T.D.C. Part III^rd^ Chem (Hons)

Paper V^th^

Unit II Wave Mechanics

Postulates of Quantum Mechanics :-

The value of an observable like momentum, energy etc. of a particle are obtained by using certain postulates.

(i) The Physical State of a particle at any time 't' is described completely by a complex wave function $\psi(r, \theta, \phi, t)$. Similarly $\psi(r, \theta, \phi)$ gives the stationary state dependent of time.

(ii) The wave function ψ and its first and second derivatives

$$\frac{d\psi}{dr}, \frac{d\psi}{d\theta}, \frac{d\psi}{d\phi}$$

$$\frac{d^2\psi}{dr^2}, \frac{d^2\psi}{d\theta^2}, \frac{d^2\psi}{d\phi^2}$$

must be ~~contein~~ contenect finite, and single valued for all values the co-ordinates r, θ, ϕ.

(iii) To every Physical observable quantity of a system their corresponds an operator such as —

Variable	operator	operation
x (distance)	$\hat{x}$	$\times x$
t (time)	$\hat{t}$	$\times t$
p_x (momentum)	$\hat{p}$	$\frac{h}{2\pi i}\frac{\partial}{\partial x}$

(iv) The wave function ψ is a solution of the dependent Schrodinger's equation

$$\hat{H}\psi = E\psi$$

where $\hat{H}$ is the Hamiltonian operator given by —

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

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

$V =$ pot. energy.

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

and,

$$\int_{+\infty}^{-\infty} \psi\psi^* \, \partial\tau = 1 \quad \text{(normalisation)}$$

(v) The only possible values of an observable ~~of~~ of a system are the eigen values ~~of~~ λ in the operator equation.

$$\hat{A}\cdot\psi = \lambda\psi$$

where $\hat{A}$ is ~~a~~ the operator for the observable. λ is the well behaved eigen function. Since the observables have real magnitude λ must be real.

(vi) The average or ~~excepected~~ excepected value $\langle A \rangle$ of a physical quantity A given by.

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi \, d\tau}{\int \psi^* \psi \, d\tau} = \int \psi^* \hat{A} \psi \, d\tau$$

where $\hat{A}$ is the operator for the quantity.

and ψ is normaliser

Wavefunction 'ψ' and its Properties :→

The wavefunction ψ is solution of Schrödinger's waveequation. It is a complex wavefunction of the type –

$$\psi = a + ib = e^{ikx}$$

So, that it has a complex conjugate,

$$\psi^* = a - ib = e^{-ikx}$$

and ~~ib~~ $\psi\psi^*$ be real

i.e

$$\psi\psi^* = (a+ib)(a-ib) = a^2 - i^2 b^2$$
$$= a^2 + b^2 = \text{real}$$

$$\psi\psi^* = \psi^2.$$

~~ψ is a~~ The wave function ψ is a three dimensional amplitude function

Properties of ψ :→

The Schrödinger equation is a second order differential equation and has infinite number of solutions. The allowed wavefunctions are those which statisfy the following properties of ψ.

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(i) ψ is single valued i.e for each va[lue] of r, θ, ϕ variables there is only one value of ψ. Thus if θ is variable,

$$\psi(\theta) = \psi(\theta + 2\pi n)$$

where n is an integer

(ii) ψ and its first and second derivati[ves] w.r.t its variables (r, θ, ϕ) are continuous. In other words there c[an] no exist sudden changes in ψ as its variables are change

(iii) ψ must be finite, i.e ψ must vanish at infinity and if ψ be a complex functi[on] then $\psi^* \psi$ vanishes at infinity.

(iv) ψ must be normalised. i.e.

$$\int_{+\infty}^{-\infty} \psi^* \psi \, d\tau = 1$$

This states that probability o[f] finding the particle in volume element $d\tau$ is unity or 100%.

If the above conditi[ons] are satisfied ψ is called a well behaved function or eigen function.