Wave function

The quantity with which Quantum Mechanics is concerned is the wave function of a body.

Wave function, ψ is a quantity associated with a moving particle. It is a complex quantity.

$|\Psi|^2$ is proportional to the probability of finding a particle at a particular point at a particular time. It is the probability density.

$$|\psi|^2 = \psi^* \psi$$

ψ is the probability amplitude.

Thus if $\psi = A + iB$ then $\psi^* = A - iB$

$$\Rightarrow |\psi|^2 = \psi^* \psi = A^2 - i^2 B^2 = A^2 + B^2$$

Normalization

$|\Psi|^2$ is the probability density.

The probability of finding the particle within an element of volume $d\tau$

$$|\psi|^2 \, d\tau$$

Since the particle is definitely be somewhere, so

$$\int_{-\infty}^{\infty} |\psi|^2 \, d\tau = 1 \qquad \therefore \text{ Normalization}$$

A wave function that obeys this equation is said to be normalized.

Properties of wave function

1. It must be finite everywhere.
   If ψ is infinite for a particular point, it mean an infinite large probability of finding the particles at that point. This would violates the uncertainty principle.

2. It must be single valued.
   If ψ has more than one value at any point, it mean more than one value of probability of finding the particle at that point which is obviously ridiculous.

3. It must be continuous and have a continuous first derivative everywhere.
   $$\frac{\partial\psi}{\partial x}, \frac{\partial\psi}{\partial y}, \frac{\partial\psi}{\partial z} \quad \text{must be continuous}$$

4. It must be normalizable.

Schrodinger's time independent wave equation

One dimensional wave equation for the waves associated with a moving particle is

$$\psi(x,t) = Ae^{\frac{-i}{\hbar}(Et-px)} \text{ and } \psi(x,t=0) = Ae^{\frac{2\pi i}{\lambda}(x)}$$

where

ψ is the wave amplitude for a given x.

A is the maximum amplitude.

λ is the wavelength

From (i)

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2}\psi \qquad \text{(ii)}$$

$$\lambda = \frac{h}{m_o v}$$

$$\Rightarrow \frac{1}{\lambda^2} = \frac{m_o{}^2 v^2}{h^2} = \frac{2m_o\left(\frac{1}{2}m_o v^2\right)}{h^2}$$

$$\frac{1}{\lambda^2} = \frac{2m_o K}{h^2}$$

where K is the K.E. for the non-relativistic case

Suppose E is the total energy of the particle

and V is the potential energy of the particle

$$\frac{1}{\lambda^2} = \frac{2m_o}{h^2}(E-V) \qquad \text{(iii)}$$

Equation (ii) now becomes

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{4\pi^2}{h^2}2m_o(E-V)\psi$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m_o}{\hbar^2}(E-V)\psi = 0$$

This is the time independent (steady state) Schrodinger's wave equation for a particle of mass m_o, total energy E, potential energy V, moving along the x-axis.

If the particle is moving in 3-dimensional space then

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m_o}{\hbar^2}(E-V)\psi = 0$$

$$\nabla^2\psi + \frac{2m_o}{\hbar^2}(E - V)\psi = 0$$

This is the time independent (steady state) Schrodinger's wave equation for a particle in 3-dimensional space.

For a free particle V = 0, so the Schrodinger equation for a free particle

$$\nabla^2\psi + \frac{2m_o}{\hbar^2}E\psi = 0$$

Schrodinger's time dependent wave equation

Wave equation for a free particle moving in +x direction is

$$\psi = Ae^{\frac{-i}{\hbar}(Et - px)} \qquad \text{(i)}$$

where E is the total energy and p is the momentum of the particle

Differentiating (i) twice w.r.t. x

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\psi \quad \Rightarrow p^2\psi = -\hbar^2\frac{\partial^2\psi}{\partial x^2} \qquad \text{(ii)}$$

Differentiating (i) w.r.t. t

$$\frac{\partial\psi}{\partial t} = -\frac{iE}{\hbar}\psi \quad \Rightarrow E\psi = i\hbar\frac{\partial\psi}{\partial t} \qquad \text{(iii)}$$

For non-relativistic case

E = K.E. + Potential Energy

$$E = \frac{p^2}{2m} + V_{x,t}$$

$$\Rightarrow E\psi = \frac{p^2}{2m}\psi + V\psi \qquad \text{(iv)}$$

Using (ii) and (iii) in (iv)

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

This is the time dependent Schrodinger's wave equation for a particle in one dimension.

