Unit - II

Schrodingee's Equation :-

It is an equation that describe the behaviouge of the wave function associated with the atomic particles.

In 1926, schroedingee using de-Broglie's idea of matteg waves developed a gegorous mathematical theogy which has geceived the name of wave mechanics. The essential feature of this theory is the incorporation of the expression foe the de-Broglie's wavelength into the general classical wave equation. By this means, a wave equation foe a moving paeticle is deeived which is known as schroedingee's fundamental wave equation.

① Time Independent schrodingee equation or schrodingee's Equation : steady - state form

According to de-Broglie theogy, a paeticle of mass m is always associated with a wave whose wavelength is given by -

$$\lambda = \frac{h}{mv} \quad ---- (1)$$

If the paeticle has wave propeeties. It is expected that theee should be some soet of wave equation which describes the behaviode of the paeticle. Consideg a system of stationaeg waves associated with a paeticle. Let x, y, z be the coodinates of the paeticle and ψ, the wave displacement foe the de-Broglie at any time t. ψ is called the wave function. It is assumed that ψ is finite, single valued and periodic

function. The classical differential equation of a wave motion is -

$$\frac{\partial^2 \psi}{\partial t^2} = v^2 \left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right]$$

$$\frac{\partial^2 \psi}{\partial t^2} = v^2 \nabla^2 \psi \quad \text{---} \quad (ii)$$

Where $\nabla = \frac{\partial}{\partial x} i + \frac{\partial}{\partial y} j + \frac{\partial}{\partial z} k$

& v - is the wave velocity.

The solution of eqn (ii) is

$$\psi = \psi_0 \sin \omega t \quad \text{---} \quad (iii)$$

Where ψ_0 = amplitude

ω - is angular frequency.

Differentiating eqn (iii) twice, we get

$$\frac{\partial \psi}{\partial t} = \omega \psi_0 \cos \omega t$$

$$\therefore \frac{\partial^2 \psi}{\partial t^2} = -\omega^2 \psi_0 \sin \omega t$$

$$\therefore \frac{\partial^2 \psi}{\partial t^2} = -\omega^2 \psi \quad \text{---} \quad (iv) \quad [\because \text{From eqn (iii)}]$$

since $\omega = 2\pi \nu$

where ν - is the frequency

$$\omega = 2\pi \nu \ \& \ \nu = \frac{v}{\lambda} \quad \text{---} \quad (v)$$

where v - is the velocity of particle

Putting eqn (v) in (iv), we get

$$\frac{\partial^2 \psi}{\partial t^2} = -\left(\frac{2\pi v}{\lambda}\right)^2 \psi$$

$$\therefore \frac{d^2\psi}{dx^2} = -\frac{4\pi^2 v^2}{d^2}\psi \quad \text{---(vi)}$$

From eqns (ii) & (vi), we get

$$v^2\nabla^2\psi = -\frac{4\pi^2 v^2}{d^2}\psi$$

$$\therefore \nabla^2\psi + \frac{4\pi^2}{d^2}\psi = 0 \quad \text{---(vii)}$$

we know that from eqn (i)

$$d = \frac{h}{m.v}$$

put this value in eqn (vii), we get

$$\nabla^2\psi + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0 \quad \text{---(viii)}$$

If E and V- be the total & potential energy then K.E.

$$E = T + V$$

$$T = E - V$$

$$\therefore \frac{1}{2}mv^2 = E - V$$

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

$\therefore m^2v^2 = 2m(E-V)$ [∵ multiple by m on both sides]

put this value in eqn (viii), we get

$$\nabla^2\psi + \frac{4\pi^2}{h^2}2m(E-V) = 0$$

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

$$\therefore \nabla^2\psi + \frac{8\pi^2 m}{h^2}[E-V]\psi = 0 \quad \text{--- (IX)}$$

Equation (IX) is known as schrodinger time independent wave equation

since $\hbar = \frac{h}{2\pi}$

$$\therefore h = \hbar \cdot 2\pi$$

substituting this value in eqn (IX), we get

$$\nabla^2\psi + \frac{8\pi^2 m}{\hbar^2 4\pi^2}[E-V]\psi = 0$$

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

The above eqn multiply by $\frac{\hbar^2}{2m}$

$$\therefore \left(\frac{\hbar^2}{2m}\right)\nabla^2\psi + \frac{2m}{\hbar^2} \times \frac{\hbar^2}{2m}[E-V]\psi = 0$$

$$\therefore \left(\frac{\hbar^2}{2m}\right)\nabla^2\psi + (E-V)\psi = 0$$

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

for a free particle $V=0$

put this value in eqn (X) we get

$$\nabla^2\psi + \frac{2mE}{\hbar^2}\psi = 0 \quad \text{--- (XII)}$$

② Schrodinger time dependent wave equation :-

The schrodinger time dependent wave equation may be obtained from schrodinger time independent wave eqn by eliminating E.

