Module – 4

QUANTUM MECHANICS

Heisenberg's Uncertainty Principle:

According to classical mechanics a particle occupies a definite place in space and possesses a definite momentum. If the position and momentum of a particle is known at any instant of time, it is possible to calculate its position and momentum at any later instant of time. The path of the particle could be traced. This concept breaks down in quantum mechanics leading to Heisenberg's Uncertainty Principle

Heisenberg's Uncertainty Principle

Statement:

It is impossible to measure simultaneously both the position and momentum of a particle accurately. If we make an effort to measure very accurately the position of a particle, it leads to large uncertainty in the measurement of momentum and vice versa.

If Δx and ΔP_x are the uncertainties in the measurement of position and momentum of the particle then the uncertainty can be written as

$$\Delta x \cdot \Delta P_x \geq \frac{h}{4\pi}$$

In any simultaneous determination of the position and momentum of the particle, the product of the corresponding uncertainties inherently present in the measurement is equal to or greater than h/4π.

Similarly

1) $\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$ where ΔE and Δt are uncertainties in measurement of energy and time

2) $\Delta L \cdot \Delta \theta \geq \frac{h}{4\pi}$ where ΔL and $\Delta \theta$ are uncertainties in measurement of angular momentum and angular displacement

Application of Uncertainty Principle:

Impossibility of existence of electrons in the atomic nucleus:

According to the theory of relativity, the energy E of a particle is: $E = mc^2 = \frac{m_o c^2}{\sqrt{1-\left(v^2/c^2\right)}}$ $\frac{m^0 c^2}{\sqrt{1 - \frac{v^2}{c^2}}}$

Where 'm_o' is the rest mass of the particle and 'm' is the mass when its velocity is 'v'.

i.e. $E^2 = \frac{m_o^2 c^4}{1-\left(v^2/c^2\right)} = \frac{m_o^2 c^6}{c^2 - v^2}$ …… 1

If '*p*' is the momentum of the particle:

i.e. $$p = mv = \frac{m_o \mathrm{v}}{\sqrt{1-\left(\mathrm{v}^2/c^2\right)}} \quad \frac{m^0 v}{\sqrt{1-\frac{v^2}{c^2}}}$$

$$p^2 = \frac{m_o^2 \mathrm{v}^2 c^2}{c^2-\mathrm{v}^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2 \quad \frac{m^0 v^2 c^2}{c^2 - v^2}$$

Multiply by c² on both side of equation 2

$$p^2 c^2 = \frac{m_o^2 \mathrm{v}^2 c^4}{c^2-\mathrm{v}^2} \quad \frac{m^0 v^2 c^4}{c^2 - v^2} \quad \ldots\ldots\ 3$$

Subtracting equation 2 by equation 1 we have

$$E^2 - p^2 c^2 = \frac{m_o^2 c^4 (c^2-\mathrm{v}^2)}{c^2-\mathrm{v}^2} \quad \frac{m^{02} c^4 (c^2 - v^2)}{(c^2 - v^2)}$$

$$E^2 = p^2 c^2 + m_o^2 c^4 \Rightarrow E^2 = c^2\left(p^2 + m_o^2 c^2\right)$$

$$E = \sqrt{c^2\left(p^2 + m_o^2 c^2\right)} \quad \ldots\ldots\ 4$$

Heisenberg's uncertainty principle states that

$$\Delta x \cdot \Delta p_x \geq \frac{h}{4\pi} \quad \ldots\ldots\ 5$$

The diameter of the nucleus is of the order 10^{-14} m. If an electron is to exist inside the nucleus, the uncertainty in its position Δx must not exceed 10^{-14}m.

i. e. $\Delta x \leq 5\times10^{-15} m$

The minimum uncertainty in the momentum

$$\Delta p_x \geq \frac{h}{4\pi\ \ \Delta x} \geq \frac{h}{4\pi\Delta x} \ \frac{6.63\times10^{-34}}{4\pi\times5\times10^{-15}} \geq 1.1\times10^{-20} \ \frac{6.63*10^{-34}}{4\pi * 10^{-14}} \text{ Ns} \quad ----- \quad 6$$

