B.Sc. ( Semester – 6 )
Subject : Physics
Course : US06CPHY01
Title : Quantum Mechanics

# Unit : 1 - Formulation of the Schrödinger Equation

## * Matter Waves : De Broglie's Hypothesis

In 1924 Louis de Broglie suggest that matter may have wave-like properties. He suggested that "if light behave like particles then it should be possible for matter to exhibit wave-like behaviour under suitable circumstances"

He made the hypothesis that the relation between the energy E of a particle and the frequency $\nu$ of the associated wave is exactly the same as that between energy of a photon and frequency of the light radiation.

$$\therefore \quad \boxed{E = h\nu = \hbar\omega} \quad \text{------ (1)}$$

where $\omega = 2\pi\nu$ is the angular frequency.

The proportionality relation like eq$^n$. (1) between E and $\omega$ must necessarily hold also between $\vec{p}$ and $\vec{k}$.

$$\therefore \quad \vec{p} = \hbar\vec{k} \quad \text{------ (2)}$$

In terms of magnitude.

$$p = \hbar k = \frac{h}{2\pi}\frac{2\pi}{\lambda} \qquad \left(\because \hbar = \frac{h}{2\pi} \text{ and } k = \frac{2\pi}{\lambda}\right)$$

$$\therefore \quad \boxed{p = \frac{h}{\lambda}} \quad \text{or} \quad \boxed{\lambda = \frac{h}{p}} \quad \text{------ (3)}$$

De Broglie's hypothesis gives dual particle-wave character to matter.

The experiments of Davisson and Germer, Kikuchi and G. P. Thomson gives the existance of 'de Broglie waves' associated with electrons.

The momentum p of the particle is then obtained from the relativistic relation

$$p^2 = 2mE_{kin} + (E_{kin}^2 / c^2)$$

$$\therefore \lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE_{kin}\left(1 + \frac{E_{kin}^2}{c^2\, 2mE_{kin}}\right)}}$$

$$\therefore \lambda = \frac{h}{\sqrt{2mE_{kin}}}\left(1 + \frac{E_{kin}}{2mc^2}\right)^{-1/2} \quad \text{---- (4)}$$

But $E_{kin} << mc^2$.

If electron accelerated through a potential difference of V volt or V/300 e.s.u., then electron acquires a kinetic energy $E_{kin} = \frac{eV}{300}$

$$\therefore \lambda = \frac{h}{\sqrt{2m\frac{eV}{300}}} = h\sqrt{\frac{150}{meV}}$$

$$\therefore \boxed{\lambda = \frac{12.25}{\sqrt{V}} \times 10^{-8}\ \text{cm.}} \quad \text{------ (5)}$$

where V is to be expressed in Volts.

The wavelength λ of the electron waves, as determined from experiment was found to be equal to h/p in agreement with de Broglie's theoretical prediction. Thus, the dual nature of matter like that of radiation was established.

After this hypothesis, Erwin Schrodinger proposed that the behaviour of matter waves associated with material particles is governed by a certain differential equation for the wave function ψ. The Schrodinger theory is called wave mechanics.

## * The motion of a free wave packet ; classical approximation and the uncertainty principle :-

According to de Broglie hypothesis a material particle in motion is associated with a wave of wavelength $\lambda = \frac{h}{mv}$, where $m$ is the mass of the particle and $v$ velocity.

If $E$ represents the energy of the particle, then the frequency $\nu$ of the wave will be given by the quantum condition $E = h\nu$.

$$\therefore \nu = \frac{E}{h} \quad ---- (1)$$

But according to Einstein's mass energy relation we have $E = mc^2$.

$$\therefore \nu = \frac{mc^2}{h}$$

de Broglie wave velocity

$$v_p = \nu \lambda$$

$$= \frac{mc^2}{h} \cdot \frac{h}{mv}$$

$$\therefore v_p = \frac{c^2}{v} \quad ---- (2)$$

The velocity of material particle ($v$) is always less than the speed of light $c$. Eqn. (2) shows that de Broglie wave velocity $v_p$ must be greater than $c$. This is not expected. The de Broglie wave associated with the particle would travel faster than the particle itself, therefore leaving the particle far behind. Hence, the material particle will not be equivalent to a single wave train.

The above difficulty was solved by Schrodinger who postulated that "a material particle in motion is equivalent to a wave packet rather than a single wave".