In order to derive time dependent wave equation, schrodinger introduced a mathematical function ψ which is a variable quantity associated with the moving particle. This is a complex function of space coordinates of the particle and time. The function ψ is called as a wave function as it characterises debroglie wave associated with particle

The differential equation representing a one-dimensional wave motion is -

$$\frac{\partial^2 \psi}{\partial t^2} = v^2 \nabla^2 \psi \quad \text{---} (1)$$

consider ψ to be a complex function of space co-ordinates of the particle and time the general soln of eqn (1) is -

$$\psi(x, y, z, t) = \psi_0(x, y, z)\, e^{-i\omega t}$$

$$\therefore \psi = \psi_0 e^{-i\omega t} \quad \text{---} (11)$$

diff. w.r.t. t, we have

$$\frac{d\psi}{dt} = \psi_0 (-i\omega) e^{-i\omega t}$$

again diff. w.r.t. t of the above eqn -

$$\frac{d^2\psi}{dt^2} = \psi_0 (-i\omega)(-i\omega) e^{-i\omega t}$$

$$\frac{d\psi}{dt} = \psi_0 (-i\omega) e^{-i\omega t}$$

$$= -i\omega \psi_0 e^{-i\omega t} \quad \text{---} (iii)$$

since $\omega = 2\pi\nu$ $\therefore E = h\nu$ (iv)

$\therefore \nu = E/h$

$$\frac{d\psi}{dt} = -i2\pi\nu\psi \quad [\because \text{from eqn iii}]$$

$$\frac{d\psi}{dt} = -\frac{i2\pi E}{h}\psi \quad \text{---} (v)$$

$\therefore \hbar = \frac{h}{2\pi}$ $\therefore \hbar 2\pi = h$

put this value in eqn (v), we get

$$\frac{d\psi}{dt} = -\frac{2\pi E i}{\hbar 2\pi}\psi$$

$$\frac{d\psi}{dt} = -\frac{iE}{\hbar}\psi$$

$$\boxed{\therefore E\psi = i\hbar \frac{d\psi}{dt}} \quad \text{---} (vi)$$

substituting the value of $E\psi$ in schrodinger time independent wave eqn,

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

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left[i\hbar\frac{\partial\psi}{\partial t} - V\right] = 0$$

$$\nabla^2\psi + \frac{2m}{\hbar^2} i\hbar\frac{\partial\psi}{\partial t} - \frac{2m}{\hbar^2}V = 0$$

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

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

$$-\frac{\hbar^2}{2m}\nabla^2\psi = i\hbar\frac{\partial\psi}{\partial t} - V\psi$$

$$\therefore \frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t}$$

$$-\left[\frac{\hbar^2}{2m}\nabla^2 + V\right]\psi = i\hbar\frac{\partial\psi}{\partial t} \quad \text{---} \quad (v)$$

This equation contains the time and hence is called time-dependent schrodinger equation.

(*) Operators :-

An operator $\hat{O}$ is a mathematical operation which may be applied to a function $f(x)$ which changes the function to another function $g(x)$. This can be represented as

$$\hat{O} f(x) = g(x) \quad \text{---} (1)$$

∴ An operator is a rule by means of which a given function is changed into another function.

$$e.g. \quad \frac{d}{dx}(x^3) = 3x^2 \quad \text{---} (2)$$

i.e. When the differential operator d/dx operates on the function x^3, the function x^3 is changed to another function $(3x^2)$.

$$i.e. \quad \frac{d}{dx} f(x) = f'(x) \quad \text{---} (3)$$

The operators used in quantum mechanics are linear operators. The operator algebra of linear operations as -

(1) Sum of the operators :-

If $\hat{A}$ and $\hat{B}$ are two linear operators then the sum.