By considering minimum uncertainty in the momentum of the electron

i.e., $\Delta p_x \geq 1.1\times10^{-20}$ Ns $= p_x$ ----- 7

Now making use of inequality of equation 6 in 3 and Substituting the values of p_x, c and m_o in equation 3, we get

$$E \geq \sqrt{c^2\left(p^2 + m_o^2 c^2\right)}$$

$$E \geq \sqrt{\left(3\times10^8\right)^2\left[\left(1.1\times10^{-20}\right)^2 + \left(9.1\times10^{-31}\right)^2\left(3\times10^8\right)^2\right]}$$

Where $m_o = 9.1 \times 10^{-31}$ kg

If the electron exists in the nucleus then its energy must be

$$E^2 \geq 1.09 \times 10^{-23} \Rightarrow E \geq 3.3 \times 10^{-12} J$$

$$E \geq 20.6 \ MeV$$

The energy must be greater than or equal to 20.6 Mev for an electron to exist inside the nucleus. But it is experimentally measured that the beta particles ejected from the nucleus during beta decay have energies of about 3 to 4 MeV. This shows that electrons cannot exist in the nucleus.

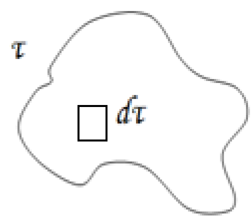
Wave Function (ψ):

A physical situation in quantum mechanics is represented by a function called wave function. It is denoted by ψ. It accounts for the wave like properties of particles. Wave function is obtained by solving Schrodinger equation. To solve Schrodinger equation it is required to know

1) Potential energy of the particle

2) Initial conditions and 3) Boundary conditions.

Physical significance of wave function:



Probability density: If ψ is the wave function associated with a particle, then $|\psi|^2$ is the probability of finding a particle in unit volume. If 'τ' is the volume in which the particle is present but where it is exactly present is not known. Then the probability of finding a particle in certain elemental volume dτ is given by $|\psi|^2 d\tau$. Thus $|\psi|^2$ is called probability density. The probability of finding an event is real and positive quantity. In the case of complex wave functions, the probability density is $|\psi|^2 = \psi^* \psi$ where ψ^* is Complex conjugate of ψ.

Normalization:

The probability of finding a particle having wave function 'ψ' in a volume 'dτ' is '$|\psi|^2 d\tau$'. If it is certain that the particle is present in finite volume 'τ', then

$$\int_0^\tau |\psi|^2 d\tau = 1 \quad \int_0^\tau |\psi|^2 d\tau = 1$$

If we are not certain that the particle is present in finite volume, then

$$\int_{-\infty}^{\infty} |\psi|^2 d\tau = 1$$

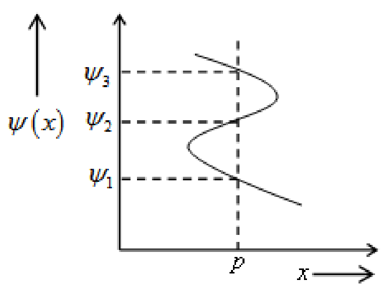
This process is called as normalization. The wave-function with constant value included is called as the normalized wave-function and the value of constant is called normalization factor.

Properties of the wave function:

A system or state of the particle is defined by its energy, momentum, position etc. If the wave function 'ψ' of the system is known, the system can be defined.

