K.T.S.P. Mandal's

Hutatma Rajguru Mahavidyalaya

Rajgurunagar, Tal- Khed, Dist. Pune 410505

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Paper II- PHY 362 Quantum Mechanics

Unit-2 Schrodinger's equation (B)

A.B.Kanawade
Associate Professor
Department of Physics

Expectation values:

The average position of a particle needs to be calculated due to inablity in getting the definite value of x coordinate.

Expectation value of x over range x and x+dx is -

$$\langle x \rangle = \frac{\int x P(x,t)\,dx}{\int P(x,t)\,dx}$$

$$= \frac{\int \psi^* x \psi \, dx}{\int \psi^* \psi \, dx}$$

For a normalized wave function, $\int \psi^* \psi \, dx = 1$

$$\therefore \langle x \rangle = \int \psi^* x \psi \, dx$$

For normalised wave functions...

$$\langle f \rangle = \int \psi^* f \psi \, dx$$

$$\langle p_x \rangle = \int \psi^* \left(-i\hbar \frac{\partial}{\partial x}\right) \psi \, dx$$

$$\langle E \rangle = \int \psi^* \left(i\hbar \frac{\partial}{\partial t}\right) \psi \, dx$$

For a dynamical variable expressed in terms of its operator, the expectation value is obtained by using the corresponding operator.

Ehrenfest Theorem:

According to Ehrenfest, Newton's laws of motion in classical physics of the form like

$$m\frac{dx}{dt} = p \quad \text{and} \quad \frac{dp}{dt} = -\frac{dV}{dx}$$

are still valid in quantum mechanics provided that we use the expectation values of the dynamical variables-

① First Theorem:

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

for all components, $m\frac{d\langle \bar{r}\rangle}{dt} = \langle \bar{P}\rangle$

Proof:

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

$$\frac{d}{dt}\langle x\rangle = \int\left(\frac{d\psi^*}{dt}x\psi + \psi^* x\frac{d\psi}{dt}\right)d\tau \quad \text{—(1)}$$

From Schrödinger's time dependent equation

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi$$

$$\& \quad \frac{\partial\psi}{\partial t} = \frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi\right)$$

Its complex conjugate is . .

$$\frac{\partial\psi^*}{\partial t} = -\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^*\right)$$

using these values in equation (1)

$$\frac{d\langle x\rangle}{dt} = \int\left[\left(-\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^*\right)\right)x\psi + \psi^* x\left(\frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi\right)\right)\right]d\tau$$

$$\frac{d}{dt}\langle x\rangle = \frac{\hbar}{2mi}\int_\tau [(\nabla^2\psi^*)x\psi - \psi^* x(\nabla^2\psi)]d\tau$$

$$= \frac{\hbar}{2mi}\left[\int_\tau (\nabla^2\psi^*)x\psi\, d\tau - \int_\tau \psi^* x(\nabla^2\psi)d\tau\right] \quad \text{—(2)}$$

From Green's second theorem...

$$\int_\tau [\psi_1(\nabla^2\psi_2) - \psi_2(\nabla^2\psi_1)]d\tau = \int_s [\psi_1\nabla\psi_2 - \psi_2\nabla\psi_1]\cdot d\bar{s}$$

S is the surface enclosing the volume τ.

Let $\psi_1 = \psi^*$ and $\psi_2 = x\psi$

using this in above equation, — we get

$$\int_\tau [\psi^*\nabla^2(x\psi) - (x\psi)\nabla^2\psi^*]d\tau = \int_s [\psi^*\nabla(x\psi) - (x\psi)\nabla\psi^*]\cdot d\bar{s} \quad \text{—(3)}$$

As $\psi \to 0$ and $\bar{\nabla}\psi \to 0$ at infinity, the above equation gives-

$$\int_\tau [\psi^*\nabla^2(x\psi) - (x\psi)\nabla^2\psi^*]d\tau = 0$$

$$\therefore \int_\tau (x\psi)\nabla^2\psi^* d\tau = \int_\tau \psi^*\nabla^2(x\psi)d\tau \quad \text{—(4)}$$

Using equation (4) in equation (2), we get

$$\frac{d}{dt}\langle x\rangle = \frac{\hbar}{2mi}\left[\int_\tau \psi^*\nabla^2(x\psi)d\tau - \int_\tau \psi^* x(\nabla^2\psi)d\tau\right]$$

$$= -\frac{i\hbar}{2m}\left[\int_\tau \psi^*\nabla^2(x\psi)d\tau - \int_\tau \psi^* x(\nabla^2\psi)d\tau\right] \quad \text{—(5)}$$

But $\nabla^2(x\psi) = \frac{\partial^2(x\psi)}{\partial x^2} + \frac{\partial^2(x\psi)}{\partial y^2} + \frac{\partial^2(x\psi)}{\partial z^2}$

$= 2\frac{\partial \psi}{\partial x} + x\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right)$

$\nabla^2(x\psi) = 2\frac{\partial \psi}{\partial x} + x\nabla^2\psi$

using this in equation (5)