$\hat{C} = \hat{A} + \hat{B}$ is also a linear operator

$$i.e. \quad \hat{C}\psi = (\hat{A} + \hat{B})\psi$$

$$= \hat{A}\psi + \hat{B}\psi \quad \text{---} (4)$$

" An operator is a rule which changes a function into another "

(ii) Multiplication of operators :- The multiplication of a linear operator $\hat{A}$ by a constant 'a' gives a linear operator $(a\hat{A})$, i.e.

$$a\hat{A}\psi = (a\hat{A})\psi \quad --$$

$$= (a\hat{A})\psi \quad ----- (5)$$

(iii) Product of two operators :- The product of two operators (say $\hat{A}$ and $\hat{B}$) $\hat{A}.\hat{B}$ need not be necessarily identical to the product $\hat{B}.\hat{A}$. For example-

$$\left(x.\frac{d}{dx}\right) f(x) = x.\frac{df(x)}{dx}$$

& $$\left(\frac{d}{dx}.x\right) f(x) = \frac{d}{dx}[x, f(x)]$$

$$= f(x) + x.\frac{df(x)}{dx}$$

$$\therefore x\frac{d}{dx} \neq \frac{d}{dx}x \quad ---- (6)$$

So in case of product of two operators, the way is most important.

(iv) commutator :- The operator $(\hat{A}\hat{B} - \hat{B}\hat{A})$ is called the commutator of two operators $\hat{A}$ and $\hat{B}$. If $\hat{A}.\hat{B} - \hat{B}\hat{A} = 0$, then the two operators $\hat{A}$ and $\hat{B}$ are called as commuting operators. Thus, for commuting operators,

$$\hat{A}.\hat{B} = \hat{B}.\hat{A} \quad ---- (7)$$

(*) Energy operator :-

The schroedinger wave equation can be expressed as

$$H\psi = E\psi \quad ---- (i)$$

This equation indicates that the operator associated with energy E is Hamiltonian H.

The schrodinger time independent wave equation is -

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

Thus, the time independent schroedinger eqn form of energy operator.

$$\hat{E} = -\frac{\hbar^2}{2m}\nabla^2 + V \quad ---- (iii)$$

The time dependent schrodinger wave equation is -

$$H\psi = i\hbar\frac{\partial\psi}{\partial t} \quad ---- (iv)$$

So the time dependent value of H is given by -

$$\hat{E} = H = i\hbar\frac{\partial}{\partial t} \quad ---- (v)$$

From eqn (iii) & (v), we get.

$$\hat{E} = H = -\frac{\hbar^2}{2m}\nabla^2 + V = i\hbar\frac{\partial}{\partial t} \quad ---- (vi)$$

This is the energy operator.

(2) Momentum operator :-

The Hamiltonian of the system represents the total energy. Hence.

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

$$= \frac{p^2}{2m} + V \quad \text{---} (i)$$

Further $$H = -\frac{\hbar^2}{2m}\nabla^2 + V \quad \text{---} (ii)$$

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

$$\therefore -\frac{\hbar^2}{2m}\nabla^2 = \frac{p^2}{2m}$$

$$-\hbar^2\nabla^2 = \frac{p^2}{2m} \times 2m$$

$$\boxed{\therefore -\hbar^2\nabla^2 = p^2} \quad \text{---} (iii)$$

Let $\hat{p}$ be the operator associated with momentum. Thus -

$$\hat{p}^2 = \frac{\hbar^2}{i^2}\nabla^2 \quad [\because i = \sqrt{-1}]$$

$$\hat{p} = \frac{\hbar}{i}\nabla \quad \text{---} (iv)$$

If p_x, p_y be the components of momentum along x, y, z axes respectively, then.

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

$$\hat{p}_y = \frac{\hbar}{i}\frac{\partial}{\partial y} \quad \& \quad \hat{p}_z = \frac{\hbar}{i}\frac{\partial}{\partial z} \quad \text{---} (v)$$

⊛ K.E. operator :-

we know that $H = K.E + P.E.$

$$\hat{H} = \hat{T} + \hat{P}$$

$$\therefore \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$$

$$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2 \quad \text{---- (i)}$$

⊛ velocity operator :-

$$\hat{T} = \frac{1}{2}m\hat{v}^2 = -\frac{\hbar^2}{2m}\nabla^2$$

$$\hat{v}^2 = -\frac{\hbar^2}{2m}\nabla^2 \quad \text{(iii)}$$

$$= \frac{\hbar^2}{i^2}\frac{\nabla^2}{m^2}$$

$$\hat{v} = \frac{\hbar}{im}\nabla$$

$$\boxed{\hat{V} = \frac{\hbar}{2m}\nabla}$$

2.0
-0.5
1.5

* Probability current Density :-

The wave function is considered to be measure of probability of finding the particle in a certain region of space. From the statistical interpretation of the wave function, As the particle is definitely to be found somewhere in space, it means that probability integral must be unity. on the other hand, it means that wave function must be normalised to unity. However this statement should be true for all the time because the particle is definitely to be found. Hence total probability has to be conserved. It means that $\psi\psi^*$ must be independent of time. i.e. $P = \int_\tau \psi\psi^* \, d\tau$