A wave packet consists of a group of wave each having slightly different velocity and wavelength with phases and amplitudes so chosen that they undergo interference constructively over only a small region of space where the particle can be located. Out side of which they undergo distructive interference so that the amplitude tends to reduce to zero rapidly.

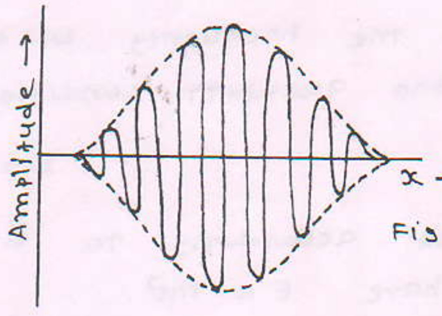

Fig: (a)

The one dimensional wave packet is shown in fig. (a). Such a packet moves with its own velocity $v_g$, called the group velocity.

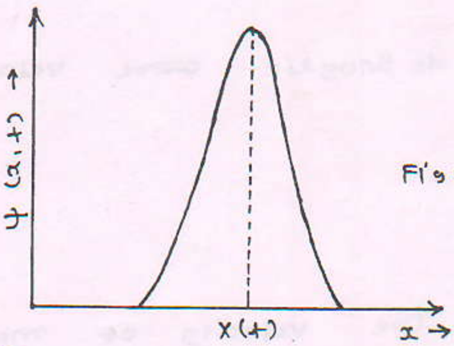

Fig: (b)

Consider a wave packet, which is represented by a wave function $\psi(x,t)$ at the instant $t$ and has a maximum at the point $X(t)$ as shown in fig (b).

If the position of the wave packet changes with time, the rate at which the maximum point moves gives the velocity $v_g$ of the packet,

$$\therefore \quad v_g = \frac{dX(t)}{dt} \quad \text{------ (3)}$$

The packet is composed of a group of harmonic waves having certain range of the wavelengths

$$\therefore \quad \psi(x,t) = \int_{-\infty}^{\infty} a(k)\, e^{i(kx-\omega t)}\, dk \quad \text{---- (4)}$$

where $a(k)$ is the amplitude of the harmonic wave with propagation constant '$k$' and angular frequency $\omega$ in the wave function. $k = \frac{2\pi}{\lambda}$.

The harmonic waves present in $\psi(x,t)$ have values of k lying within a small range centred about some value $\bar{k}$. When k is restricted to a narrow range, the momentum associated with it according to the de Broglie relation is also restricted. The frequency $\omega$ of these harmonic wave will also very close to $\bar{\omega} = \omega(\bar{k})$.

The exansion of $\omega(k)$ in Taylor series of power $(k-\bar{k})$ is given by

$$\omega(k) = \bar{\omega} + \bar{\omega}'.(k-\bar{k}) \quad \text{------ (5)}$$

(neglecting the higher powers)

where, $\bar{\omega} = \omega(\bar{k})$ and, $\bar{\omega}' = \left(\frac{d\omega}{dk}\right)_{\bar{k}} = \frac{d\bar{\omega}}{d\bar{k}}$.

The position $x(t)$ of the maximum of $\psi$ is the point at which $\frac{\partial\psi}{\partial x}$ vanishes. i.e $\frac{\partial\psi}{\partial x} = 0$.

$\therefore$ From eqn. (4) we can write

$$\left(\frac{\partial\psi}{\partial x}\right)_{x=x(t)} = \int a(k) \cdot ik\, e^{i[kx(t)-\omega t]}\, dk = 0 \quad \text{---- (6)}$$

Diffn. of above eqn. w.r.t t gives

$$\int a(k) \cdot ik \cdot i\,[kx'(t) - \omega] \cdot e^{i[kx(t)-\omega t]}\, dk = 0 \quad \text{---- (7)}$$

Now, substituting the value of $\omega$ from eqn (5) in eqn. (7) we get

$$\int a(k).\, i^2 k\,[kx'(t) - \bar{\omega} - \bar{\omega}'.(k-\bar{k})] \cdot e^{i[kx(t)-\omega t]}\, dk = 0$$

$$\therefore \int a(k) \cdot i^2 k\,[kx'(t) - \bar{\omega} - \bar{\omega}'k + \bar{\omega}'\bar{k}] \cdot e^{i[kx(t)-\omega t]}\, dk = 0$$

$$\therefore \int a(k)\, i^2 k\,[(x'(t) - \bar{\omega}')k - (\bar{\omega} - \bar{\omega}'\bar{k})]\, e^{i[kx(t)-\omega t]}\, dk = 0$$

$$\therefore [x'(t) - \bar{\omega}'] \int a(k)\, i^2 k^2\, e^{i[kx(t)-\omega t]}\, dk - (\bar{\omega} - \bar{\omega}'\bar{k}) \int a(k)\, i^2 k\, e^{i[kx(t)-\omega t]}\, dk = 0 \quad \text{---- (8)}$$

