Dr. Vijay Kumar
P.G. Deptt. of Chem.
R.N. College, Hajipur.

P.G. Sem. IInd

Quantum Mechanics
Core Course — VII (physical chemistry)

Postulates of Quantum mechanics :→

Quantitative value of energy, momentum or any physicaly measurable or observable quantity of a system are obtained without solving the Schrödinger wave equation, by using certain postulates, known as postulates of quantum mechanics. These are —

(i) The Physical State of a particle at any time 't' is described compeletely by a complex wavefunction, $\psi(r, t)$. $\psi(r)$ gives the stationary states independent of time, and

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

(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 contineous, finite and single valued for all values of sperical co-ordinates, (r, θ, and ϕ).

(iii) To every Physicaly observable quantity their corre-sponds an operator.

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

(iv) In the operator equation —

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

Where $\hat{A}$ is the operator for the physical quantity, ψ is the well behaved eigen function and λ is the eigen value. Thus the Hamiltonian operator $\hat{H}$ is the operator for energy, and by the operator equation —

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

The value of E is obtained.

Where —

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

and

$$\hat{E} = -\frac{h}{2\pi i}\frac{\partial}{\partial t}$$

(V) The average or expectation value of a quantity is given by —

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

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

If $\int \psi^*\psi \, d\tau = 0$ ~~than~~

then $\langle A\rangle = \int \psi^* \hat{A}\psi \, d\tau = 1$

(vi) A Physicaly observable quantity can be represented by Hermitian operator. i.e

$$\int \psi_1^* \hat{A}\, \psi_2 \, d\tau = \int \psi_2 \hat{A}\, \psi_1^* \, d\tau$$

ψ_1 and ψ_2 are a pair of function representing physical states of a particle.

Scanned by TapScanner

Quantum mechanics.

Commutation :→ If the results of two operations is the same regardless of the sequence in which the operations are performed the two operators are said to commute. i.e

If $\hat{A}\hat{B} f(x) = \hat{B}\hat{A} f(x)$

$\hat{A}$ and $\hat{B}$ commute.

Let of $\hat{A} = \frac{\partial}{\partial x}$ and $\hat{B} = \times x$ then

$$\hat{A}\hat{B} f(x) = \hat{A}\, x f(x)$$

$$= \frac{\partial}{\partial x} x f(x)$$

$$= x f'(x) + f(x) \quad \text{---} \quad (1)$$

and

$$\hat{B}\hat{A} f(x) = x \frac{\partial}{\partial x} f(x)$$

$$= x f' x \quad (2)$$

As (1) and (2) are not equal

$$\hat{A}\hat{B} f(x) \neq \hat{B}\hat{A} f(x)$$

and the operator $\hat{A}$ and $\hat{B}$ do not commute.

Commutator :→ If two operator $\hat{A}$ and $\hat{B}$ commut then —

$$\hat{A}.\hat{B} - \hat{B}\hat{A} = (\hat{A}\hat{B}) = 0$$

Thus behave a new operator $(\widehat{AB - BA})$ which means multiplication with zero

8.12.80

Schrödinger equation using Hamiltonian operator: →

The wave equation for stationary state of a system is —

$$H\psi = E\psi$$

or, $$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V\right\}\psi = E\psi$$

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

or, $$\frac{\hbar^2}{2m}\nabla^2\psi - V\psi = -E\psi \qquad \boxed{\hbar = \frac{h}{2\pi}}$$

or, $$\frac{\hbar^2}{2m}\nabla^2\psi + (E-V)\psi = 0$$

which is schrödinger equation.

Schrödinger equation in operator form

One dimensional schrödinger equation is —

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0$$

or, $$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi - \frac{2m}{\hbar^2}V\psi = 0$$

or, $$\frac{2mE\psi}{\hbar^2} = \frac{2mV\psi}{\hbar^2} - \frac{d^2\psi}{dx^2}$$

or, $$E\psi = V\psi - \frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}$$

or, $$E\psi = \left(-\frac{\hbar^2}{2m}\frac{d}{dx^2} + V\right)\psi$$

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

where $\hat{H} = -\frac{\hbar^2}{2m}\cdot\frac{d}{dx^2} + V$

Scanned by TapScanner