Physical Interpretation of wavefunction ψ

It is an essential requirement in QM that the wavefunc^n associated with a physical system contains all relevant information about the system and its future behavior and thus describes it completely. The finite region in which the wavefunction ψ is appreciably different from zero is called the wave packet.

The probability per unit volume of finding the particle at some position r at any given time t in the wave packet is given by $|\psi|^2$. More exactly the probability of finding the particle in a volume element dv is

$$P(r,t)\,dv = |\psi(r,t)|^2 dv \quad \text{where } P(r,t) = \psi^*(r,t)\psi(r,t) = |\psi|^2$$

is known as position probability density.

The fun^n $\psi(r,t)$ sometimes called probability amplitude of the particle at position r at time t. The total probality of finding the particle in the region is of course unity ie the particle is certainly to be found some where in space

$$\iiint |\psi(r,t)|^2 dv = 1 \Rightarrow \psi(r,t) \text{ satisfying this}$$

condition is known as normalized wave func^n.

Limitation on ψ

(I) ψ must be finite for all values of x, y, z of region

(II) ψ must be single valued ie for each set of values of x, y, z, ψ must have one value

(III) ψ and its derivative $\frac{d\psi}{dr}$ must be continuous in all region

(IV) ψ vanishes at boundaries (at infinity)

Schrodinger Equation for a free particle

We know that a plane propagating matter wave is described by the wave function

$$\psi(x,t) = A e^{i(kx-\omega t)} \quad \text{——} (1)$$

which represents a free particle propagating in +ve x-direction with linear momentum $p = \hbar k$

The position probability density $P(x,t)$ of the particle is

$$P(x,t) = |\psi(x,t)|^2 = A^* e^{-i(kx-\omega t)} \, A e^{i(kx-\omega t)}$$

$$= A^2 \quad \text{——} (2)$$ which is a constant quantity and independent of position x. This implies that the particle is equally probable everywhere in a region where $\psi(x,t)$ is non zero. That also means that the position of the particle which is described by the wavefunction $\psi(x,t)$ is totally uncertain; ie $\Delta x = \infty$ if the wavefunction is extended in an infinite region.

For a particle which is moving freely (ie, no force is acting on the particle) in +ve x-direction, the total energy is

$$E = \frac{p_x^2}{2m} \quad \text{——} (3)$$

This particle is described by a plane propagating matter wave of wave vector $k = \left(\frac{2\pi}{\lambda}\right)$ and angular frequency $\left(\omega = \frac{E}{\hbar}\right)$

$$\psi(x,t) = A e^{i(kx-\omega t)}$$

[We know $E = \hbar\omega$, $p = \hbar k$]

$$\therefore \psi(x,t) = A e^{\frac{i}{\hbar}(p_x x - Et)} \quad \text{——— (4)}$$

Now operating the operator $-i\hbar\frac{\partial}{\partial x} = \hat{p}_x$ twice on $\psi(x,t)$ given in eqn. (4) we get

$$-i\hbar\frac{\partial}{\partial x}\psi(x,t) = (-i\hbar)\frac{\partial}{\partial x}\left\{A e^{\frac{i}{\hbar}(p_x x - Et)}\right\}$$

$$= (-i\hbar)\underbrace{A e^{\frac{i}{\hbar}(p_x x - Et)}}_{\psi(x,t)} \cdot \left(\frac{i}{\hbar}p_x\right)$$

$$\therefore -i\hbar\frac{\partial}{\partial x}\psi(x,t) = p_x\psi(x,t)$$

Again operating the operator $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$ on ~~both si~~ the above eqn. we get

$$-i\hbar\frac{\partial}{\partial x}\left\{-i\hbar\frac{\partial}{\partial x}\psi(x,t)\right\} = -i\hbar\frac{\partial}{\partial x}\left\{p_x\psi(x,t)\right\}$$

or, $$-\hbar^2\frac{\partial^2}{\partial x^2}\psi(x,t) = (-i\hbar)p_x\frac{\partial}{\partial x}A e^{i/\hbar(p_x x - Et)}$$

or, $$-\hbar^2\frac{\partial^2}{\partial x^2}\psi(x,t) = (-i\hbar)p_x A e^{i/\hbar(p_x x - Et)} \cdot \left(\frac{i}{\hbar}p_x\right)$$

$$\therefore -\hbar^2\frac{\partial^2}{\partial x^2}\psi(x,t) = p_x^2\psi(x,t) \quad \text{—— (5)}$$