The second term in above equation vanishes using equation (6). Hence eqn (8) reduced to

$$[x'(t) - \bar{\omega}'] \int a(k)\, i^2 k^2\, e^{i[kx(t) - \omega t]}\, dk = 0. \qquad ---- (9)$$

We have

$$\psi(x,t) = \int a(k)\, e^{i(kx - \omega t)}\, dk$$

$$\therefore \quad \frac{\partial^2 \psi}{\partial x^2} = \int a(k)\, i^2 k^2\, e^{i(kx-\omega t)}\, dk \quad ---- (10)$$

Therefore in eqn (9) the term

$$\int a(k)\, i^2 k^2\, e^{i[kx(t) - \omega t]}\, dk \neq 0.$$

$\therefore$ We get

$$[x'(t) - \bar{\omega}'] = 0$$

$$\therefore \quad x'(t) = \bar{\omega}'$$

$$\therefore \boxed{v_g = x'(t) = \frac{d\bar{\omega}}{d\bar{k}}} \qquad ------ (11)$$

This is the velocity of the wave packet.

For a particle of mass m

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

$$\therefore \frac{dE}{dp} = \frac{2p}{2m} = \frac{p}{m} = \frac{mv}{m} = v.$$

$\therefore$ The velocity $v$ of the particle is given by

$$\boxed{v = \frac{dE}{dp}} \qquad ------ (12)$$

Eqns. (11) and (12) shows that the two velocities becomes identical if the particle parameters E, p are related to the wave parameters $\bar{\omega}$, $\bar{k}$ through the de Broglie relation $E = \hbar\bar{\omega}$, $p = \hbar\bar{k}$.

Therefore, we conclude that a small wave packet composed of a small band of de Broglie waves does move like a classical particle at least in the case of free particle.

→ Heisenberg's Uncertainty Principle :-

According to Newtonian physics, it is possible to determine exactly the position and momentum of a particle simultaneously. But the concept of dual nature of matter presents difficulty in locating the exact position and momentum at the same time. A moving particle, according to quantum mechanics, may be considered a group of waves (wave - packet) and the particle may be any where within the wave packet. Thus the position of the particle is uncertain within the limit of the wave packet. Also since the wave packet has a velocity spread, there is uncertainty about the velocity or momentum of the particle. Hence, it is impossible to know exactly where within the wave packet the particle is and what is its ~~exa~~ exact momentum.

Heisenberg in 1927, proposed the uncertainty principle which states that "the simultaneous determination of the exact position and momentum of a moving particle is impossible."

If $\Delta x$ denote the error in determining its position and $\Delta p$ the error in momentum, then according to this principle

$$\boxed{(\Delta p)(\Delta x) \gtrsim \hbar} \quad \text{----- (13)}$$

In case of three dimensional wave packet

$$\psi(\vec{x}, t) = \int a(\vec{k})\, e^{i(\vec{k}\cdot\vec{x} - \omega t)}\, d^3k \quad \text{----- (14)}$$

There are three uncertainty relations

$$\left.\begin{array}{l} (\Delta x)(\Delta p_x) \gtrsim \hbar \\ (\Delta y)(\Delta p_y) \gtrsim \hbar \\ (\Delta z)(\Delta p_z) \gtrsim \hbar \end{array}\right\} \quad \text{-------- (15)}$$

## * Uncertainties introduced in the process of measurement :-

Suppose we ~~wh~~ wish to determine the position of a small object with precision. We use microscope for this purpose. The limit of accuracy $\Delta x$ can be made by the microscope is given by its resolving power

$$\Delta x = \frac{\lambda}{\sin\alpha} \quad \text{------ (1)}$$

Here $\lambda$ is the wavelength of the light and $\alpha$ is ~~is~~ the half-angle substended by the objective ~~lens~~ lens of the microscope at the position of the object.