Linearity and Superposition

If ψ_1 and ψ_2 are two solutions of any Schrodinger equation of a system, then linear combination of ψ_1 and ψ_2 will also be a solution of the equation..

$$\psi = a_1\psi_1 + a_2\psi_2 \quad \text{is also a solution}$$

Here a_1 & a_2 are constants

Above equation suggests:

(i) The linear property of Schrodinger equation

(ii) ψ_1 and ψ_2 follow the superposition principle

If P_1 is the probability density corresponding to ψ_1 and P_2 is the probability density corresponding to ψ_2

Then $\psi \rightarrow \psi_1 + \psi_2$ due to superposition principle

Total probability will be

$$P = |\psi|^2 = |\psi_1 + \psi_2|^2$$

$$= (\psi_1 + \psi_2)^* (\psi_1 + \psi_2)$$

$$= (\psi_1^* + \psi_2^*)(\psi_1 + \psi_2)$$

$$= \psi_1^*\psi_1 + \psi_2^*\psi_2 + \psi_1^*\psi_2 + \psi_2^*\psi_1$$

$$P = P_1 + P_2 + \psi_1^*\psi_2 + \psi_2^*\psi_1$$

$$P \neq P_1 + P_2$$

Probability density can't be added linearly

Expectation values

Expectation value of any quantity which is a function of 'x' ,say f(x) is given by

$$< f(x) > = \int_{-\infty}^{\infty} f(x) |\psi|^2 dx \qquad \text{for normalized } \psi$$

Thus expectation value for position 'x' is

$$< x > = \int_{-\infty}^{\infty} x |\psi|^2 dx$$

Expectation value is the value of 'x' we would obtain if we measured the positions of a large number of particles described by the same function at some instant 't' and then averaged the results.

Q. Find the expectation value of position of a particle having wave function ψ = ax between x = 0 & 1, ψ = 0 elsewhere.

Solution

$$<x> = \int_0^1 x\,|\psi|^2 dx \quad = a^2 \int_0^1 x^3 dx$$

$$= a^2 \left[\frac{x^4}{4} \right]_0^1$$

$$<x> = \frac{a^2}{4}$$

Operators

(Another way of finding the expectation value)

An operator is a rule by means of which, from a given function we can find another function.

For a free particle

$$\psi = Ae^{\frac{-i}{\hbar}(Et-px)}$$

Then

$$\frac{\partial \psi}{\partial x} = \frac{i}{\hbar} p \psi$$

Here

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x} \qquad \text{(i)}$$

is called the momentum operator

Similarly $$\frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} E\psi$$

Here $$\hat{E} = i\hbar \frac{\partial}{\partial t} \qquad \text{(ii)}$$

is called the Total Energy operator

Equation (i) and (ii) are general results and their validity is the same as that of the Schrodinger equation.

If a particle is not free then

$$\hat{E} = \hat{K.E.} + \hat{U} \qquad \Rightarrow \hat{E} = \frac{\hat{p}^2}{2m_o} + \hat{U}$$

$$i\hbar\frac{\partial}{\partial t} = \frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 + U \qquad \therefore \hat{U} = U$$

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

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

This is the time dependent Schrodinger equation

If Operator is Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U$$

Then time dependent Schrodinger equation can be written as

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

This is time dependent Schrodinger equation in Hamiltonian form.

Eigen values and Eigen function

Schrodinger equation can be solved for some specific values of energy i.e. Energy Quantization.

The energy values for which Schrodinger equation can be solved are called 'Eigen values' and the corresponding wave function are called 'Eigen function'.

Suppose a wave function (ψ) is operated by an operator 'α' such that the result is the product of a constant say 'a' and the wave function itself i.e.

$$\hat{\alpha}\psi = a\psi$$

then

ψ is the eigen function of $\hat{\alpha}$

a is the eigen value of $\hat{\alpha}$

Q. Suppose $\psi = e^{2x}$ is eigen function of operator $\frac{d^2}{dx^2}$ then find the eigen value.

Solution.

$$\hat{G} = \frac{d^2}{dx^2}$$

$$\hat{G}\psi = \frac{d^2\psi}{dx^2} = \frac{d^2}{dx^2}(e^{2x})$$

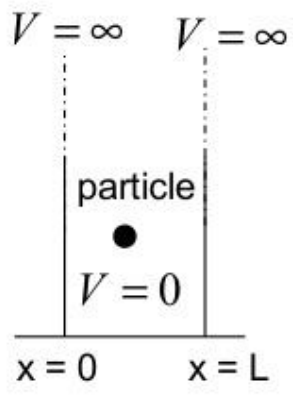
$$\hat{G}\psi = 4e^{2x}$$

$$\hat{G}\psi = 4\psi$$

The eigen value is 4.

