2\psi_x}{\partial x^2} = k_x^2; \frac{1}{\psi_y}\frac{\partial^2\psi_y}{\partial y^2} = k_y^2; \frac{1}{\psi_z}\frac{\partial^2\psi_z}{\partial z^2} = k_z^2$ ....(5)

equation (4) becomes

$$k_x^2 + k_y^2 + k_z^2 = \frac{2mE}{\hbar^2}$$

Now the equations (5) can be rewritten as

$$\left(\frac{\partial^2\psi_x}{\partial x^2}\right)+k_x{}^2\psi_x=0 \quad \text{..........(x)}$$

$$\left(\frac{\partial^2\psi_y}{\partial y^2}\right)+k_y{}^2\psi_y=0 \quad \text{..........(y)}$$

$$\left(\frac{\partial^2\psi_z}{\partial z^2}\right)+k_z{}^2\psi_z=0 \quad \text{..........(z)}$$

The general solution of these differential equations is of the form

$$\psi_x = A\sin K_x.x + B\cos K_x.x \qquad \text{..........(6)}$$

where A and B are arbitrary constants. To find the values of A and B we apply the boundary conditions. For continuity of the wave function at the boundary, we have

$$\psi_x = 0 \text{ when } x = 0 \;\&\; x = L_x, \text{both}$$

Using boundary condition

$\psi_x = 0$ when $x = 0$, we get from equation (6)

$$B = 0$$

Therefore equation (6) now becomes

$$\psi_x = A\sin K_x.x \qquad \text{..........(7)}$$

Using boundary condition $\psi_x = 0$ when $x = L_x$ we get from equation (7)

$$0 = A \sin K_x.L_x$$

$$\therefore\; k_x.L_x = n_x\pi \text{ where } n = 1, 2, 3, ...$$

$$\therefore\; k_x = \frac{n_x\pi}{L_x} \qquad \text{..........(8)}$$

Therefore equation (7) becomes

$$\psi_x = A_x \sin\left(\frac{n_x\pi}{L_x}\right).x$$

Similarly

$$\psi_y = A_y \sin\left(\frac{n_y\pi}{L_y}\right).y \text{ when } k_y = \frac{n_y\pi}{L_y} \text{ and}$$

$$\psi_z = A_z \sin\left(\frac{n_z \pi}{L_z}\right).z \text{ when } k_z = \frac{n_z \pi}{L_z}$$

Hence the complete solution can be written as $\Psi(x, y, z) = \Psi_{x.}\Psi_{y.}\Psi_z$

$$\therefore \quad \psi = A_x \cdot A_y \cdot A_z \cdot \sin\left(\frac{n_x \pi}{L_x}\right).x \sin\left(\frac{n_y \pi}{L_y}\right).y \sin\left(\frac{n_z \pi}{L_z}\right)z \qquad ....(9)$$

The particle is somewhere inside the box. Hence for a normalized wave function

$$\int_0^{L_x}\int_0^{L_y}\int_0^{L_z} \psi^* \psi.dV = 1$$

$$\therefore \quad \int_0^{L_x} A_x^{\,2} \sin^2\left(\frac{n_x \pi}{L_x}\right).x.dx = 1$$

But $A_x^{\,2}\int_0^{L}\left(\frac{1-\cos 2n_x \pi x / L}{2}\right).x.dx = 1 \Rightarrow A_x^{\,2}\frac{L_x}{2} = 1.\text{gives}.A_x = \sqrt{\frac{2}{L_x}}$

Similarly $A_y = \sqrt{\frac{2}{L_y}}$ and $A_z = \sqrt{\frac{2}{Lz}}$

Hence, the complete wave function for various values of quantum numbers n_x, n_y and n_z has the form,

$$\psi = \sqrt{\frac{8}{L_x \cdot .L_y \cdot L_z}} \cdot \sin\left(\frac{n_x \pi}{L_x}\right).x \sin\left(\frac{n_y \pi}{L_y}\right).y \sin\left(\frac{n_z \pi}{L_z}\right)z$$