The higher the accuracy, smaller is the wavelength. But the light consists of photons of momentum $p = \frac{h}{\lambda}$. The x-component of the momentum of a photon scattered by the object into the microscope is uncertain by an amount $\pm\left(\frac{h}{\lambda}\right)\sin\alpha$.

$$\therefore \quad \Delta p_x \approx \frac{h}{\lambda}\sin\alpha \approx \frac{h}{\Delta x}.$$

$$\therefore \quad (\Delta p_x)(\Delta x) \sim h. \quad \text{------ (2)}$$

# THE SCHRÖDINGER EQUATION

## *. A free particle in one dimension :-

Consider a free particle of velocity $v$, momentum $p$ and energy $E$ moving in one dimension. For non relativistic particle $p = mv$ and energy $E = \frac{1}{2}mv^2$. Potential energy is zero for free particle.

The energy - momentum relation is given by

$$E = \frac{1}{2} m v^2 = \frac{1}{2} \frac{m^2 v^2}{m}$$

$$\therefore \quad E = \frac{p^2}{2m} \quad \text{------ (1)}$$

According to the de Broglie hypothesis, there is a harmonic wave of propagation constant k and angular frequency $\omega$ associated with the moving particle

$$\therefore \quad \hbar k = p \quad \text{and} \quad \hbar\omega = E \quad \text{---- (2)}$$

substituting these values of p and E in eq$^n$. (1) we get

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \quad \text{------ (3)}$$

The harmonic wave is represented by

$$\psi(x,t) = a\cos(kx-\omega t) + b\sin(kx-\omega t) \quad \text{---- (4)}$$

$$\left.\begin{aligned}
\therefore \quad \frac{\partial\psi}{\partial x} &= k\left[-a\sin(kx-\omega t) + b\cos(kx-\omega t)\right] \\
\frac{\partial^2\psi}{\partial x^2} &= -k^2\left[a\cos(kx-\omega t) + b\sin(kx-\omega t)\right] \\
&= -k^2\psi \\
\frac{\partial\psi}{\partial t} &= -\omega\left[-a\sin(kx-\omega t) + b\cos(kx-\omega t)\right] \\
\frac{\partial^2\psi}{\partial t^2} &= -\omega^2\left[a\cos(kx-\omega t) + b\sin(kx-\omega t)\right] \\
&= -\omega^2\psi
\end{aligned}\right\} \quad \text{---. (5)}$$

The possible differential equations are

$$\frac{\partial\psi}{\partial t} = -\frac{\omega}{k}\frac{\partial\psi}{\partial x} \quad \text{and} \quad \frac{\partial^2\psi}{\partial t^2} = \frac{\omega^2}{k^2}\frac{\partial^2\psi}{\partial x^2} \quad \text{---- (6)}$$

But these are unsuitable for the description of matter waves because

$\frac{\omega}{k} = \frac{E}{p} = \frac{p^2/2m}{p} = \frac{p}{2m}$ depends on the particular state of motion of the particle. $\frac{\omega}{k}$ is not independent of p.

But, $\frac{\omega}{k^2} = -\frac{\hbar}{2m}$ is independent of p.

Hence, $\frac{\omega}{k^2}$ is suitable for matter waves.

We can equate $\frac{\partial \psi}{\partial t}$ to $\frac{\partial^2 \psi}{\partial x^2}$.

The ratio of the coefficients of the cosine function in the two cases should be the same as that of the coefficients of the sine functions.

$$\therefore \quad \frac{a}{b} = -\frac{b}{a} \qquad \therefore \quad b^2 = -a^2$$

$$\text{or} \quad b = \pm ia \qquad \text{-----} (7)$$

We can write

$$\psi(x,t) = a\left[\cos(kx-\omega t) + i\sin(kx-\omega t)\right]$$

$$\therefore \psi(x,t) = a\, e^{i(kx-\omega t)} \qquad \text{------} (8)$$

Thus, matter waves for a particle of momentum p are to be represented by a complex harmonic functions of x and t.

$$\therefore \quad \frac{\partial \psi}{\partial t} = a\, e^{i(kx-\omega t)}(-i\omega)$$

$$= -i\omega\psi \qquad \text{------} (9)$$

and, $$\frac{\partial \psi}{\partial x} = a\, ik\, e^{i(kx-\omega t)}$$

$$\therefore \quad \frac{\partial^2 \psi}{\partial x^2} = -i^2k^2 a\, e^{i(kx-\omega t)}$$

$$= -k^2\psi \qquad (\because i^2 = -1)$$

$$= -\frac{2m\omega}{\hbar}\psi \qquad \text{-----} (10)$$

From eq$^n$ (9) $\quad \psi = -\frac{1}{i\omega}\frac{\partial \psi}{\partial t}$

Substituting this value of $\psi$ in eq$^n$ (10) we get

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{2m\omega}{\hbar} \times -\frac{1}{i\omega}\frac{\partial \psi}{\partial t}$$

$$= \frac{2m}{i\hbar}\frac{\partial \psi}{\partial t} = -\frac{i\hbar\, 2m}{\hbar^2}\frac{\partial \psi}{\partial t} \qquad (\because i^2 = -1)$$

$$\therefore \quad \boxed{i\hbar\frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2}} \qquad \text{-----} (11)$$

This is the Schrodinger equation for a free particle in one dimension.

