Expectation values

The average or expectation value of A of an observable is defined as

$$\langle A \rangle = \int_\tau \psi^*(\vec{r},t)\, \hat{A}\, \psi(\vec{r},t)\, d\tau$$

where, τ is entire vol^m.

1. Position vector $\vec{r}$

then $\langle \vec{r} \rangle = \int_\tau \psi^*(\vec{r},t)\, \vec{r}\, \psi(\vec{r},t)\, d\tau$

2.
- for $\vec{x}$ $= \int_\tau \psi^*(\vec{r},t)\, x\, \psi(\vec{r},t)\, d\tau$
- for $\vec{y}$ $= \int_\tau \psi^*(\vec{r},t)\, y\, \psi(\vec{r},t)\, d\tau$
- for $\vec{z}$ $= \int_\tau \psi^*(\vec{r},t)\, z\, \psi(\vec{r},t)\, d\tau$

3. Potn energy (V)

$$\langle V \rangle = \int_\tau \psi^*(\vec{r},t)\, V\, \psi(\vec{r},t)\, d\tau$$

4. Total energy (E)

$$\langle E \rangle = \int_\tau \psi^*(\vec{r},t)\, E\, \psi(\vec{r},t)\, d\tau$$

$$= \int_\tau \psi^*(\vec{r},t)\, i\hbar \frac{\partial \psi(\vec{r},t)}{\partial t}\, d\tau$$

5. Momentum (P)

$$\langle P \rangle = \int_\tau \psi^*(\vec{r},t)\, (-i\hbar \nabla)\, \psi(\vec{r},t)\, d\tau$$

Similarly x, y, z component same as sl. no. ②.

The Ehrenfest theorem:—

Ehrenfest showed that the classical eqn of motion

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

are also valid in quantum mechanics if all classical quantities be replaced by the expectation values of their corresponding quantum mechanical operators.

Statement:— In quantum mechanics the expectation or average values of observables behave in the same manner as the observables themselves do in classical mechanics.

(a) Proof:—

$$\frac{d\langle x\rangle}{dt} = \frac{d}{dt}\int_{-\infty}^{+\infty} \psi^*(x,t)\, x\, \psi(x,t)\, dx$$

$$= \int_{-\infty}^{+\infty} \psi^*\, x \frac{\partial \psi}{\partial t} dx + \int_{-\infty}^{+\infty} \frac{\partial \psi^*}{\partial t} x \psi\, dx \quad \text{—— (1)}$$

Substituting $\psi(x,t)$ from eqn $\psi(x,t) = u(x,t) + i\,v(x,t)$ in time dependent Schrödinger eqn and then equating the real and imaginary parts on both sides we get,

$$-\hbar\frac{\partial v}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 u + Vu \quad \text{—— (2)}$$

$$\& \quad \hbar\frac{\partial u}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 v + Vv \quad \text{—— (3)}$$

Multiplying eqn (3) by $-i$ and adding to eqn (2) we get,

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

(where, $\psi^* = u - iv$)

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

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

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

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

$$= \left[\psi^* x \frac{\partial \psi}{\partial x}\right]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty}\left[\frac{\partial \psi^*}{\partial x} x \frac{\partial \psi}{\partial x} + \psi^* \frac{\partial \psi}{\partial x}\right] dx$$

$$- \left[\frac{\partial \psi^*}{\partial x} x\psi\right]_{-\infty}^{+\infty} + \int_{-\infty}^{+\infty}\left[\frac{\partial \psi^*}{\partial x} x \frac{\partial \psi}{\partial x} + \frac{\partial \psi^*}{\partial x}\psi\right] dx$$

[since, ψ and $\frac{\partial \psi}{\partial x} \to 0$ as $x \to \infty$ & $-\infty$ then]

$$= \int_{-\infty}^{+\infty}\left[\frac{\partial \psi^*}{\partial x}\psi - \psi^* \frac{\partial \psi}{\partial x}\right] dx$$

again, $$\int_{-\infty}^{+\infty} \frac{\partial \psi^*}{\partial x}\psi\, dx = \left[\psi^* \psi\right]_{-\infty}^{\infty} - \int_{-\infty}^{+\infty} \psi^* \frac{\partial \psi}{\partial x} dx$$

$$= -\int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x} dx$$

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

$\because p_x = -i\hbar \frac{\partial}{\partial x}$

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

In 3-D. $$\boxed{\frac{d\langle \vec{r}\rangle}{dt} = \frac{\langle \vec{p}\rangle}{m}}$$

