P. G. Sem. IInd Dr. Vijay Kumar

Core course VII Physical chemistry

Quantum mechanics

Hamiltonian operator :→

for expression for total energy of a single particle of mass m is called the Hamiltonian and is denoted by $\hat{H}$. The classical expression

$$\therefore \hat{H} = E + V$$
$$= \frac{1}{2} m v^2 + V$$
$$= \frac{1}{2} \frac{m^2 v^2}{m} + V$$
$$= \frac{p^2}{2m} + V$$

(where
V = P.E of the particle
v = velocity
p = momentum
E = K.E of the particle)

If p_x, p_y and p_z be the component of linear momentum momentum p,

$$p^2 = p_x^2 + p_y^2 + p_z^2$$

and $$\hat{H} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V$$

The momentum operator is

$$\hat{p} = \frac{h}{2\pi i} \frac{\partial}{\partial x}$$
$$= \frac{i h}{2\pi i^2} \frac{\partial}{\partial x}$$
$$= -i \hbar \frac{\partial}{\partial x}$$

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

and $i^2 = -1$

$$\therefore \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2 = \left(-i\hbar \frac{\partial}{\partial x}\right)\left(-i\hbar \frac{\partial}{\partial x}\right) + \left(-i\hbar \frac{\partial}{\partial y}\right)\left(-i\hbar \frac{\partial}{\partial y}\right) + \left(-i\hbar \frac{\partial}{\partial z}\right)\left(-i\hbar \frac{\partial}{\partial z}\right)$$
$$= -\hbar^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$
$$= -\hbar^2 \nabla^2$$
$$= \cancel{-\frac{h^2}{4\pi}} - \frac{h^2}{4\pi^2} \nabla^2$$

$\therefore$ Hamiltonian operator is

$$\hat{H} = -\frac{h^2}{4\pi^2 \cdot 2m} \nabla^2 + V = -\frac{h^2}{8\pi^2 m} \nabla^2 + V$$

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To set up an operator for momentum

An electron moving along x-direction is like a sine wave propagating along the direction for which the wave function may be written as —

$$\psi = A \sin 2\pi x/\lambda$$

where λ = wavelength.

An equivalent form for the time independent wave is —

$$\psi = C e^{\pm 2\pi i x/\lambda}$$

Then,

$$\frac{\partial \psi}{\partial x} = \pm C \frac{2\pi i}{\lambda} e^{\pm 2\pi i x/\lambda}$$

$$= \pm \frac{2\pi i}{\lambda} \psi$$

$$= \pm 2\pi i \psi / h/p \qquad \left(\text{since } \lambda = \frac{h}{p}\right)$$

or, $$p\psi = \pm \frac{h}{2\pi i} \frac{\partial \psi}{\partial x}$$

$$\therefore \hat{p}_x = \pm \frac{h}{2\pi i} \frac{\partial}{\partial x}$$

$\hat{p}_x$ = the linear momentum operator along x-direction.

$$\therefore \hat{p}_x = + \frac{h}{2\pi i} \frac{\partial}{\partial x} \quad \text{and} \quad \hat{p}_x^* = - \frac{h}{2\pi i} \partial/\partial x$$

Similarly,

$$\hat{p}_y = + \frac{h}{2\pi i} \frac{\partial}{\partial y} \quad \text{and} \quad \hat{p}_y^* = - \frac{h}{2\pi i} \frac{\partial}{\partial y}$$

$$\hat{p}_z = + \frac{h}{2\pi i} \frac{\partial}{\partial z} \quad \text{and} \quad \hat{p}_z^* = - \frac{h}{2\pi i} \frac{\partial}{\partial z}.$$

The linear momentum operator is ~~herm~~ hermition.

To prove that linear momentum operator is Hermitian or observable (can be measured).