The solⁿ of above eqⁿ. is

$$\boxed{\psi(x,t) = \int a(k)\, e^{i(kx-\omega t)}\, dk} \quad ---(12)$$

The function $\psi$ representing matter waves must be necessarily a complex function of $x$ and $t$.

## * Generalization to three dimensions :-

The energy - momentum relation for a free particle moving in three - dimensional space is given by

$$E = \frac{p^2}{2m} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \quad ----(1)$$

where $p_x, p_y, p_z$ are the components of the momentum vector $\vec{p}$. The harmonic wave to be associated with the particle must have the form

$$\psi(x,t) = a\, e^{i[\vec{k}\cdot\vec{x} - \omega t]} \quad -----(2)$$

Using deBroglie relations $\hbar\vec{k} = \vec{p}$ and $\hbar\omega = E$ together with eqⁿˢ. ① & ② we get

$$\boxed{i\hbar \frac{\partial \psi(\vec{x},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x},t)} \quad ----(3)$$

Here, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian operator.

This is the Schrodinger equation for a free particle in three dimensions.

The solⁿ of eqⁿ (3) is

$$\boxed{\psi(\vec{x},t) = \int a(\vec{k})\, e^{i(\vec{k}\cdot\vec{x} - \omega t)}\, d^3k} \quad ---(4)$$

## * The operator correspondence and the Schrodinger equation for a particle subject to forces :-

For a free particle, the schrodinger equation can also be obtained as follows.

Replace the energy E and the momentum $\vec{p}$ by the following differential operators

$$E \rightarrow i\hbar \frac{\partial}{\partial t}, \quad \vec{p} \rightarrow -i\hbar \vec{\nabla}$$

We have, $E = \frac{p^2}{2m}$

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

$$\therefore i\hbar \frac{\partial \psi}{\partial t} = \frac{(-i\hbar\vec{\nabla})^2}{2m}\psi$$

$$\therefore \boxed{i\hbar \frac{\partial \psi(\vec{x},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x},t)} \quad \text{---} (1)$$

$(\because i^2 = -1)$

Eq$^n$ (1) represents the three dimensional Schrodinger equation for a free particle.

Let $\vec{F}$ be the total force acting on the particle

$$\therefore \vec{F} = -\vec{\nabla} V(\vec{x}, t) \quad \text{-------} (2)$$

where $V(\vec{x}, t)$ is the potential energy.

The total energy E of the particle can be expressed as

$$E = \frac{p^2}{2m} + V(\vec{x}, t)$$

Now operating wave function $\psi$ we get

$$E\psi = \left[\frac{p^2}{2m} + V(\vec{x}, t)\right]\psi$$

$$\therefore \boxed{i\hbar \frac{\partial \psi(\vec{x},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x},t) + V(\vec{x},t)\psi(\vec{x},t)} \quad \text{---} (3)$$

This is the Schrodinger equation for a particle moving in a potential.

In above equation

$$\frac{p^2}{2m} + V(\vec{x}, t) = H$$

or $-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x}, t) = H$ is called Hamiltonian operator.

The energy of a particle is given by

$$E = H(\vec{x}, \vec{p}, t) \quad ---- (4)$$

Eq$^n$. (3) becomes

$$\boxed{i\hbar \frac{\partial \psi}{\partial t} = H(\vec{x}, -i\hbar\vec{\nabla}, t)\psi} \quad ---- (5)$$

The operator $H(\vec{x}, -i\hbar\vec{\nabla}, t)$ is the quantum mechanical Hamiltonian for the particle.

## * Normalization and Probability Interpretation :-

The Schrodinger equation is linear and homogeneous in $\psi$ and its derivatives. If we multiply any solution of the equation by a constant, the resulting function is still a solution.

