Ehrenfest's Theorem

According to Ehrenfest's theorem, The expectation values of the position and momentum vectors for a wave packets are formally identical to newton's equations of classical mechanics:

$$\frac{d}{dt}\langle r\rangle = \frac{\langle p\rangle}{m}$$

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

Heisenberg Uncertainity Relation Proof

It is simple to define uncertainity as the root mean square deviation from the mean value:

$$\Delta x = \langle (x-\langle x\rangle)^2\rangle^{1/2}$$

$$\Delta p = \langle (p-\langle p\rangle)^2\rangle^{1/2}$$

Let

$$A = x-\langle x\rangle$$

$$B = p-\langle p\rangle = i\hbar\left[\frac{d}{dx}-\left\langle\frac{d}{dx}\right\rangle\right]$$

Then

$$(\Delta x)^2(\Delta p)^2 = \int_{-\infty}^{\infty}\psi^* A^2\psi\,dx\int_{-\infty}^{\infty}\psi^* B^2\psi\,dx$$

$$= \int_{-\infty}^{\infty}(A^*\psi^*)(A\psi)\,dx\int_{-\infty}^{\infty}(B^*\psi^*)(B\psi)\,dx$$

from the schwarz inequality

$$\int|f|^2dx\int|g|^2dx \geq \left|\int f^* g\,dx\right|^2$$

$$(\Delta x)^2(\Delta p)^2 \geq \left|\int(A^*\psi^*)(B\psi)\,dx\right|^2 = \left|\int\psi^* AB\psi\,dx\right|^2$$

$$\left[\int \psi^* A B \psi \, dx\right]^* = \int \psi A^* B^* \psi^* \, dx$$

$$= \int B^* \psi^* A \psi \, dx$$

$$= \int \psi^* B A \psi \, dx$$

$$(AB - BA)\psi = -i\hbar\left[x\frac{d\psi}{dx} - \frac{d}{dx}(x\psi)\right]$$

$$= -i\hbar\left[x\frac{d\psi}{dx} - x\frac{d\psi}{dx} - \psi\right]$$

$$= +i\hbar\psi$$

Therefore

$$\int \psi^* (AB - BA)\psi \, dx = i\hbar \int \psi^* \psi \, dx$$

$$= i\hbar \quad \text{—} (2)$$

from (1), R.H.S side can be written as

$$\left|\int \psi^* AB\psi \, dx\right|^2 = \left|\int \psi^* \left[\tfrac{1}{2}(AB - BA) + \tfrac{1}{2}(AB + BA)\right]\psi \, dx\right|^2 \quad \text{—} (3)$$

using (2) & (3), we get

$$(\Delta x)^2 (\Delta P)^2 \geq \hbar^2/4$$

$$\Delta x \Delta P \geq \hbar/2$$

Time independent schrodinger equation

There are many Physical Problems in which the potential energy of the particle doesnot depend on time ; $V = V(\vec{r})$ — (1)

In such cases, $\psi(\vec{r},t) = \psi(\vec{r})\,\phi(t)$

Then schrodinger equation becomes

$$i\hbar\,\psi(\vec{r})\frac{d\phi(t)}{dt} = \phi(t)\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r})$$

dividing both side by $\psi(\vec{r})\,\phi(t)$, we get

$$i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = \frac{1}{\psi(\vec{r})}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) \quad \text{— (2)}$$

Thus each side must depend upon a constant 'E' such that,

$$\left.\begin{aligned} E\phi &= i\hbar\frac{d\phi}{dt} \\ \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) &= E\,\psi(\vec{r}) \end{aligned}\right] \quad (3)$$

$$\phi(t) = \exp\left(-\frac{iEt}{\hbar}\right) \quad \text{— (4)}$$

$$\psi(\vec{r},t) = \psi(\vec{r})\exp\left(-\frac{iEt}{\hbar}\right)$$

$$\boxed{H\psi(\vec{r}) = E\,\psi(\vec{r})}$$

where H is the Hamiltonian operator,

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

The operator H acting on the function $\psi(\vec{r})$ gives back the function multiplied by the constant, E.

$$\boxed{H\psi = E\psi}$$

eigen function

eigen value

eigenvalue equation

Degeneracy

- Sometimes it happens that more than one linearly independent eigenfunctions correspond to the same eigenvalue. This type of eigen values are called degenerate.
- If $\psi_1, \psi_2 \,--\, \psi_n$ are linearly independent eigen functions corresponding to eigen value E, then $\psi = c_1\psi_1 + c_2\psi_2 + --- + c_n\psi_n$ is also eigen function corresponding to E.