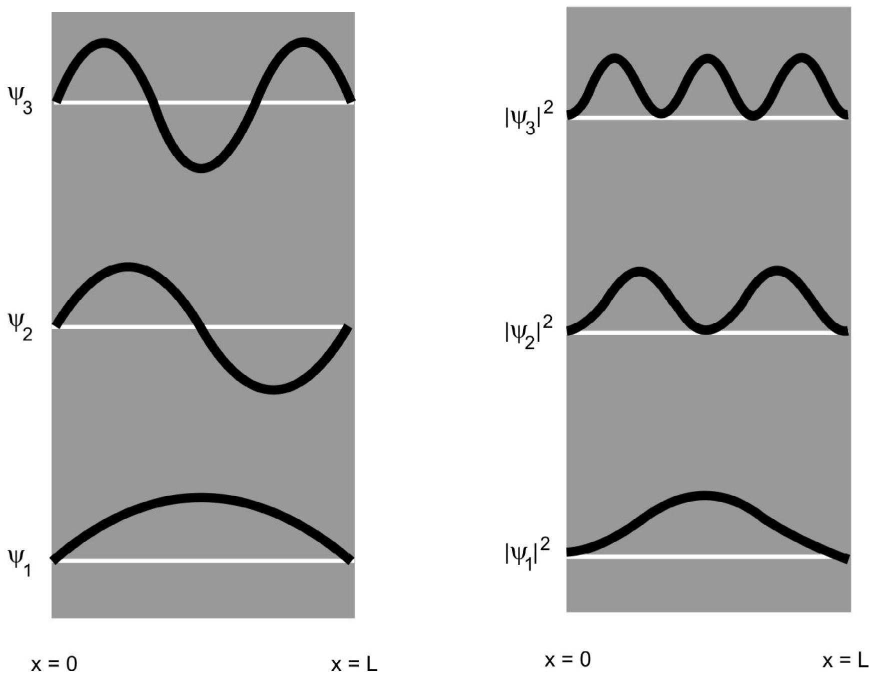

Fig. 2.6

Figure represents first three normalized wave functions and probability density for a particle in a box.

Eigen Values of the Energy:

We know, $k_x{}^2 + k_y{}^2 + k_z{}^2 = \frac{2mE}{\hbar^2}$ and $k_x = \frac{n_x \pi}{L_x}$ $k_y = \frac{n_y \pi}{L_y}$

$$k_z = \frac{n_z \pi}{L_z}$$

$$\therefore \frac{2mE}{\hbar^2} = \pi^2 \left(\frac{n_x{}^2}{L_x{}^2} + \frac{n_y{}^2}{L_y{}^2} + \frac{n_z{}^2}{L_z{}^2} \right)$$

$$\therefore \quad E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x{}^2}{L_x{}^2} + \frac{n_y{}^2}{L_y{}^2} + \frac{n_z{}^2}{L_z{}^2} \right) \qquad ....(11)$$

For cubical box, the ground state energy value is obtained by putting nx = ny = nz = 1

$$E_{1,1,1} = \frac{3\pi^2 . \hbar^2}{2mL^2}$$

There is only one set of quantum numbers that gives this energy state, and this level is said to be non-degenerate.

$$E_{211} = E_{121} = E_{112} = \frac{3\pi^2\hbar}{ma^2}$$

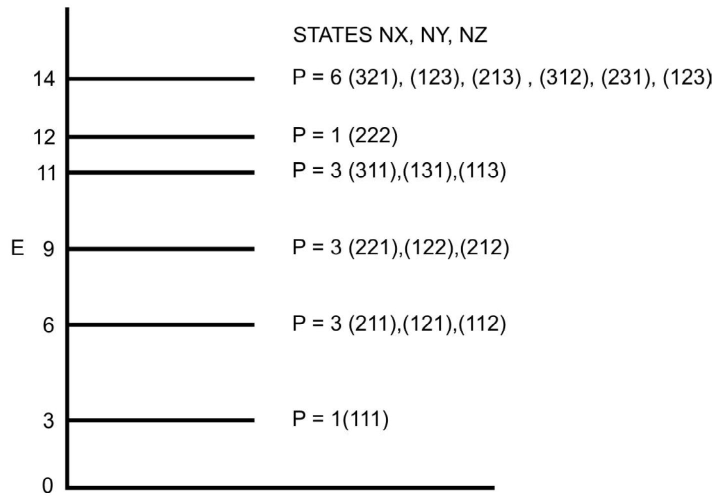

Fig. 2.7

Figure shows energy levels, degree of degeneracy and quantum numbers of a particle in a cubical box.