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

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

$\frac{d}{dt}\langle x\rangle = -\frac{i\hbar}{2m}\int_\tau \psi^*\left(2\frac{\partial\psi}{\partial x}\right)d\tau$

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

$\boxed{\frac{d}{dt}\langle x\rangle = \frac{1}{m}\langle P_x\rangle}$

(2) Second theorem:

$$\frac{d\langle P_x\rangle}{dt} = \left\langle -\frac{dV}{dx} \right\rangle$$

For all components, $\frac{d}{dt}\langle \bar{P} \rangle = \langle -\nabla V \rangle$

Proof:
$$\langle P_x \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} d\tau$$

Differentiating w.r.t. t

$$\frac{d}{dt}\langle P_x \rangle = -i\hbar \frac{\partial}{\partial t} \int \psi^* \frac{\partial \psi}{\partial x} d\tau$$

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

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

$$= \int_\tau \left[\left(-i\hbar \frac{\partial \psi^*}{\partial t}\right) \frac{\partial \psi}{\partial x} - \psi^* \frac{\partial}{\partial x} \left(i\hbar \frac{\partial \psi}{\partial t} \right) \right] d\tau \quad \text{---(1)}$$

From schrödinger's time dependent equation

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi$$

and $-i\hbar \frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi^* + V\psi^*$ (Complex Conjugate)

using these in equation (1), we get

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

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

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

$$\therefore \frac{d}{dt}\langle P_x\rangle = \frac{\hbar^2}{2m}\int_\tau \left[\psi^* \nabla^2\left(\frac{\partial\psi}{\partial x}\right) - \nabla^2\psi^* \frac{\partial\psi}{\partial x}\right] d\tau + \int \left[V\psi^* \frac{\partial\psi}{\partial x} - \psi^* \frac{\partial V\psi}{\partial x}\right] d\tau \quad \text{—(2)}$$

Consider the first term and use Green's second theorem

$$\int_\tau \left[\psi^* \nabla^2\left(\frac{\partial\psi}{\partial x}\right) - \nabla^2\psi^* \frac{\partial\psi}{\partial x}\right] d\tau = \int_S \left[\psi^* \nabla\left(\frac{\partial\psi}{\partial x}\right) - \nabla\psi^* \frac{\partial\psi}{\partial x}\right] \cdot d\vec{S}$$

As $\psi \to 0$ and its first order derivative becomes zero, the surface integral is zero.

$$\therefore \int \left[\psi^* \nabla^2\left(\frac{\partial\psi}{\partial x}\right) - \nabla^2\psi^* \frac{\partial\psi}{\partial x}\right] d\tau = 0$$

Using this in equation (2), we get

$$\frac{d}{dt}\langle P_x\rangle = \int_\tau \left[V\psi^* \frac{\partial\psi}{\partial x} - \psi^* \frac{\partial V\psi}{\partial x}\right] d\tau$$

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

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

$$\therefore \frac{d}{dt}\langle P_x\rangle = \int_\tau \psi^* \left(-\frac{\partial V}{\partial x}\right)\psi \, d\tau$$

$$\boxed{\frac{d}{dt}\langle P_x\rangle = \left\langle -\frac{dV}{dx}\right\rangle}$$

$$\therefore \frac{d}{dt}\langle P_x\rangle = \frac{\hbar^2}{2m}\int_\tau \left[\psi^* \nabla^2\left(\frac{\partial \psi}{\partial x}\right) - \nabla^2\psi^* \frac{\partial \psi}{\partial x}\right] d\tau + \int \left[V\psi^* \frac{\partial \psi}{\partial x} - \psi^* \frac{\partial V\psi}{\partial x}\right] d\tau \quad \text{— (2)}$$

Consider the first term and use Green's second theorem

$$\int_\tau \left[\psi^* \nabla^2\left(\frac{\partial \psi}{\partial x}\right) - \nabla^2\psi^* \frac{\partial \psi}{\partial x}\right] d\tau = \int_S \left[\psi^* \nabla\left(\frac{\partial \psi}{\partial x}\right) - \nabla\psi^* \frac{\partial \psi}{\partial x}\right] \cdot d\vec{S}$$

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

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

$$\therefore \frac{d}{dt}\langle P_x\rangle = \int_\tau \psi^* \left(-\frac{\partial V}{\partial x}\right)\psi \, d\tau$$

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

Consider the first term and use Green's second theorem

$$\int_\tau \left[\psi^* \nabla^2\left(\frac{\partial \psi}{\partial x}\right) - \nabla^2\psi^* \frac{\partial \psi}{\partial x}\right] d\tau = \int_S \left[\psi^* \nabla\left(\frac{\partial \psi}{\partial x}\right) - \nabla\psi^* \frac{\partial \psi}{\partial x}\right] \cdot d\bar{S}$$

As $\psi \to 0$ and its first order derivative becomes zero, the surface integral is zero.

$$\therefore \int \left[\psi^* \nabla^2\left(\frac{\partial \psi}{\partial x}\right) - \nabla^2\psi^* \frac{\partial \psi}{\partial x}\right] d\tau = 0$$

