Ehrenfest's theorem

The theorem states that quantum mechanics gives the same results as classical mechanics for a particle for which the average or expectation values of dynamical quantities are involved.

We prove the theorem for one-dimensional motion of a particle by showing that

(a) $\dfrac{d\langle x\rangle}{dt} = \dfrac{\langle P_x\rangle}{m}$

(b) $\dfrac{d\langle P_x\rangle}{dt} = \langle F_x\rangle$

Proof :—

(a) To show that $\dfrac{d\langle x\rangle}{dt} = \dfrac{\langle P_x\rangle}{m}$

Let x be the position coordinate of a particle of mass m at time t.

The expectation value of x is given by

$$\langle x\rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\cdot x\,\psi(x,t)\,dx \quad ; \text{———} (1)$$

Differentiating this equation w.r.t t

$$\frac{d\langle x\rangle}{dt} = \int_{-\infty}^{\infty} x\,\frac{\partial(\psi\psi^*)}{\partial t}\,dx \quad ; \text{———} (2)$$

from Schrodinger wave equations

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi \quad \text{———} (3)$$

and its conjugate

$$-i\hbar\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi^*}{\partial x^2} + V\psi^* \quad \text{———} (4)$$

Multiplying equation (3) by ψ^* and equation (4) by ψ both sides we get

$$i\hbar\,\psi^*\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\psi^*\frac{\partial^2\psi}{\partial x^2} + \psi^* V\psi \quad \text{———} (5)$$

$$-i\hbar\,\psi\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\psi\frac{\partial^2\psi^*}{\partial x^2} + \psi V\psi^* \quad \text{———} (6)$$

Subtracting (6) from equation (5) we get.

$$i\hbar\left(\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right) = -\frac{\hbar^2}{2m}\left[\psi^*\frac{\partial^2\psi}{\partial x^2} - \psi\frac{\partial^2\psi^*}{\partial x^2}\right]$$

or $$i\hbar\frac{\partial}{\partial t}(\psi\psi^*) = -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left[\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right]$$

$$\frac{\partial}{\partial t}(\psi\psi^*) = \frac{i\hbar}{2m}\frac{\partial}{\partial x}\left[\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right] \quad \text{———} (7)$$

Putting equation (7) in (2) we get

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

Integrating R.H.S by parts we get

$$= \frac{i\hbar}{2m}\left[x\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)\right]_{-\infty}^{\infty} - \frac{i\hbar}{2m}\int_{-\infty}^{\infty}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)dx$$

As x approaches either ∞ or $-\infty$, ψ and $\frac{\partial\psi}{\partial x}$ approach zero, and therefore the first term becomes zero.

Hence we get

$$\frac{d\langle x\rangle}{dt} = -\frac{i\hbar}{2m}\int_{-\infty}^{\infty}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)dx; \quad \text{———} (8)$$

The expectation value of P_x is given by

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

$$\therefore \int_{-\infty}^{\infty}\psi^*\frac{\partial\psi}{\partial x}dx = \frac{i}{\hbar}\langle P_x\rangle; \quad \text{———} (9)$$

Similarly,

$$\int_{-\infty}^{\infty}\psi\frac{\partial\psi^*}{\partial x}dx = -\frac{i}{\hbar}\langle P_x\rangle; \quad \text{———} (10)$$

Substituting the values of (9) and (10) in equation (8)

$$\frac{d\langle x\rangle}{dt} = -\frac{i\hbar}{2m}\left[\frac{i}{\hbar}\langle P_x\rangle + \frac{i}{\hbar}\langle P_x\rangle\right]$$

$$\therefore \frac{d\langle x\rangle}{dt} = \frac{\langle P_x\rangle}{m} \quad \text{———} (11)$$

Proved.

(b) To show that

$$\frac{d\langle P_x\rangle}{dt} = \langle F_x\rangle$$

The expectation value of the momentum P_x is given by

$$\langle P_x\rangle = \int_{-\infty}^{\infty}\psi^*(x,t)\frac{\hbar}{i}\frac{\partial}{\partial x}\psi(x,t)\,dx \quad \text{———} (12)$$

$$= \frac{\hbar}{i}\int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x}\,dx \; ; \text{ ——— } (13)$$

Differentiating equation (13) w.r.t t we get

$$\frac{d\langle p_x\rangle}{dt} = \frac{\hbar}{i}\int_{-\infty}^{\infty}\left[\frac{\partial \psi^*}{\partial t}\frac{\partial \psi}{\partial x} + \psi^* \frac{\partial^2 \psi}{\partial x \partial t}\right]dx \; ; \text{ ——— } (14)$$

Now the time-dependent Schrodinger equations for ψ and ψ^* are

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi \; ; \text{ ——— } (15)$$

and its complex conjugate

$$-i\hbar \frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi^*}{\partial x^2} + V\psi^* \; ; \text{ ——— } (16)$$

Differentiating (15) w.r.t x

$$i\hbar \frac{\partial^2 \psi}{\partial x \partial t} = -\frac{\hbar^2}{2m}\frac{\partial^3 \psi}{\partial x^3} + \frac{\partial}{\partial x}(V\psi) \; ; \text{ ——— } (17)$$

We write equation (14) in the form

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

Substituting the expressions for $-i\hbar \frac{\partial \psi^*}{\partial t}$ and $i\hbar \frac{\partial^2 \psi}{\partial x \partial t}$ in this equation, we obtain

$$\frac{d\langle p_x\rangle}{dt} = \int_{-\infty}^{\infty}\left[\left(-\frac{\hbar^2}{2m}\frac{\partial^2 \psi^*}{\partial x^2} + V\psi^*\right)\frac{\partial \psi}{\partial x} - \psi^*\left(-\frac{\hbar^2}{2m}\frac{\partial^3 \psi}{\partial x^3} + \frac{\partial (V\psi)}{\partial x}\right)\right]dx$$

$$= -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\left[\frac{\partial^2 \psi^*}{\partial x^2}\cdot\frac{\partial \psi}{\partial x} - \psi^* \frac{\partial^3 \psi}{\partial x^3}\right]dx + \int_{-\infty}^{\infty}\left[V\psi^* \frac{\partial \psi}{\partial x} - \psi^* \frac{\partial}{\partial x}(V\psi)\right]dx$$

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

$$= -\frac{\hbar^2}{2m}\left[\frac{\partial \psi}{\partial x}\cdot\frac{\partial \psi^*}{\partial x} - \psi^* \frac{\partial^2 \psi}{\partial x^2}\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty}\psi^* \frac{\partial V}{\partial x}\psi\,dx \text{ ——— } (18)$$

As x approaches either ∞ or $-\infty$, ψ and $\frac{\partial \psi}{\partial x}$ approach zero. (4)
Therefore, the first term on the right hand side of equation (18) is zero. The second term represents the expectation value of the differential coefficient of the potential energy V with respect to x i.e

$$\left\langle \frac{\partial V}{\partial x} \right\rangle = \int_{-\infty}^{\infty} \psi^* \frac{\partial V}{\partial x} \psi \, dx$$

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

But $-\frac{\partial V}{\partial x}$ is the classical force F_x

$$\therefore \quad \frac{d\langle P_x \rangle}{dt} = \langle F_x \rangle \quad \text{------} \quad (19)$$

This equation represents Newton's second law of motion. Thus if the expectation values of the dynamical quantities for a particle are considered, quantum mechanics gives the equations of classical mechanics.