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(b) Proof of, $\frac{d\langle p_x \rangle}{dt} = -\left\langle \frac{\partial V}{\partial x} \right\rangle$

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

$$= -i\hbar \left(\int_{-\infty}^{+\infty} \psi^* \frac{\partial}{\partial x}\frac{\partial \psi}{\partial t}\, dx + \int_{-\infty}^{+\infty} \frac{\partial \psi^*}{\partial t}\frac{\partial \psi}{\partial x}\, dx \right)$$

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

$$+ \int_{-\infty}^{+\infty} \left(-\frac{\hbar}{2m}\nabla^2\psi^* + V\psi^*\right)\frac{\partial \psi}{\partial x}\, dx$$

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

$$= -\int_{-\infty}^{+\infty} \psi^* \frac{\partial V}{\partial x}\psi\, dx$$

$$= \left\langle -\frac{\partial V}{\partial x} \right\rangle$$

In 3-D

$$\boxed{\frac{d}{dt}\langle p \rangle = \langle -\nabla V \rangle}$$

Different type of operators

1. Linear operator:–

$$\hat{A}(\psi_1 + \psi_2) = \hat{A}\psi_1 + \hat{A}\psi_2$$

2. Commutator operator:–

$$[\hat{A}, \hat{B}] = (\hat{A}\hat{B} - \hat{B}\hat{A})$$

$$\hat{A}\hat{B} = \hat{B}\hat{A}$$

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(3) Hermitian operator :-

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

Eigen function and eigen value:-

$$\hat{A}\psi_n(x) = \lambda_n \psi_n(x)$$

Exple. If $\hat{A} = \frac{d^2}{dx^2}$ & $\psi(x) = ae^{-2x}$

$$\hat{A}\psi(x) = \frac{d^2}{dx^2}\psi(x) = \frac{d^2}{dx^2}(ae^{-2x})$$

$$= 4ae^{-2x}$$

$$= 4\psi(x)$$

∴ 4 is the eigen value.

Condition for well behaved function:-

a) $\psi(x)$ must be single valued and continuous everywhere,

b) $\psi(x)$ must be square-integrable; so that the integral of its modulus squared is finite.

$$\int |\psi|^2 dx = \text{finite}$$

c) Except at some isolated pt. the derivative $\frac{d\psi}{dx}$ should be continuous everywhere,

d) $\psi(x)$ must remain finite and $\psi(x) \to \alpha$ as $x \to \pm\infty$.

Hamiltonian operator:-

$$H = \frac{p^2}{2m} + V$$

$$\hat{H} = \hat{T} + \hat{V}$$

$$= -\frac{\hbar^2}{2m}\nabla^2 + \hat{V} \quad \left(\because p = -i\hbar\nabla\right)$$

$$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$$

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

Parity operator:-

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

$\rightarrow \hat{P}$ is parity operator.

a) Parity operator $\hat{P}$ is Hermitian :

$$\int \psi^*(\vec{r})\, \hat{P}\, \phi(\vec{r})\, d\vec{r}$$

$$= \int \psi^*(\vec{r})\, \phi(-\vec{r})\, d\vec{r} = \int \psi^*(-\vec{r})\, \phi(\vec{r})\, dr$$

$$= \int \left[\hat{P}\,\psi(\vec{r})\right]^* \phi(\vec{r})\, d\vec{r}$$

(b) Eigen values of $\hat{P}$:-

$$\hat{P}\,\psi_\alpha(\vec{r}) = \alpha\,\psi_\alpha(\vec{r})$$

$\rightarrow \alpha$ is an eigen value.

$$\hat{P} f(-\vec{r}) = f(\vec{r})$$

$$\hat{P}\left[\hat{P} f(-\vec{r})\right] = \hat{P} f(\vec{r}) = f(-\vec{r}) = I f(-\vec{r})$$

$$\Rightarrow P^2 f(-\vec{r}) = \hat{I} f(-\vec{r})$$

$\Rightarrow P^2 = \hat{I} \rightarrow$ unit operator.