$$\frac{dP}{dt} = \frac{\partial}{\partial t}\int \psi^*\psi \cdot d\tau = \int \frac{\partial}{\partial t}(\psi^*\psi)\cdot d\tau = 0 \quad \text{--- (1)}$$

The time-dependent schroedinger's wave equation as -

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = -\frac{\hbar}{i}\frac{d\psi}{dt} \quad \text{--- (II)}$$

Its complex conjugate may be as.

$$-\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^* = +\frac{\hbar}{i}\frac{\partial\psi^*}{\partial t} \quad \text{--- (III)}$$

The eqn (II) is multiplied on the left ψ^* and eqn (III) by ψ, we obtain

$$-\frac{\hbar^2}{2m}\psi^*\nabla^2\psi + V\psi\psi^* = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t}\psi^* \quad \text{--- (IV)}$$

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

eqn (v) is substracted from eqn (iv), we get

$$-\frac{\hbar^2}{2m}\psi^*\nabla^2\psi + V\psi\psi^* = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t}\psi^*$$

$$-\frac{\hbar^2}{2m}\psi\nabla^2\psi^* + V\psi\psi^* = +\psi\frac{\hbar}{i}\frac{\partial\psi^*}{\partial t}$$

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

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

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

$$-\frac{\hbar}{2mi}\left[\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right] = \left[\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right] \quad \text{--- (vi)}$$

Now L.H.S. of eqn (i) may be as

$$\frac{\partial\rho}{\partial t} = \int\frac{\partial}{\partial t}\int_v \psi\psi^* d\tau$$

$$\frac{\partial\rho}{\partial t} = \int_v\left[\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right]d\tau \quad \text{--- (vii)}$$

Put this value in eqn (vi), we get

we get

$$\frac{\partial \rho}{\partial t} = -\frac{\hbar}{2mi}\int_v [\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*]\, d\tau \quad \text{— (VIII)}$$

using Green's theorem, it is possible to convert into surface integral as,

$$\frac{\partial \rho}{\partial t} = \frac{-\hbar}{2mi}\int_v [\psi^* \nabla \psi - \psi \nabla^2 \psi^*].d\vec{A} \quad \text{— (IX)}$$

Now a vector $S(r,t)$ is,

$$S(r,t) = \frac{\hbar}{2mi}(\psi^* \nabla \psi - \psi \nabla \psi^*) \quad \text{— (X)}$$

Put this value in eqn (IX), we get

$$\frac{\partial \rho(r,t)}{\partial t} = -\int S.d\vec{A} \quad \text{— (XI)}$$

using Divergence Gauss theorem the above eqn is modified

$$\frac{\partial}{\partial t}\int \rho(r,t).d\tau = -\int_v \text{div}\, S.\, d\tau \quad \text{— (XII)}$$

$$\boxed{\frac{\partial \rho}{\partial t} + \text{div}\, S = 0} \quad \text{— (XIII)}$$

$$\left(\frac{\partial \rho}{\partial t} + \text{div}\, j\right) = 0$$

Eq (XIII) has been found to be analogous to the well known equation of continuity in hydrodynamics as

$$\left(\frac{\partial \rho}{\partial t} + \operatorname{div} j\right) = 0 \quad \text{---} \quad (xiv)$$

where ρ represents the fluid density and j the current density. By eqn (xiii) it means that the changes in fluid density are due to unbalanced flow of current j across the boundaries. Thus, it becomes reasonable to interpret the vector $S(r,t)$ as a probability current density. As eqn (xii) reveals that the changes in probability have been due to the flow of probability current S. Therefore the interpretation of quantity $\psi\psi^*$ as probability density gives rise to the concept of probability.

The increase of the total probability inside a finite volume τ has been attributed to the influx of the probability current across the surface A which is bounding the volume. Hence it is possible to describe the decrease of the probability interms of an outward flow of probability current through the surface. Consequently the decrease or increase of the probability takes place by the change in ψ with time.