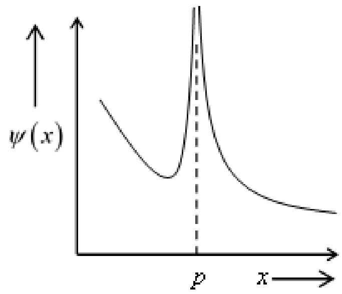
The wave function 'ψ' of the system changes with its state. To find 'ψ' Schrodinger equation has to be solved. As it is a second order differential equation, there are several solutions. All the solutions may not be correct. We have to select those wave functions which are suitable to the system. The acceptable wave function has to possess the following properties:

1) **Ψ is single valued everywhere:**



Consider the function $\psi(x)$ which varies with position as represented in the graph. The function $\psi(x)$ has three values ψ_1, ψ_2 and ψ_3 at x = p. i.e., the probability of finding the particle has three different values at the same location which is not allowed. Thus the wave this wave function is not acceptable.

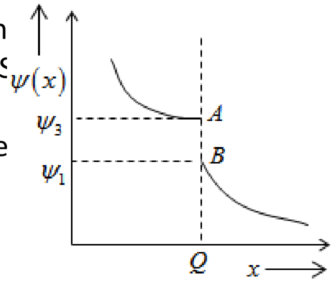
2) Ψ is finite everywhere:



Consider the function $\psi(x)$ which varies with position as represented in the graph. The function $\psi(x)$ is not finite at x =R but $\psi(x) = \infty$. Thus it indicates large probability of finding the particle at a location. It violates uncertainty principle. Thus the wave function is not acceptable.

3) Ψ and its first derivatives with respect to its variables are continuous everywhere:

Consider the function $\psi(x)$ which varies with position as represented in the graph. The function $\psi(x)$ is truncated at x = Q between the points A & B, the state of th o obtain the wave function associated with the system, we have to solve S n. Since it is a second order differential wave equation, the wave function st be continuous at x = Q. As it is a discontinuous wave function, the wave e.



4) For bound states 'ψ' must vanish at potential boundary and outside. If 'ψ*' is a complex function, then ψ* ψ must also vanish at potential boundary and outside.

The wave function which satisfies the above 4 properties are called Eigen functions.

Eigen functions:

Eigen functions are those wave functions in quantum mechanics which possesses the properties they are single valued, Finite everywhere and the wave functions and their first derivatives with respect to their variables are continuous are called Eigen wave functions

Eigen values:

Eigen functions should be such that, the operator operating on it produces back the wave function multiplied by constant, such constant value obtained for a physical observable are called Eigen values

$\hat{A}\psi = \lambda\psi$ here ψ is Eigen wave function and λ is Eigen value

There are two types of Schrodinger equations:

1) The time dependent Schrodinger equation: It takes care of both the position and time variations of the wave function. It involves imaginary quantity i.

The equation is:

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} + V\psi = -\frac{ih}{2\pi}\frac{d\psi}{dt} \quad \frac{-h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2}\frac{-i\hbar}{2\pi}\frac{d\psi}{dt}$$

2) The time independent Schrodinger equation: It takes care of only position variation of the wave function.

The equation is: $$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

Expression for time independent Schrodinger wave equation

Consider a particle of mass 'm' moving with velocity 'v'. The de-Broglie wavelength 'λ' is

$$\lambda = \frac{h}{mv} = \frac{h}{P}$$ ----- 1 where $'mv'$ is the momentum of the particle

The wave equation is given as

$$\Psi = A\,e^{i(kx-\omega t)}$$ ----- 2

Where 'A' is a constant and 'ω' is the angular frequency of the wave. The time independent part in equation 2 is represented as

$$\psi = A\,e^{ikx}$$

Hence equation 2 becomes

$$\Psi = \psi\; e^{-i\omega t}$$ ----- 3

Differentiating equation 3 with respect to t twice

$$\frac{d^2\Psi}{dt^2} = -\omega^2 e^{-i\omega t}\,\psi \qquad \frac{d^2\psi}{dt^2}$$ ----- 4

Differentiating equation 3 with respect to x twice

$$\frac{d^2\Psi}{dx^2} = e^{-i\omega t}\,\frac{d^2\psi}{dx^2} \qquad \frac{d^2\psi}{dt^2}$$ ----- 5