Important properties

1.) Stationary states

If $P(\vec{r},t) = \psi^*(\vec{r},t)\,\psi(\vec{r},t)$

$$= \psi^*(\vec{r})\, e^{iEt/\hbar}\, \psi(\vec{r})\, e^{-iEt/\hbar}$$

$$= \psi^*(\vec{r})\,\psi(\vec{r})$$

These states are called stationary states. This name is furthur justified by the fact that expectation value of the total energy operator in a state;

$$\int \psi^*(\vec{r},t)\, H\, \psi(\vec{r},t)\, d\vec{r}$$

$$= \int \psi^*(\vec{r},t)\, e^{iEt/\hbar}\, H\, \psi(\vec{r})\, e^{-iEt/\hbar}\, d\vec{r}$$

$$= \int \psi^*(\vec{r})\, E\, \psi(\vec{r})\, d\vec{r}$$

$$= E \int \psi^*(\vec{r})\, \psi(\vec{r})\, d\vec{r}$$

$$= E$$

2.) orthogonality of eigen functions.

let ψ_k and ψ_n be eigen functions such that

$$H\psi_k = E_k\psi_k \quad —(1)$$

$$H\psi_n = E_n\psi_n \quad —(2)$$

Taking complex conjugate

$$(H\psi_n)^* = E_n\psi_n^* \quad —(3)$$

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Prepmultiplying eq (1) by ψ_n^* and postmultiply eq (3) by ψ_k given

$$\psi_n^* (H\psi_k) = E_k \psi_n^* \psi_k \quad -(4)$$

$$(H\psi_n)^* \psi_k = E_n \psi_n^* \psi_k \quad -(5)$$

Substracting eq (5) - (4)

$$(E_n - E_k) \int \psi_n^* \psi_k \, d\vec{r} = \int [\psi_n^* (H\psi_k) - (H\psi_n)^* \psi_k] \, d\vec{r}$$

$$(E_n - E_k) \int \psi_n^* \psi_k \, d\vec{r} = 0$$

since, $E_k \neq E_n$

$$\int \psi_n^* \psi_k \, d\vec{r} = 0$$

This shows that eigen function are orthogonal.

In general

$$\int \psi_k^* \psi_n \, d\vec{r} = \delta_{kn} = \begin{cases} 0, & k \neq n \\ 1, & k = n \end{cases}$$

3.) Parity

The one dimensional schrodinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

Replacing x by $-x$, we get

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(-x)}{dx^2} + V(x)\psi(-x) = E\psi(-x)$$

Case 1 If eigen value is non degenerate then $\psi(x)$ and $\psi(-x)$ can be written as

$$\psi(-x) = c\,\psi(x)$$

Changing the sign of x in this equation, we get

$$\psi(x) = c\,\psi(-x)$$

Combining these two equations,

$$\psi(x) = c^2\,\psi(x)$$

$$c^2 = 1$$

$$c = \pm 1$$

Therefore

$$\psi(-x) = \pm\,\psi(x)$$

even Parity

$$\psi(-x) = \psi(x)$$

odd Parity

$$\psi(-x) = -\psi(x)$$

4) Continuity and Boundary Conditions

1.) The second order schrodinger equation wave function must have single-valued, finite and continous at every point in space.

2.) The wave functions are bounded at large distances in all directions.

3.) If there is an infinite potential step at a surface, then the wave function at the surface is zero and the component of the gradient of the wave function normal to the surface is not determined.