From eqn (xii) it can be concluded that if the volume is so large as to be having the particle with certainty when it is corresponding to the total probability of one then the surface is at infinity. If boundary condition is applied on ψ at infinity it is evident that ψ and $\nabla\psi$ have to vanish there. Consequently S has to be vanished and R.H.S. of eqn (xii) has to be zero and it is verified that $\partial/\partial t \int_{\tau\to\infty} \psi^* \psi \cdot d\tau = 0$

④ Eigen values and Eigen Functions :-

Schroedinger's equation will have many solutions. some of them being imaginary which have no significance. The solutions have significance only for the certain values called the eign values of the total energy E.

For an atom, these correspond to the energy values associated with different orbits in the atom. Thus, the existence of various energy levels in an atom as postulated by Bohr is a direct consequence of the wave-mechanical concepts.

"solution of the wave equation for these definite value of E, gives the corresponding values of the wave functions ψ known as eign functions."

The eigen function must satisfy certain conditions in order to have a physical significance. They must have only one value which should be finite and continuous throughout the whole of space of system under consideration i.e. for all possible values of the co-ordinates (x, y, z) including infinity

1. The first Interpretation of ψ :-

The first attempt to this problem was made by schroedinger himself. Interms of charge density. In any electromagnetic wave system ie -

The energy density $\propto A^2$ ---①

where energy density is the energy per unit volume and A the amplitude of the wave.

The number of photons per unit volume is equal to the energy density divided by hν is the energy of photon.

Thus,

No. of photon per unit volume = $\frac{\text{Energy density}}{h\nu}$ ——— (i)

But the number of photons per unit volume is defined as the photo density. It means that

photon density = $\frac{\text{Energy density}}{h\nu} = \frac{A^2}{h\nu}$ ——— (ii)

Thus, we conclude that photon density is proportional to A^2 since $h\nu$ is constant. i.e.

photon density $\propto A^2$ ——— (iii)

If ψ is the amplitude of the matter wave at any point in space, we may consider the particle density (no. of particles per unit volume at the point) to be proportional to $|\psi|^2$. Hence, the square of ψ is a measure of the particle density. If we multiply the particle density by electric charge (e) of the particle, we get the charge density. Therefore, the quantity $|\psi|^2$ is also the measure of charge density.

The interpretation given above led to satisfactory result when wave mechanics was applied to the stable states of the Bohr theory. But certain difficulties arose against this interpretation of ψ i.e.

① The wave packet associated with material particle must in course of time become dissipated so that it might no represent for long the particle concerned.

② consideration of the mutual action of the particles must in course as a collision of the corresponding wave packets in ordinary three-dimensional space leads to very serious difficulties.

The IInd Interpretation of ψ :-

Born (1926) in collaboration with Bohr and Heisenberg's put forward the interpretation of ψ. According to them, $|\psi|^2$ does not measure the particle density or charge density at any point but it is related to the probability of finding the particle at that point at any given moment.

Accordingly, the probability 'p' of finding the electron at the point (x, y, z) is given by

$$p = \psi(x,y,z) \cdot \psi^*(x,y,z)$$

where ψ^* is the complex conjugate of ψ.

As ψ may have imaginary values, one must therefore multiply by complex conjugate in order to make p real.

The probability of finding the electron or particle at any point, may be large small or zero, but it cannot be imaginary. Of course if ψ is real, $\psi^* = \psi$, and the probability p equals to the square of ψ.

Thus, we conclude that ψ must satisfy the following conditions.

a) It must be single valued at each and every point

b) It must not have the value infinite at any point

c) Its absolute values at all points must be such that

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \psi(x,y,z)\,\psi^*(x,y,z)\,dx\,dy\,dz$$

$$= \int \psi^* \psi \cdot d\tau = 1$$

τ is a general symbol for all conditions

As there is one electron it means that the total probability must be one.

⊛ Expectation values :-

According to Max Born, the wave function Ψ has a probabilistic interpretation as it is a measure of the probability amplitude. Hence it becomes necessary to find out the average or expectation values of the dynamical quantities (the space coordinates, momenta and energy) of our interest.

" The expectation or average values of a dynamical quantity is defined as its mathematical average for the result of a single measurement." conversely, it can also be defined as the mathematical average of the result of a large number of measurement made on independent systems.