Suppose $\psi'(\vec{x}, t)$ is the solution of the Schrodinger equation

let $$\int |\psi'(\vec{x}, t)|^2 d^3x = N^2 \quad ------ (1)$$

Since, $|\psi'|^2$ is the absolute value squared of a complex number and is also a real number denoted by $N^2$. The number $N^2$ is called the norm of the wave function $\psi'$.

Let us now define

$$\psi(\vec{x}, t) = \frac{1}{N}\psi'(\vec{x}, t) \quad ---- (2)$$

Here, $\psi$ differs from $\psi'$ only by a constant factor and it will also be a solution.

Now,
$$\boxed{\int |\psi(\vec{x}, t)|^2 d^3x = 1} \quad ---- (3)$$

or

$$\boxed{\int |\psi(\vec{x}, t)|^2 d\tau = 1}$$

The wave functions that satisfy the condition (3) are known as normalized wave functions.

The normalizable wave functions are those with finite norm.

The norm is defined as the integral of $|\psi|^2$ overall of space, it finiteness implies that $|\psi(\vec{x},t)|^2$ vanishes at infinity.

Hence, $$\psi(\vec{x},t) \to 0 \quad \text{as} \quad r \to \infty$$
$$\text{where} \quad r = |\vec{x}| \quad \text{- - - - (4)}$$

This is a boundary condition for normalizable wave function.

The position of a particle can not be precisely defined. There is a certain probability that the particle is within any specified volume element. The probability is proportional to the value of $|\psi|^2$ within the volume element.

Thus $|\psi|^2$, i.e the square of the magnitude of the wave function $\psi$ gives the probability density of finding the physical system at a particular place at a given time.

$|\psi(\vec{x},t)|^2 d^3x$ is equal to the probability that the particle is within the volume element $d^3x$ around the point x. The total probability that the particle is somewhere in space is then $\int|\psi|^2 d^3x$. Since the particle certainly is somewhere in space is ~~then~~, this total probability must be unity.

$$\therefore \boxed{\int |\psi|^2 d^3x = 1.} \quad \text{- - - - (5)}$$

## * Non - normalizable Wave Functions and Box Normalization :-

For normalization integral of $|\psi|^2$ overall space should be finite. There exist wave function or some physical problems for which the integral is infinite. This types of wave function is called non-normalized wave function. The infinite value of $\int |\psi|^2 d^3x$ represents an infinite number of non-interacting particles. Then $|\psi|^2 d^3x$ is the number of particles in the volume $d^3x$ at any instant.

By considering some ~~limit~~ limit, we can handle non-normalizable wave function. Imagine the particle to be confined within a large box and integral of $|\psi|^2$ taken over the interior of the box gives norm. This makes the norm finite, it can be made unity by multiplying the wave function by a suitable constant. This procedure is called box normalization.

The harmonic wave to be associated with the particle must have the form

$$\psi(\vec{x}, t) = a \exp[i(\vec{k}\cdot\vec{x} - \omega t)] \quad \text{----} (1)$$

If the box is taken to be a cube with edges of length L parallel to the x, y, z axes, the wave function at time $t = 0$

$$\psi_k(\vec{x}) = L^{-3/2} e^{i\vec{k}\cdot\vec{x}} \quad \text{-----} (2)$$

are normalized within the box., since

$$\iiint_{-\frac{1}{2}L}^{+\frac{1}{2}L} |\psi_k(\vec{x})|^2 dx\,dy\,dz = \iiint_{-\frac{1}{2}L}^{+\frac{1}{2}L} \frac{dx\,dy\,dz}{L^3} = 1 \quad \text{---} (3)$$

The boundary conditions is not applicable in this case.

We require that function (2) be periodic with respect to the size of the box. This means that if x, y or z is increased by L, the wave function should remain unchanged.

Hence, $e^{ik_xL} = e^{ik_yL} = e^{ik_zL} = 1 \quad \text{-----} (4)$

so that $k_x, k_y, k_z$ must be integer multiples of $(2\pi/L)$.

$$\therefore \vec{k} = \frac{2\pi}{L}\vec{n}, \quad (n_x, n_y, n_z = 0, \pm 1, \pm 2 \ldots) \quad \text{----(5)}$$

Thus, the admissible momentum vectors get quantized for the 'particle in a Box'.