SOLVED PROBLEMS

Ex. 1. Calculate the expectation value of p and p^2 for the normalized wave function $\psi(x) = \left(\frac{2}{L}\right)^{1/2} \sin\frac{\pi.x}{L}$ in the region $0 < x < L$ and $\Psi(x) = 0$ for $|x| > L$

Solution: A) *The expectation value of a dynamical variable p for normalized wave function ø is given by*

$$< p >= \int \psi^* \hat{p}\psi.dx \qquad ....(1)$$

The operator associated with x component of momentum is $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$

$$\therefore \quad < p >= \int \psi * \frac{\hbar}{i}\frac{\partial \psi}{\partial x}.dx$$

Here $\psi(x)=\left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi.x}{L}$

in the region 0 < x < L

$$\therefore \quad <P>=\int_O^L\left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi x}{L}\left\{\frac{\hbar}{i}.\frac{\partial}{\partial x}\left(\frac{2}{L}\right)^{1/2}\right\}.dx$$

$$=\frac{2}{L}\frac{\hbar}{i}\frac{\pi}{L}\int_0^L\sin\frac{\pi x}{L}.\cos\frac{\pi x}{L}.dx$$

$$=\frac{\hbar}{i}\frac{\pi}{L^2}\int_0^L\sin\frac{2\pi x}{L}.dx$$

$$=-\frac{\hbar}{i}\frac{\pi}{L^2}\left[\frac{\cos 2\frac{\pi x}{L}}{2\pi/L}\right]_0^L$$

$$=-\frac{\hbar}{2iL}\left[\cos 2\pi-\cos 0\right]=0$$

$$\therefore \quad <p>=0$$

B) *The expectation value of a dynamical variable p^2 for normalized wave function ø is given by*

$$<p^2>=\int\psi^*\left(\hat{p}^2\right)\psi.dx \qquad ....(1)$$

The operator associated with x component of momentum is

$$\hat{p}^2=\hbar^2\frac{\partial^2}{\partial x^2}$$

$$\therefore \quad <p^2>=\int\psi^*\hbar^2\frac{\partial^2\psi}{\partial x^2}.dx$$

Here $\psi(x)=\left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi.x}{L}$ in the region 0 < x < L

$$\therefore \quad <p^2>=-\hbar^2\int_0^L\left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi x}{L}\left\{.\frac{\partial^2}{\partial x^2}\left(\left(\frac{2}{L}\right)^{1/2}.\sin\frac{\pi x}{L}\right)\right\}.dx$$

$$= \frac{2}{L}\hbar^2 \int_0^L \sin\frac{\pi x}{L}.\left(\frac{\pi}{L}\right).\sin\frac{\pi x}{L}.dx$$

$$= \frac{\pi^2\hbar^2}{L^3}\int_0^L 2\sin^2\frac{\pi x}{L}.dx$$

$$= \frac{\pi^2\hbar^2}{L^3}\int_0^L \left[1-\cos\frac{2\pi x}{L}\right].dx$$

$$= \frac{\pi^2\hbar^2}{L^3}\left[x - \left\{\frac{\sin\left(2\pi x/L\right)}{2\pi/L}\right\}\right]_0^L$$

$$= \frac{\pi^2\hbar^2}{L^3}\left[L - \frac{L}{2\pi}\{\sin 2\pi - \sin 0\}\right] = \frac{\pi^2\hbar^2}{L^2}$$