Particle in a Box

Consider a particle of rest mass m_o enclosed in a one-dimensional box (infinite potential well).



Boundary conditions for Potential

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < L \\ \infty & \text{for } 0 > x > L \end{cases}$$

Boundary conditions for ψ

$$\Psi = \begin{cases} 0 & \text{for } x = 0 \\ 0 & \text{for } x = L \end{cases}$$

Thus for a particle inside the box Schrodinger equation is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m_o}{\hbar^2}E\psi = 0 \qquad \text{(i)} \qquad \therefore V = 0 \text{ inside}$$

$$\lambda = \frac{h}{p} = \frac{2\pi}{k}$$ (k is the propagation constant)

$$\Rightarrow k = \frac{p}{\hbar} = \frac{\sqrt{2m_o E}}{\hbar}$$

$$\Rightarrow k^2 = \frac{2m_o E}{\hbar^2} \qquad \text{(ii)}$$

Equation (i) becomes

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0 \qquad \text{(iii)}$$

General solution of equation (iii) is

$$\psi(x) = A \sin kx + B \cos kx \qquad \text{(iv)}$$

Boundary condition says ψ = 0 when x = 0

$$\psi(0) = A\sin k.0 + B\cos k.0$$

$$0 = 0 + B.1 \qquad \Rightarrow B = 0$$

Equation (iv) reduces to

$$\psi(x) = A\sin kx \qquad \text{(v)}$$

Boundary condition says ψ = 0 when x = L

$$\psi(L) = A\sin k.L$$

$$0 = A\sin k.L$$

$$A \neq 0 \quad \Rightarrow \sin k.L = 0$$

$$\Rightarrow \sin k.L = \sin n\pi$$

$$kL = n\pi$$

$$k = \frac{n\pi}{L} \qquad \text{(vi)}$$

Put this in Equation (v)

$$\psi(x) = A\sin\frac{n\pi x}{L}$$

When n # 0 i.e. n = 1, 2, 3…., this gives ψ = 0 everywhere.

Put value of k from (vi) in (ii)

$$k^2 = \frac{2m_o E}{\hbar^2}$$

$$\left(\frac{n\pi}{L}\right)^2 = \frac{2m_o E}{\hbar^2}$$

$$\Rightarrow E = \frac{\hbar^2 k^2}{2m_o} \quad = \frac{n^2 h^2}{8m_o L^2} \qquad \text{(vii)}$$

Where n = 1, 2, 3….

Equation (vii) concludes

1. Energy of the particle inside the box can't be equal to zero. The minimum energy of the particle is obtained for n = 1

$$E_1 = \frac{h^2}{8m_o L^2} \qquad \textbf{(Zero Point Energy)}$$

If $E_1 \to 0$ momentum $\to 0$ i.e. $\Delta p \to 0$

$$\Rightarrow \Delta x \to \infty$$

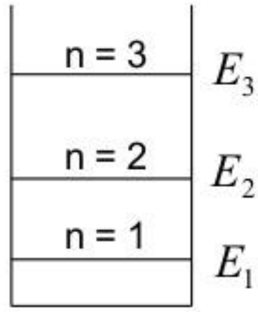
But $\Delta x_{\max} = L$ since the particle is confined in the box of dimension L.

Thus zero value of zero point energy violates the Heisenberg's uncertainty principle and hence zero value is not acceptable.

2. All the energy values are not possible for a particle in potential well.

   Energy is Quantized

3. E_n are the eigen values and 'n' is the quantum number.
4. Energy levels (E_n) are not equally spaced.



$$\psi_n(x) = A \sin \frac{n\pi x}{L}$$

Using Normalization condition

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = 1$$

$$A^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx = 1$$

$$A^2 \left(\frac{L}{2} \right) = 1 \Rightarrow A = \sqrt{\frac{2}{L}}$$

The normalized eigen function of the particle are

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi n x}{L}$$

Probability density figure suggest that:

1. There are some positions (nodes) in the box that will never be occupied by the particle.
2. For different energy levels the points of maximum probability are found at different positions in the box.

$|\psi_1|^2$ is maximum at L/2 (middle of the box)

$|\psi_2|^2$ is zero L/2.