## * Conservation of Probability :-

The probability interpretation of the normalized wave function says that the particle is sure to be found somewhere in space. This statement has to be true at all times as long as the particle is stable which can not decay or disappear. Therefore, the total probability must be conserved. i.e $|\psi|^2$ must be time independent, and

$$\frac{\partial}{\partial t}\int |\psi|^2 d^3x = \int \frac{\partial}{\partial t}|\psi|^2 d^3x = 0 \quad \text{----(1)}$$

Let us verify this requirement.

$$\frac{\partial}{\partial t}|\psi|^2 = \frac{\partial}{\partial t}(\psi^*\psi) = \psi^*\frac{\partial \psi}{\partial t} + \frac{\partial \psi^*}{\partial t}\psi \quad \text{----(2)}$$

But $\quad E\psi = H\psi$

$$\therefore i\hbar\frac{\partial \psi}{\partial t} = H\psi \quad \text{and,} \quad -i\hbar\frac{\partial \psi^*}{\partial t} = (H\psi)^*$$

$$\therefore \frac{\partial \psi}{\partial t} = (i\hbar)^{-1}H\psi \quad \text{and} \quad \frac{\partial \psi^*}{\partial t} = -(i\hbar)^{-1}(H\psi)^*$$

$\therefore$ From eqn (2) we can write

$$\frac{\partial}{\partial t}|\psi|^2 = \psi^*(i\hbar^{-1}H\psi) - [(i\hbar)^{-1}(H\psi)^*\psi]$$

$$= (i\hbar)^{-1}[\psi^*(H\psi) - (H\psi)^*\psi] \quad \text{----(3)}$$

But $\quad H = -\frac{\hbar^2}{2m}\nabla^2 + V(x,t)$

$\therefore$ Eqn. (3) becomes,

$$\frac{\partial}{\partial t}|\psi|^2 = (i\hbar)^{-1}\left[\psi^*\left(-\frac{\hbar^2}{2m}\right)\nabla^2\psi + \psi^*\cancel{V(x,t)}\psi + \left(\frac{-\hbar^2}{2m}\right)\nabla^2\psi^*\psi - \cancel{V\psi^*}\psi\right]$$

$$\therefore \frac{\partial}{\partial t}|\psi|^2 = \frac{i\hbar}{2m}\left[\psi^*\nabla^2\psi - (\nabla^2\psi^*)\psi\right]$$

$$= \frac{i\hbar}{2m}\vec{\nabla}\cdot\left[\psi^*\vec{\nabla}\psi - (\vec{\nabla}\psi^*)\psi\right]$$

$$\therefore \boxed{\frac{\partial}{\partial t}P(\vec{x},t) + \operatorname{div}\vec{S}(\vec{x},t) = 0} \quad \text{----- (4)}$$

where, $P(\vec{x},t) = \psi^*\psi$

and, $\vec{S}(\vec{x},t) = -\frac{i\hbar}{2m}\left[\psi^*\vec{\nabla}\psi - (\nabla\psi^*)\psi\right]$ ---- (5)

On integrating eqn. (4) overall space, we get

$$\frac{\partial}{\partial t}\int P\,d^3x = -\int \operatorname{div}\vec{S}\,d^3x$$

Now, converting R.H.S of volume integral of $\operatorname{div}\vec{S}$ in to surface integral $\sigma$ bounding the volume by Gauss theorem, we get

$$\frac{\partial}{\partial t}\int P\,d^3x = -\int_\sigma \vec{S}\cdot\hat{n}\,d\sigma \quad \text{----- (6)}$$

Since, the volume integral in eqn. (6) is overall of space, the surface $\sigma$ is infinity Hence eqn (6) is zero.

$$\therefore \frac{\partial}{\partial t}\int P\,d^3x = 0$$

$$\therefore \boxed{\frac{\partial}{\partial t}\int|\psi|^2 d^3x = 0} \quad \text{------ (7)}$$

Thus we have varified that the condition ① for conservation of total probability is satisfied., and the normalization ⑥ is time independent

## * Expectation Values ; Ehrenfest's Theorem :-

Suppose we take large number of observation of the position of the particle. We do not expect to get the same result each time. Therefore we take the mean or average of all the observed value of the position vectors, and the result is expected to be

$$\langle \vec{x} \rangle = \int \vec{x} \, |\psi|^2 \, d^3x = \int \psi^* \vec{x} \psi \, d^3x \quad \text{---- (1)}$$

The possible results $\vec{x}$ weighted by the function $|\psi(\vec{x})|^2$. Eqn. (1) gives mean position or expectation value of the position variable $\vec{x}$.