$$\therefore \quad <p^2> = \frac{\pi^2\hbar^2}{L^2}..$$

Ex. 2. Find the expectation value of position and x-component of momentum of a particle trapped in a box L wide. Whose normalized wave function is

$$\boldsymbol{\psi(x) = \left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi.x}{L}} \text{ **in the region 0 < x < L and**}$$

$$\boldsymbol{\psi(x) = 0 \text{ for } |x| > L}$$

Solution: **:** A) *The expectation value of a dynamical variable x for normalized wave function ψ is given by*

$$<x> = \int \psi^* \hat{x}\psi.dx \qquad ....(1)$$

The operator associated with x component of momentum is x = multiplication by x

$$\therefore \quad <x> = \int \psi * x.\frac{\partial\psi}{\partial x}.dx$$

Here $\psi(x) = \left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi.x}{L}$ in the region 0 < x < L

$$\therefore \quad <x> = \int_0^L \left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi x}{L}\left\{x\left(\frac{2}{L}\right)^{1/2}.\sin\frac{\pi x}{L}\right\}.dx$$

$$= \frac{2}{L}\int_0^L x.\sin^2\frac{\pi x}{L}.dx$$

$$= \frac{2}{L}\int_0^L x.\left[\frac{1-\cos 2\pi x/L}{2}\right].dx$$

$$= \frac{1}{L}\int_0^L x.dx - \frac{1}{L}\int_0^L x.\cos\frac{2\pi x}{L}.dx$$

Now, $\int_0^L x.dx = \left[\frac{x^2}{2}\right]_0^L = \frac{L^2}{2}$ and $-\int_0^L x.\cos\frac{2\pi x}{L}.dx = 0$

$\therefore \quad \langle x \rangle = \frac{L}{2}$

B) *The expectation value of a dynamical variable p_x for normalized wave function ø is given by*

$$\langle p_x \rangle = \int \psi^* \hat{p}_x \psi.dx \qquad ....(1)$$

The operator associated with x component of momentum is

$$\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$\therefore \quad \langle p \rangle = \int \psi^* \frac{\hbar}{i}\frac{\partial \psi}{\partial x}.dx$$

Here $\psi(x) = \left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi.x}{L}$ in the region $0 < x < L$

$$\therefore \quad \langle p \rangle = \int_0^L \left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi x}{L}\left\{\frac{\hbar}{i}.\frac{\partial}{\partial x}\left(\frac{2}{L}\right)^{1/2}.\sin\frac{\pi x}{L}\right\}.dx$$

$$= \frac{2}{L}\frac{\hbar}{i}\frac{\pi}{L}\int_0^L \sin\frac{\pi x}{L}.\cos\frac{\pi x}{L}.dx$$

$$= \frac{\hbar}{i}\frac{\pi}{L^2}\int_0^L \sin\frac{2\pi x}{L}.dx$$

$$= -\frac{\hbar}{i}\frac{\pi}{L^2}\left[\frac{\cos 2\frac{\pi x}{L}}{2\pi/L}\right]_0^L$$

$$= -\frac{\hbar}{2iL}\left[\cos 2\pi - \cos 0\right] = 0$$

Ex. 3 A particle limited to the x axis has the wave function ψ = ax between x = 0 and x = 1; ψ = 0 elsewhere. a) Find the probability that the particle can be found between x = 0.45 and x = 0.55. b) Find the expectation value <x> of the particles position.

Solution: a) The probability is

$$\int_{x1}^{x2} |\psi|^2\, dx = a^2 \int_{0.45}^{0.55} x^2.dx = a^2\left[\frac{x^3}{3}\right]_{0.45}^{0.55} = 0.0251 \times a^2$$

b) The expectation value is

$$< x > = \int_0^1 x.|\psi|^2\, dx = a^2 \int_0^1 x^3 dx = a^2\left[\frac{x^4}{4}\right]_0^1 = \frac{a^2}{4}$$

Ex. 4. Which of the following are eigen functions of the operator $\frac{d}{dx}$

i) e^{-ax} and ii) $\sin(\lambda x)$

Solution: i) $\frac{d}{dx}e^{-ax} = -a.e^{-ax}$, here function $\mathbf{e^{-ax}}$ remains unchanged, hence $\mathbf{e^{-ax}}$ is an eigen function and –a is an eigen value of the operator $\frac{d}{dx}$.

ii) $\frac{d}{dx}\sin(\lambda x) = \lambda.\cos(\lambda x)$, here function $\sin(\lambda x)$ has changed after the operation, hence $\sin(\lambda x)$ cannot be the eigen function of the operator $\frac{d}{dx}$.

