Quantum Mechanics

Lecture #5

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Ehrenfest Theorem:

"Ehrenfest Theorem" (...Bohr's correspondence principle...

Statement :-

- According to Ehrenfest's theorem the classical equations

$$m\frac{d\vec{r}}{dt} = \vec{p} \quad \text{and} \quad \frac{d\vec{p}}{dt} = -\nabla V$$

are also valid in quantum mechanics, provided we replace all the classical quantities by the expectation values of their corresponding quantum mechanical operators.

$\Longrightarrow$ This theorem states that

"The average motion of a wave-packet agrees with the motion of the corresponding classical particle."

Proof :- Ehrenfest proved that if $\langle x \rangle$ and $\langle P_x \rangle$ be the average values of position and momentum respectively, then

Cont.

$$m \frac{d\langle x\rangle}{dt} = \langle P_x \rangle \quad \text{—— (i)}$$

and if V is the P.E of particle

$$\frac{d\langle P_x\rangle}{dt} = -\left\langle \frac{\partial V}{\partial x} \right\rangle \quad \text{—— (ii)}$$

Now we'll prove (i) and (ii) respectively.
Consider the average value of position i-e

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

Diff. w.r.t 't'

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

$$= \int \psi^* \left[\frac{\partial x}{\partial t} + \frac{i}{\hbar}[H, x] \right] \psi \, d\tau$$

$\because$ x is independent of time $\frac{\partial x}{\partial t} = 0$

$$\frac{d\langle x\rangle}{dt} = \int \psi^* \left[\frac{i}{\hbar}[H, x] \right] \psi \, d\tau$$

$$= \frac{i}{\hbar}\int \psi^* [Hx - xH] \psi \, d\tau \quad \text{—— (iii)}$$

where $\hat{H}$ is hamiltonian operator and

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

Put in (iii)

Cont.

$$\because \nabla^2 x\psi = \frac{\partial^2}{\partial x^2} x\psi = \frac{\partial}{\partial x}\left[\frac{\partial}{\partial x}(x\psi)\right] = x\frac{\partial^2\psi}{\partial x^2} + \frac{\partial\psi}{\partial x} + \frac{\partial\psi}{\partial x}$$

$$\frac{d\langle x\rangle}{dt} = \frac{i}{\hbar}\int \psi^*\left[\left(\frac{-\hbar^2}{2m}\nabla^2 + V(x)\right)x - x\left(\frac{-\hbar^2}{2m}\nabla^2 + V(x)\right)\right]\psi\, d\tau$$

$$= \frac{i}{\hbar}\int \left[-\frac{\hbar^2}{2m}\psi^*\nabla^2 x\psi + \psi^* V(x)x\psi + \frac{\hbar^2}{2m}\psi^* x\nabla^2\psi - \psi^* x V\psi\right] d\tau$$

$\because V$ is constt.

$$= \frac{i}{\hbar}\int\left[\frac{-\hbar^2}{2m}\psi^*\left\{x\frac{\partial^2\psi}{\partial x^2} + 2\frac{\partial\psi}{\partial x}\right\} + \frac{\hbar^2}{2m}\psi^* x\frac{\partial^2\psi}{\partial x^2}\right] d\tau$$

$$= \frac{i}{\hbar}\int\left[\frac{-\hbar^2}{2m}\psi^*\cancel{x}\frac{\partial^2\psi}{\partial x^2} - \frac{\hbar^2}{m}\psi^*\frac{\partial\psi}{\partial x} + \frac{\hbar^2}{2m}\psi^*\cancel{x}\frac{\partial^2\psi}{\partial x^2}\right] d\tau$$

$$= \frac{i}{\hbar}\int -\frac{\hbar^2}{m}\psi^*\frac{\partial\psi}{\partial x}\, d\tau$$

$$= -\frac{i\hbar^2}{m\hbar}\int \psi^*\frac{\partial\psi}{\partial x}\, d\tau$$

$$= \frac{1}{m}\int \psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\, d\tau$$

$$= \frac{1}{m}\langle P_x\rangle$$

$$\boxed{m\frac{d\langle x\rangle}{dt} = \langle P_x\rangle}$$

Hence proved.

is eq. bears the same relation b/w expected values of displacement and momentum in classical case.

Cont.