Now,

$$\frac{d\langle \vec{x} \rangle}{dt} = \int \left( \frac{\partial \psi^*}{\partial t} \vec{x} \psi + \psi^* \vec{x} \frac{\partial \psi}{\partial t} \right) d^3x \quad \text{---- (2)}$$

But

$$E\psi = H\psi$$

$$\therefore \; i\hbar \frac{\partial \psi}{\partial t} = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{x}, t) \right] \psi$$

$$\therefore \; \frac{\partial \psi}{\partial t} = \frac{1}{i\hbar} \left[ -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi \right]$$

and,

$$\frac{\partial \psi^*}{\partial t} = -\frac{1}{i\hbar} \left[ -\frac{\hbar^2}{2m} \nabla^2 \psi^* + V\psi^* \right]$$

substituting these values of $\frac{\partial \psi}{\partial t}$ and $\frac{\partial \psi^*}{\partial t}$ in eqn (2), we get

$$\frac{d\langle \vec{x} \rangle}{dt} = \frac{1}{i\hbar} \int \left[ -\left( -\frac{\hbar^2}{2m} \nabla^2 \psi^* + V\psi^* \right) \vec{x} \psi + \psi^* \vec{x} \left( -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi \right) \right] d^3x$$

$$\therefore \; \frac{d\langle \vec{x} \rangle}{dt} = \frac{i\hbar}{2m} \int \left[ \psi^* \vec{x} \nabla^2 \psi - (\nabla^2 \psi^*) \vec{x} \psi \right] d^3x \quad \text{---- (3)}$$

By using integration by parts this eqn. reduced to

$$\frac{d\langle \vec{x} \rangle}{dt} = -\frac{i\hbar}{m} \int \psi^* \vec{\nabla} \psi \, d^3x \quad \text{------ (4)}$$

Now, in the classical mechanic $\vec{p} = m \frac{d\vec{x}}{dt}$. For the quantum mechanical wave packet as a whole, the classical relations should be apply approximately.

Hence, from eqn. (4) we define the mean momentum or expectation value of the momentum as

$$\langle \vec{P} \rangle = m\frac{d\langle \vec{x} \rangle}{dt} = \int \psi^* (-i\hbar\vec{\nabla})\psi \, d^3x \quad \text{-----} (5)$$

Eqn (5) is the integral of the product of $\psi^*$ and $\vec{P}_{op}\psi$ where $\vec{P}_{op}$ is the operator $(-i\hbar\vec{\nabla})$ represents the momentum in quantum mechanics.

Hence, the expectation value of any dynamical variable $A(\vec{x}, \vec{P})$ is defined as

$$\langle A \rangle = \int \psi^* A_{op} \psi \, d^3x \quad \text{-----} (6)$$

where $A_{op}$ is the operator $A(\vec{x}, -i\hbar\vec{\nabla})$.

$A_{op}$ acts only on the wave function $\psi$ standing to its right. When the wave function is not normalized then

$$\langle A \rangle = \frac{\int \psi^* A_{op} \psi \, d^3x}{\int \psi^* \psi \, d^3x} \quad \text{-------} (7)$$

Now, differentiating eqn. (5) we can get

$$\frac{d\langle \vec{P} \rangle}{dt} = -\langle \vec{\nabla} V(\vec{x}, t) \rangle \quad \text{-----} (8)$$

since, $\langle \vec{P} \rangle = m\frac{d\langle \vec{x} \rangle}{dt}$ is similar to Newton's equation of motion. The expected value of R.H.S of eqn (8) can be written as $-\left[\vec{\nabla} V(\vec{x}, t)\right]_{\vec{x} = \langle \vec{x} \rangle}$.

The difference between this expression $\vec{\nabla}V$ at $\langle \vec{x} \rangle$ and the average of $\vec{\nabla}V$ is small when the size of the wave packet is small. In this limit, the overall motion of the quantum wave packet is well approximated by classical mechanics. This statement is known as Ehrenfest's theorem.

## * Admissibility conditions on the wave function:-

1. The wave function $\psi$ should be finite and single valued everywhere.
2. The wave function $\psi$ and its first partial derivatives $\frac{\partial \psi}{\partial x}$, $\frac{\partial \psi}{\partial y}$ and $\frac{\partial \psi}{\partial z}$ should be continuous functions of $\vec{x}$, for all $\vec{x}$.
3. At any point where the potential $V$ makes a sudden jump of infinite magnitude, $\frac{\partial \psi}{\partial x}$ has a finite discontinuity but $\psi$ remains continuous.