And operating the operator $\hat{E} = \hat{H} = +i\hbar \frac{\partial}{\partial t}$ on ψ gives

$$i\hbar \frac{\partial}{\partial t}\psi(x,t) = i\hbar \frac{\partial}{\partial t} A e^{\frac{i}{\hbar}(p_x x - Et)}$$

$$\therefore i\hbar \frac{\partial}{\partial t}\psi(x,t) = i\hbar A e^{\frac{i}{\hbar}(p_x x - Et)} \left(-\frac{i}{\hbar}E\right)$$

$$\therefore i\hbar \frac{\partial}{\partial t}\psi(x,t) = E\psi(x,t) \quad \text{— (6)}$$

Hence from eqⁿs. (3) we get $E = \frac{p_x^2}{2m}$. Now we find that the wave function $\psi(x,t)$ given by $\psi(x,t) = A e^{i/\hbar (p_x x - Et)}$ satisfies the partial differential eqⁿ:

$$\boxed{i\hbar \frac{\partial}{\partial t}\psi(x,t) = \frac{p_x^2}{2m}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t)} \quad \text{— (7)}$$

This is known as time-dependent Schrodinger eqⁿ. for a free particle (P.E $V(x) = 0$) moving along x-axis.

In 3-dimensions the generalization of the above eqⁿ. (7) is

$$\boxed{i\hbar \frac{\partial}{\partial t}\psi(r,t) = -\frac{\hbar^2}{2m}\nabla^2\psi(r,t)} \quad \text{— (8)}$$

where $\vec{\nabla} = \frac{\partial}{\partial x}\hat{i} + \frac{\partial}{\partial y}\hat{j} + \frac{\partial}{\partial z}\hat{k}$

and $\nabla^2 = \vec{\nabla}\cdot\vec{\nabla} = \left(\frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}\right)$

Schrodinger equation for a particle in a potential

We know that the operators $\hat{p} = -i\hbar \frac{\partial}{\partial x}$ and $\hat{E} = \hat{H} = i\hbar \frac{\partial}{\partial t}$ when operating on free particle of wave function $\psi(x,t)$ give respectively the values of linear momentum ($p = \hbar k$) and energy ($E = \hbar\omega$) of the particle.

The Schrodinger equation for a free particle is given by

$$i\hbar \frac{\partial}{\partial t}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2}$$

may be written in the form

$$i\hbar \frac{\partial}{\partial t}\psi(x,t) = \frac{\hat{p}^2}{2m}\psi(x,t) \quad \text{——— (9)}$$

Now the operator $\frac{\hat{p}^2}{2m}$ when operating on $\psi(x,t)$ will give the value of the kinetic energy (K.E) of the free particle which is $\left(= \frac{p^2}{2m} = \frac{1}{2}mv^2\right)$ the total energy of the free particle because its potential energy is zero.

For a particle in a potential $V(x)$, the total energy would be $E = \frac{p^2}{2m} + V(x)$. Therefore we can generalize the eq^n (9) by replacing the total energy (K.E) of the free particle by total energy E ($=$ K.E $+$ P.E) of the particle in a potential $V(x)$ as

$$i\hbar \frac{\partial}{\partial t}\Psi(x,t) = \left[\frac{p^2}{2m} + V(x)\right]\Psi(x,t) \quad \text{--- (10)}$$

$$\therefore\ i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x,t) \quad \text{--- (11)}$$

This equation (11) is the famous time-dependent Schrodinger equation for a particle in a potential $V(x)$.

The three dimensional generalization of Schrodinger eqn. is

$$i\hbar \frac{\partial \Psi(r,t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\Psi(r,t) \quad \text{--- (12)}$$

The operator inside the third bracket on the right hand side of eqn (12) plays a very important role. It is called Hamiltonian operator of the particle and is denoted by $\hat{H}$.

i.e. $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \Rightarrow$ Hamiltonian operator

So Schrodinger eqn. can be rewritten as

$$i\hbar \frac{\partial}{\partial t}\Psi(r,t) = \hat{H}\Psi(r,t) \quad \text{--- (13)}$$

with $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \quad \text{--- (14)}$

Expectation value and Operators

We know that the operator $\hat{p} = -i\hbar\frac{\partial}{\partial x}$ operating on a state func^n $\psi(x,t) = Ae^{+i(kx-\omega t)}$ of a free particle gives us the value of linear momentum ($p = \hbar k$) of the particle.