Part II

Let $\langle P_x \rangle = \int \psi^* \hat{P}_x \psi \, d\tau$

Diff. w.r.t 't'

$$\frac{d\langle P_x \rangle}{dt} = \int \psi^* \left[\frac{\partial P_x}{\partial t} + \frac{i}{\hbar} [H, P_x] \right] \psi \, d\tau$$

$$= \int \psi^* \left[\frac{i}{\hbar} [H, P_x] \right] \psi \, d\tau \qquad \because \frac{\partial P_x}{\partial t} = 0$$

$$= \frac{i}{\hbar} \int \psi^* [H P_x - P_x H] \psi \, d\tau \quad \text{——— (iv)}$$

Now as

$$P_x = -i\hbar \frac{\partial}{\partial x} \quad \text{and} \quad \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x).$$

Put in (iv)

$$\frac{d\langle P_x \rangle}{dt} = \frac{i}{\hbar} \int \psi^* \left[\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \left(-i\hbar \frac{\partial}{\partial x} \right) - \left(-i\hbar \frac{\partial}{\partial x} \right) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \right] \psi \, d\tau$$

$$= \frac{i}{\hbar} \int \psi^* \left[\cancel{\frac{i\hbar^3}{2m} \frac{\partial^3}{\partial x^3}} - i\hbar \cancel{\frac{\partial}{\partial x}} V(x) \frac{\partial}{\partial x} - \cancel{\frac{i\hbar^3}{2m} \frac{\partial^3}{\partial x^3}} + i\hbar \frac{\partial}{\partial x} V(x) \right] \psi \, d\tau$$

$$= \frac{i}{\hbar} \int \psi^* \left[-i\hbar \left[V(x) \frac{\partial}{\partial x} - \frac{\partial}{\partial x} V(x) \right] \right] \psi \, d\tau$$

$$= \int \psi^* \left[V(x) \frac{\partial \psi}{\partial x} - \frac{\partial}{\partial x} (V(x) \psi) \right] d\tau$$

Cont.

$$= \int \left[\psi^* V(x) \frac{\partial \psi}{\partial x} - \psi^* V(x) \frac{\partial \psi}{\partial x} - \psi^* \frac{\partial V}{\partial x} \psi \right] d\tau$$

$$= \int - \psi^* \frac{\partial V}{\partial x} \psi \, d\tau$$

So,

$$\boxed{\frac{d\langle P_x \rangle}{dt} = - \left\langle \frac{\partial V}{\partial x} \right\rangle}$$

Hence proved

Parity:

Parity:- "Parity is a property of a wave function that describes its behaviour under inversion of the coordinate system."

It describes the behaviour of eigen function when the coordinates are changed.

The parity operator is defined as

$$\hat{P} f(x) = f(-x)$$

or

$$\hat{P} f(-x) = f(x)$$

f the wavefunction changes by inverting he coordinates then it is Antisymmetrical nd if it does'nt change then symmetrical

Cont.

→ what are eigen values of $\hat{P}$?
let $g(x)$ an eigen function of $\hat{P}$ with eigen value α.

$$\hat{P} g(x) = \alpha g(x)$$
$$\Rightarrow \quad g(-x) = \alpha g(x)$$

Again applying parity $\hat{P}$

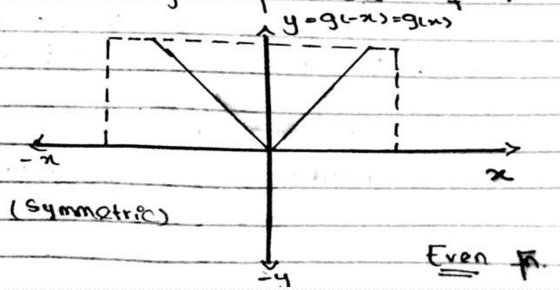
$$\hat{P} g(-x) = \alpha \hat{P} g(x)$$
$$g(x) = \alpha \alpha g(x)$$
$$g(x) = \alpha^2 g(x)$$
$$\Rightarrow \quad \alpha^2 = 1$$
or
$$\alpha = \pm 1 \qquad \text{(It has two eigen values always).}$$

{Case : 1}

when $\alpha = 1$

$$\hat{P} g(x) = \alpha g(x)$$
$$g(-x) = (1) g(x)$$
$$\Rightarrow \quad g(-x) = g(x) \qquad \text{even function}$$

Thus an even function is an eigen function of $\hat{P}$ with eigen value $+1$.



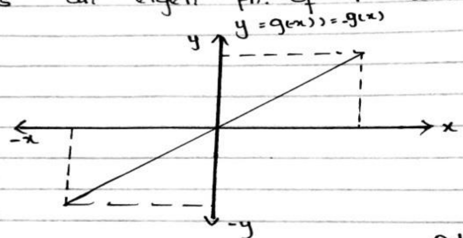
Cont.