The expectation values for a function $f(\vec{\varepsilon})$ depending only a space co-ordinates can be expressed as -

$$\langle f(\varepsilon) \rangle = \int P(\vec{\varepsilon})\, f(\vec{\varepsilon})\, d\tau$$

where $d\tau$ being a small volume of element.

$$\langle f(\varepsilon) \rangle = \int \Psi^*(\vec{\varepsilon}, t)\, \Psi(\vec{\varepsilon}, t)\, f(\vec{\varepsilon})\, d\tau \quad \text{---- (i)}$$

Thus the average value of position vector $\vec{\varepsilon}$ becomes

$$\langle \vec{\varepsilon} \rangle = \int \Psi^*(\vec{\varepsilon}, t)\, \vec{\varepsilon}\, \Psi(\vec{\varepsilon}, t)\, d\tau \quad \text{--- (ii)}$$

For the position co-ordinates x, y, z as -

$$\left.\begin{aligned} \langle x \rangle &= \int \Psi^* x \Psi\, d\tau \\ \langle y \rangle &= \int \Psi^* y \Psi\, d\tau \\ \langle z \rangle &= \int \Psi^* z \Psi\, d\tau \end{aligned}\right\} \quad \text{--- (iii)}$$

since the probability density depends on time. These average values are only the function time.

The expectation value of potential energy V, which also a function of position co-ordinate ie.

$$\langle V \rangle = \int \Psi^*(\vec{r},t)\, V(\vec{r},t)\, \Psi(\vec{r},t)\, d\tau \quad \text{— (iv)}$$

Now momentum and energy is

$$\therefore E\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Hence total Energy E as operator operating on Ψ

$$E = i\hbar \frac{\partial}{\partial t} \quad \text{— (v)}$$

$\therefore$ Total Energy = K.E + P.E

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

$$\therefore \langle E \rangle = \left\langle \frac{p^2}{2m} \right\rangle + \langle V \rangle \quad \text{— (vi)}$$

But

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

$$\langle E \rangle = \left\langle -\frac{\hbar^2}{2m}\nabla^2 \right\rangle + \langle V \rangle \quad \text{— (vii)}$$

From eqn (vi) & (vii), we have

$$p^2 = -\hbar^2 \nabla^2$$

$$\therefore p = -i\hbar\nabla \quad \text{— (viii)}$$

$\therefore$ Expectation values of Energy & momentum

$$\left.\begin{aligned} \langle E \rangle &= \int \Psi^* i\hbar \frac{\partial \Psi}{\partial t}\, d\tau \\ \langle p \rangle &= \int \Psi^* (-i\hbar \nabla \Psi)\, d\tau \end{aligned}\right\} \quad \text{— (ix)}$$

The expectation values of the components p_x, p_y & p_z of the momentum can be

$$\langle p_x \rangle = -i\hbar \int \Psi^* \frac{\partial \Psi}{\partial x}\, dx$$

$$\langle p_y \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial y} \, dy$$

$$\langle p_z \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial z} \, dz \quad \Big\} - (X)$$

The wave function is not properly normalized, the average value of a function $f(x)$ of position co-ordinate is

$$\langle f(x) \rangle = \frac{\int \psi^* f(x) \psi \, d\tau}{\int \psi^* \psi \, d\tau} \quad - (X_1)$$

(*) Eigen values and Eigen Functions :-

Let us consider a function $f(x)$, which is such that an operator $\hat{A}$ operating on $f(x)$ gives

$$\hat{A} f(x) = a f(x)$$

$$a = \frac{1}{f(x)} [\hat{A} f(x)] \quad - (I)$$

Where 'a' is a constant, then the function $f(x)$ is called the eign function of the operator the 'a' constant is termed as the eign values of the operator belonging to the eign function $f(x)$ and an equation such as the eqn (I) is called the eigen values equation.

Equation shows that an operator acting on function reproduces the same function multiplied by a constant factor.

For example :

The operand $\sin 4x$ when operated by an operator $\left[-\frac{d^2}{dx^2}\right]$ gives

$$-\frac{d^2}{dx^2} \sin 4x = 16 \sin 4x \quad - (II)$$

we say that the number 16 is an eign values of the operator $\left[-\frac{d^2}{dx^2}\right]$ & the operand $\sin 4x$ is an eign function of the operator. Also the eign value and the eign function belong to each other.

All operators in quantum mechanics have eign functions and eign values. Let us derive some important operators that are valid not only for free particles but also the bound states.

—xox— xox —— xox —— xox ——

The end.