We know that $P(x,t)\,dx = |\psi(x,t)|^2 dx$ is the probability of finding the particle in the length dx about the point x at time t. Therefore, the quantity $\left[-i\hbar\frac{\partial}{\partial x}\right]|\psi(x,t)|^2 dx$ in a way, gives us information about the probable value of the linear momentum of the particle in the region x and $x+dx$ at time t.

And $\int_{-\infty}^{\infty}\left(-i\hbar\frac{\partial}{\partial x}\right)|\psi(x,t)|^2 dx$ or $\int_{-\infty}^{\infty}\psi^*(x,t)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x,t)\,dx$

gives us the information about the probable value or the average value or expectation value of the linear momentum of the particle in state $\psi(x,t)$.

Technically we state it as the value of the x component of the linear momentum (p_x) of a particle in a state $\psi(r,t)$ is equal to the expectation value of the corresponding operator $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$ in the state $\psi(x,t)$ that is

$$p_x = \langle\hat{p}_x\rangle = \int_{-\infty}^{\infty}\psi^*(x,t)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x,t)\,dx \qquad (15)$$

p_x: value of the x component of linear momentum

$\langle\hat{p}_x\rangle$: expectation value of the corresponding operator in the state $\psi(x,t)$.

Any physical quantity (eg position, momentum, energy) that can be measured experimentally is known as observables.

Thus the value of 'A' of any observable in state $\psi(r,t)$ is obtained as the expectation value of the corresponding operator $\hat{A}$ in state $\psi(r,t)$, that is

$$A = \langle \hat{A} \rangle = \int_{-\infty}^{\infty} \psi^*(r,t)\, \hat{A}\, \psi(r,t)\, dr \quad \text{—— (16)}$$

The observables are represented by hermitian operators which have real eigenvalues.

Probability Current Density : Equation of Continuity

In quantum mechanics, wave function is not a physical wave function like water wave, sound wave etc. It is probability wave function.

We know that wave func^n must be square integrable and therefore can be normalized to unity ie, it satisfies the condition

$$\int |\psi(r,t)|^2 dr = \int \rho(r,t)\, dr = 1 \quad \text{—— (17)}$$

Here the integral extends over all space where the wave function of the particle $\psi(r,t)$ is nonzero. The wavefunc^n is normalized to unity at time t, and it remains normalized to unity at all times. The square of the wavefunc^n $|\psi(r,t)|^2$ is is defined as the position probability density. And this requires that the probability of finding the particle somewhere must remain unity at all times. So the total probability is conserved at all times, that is

$$\frac{\partial}{\partial t}\int |\psi(r,t)|^2 dr = \frac{\partial}{\partial t}\int \rho(r,t)\, dr = 0 \quad \text{— (18)}$$

Let us now consider the three dimensional time dependent Schrodinger equation and its complex conjugate

$$i\hbar \frac{\partial}{\partial t}\psi(r,t) = -\frac{\hbar^2}{2m}\nabla^2\psi(r,t) + V(r)\,\psi(r,t) \rightarrow (19)$$

and its complex conjugate

$$-i\hbar \frac{\partial}{\partial t}\psi^*(r,t) = -\frac{\hbar^2}{2m}\nabla^2\psi^*(r,t) + V(r)\,\psi^*(r,t) \rightarrow (20)$$

Multiplying eq^n (19) from left by ψ^* and eq^n (20) by ψ we get

$$i\hbar\,\psi^*\frac{\partial}{\partial t}\psi = -\frac{\hbar^2}{2m}\psi^*\nabla^2\psi + V(r)\,\psi^*\psi \quad \text{— (21)}$$

and $$-i\hbar\,\psi\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\psi\,\nabla^2\psi^* + V(r)\,\psi\psi^* \quad \text{— } \boxed{21}$$

Taking the difference of these two eq^{n}s. we have

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

or, $-i\hbar\left(\psi^*\frac{\partial\psi}{\partial t}+\psi\frac{\partial\psi^*}{\partial t}\right)=\frac{\hbar^2}{2m}\left(\psi^*\nabla^2\psi-\psi\nabla^2\psi^*\right)$ (24)