Case : II

when $\alpha = -1$

$$\hat{P}g(x) = \alpha g(x)$$
$$g(-x) = (-1)g(x)$$
$$g(-x) = -g(x) \quad \text{odd function}$$

An odd is an eigen Fn. of $\hat{P}$ with eigen value '-1'.



(non-symmetric)

Odd function

Note :- The order of degeneracy of $\alpha = \pm 1$ is infinite.

- Show that $\hat{P}$ commutes with $V(x)$ (symmetrical)?

let $g(x)$ be any arbitrary function of x

$$\hat{P}\,V g(x) = V(-x)\,g(-x)$$
$$= V(x)\,\hat{P}g(x)$$
$$\Rightarrow \quad \hat{P}V g(x) = V(x)\,\hat{P}\,g(x)$$

then

$$PV = VP$$

$\hat{P}$ commutes with $V(x)$.

Cont.

⇒ Show that $\hat{P}$ commutes with $\hat{p}$.

Now Taking

$$[\hat{P}, \hat{p}]\, g(x)$$

$$= \left[\hat{P} \cdot -i\hbar \frac{\partial}{\partial x} g(x) + i\hbar \frac{\partial}{\partial x} \hat{P} g(x)\right]$$

$$= \hat{P}\left(-i\hbar \frac{\partial}{\partial x} g(x)\right) + i\hbar \frac{\partial}{\partial x} g(-x)$$

$$= -i\hbar \frac{\partial}{\partial x} g(-x) + i\hbar \frac{\partial}{\partial x} g(-x)$$

$$= 0$$

Thus

$$[\hat{P}, \hat{p}] = 0$$

⇒ $\hat{P}\hat{p} - \hat{p}\hat{P} = 0$ Hence $\hat{P}$ commutes with $\hat{p}$.

⇒ Show that $\hat{P}$ commutes with $\hat{p}^2$.

As

$$\hat{P}\hat{p}^2 = \hat{P}\hat{p}\hat{p}$$

$$= \hat{p}\hat{P}\hat{p}$$

$$= \hat{p}\hat{p}\hat{P}$$

$$= \hat{p}^2\hat{P}$$

Thus $\hat{P}$ does commute with $\hat{p}^2$.

Cont.

⇒ Show that $\hat{P}$ commutes with $\hat{H}$.
we know that

$$[\hat{P}, \hat{H}] = \hat{P}\hat{H} - \hat{H}\hat{P}$$
$$= \hat{P}\left(\frac{\hat{p}^2}{2m} + V(x)\right) - \left(\frac{\hat{p}^2}{2m} + V(x)\right)\hat{P}$$
$$= \frac{1}{2m}\hat{P}\hat{p}^2 + \hat{P}V(x) - \frac{1}{2m}\hat{p}^2\hat{P} - V(x)\hat{P}$$
$$= \frac{1}{2m}\hat{p}^2\hat{P} + V\hat{P} - \frac{1}{2m}\hat{p}^2\hat{P} - V\hat{P}$$
$$= 0 \quad \because \hat{P} \text{ commutes with } V(x)$$

Thus $\hat{P}$ commutes with $\hat{H}$.

· Show that $\hat{P}$ is constant.
As we know that if $\hat{P}$ cannot depend upon time then

$$\frac{d\langle\hat{P}\rangle}{dt} = \int \frac{\partial\hat{P}}{\partial t} + \frac{i}{\hbar}[H, \hat{P}]\, d\tau$$

Now

$$\frac{\partial\hat{P}}{\partial t} = 0$$

$$[\hat{H}, \hat{P}] = 0$$

So,

$$\langle\hat{P}\rangle = \text{constant}$$

Cont.

→ Thus parity of the state of system is constant motion.

⇒ Show that if $V(x)$ is symmetric about $r=0$ then the eigen fn. satisfying SWQ have define parity.

As

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r) \qquad \because H\psi = E\psi$$

Now change $r \to -r$

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

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

Thus $\psi(r)$ and $\psi(-r)$ satisfy the eigen value eq. Simply we can reduce the above eq.

$$\psi(-r) = K\psi(r) \quad \text{--- (i)} \quad \text{if } r \to -r$$

$$\Rightarrow \psi(r) = K\psi(-r)$$
$$= K[K\psi(r)] \qquad \text{By (i)}$$
$$= K^2\psi(r)$$
$$\Rightarrow K = \pm 1$$

Hence wave fn. $\psi(\pm r)$ have eithe $K=+1$ even or $K=-1$ Odd parity.