Using this in equation (2), we get

$$\frac{d}{dt}\langle P_x\rangle = \int_\tau \left[V\psi^* \frac{\partial \psi}{\partial x} - \psi^* \frac{\partial V\psi}{\partial x}\right] d\tau$$

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

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

$$\therefore \frac{d}{dt}\langle P_x\rangle = \int_\tau \psi^* \left(-\frac{\partial V}{\partial x}\right)\psi \,] d\tau$$

$$\boxed{\frac{d}{dt}\langle P_x\rangle = \left\langle -\frac{dV}{dx}\right\rangle}$$

Problems:

(1) Find the current density if the wave function is

$$\psi(x) = A e^{ikx}$$

Solution:

$$\bar{J} = \frac{\hbar}{2mi}\left[\psi^* \nabla\psi - \psi \nabla\psi^*\right]$$

$$J_x = \frac{\hbar}{2mi}\left[\psi^* \frac{d\psi}{dx} - \psi \frac{d\psi^*}{dx}\right]$$

$$\psi(x) = A e^{ikx} \quad \& \quad \psi^*(x) = A^* e^{-ikx}$$

$$\therefore J_x = \frac{\hbar}{2mi}\left[A^* e^{-ikx} \frac{d}{dx} A e^{ikx} - A e^{ikx} \frac{d}{dx} A^* e^{-ikx}\right]$$

$$= \frac{\hbar}{2mi} AA^*\left[e^{-ikx}(ik)e^{ikx} - e^{ikx}(-ik)e^{-ikx}\right]$$

$$= \frac{\hbar}{2mi} AA^* (2ik)$$

$$= \frac{\hbar k}{m}|A|^2 \qquad \{\text{As } \hbar k = p = mv\}$$

$$= \frac{mv}{m}|A|^2$$

$$J_x = v|A|^2$$

(2) Normalise the wave function $\psi(x) = A e^{-\frac{x^2}{2a^2} + ikx}$

The range is from $-\infty$ to $+\infty$.

Solution:

$$\int \psi \psi^* dx = 1$$

$$\therefore \int A e^{-\frac{x^2}{2a^2} + ikx} \cdot A^* e^{-\frac{x^2}{2a^2} - ikx} dx = 1$$

But general integral $\int_{-\infty}^{+\infty} e^{-\beta x^2} dx = \sqrt{\pi/\beta}$

$$\therefore |A|^2 \sqrt{\frac{\pi}{1/a^2}} = 1$$

$$\therefore |A|^2 a \sqrt{\pi} = 1$$

$$\therefore |A| = \frac{1}{\sqrt{a}\,\pi^{1/4}}$$

$$\therefore \psi(x) = \frac{1}{\sqrt{a}\,\pi^{1/4}} e^{-x^2/2a^2 + ikx}$$

(3) Find the expectation value of momentum and position for a particle having wave function

$$\psi(x,t) = A e^{-\frac{x^2}{2a} + ikx}$$

The range of x is from $-\infty$ to $+\infty$

solution:

$$\int \psi \psi^* dx = 1$$

$$\therefore \int_{-\infty}^{+\infty} A e^{-\frac{x^2}{2a} + ikx} \cdot A^* e^{-\frac{x^2}{2a} - ikx} dx = 1$$

$$\text{or} \quad |A|^2 \int_{-\infty}^{+\infty} e^{-x^2/a} dx = 1$$

$$\therefore \langle x \rangle = \int_{-\infty}^{+\infty} \psi \, x \, \psi^* dx$$

$$\langle x \rangle = |A|^2 \int_{-\infty}^{+\infty} x \, e^{-x^2/a} dx$$

Integral on RHS is odd integral. Its value is zero.

$$\therefore \langle x \rangle = 0$$

$$\langle P_x \rangle = -i\hbar \int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x} dx$$

$$= -i\hbar \int_{-\infty}^{+\infty} A^* e^{-x^2/2a - ikx} \frac{\partial}{\partial x}\left(A e^{-x^2/2a + ikx}\right) dx$$

$$= -i\hbar |A|^2 \int_{-\infty}^{+\infty} e^{-x^2/2a + ikx}\left(-x/a + ik\right) e^{-x^2/2a + ikx} dx$$

$$= -i\hbar |A|^2 \int_{-\infty}^{\infty} \left(e^{-x^2/2a - ikx}\left(-\frac{x}{a}\right) e^{-x^2/2a + ikx} + e^{-x^2/2a - ikx} ik\, e^{-x^2/2a + ikx}\right) dx$$

$$= |A|^2 \frac{i\hbar}{a} \int_{-\infty}^{\infty} x\, e^{-x^2/a} dx + \hbar k |A|^2 \int_{-\infty}^{\infty} e^{-x^2/a} dx$$

First term on RHS is zero.

Using $|A|^2 \int_{-\infty}^{\infty} e^{-x^2/a} dx = 1$ in above, we get

$$\langle P_x \rangle = \hbar k$$