Ex. 5. Which of followings are the eigen functions of the operator $\frac{d^2}{dx^2}$? i) sin x ii) cos x iii) e^{-2x}

Solution: i) $\frac{d^2}{dx^2}\sin x = -\sin x$, Hence, eigen value = –1

ii) $\dfrac{d^2}{dx^2}\cos x = -\cos x$ Hence, eigen value = –1

iii) $\dfrac{d^2}{dx^2}e^{-x} = 4e^{-2x}$, Hence, eigen value = 4

Here all functions remain unchanged; hence **all three** are the eigen functions of the operator $\dfrac{d^2}{dx^2}\partial$.

Ex. 6. The wave function of a particle confined in a box of length L is $\psi(x) = \left(\frac{2}{L}\right)^{1/2} \sin\frac{\pi.x}{L}$ in the region 0 < x < L and zero elsewhere. Calculate the probability of finding the particle in the region 0 < x < L.

Solution: Probability of finding the particle per unit length = $\psi\psi^*$.

Here $\psi^* = \psi = \sqrt{\left(\frac{2}{L}\right)}\sin\frac{\pi.x}{L}$

Probability of finding the particle in the length 0 to L/2; we get

$$P = \int_0^{L/2}\left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi x}{L}\left\{\left(\frac{2}{L}\right)^{1/2}.\sin\frac{\pi x}{L}\right\}.dx$$

$$= \frac{2}{L}\int_0^{L}.\sin^2\frac{\pi x}{L}.dx$$

$$= \frac{2}{L}\int_0^{L}.\left[\frac{1-\cos 2\pi x/L}{2}\right].dx$$

$$= \frac{1}{L}.\left[x - \frac{\sin 2\pi x/L}{2\pi/L}\right]_0^{L/2}$$

$$= \frac{1}{L}.\left[\frac{L}{2} - \frac{(\sin\pi - \sin 0)}{2\pi/L}\right] = \frac{1}{2}$$

Hence, Probability of finding the particle in the length 0 to L/2 = ½.

Ex. 7. Calculate the energy difference between the ground state and the first excited state for an electron in one dimensional rigid box of length 10-10m. (mass of electron = 9.1 × 10⁻³1 kg and h = 6.626× 10⁻³⁴ joule-sec)

Solution: The energy of a particle in one dimensional rigid box of side L is given by

$$\therefore \quad E_n = \left(\frac{\hbar^2\pi^2}{2mL^2}\right).n^2 = \frac{n^2h^2}{8mL^2} \qquad \text{..........(1)}$$

where n = 1, 2, 3,....... Substituting given values

$$E_n = n^2 \frac{(6.626\times10^{-34})^2}{8(9.1\times10^{-31})\times10^{-10}} = 0.603\times10^{-17}\times n^2 \text{ in joules}$$

$$= \frac{0.603\times10^{-17}.n^2}{1.6\times10^{-19}} \text{ in eV} = 37.7n^2 \text{ eV}$$

In the ground state n = 1, E_1= 37.7 eV

For first excited state n = 2, E_2 = 37.7 × 4 eV = 150.8 eV

Therefore, the energy difference, E_2–E_1 = 113.1 eV

References and Text books –

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5. ***Quantum Mechanics, by- A. K. Ghatak, S. lokanathan.***
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7. ***Quantum Mechanics, by-Chatwal, Anand, Himalaya publications.***
8. ***Advanced Quantum Mechanics, by- SatyaPrakash, Pragati Publications.***