Since,

$$\int_{-\infty}^{+\infty} \psi_1^* \hat{p} \psi_2 \, dx$$

$$= \int_{-\infty}^{+\infty} \psi_1^* \left(\frac{h}{2\pi i} \frac{\partial}{\partial x}\right) \psi_2 \, dx$$

$$= \frac{h}{2\pi i} \int_{-\infty}^{+\infty} \psi_1^* \frac{\partial}{\partial x} \cdot \psi_2 \, dx$$

$$= \frac{h}{2\pi i} \left[\psi_1^* \psi_2\right]_{-\infty}^{+\infty} - \frac{h}{2\pi i} \int_{-\infty}^{+\infty} \psi_2 \frac{\partial \psi_1^*}{\partial x} d$$

The first term on the right hand side is zer both ψ_1 and ψ_2 vanish at infinity. The sec term on the right hand side can be writt

$$\int_{-\infty}^{+\infty} \psi_2 \cdot \left(\frac{h}{2\pi i} \frac{\partial}{\partial x}\right) \cdot \psi_1^* \, dx$$

$$= \int_{-\infty}^{+\infty} \psi_2 \hat{p} \psi_1^* \, dx.$$

us, the linear momentum operator is hermi hence linear momentum is observable.

operator.

To prove that Hamiltonian is hermitian :→

As,
$$\hat{H} = -\frac{h^2}{8\pi^2 m}\nabla^2 + V$$
$$= -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V$$

If ψ and ϕ be the two wave functions for th operator $\partial^2/\partial x^2$

$$\iiint_{-\infty}^{+\infty} \phi^* \frac{\partial^2}{\partial x^2}\psi . dx . dy . dz.$$

$$= \iint_{-\infty}^{+\infty} \phi^* \frac{\partial \psi}{\partial x} . dy . dz. - \iiint_{-\infty}^{+\infty} \frac{\partial \phi^*}{\partial x} . \frac{\partial \psi}{\partial x} . dx . dy . d$$

ϕ^* vanishes at infinity & $\frac{\partial \psi}{\partial x}$ is finite or ze

i.e $\iint_{-\infty}^{+\infty} \phi^* . \frac{\partial \psi}{\partial x} dy . dz = 0$

$$= -\iiint_{-\infty}^{+\infty} \frac{\partial \phi^*}{\partial x} \cdot \frac{\partial \psi}{\partial x} \, dx. dy. dz. \quad \text{——— (1)}$$

Similarly,

$$\iiint_{-\infty}^{+\infty} \psi \frac{\partial^2}{\partial x^2} \phi^* . dx. dy. dz$$

$$= \iiint_{-\infty}^{+\infty} \frac{\partial \psi}{\partial x} \cdot \frac{\partial \phi^*}{\partial x} . dx. dy. dz. \quad \text{——— (2)}$$

As (1) and (2) are the same,

hence $\frac{\partial^2}{\partial x^2}$ is hermitian

Similarly $\frac{\partial^2}{\partial y^2}$ and $\frac{\partial^2}{\partial z^2}$ are hermitian.

hence $\hat{H} = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V$ being the sum of hermitian operator is hermitian.

<u>express</u> <u>Hamiltonian</u> <u>in the</u> <u>cartesian</u> <u>co-ordinate</u>.

$$\hat{H} = \frac{1}{2m}\left(\hat{p}_x^{\,2} + \hat{p}_y^{\,2} + \hat{p}_z^{\,2}\right) + V$$

$$= \frac{1}{2m}\left\{\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^2 + \left(\frac{h}{2\pi i}\frac{\partial}{\partial y}\right)^2 + \left(\frac{h}{2\pi i}\frac{\partial}{\partial z}\right)^2\right\} + V$$

$$= \frac{1}{2m}\left\{-\frac{h^2}{4\pi^2}\frac{\partial^2}{\partial x^2} - \frac{h^2}{4\pi^2}\frac{\partial^2}{\partial y^2} - \frac{h^2}{4\pi^2}\frac{\partial^2}{\partial z^2}\right\} + V$$

$$= -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V$$

<u>which is the required form</u>