Normalization of wave function:

$|\psi|^2$ or $\psi\psi^*$ gives the probability of finding the particle in a given region of space is 100% or unity. This can be mathematically written as

$$\int |\psi(r,t)|^2 d\tau = 1 \quad \text{--- (1)}$$

$\because d\tau$ = elemental volume of the said region and the integration extends over the entire space.

Eqn. (1) can be rewritten as

$$\int \psi^*(r,t)\,\psi(r,t)\,d\tau = 1 \quad \text{--- (2)}$$

A wave function which satisfies the above eqn is said to be normalized or normalized to unity.

Generally ψ is not a normalized wave function rather it is the solution of a wave function i.e. also $(N\psi)$ is a solution. where N is a constant quantity. The choice of the value of N should be such that the new wave function is a normalized wave function.

For normalization of new wave function, it must satisfy the following requirement i.e.

$$\int N(\psi)^* (N\psi)\, dx\,dy\,dz = 1 \quad \text{where } d\tau = dx\,dy\,dz.$$

or $|N|^2 \int \psi^* \psi \, dx\,dy\,dz = 1 \Rightarrow |N|^2 = \dfrac{1}{\int \psi^*\psi\, dx\,dy\,dz}$.

where $|N|$ is known as normalization const. and $N\psi$ is known as normalized wave function.

Condn of orthogonality :→ If ψ_i and ψ_j are two diff. wave function. both satisfies the soln of wave eqn. then the function will be normalized.

if $\int \psi_i^* \psi_i \, d\tau = 1$ and $\int \psi_j^* \psi_j \, d\tau = 1$.

If the two wave functions ψ_i and ψ_j are such that the integral $\int \psi_i^* \psi_j \, d\tau$ or $\int \psi_j^* \psi_i \, d\tau$ vanishes over the entire space i.e.

$$\int \psi_i^* \psi_j \, d\tau = 0 \quad \text{or} \quad \int \psi_j^* \psi_i \, d\tau = 0$$

where $i \neq j$

Then the wave functions ψ_i and ψ_j are said to be mutually orthogonal.

Eigenvalues and Eigenfunctions:

Schrodinger's eqn. may have many solution. out of these some are imaginary and have no significance. The solutions have significance only for certain values called eigen values of the total energy E. These eigen values corresponds to the energy values associated with the different orbitals in the atom. Thus, according to Bohr's postulated, the different energy levels exist in an atom is the direct consequence of wave mechanical concept. The solution of the wave eqn. at these definite energy values E gives the corresponding values of wave function ψ, known as eigen function.

Only those eigen functions have physical significance which satisfy the following condn

① They must be single valued fn

② They should be finite

③ They should be continuous throughout the entire space under consideration.

Example-: Let ψ be a well behave fn of the state of the system and let this be operated on by the operator $\hat{A}$ such that a satisfies the equation

$$\hat{A}\psi(x) = \lambda\psi(x) \quad \text{—— ①}$$

Then we say that λ is an eigenvalue of the operator $\hat{A}$ and ~~operator~~ operand $\psi(x)$ is an eigen function of $\hat{A}$. The eigenvalue λ and the eigen function $\psi(x)$ of operator $\hat{A}$ belong to each other.

The above eqn. ① is termed as eigenvalue equation for the operator $\hat{A}$.

where r is an observable

r_{op} is the operator associated with the observable.

$d^3 r$ is the volume element.

Thus eqn (1) can be rewritten as

$$\langle r \rangle = \frac{\int \psi^*(r,t)\, r\, \psi(r,t)\, d^3 r}{\int \psi^*(r,t)\, \psi(r,t)\, d^3 r} \quad \text{-----} \quad (2)$$

If ψ is normalized, then

$$\langle r \rangle = \int \psi^*(r,t)\, r\, \psi(r,t)\, d^3 r \quad \text{-----} \quad (3)$$

because $\int \psi^*(r,t)\, \psi(r,t)\, d^3 r = 1$

Thus the expectation value of position vector is

$$\langle r \rangle = \int_{-\infty}^{+\infty} \psi^*(r,t)\, r\, \psi(r,t)\, d^3 r \quad \text{-----} \quad (4)$$

Similarly for momentum the expectation value is

$$\langle P \rangle = \int_{-\infty}^{+\infty} \psi^* \, p \, \psi \, dr$$

$$= \int_{-\infty}^{+\infty} \psi^* \left(\frac{\hbar}{i} \nabla \psi\right) dr \quad \text{-----} \quad (5)$$

And for energy, the expectation value is

$$\langle E \rangle = \int_{-\infty}^{+\infty} \psi^* \left(i\hbar \frac{\partial}{\partial t}\right) \psi \, dr$$

$$= i\hbar \int_{-\infty}^{+\infty} \psi^* \frac{\partial \psi}{\partial t} \, dr \quad \text{-----} \quad (6)$$

7.12. Observables and Operators

Any physical quantity like energy, momentum, position etc. that can be observed or measured is called observables. Each observable is associated with a definite operator.

e.g. Schrödinger equation $E\psi = H\psi$ informs that the observable E (energy) is associated with operator H called hamiltonian i.e. $E = H$.

An operator is a rule which changes a given function into another function. If the operator A satisfies the condition or rule $A(a_1\psi_1 + a_2\psi_2) = a_1 A\psi_1 + a_2 A\psi_2$, then the operator A is said to be linear. In quantum mechanics operators are linear.

Operators Associated with different observables

Observables	Symbol	Associated operators in Three Dimension	in One Dimension
Energy	E_{op} or H	$-\frac{\hbar^2}{2m}\nabla^2 + V$	$i\hbar\frac{\partial}{\partial t}$
Kinetic energy	T_{op}	$-\frac{\hbar^2}{2m}\nabla^2$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
Potential energy	V_{op}	V	V
Momentum	P_{op}	$\frac{\hbar}{i}\nabla$	$\frac{\hbar}{i}\frac{\partial}{\partial x}, \frac{\hbar}{i}\frac{\partial}{\partial y}, \frac{\hbar}{i}\frac{\partial}{\partial z}$
Velocity	v_{op}	$\frac{\hbar}{im}\nabla$	$\frac{\hbar}{im}\frac{\partial}{\partial x}, \frac{\hbar}{im}\frac{\partial}{\partial y}, \frac{\hbar}{im}\frac{\partial}{\partial z}$
Position	r_{op}	r	$x, y, z.$

7.13. EXPECTATION VALUE:

Any dynamical quantity like position co-ordinates, momenta, energy etc are defined by wave function. According to Born the wave function has probabilistic interpretation. So thus it is essential to calculate the expectation or average value of the dynamical quantity.

Expectation value is defined as the average of a result of a large number of measurements on independent systems.

Mathematically it can be written as

$$\langle r \rangle = \frac{\int P(r,t)\, r_{op}\, d^3r}{\int \psi^*(r,t)\, \psi(r,t)\, d^3r} \qquad (1)$$