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

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

or, $\frac{\partial}{\partial t}(\psi^*\psi)=-\frac{\hbar}{2mi}\vec{\nabla}\cdot\left[\psi^*(\vec{\nabla}\psi)-(\nabla\psi^*)\psi\right]$

or, $\frac{\partial}{\partial t}(\psi^*\psi)=-\vec{\nabla}\cdot\vec{J}(r,t)$

or, $\frac{\partial\rho}{\partial t}+\vec{\nabla}\cdot\vec{J}=0$ —— (23)

where $\psi^*\psi=\rho$ is known as charge probability density

and $\vec{J}(r,t)=-\frac{\hbar^2}{2mi}\left[\psi^*\vec{\nabla}\psi-(\vec{\nabla}\psi^*)\psi\right]$ is —— (24)

known as current probability density.

The relation in eq^n (23) is the familiar form of equation of continuity.

It can be shown that

$$\vec{J}(r,t) = \left| \frac{\hbar}{2mi} \left[\psi^*(\nabla\psi) - (\nabla\psi^*)\psi \right] \right|$$

$$= \frac{\hbar}{2mi} \left[A^* e^{-i(kx-\omega t)} \frac{\partial}{\partial x} \left\{ A e^{i(kx-\omega t)} \right\} - \frac{\partial}{\partial x} \left\{ A^* e^{-i(kx-\omega t)} \right\} . A e^{i(kx-\omega t)} \right]$$

$$= \frac{\hbar}{2mi} (ik) \left[\psi^*\psi + \psi^*\psi \right]$$

$$= \frac{\hbar k}{2m} 2\psi^*\psi = \frac{p}{m}(\psi^*\psi) = v\rho$$

$$\therefore \boxed{\vec{J} = \rho\vec{v}} \quad \text{where } \vec{v} = \frac{\vec{p}}{m} \text{ and } \rho = \psi\psi^* \longrightarrow (25)$$

$= \text{position prob. density}$

Probability Conservation and Hermiticity of the Hamiltonian :—

We know that the total probability of finding the particle somewhere at all time is conserved

i.e, $$\frac{\partial}{\partial t} \int_{-\infty}^{\infty} P(r,t)\, dr = 0 \quad \left[\text{Since } \int_{-\infty}^{\infty} P(r,t)\, dr = 1 \right] \quad \text{—— (26)}$$

This may be obtained in terms of the Hamiltonian operator $\hat{H}$. For this we consider the time dependent Schrodinger equation and its complex conjugate

$$i\hbar \frac{\partial}{\partial t}\psi(r,t) = \hat{H}\,\psi(r,t) \quad \text{—— (27)}$$

and $$-i\hbar \frac{\partial}{\partial t}\psi^*(r,t) = \hat{H}\,\psi^*(r,t) \quad \text{—— (28)}$$

Let us start with the L.H.S of eq^n. (26)

$$\frac{\partial}{\partial t}\int \rho(r,t)\,dr = \frac{\partial}{\partial t}\int \psi^*(r,t)\,\psi(r,t)\,dr$$

$$= \int\left[\psi^*\left(\frac{\partial \psi}{\partial t}\right) + \left(\frac{\partial \psi^*}{\partial t}\right)\psi\right] dr$$

using eq^{n}s. (27) and (28) we get

$$\frac{\partial}{\partial t}\int \rho(r,t)\,dr = \int\left[\psi^*\left(\frac{\hat{H}}{i\hbar}\psi\right) + \left(\frac{\hat{H}}{-i\hbar}\psi^*\right)\psi\right] dr = 0$$

$$= \frac{1}{i\hbar}\int\left[\psi^*(\hat{H}\psi) - (\hat{H}\psi)\psi\right] dr = 0$$

So we get $$\int \psi^*(\hat{H}\psi)\,dr = \int(\hat{H}\psi^*)\psi\,dr \quad \text{—— (29)}$$

Operators which satisfy the condition given in eq^n (29) are called Hermitian operators. It is clear that Hamiltonian operator $\hat{H} = -\frac{\hbar^2\nabla^2}{2m} + V(r)$ where $V(r)$ is a real potential is a Hermitian operator