The equation of a travelling wave is given by

$$\frac{\frac{d^2y}{dx^2} = \frac{1}{v^2}\,d^2y}{dt^2} \qquad \frac{d^2y}{dx^2} = \frac{1}{\mathrm{v}^2}\frac{d^2y}{dt^2}$$ Where 'y' is the displacement and 'v' is the velocity

By replacing y with ψ we get the de-Broglie wave associated with the particle as

$$\frac{d^2\Psi}{dx^2} = \frac{1}{\mathrm{v}^2}\frac{d^2\Psi}{dt^2}$$ ------ 6

Substituting equations 4 & 5 in 6, we get

$$e^{-i\omega t}\frac{d^2\psi}{dx^2} = \frac{1}{\mathrm{v}^2} \times -\omega^2 e^{-i\omega t}\,\psi \quad \Rightarrow \frac{d^2\psi}{dx^2} = -\frac{\omega^2}{\mathrm{v}^2}\psi \qquad \frac{d^2\psi}{dx^2} = \frac{-\omega^2}{v^2\psi}$$

But $\omega = 2\pi\nu$ and $\mathrm{v} = \nu\lambda$ where ν is the frequency and 'λ' is the wavelength

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \quad \Rightarrow \frac{1}{\lambda^2} = -\frac{1}{4\pi^2\psi}\frac{d^2\psi}{dx^2}$$ ------ 7

We know that $K.E = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$ ------ 8 $\quad \because \lambda = \frac{h}{p} \Rightarrow \; p = \frac{h}{\lambda}$

Using equation 7 in equation 8

$$K.E = \frac{h^2}{2m}\left[\left(-\frac{1}{4\pi^2\psi}\right)\frac{d^2\psi}{dx^2}\right] = -\frac{h^2}{8\pi^2 m\psi}\frac{d^2\psi}{dx^2}$$ ------ 9

Total Energy E = K.E + P.E

$$E = -\frac{h^2}{8\pi^2 m\psi}\frac{d^2\psi}{dx^2} + V \quad \Rightarrow \quad E - V = -\frac{h^2}{8\pi^2 m\psi}\frac{d^2\psi}{dx^2}$$ Multiply by $\frac{8\pi^2 m}{h^2}\psi$

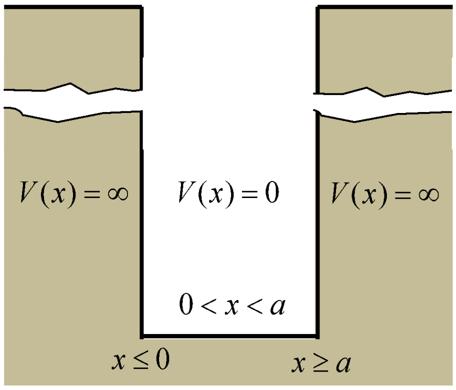
$$\frac{d^2\psi}{dx^2} = -\frac{8\pi^2 m}{h^2}(E - V)\psi$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$ This is the time independent Schrodinger wave equation

Application of Schrodinger wave equation:

Energy Eigen values of a particle in one dimensional, infinite potential well (One dimension potential well of infinite depth) or of a particle in a box.

Consider a particle of a mass 'm' free to move in one dimension along positive x -direction between $x=0$ to $x=a$. The potential energy outside this region is infinite and within the region is zero. The particle is in bound state. Such a configuration of potential in space is called infinite potential well. It is also called particle in a box.



The Schrödinger equation outside the well is

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2 m}{h^2}(E-\infty)\psi=0 \qquad \frac{d^2\psi}{dx^2}+\frac{8m\pi^2}{h^2}(E-v)\psi=0$$

------ (1) $\qquad \because \; V=\infty$

For outside the well, the value of $\psi=0$ & $|\psi|^2=0$. That is particle cannot be found outside the well and also at the walls

The Schrodinger's equation inside the well is:

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2 m}{h^2}E\psi=0$$

---- (2) $\qquad \because \; V=0$

Let $\frac{8m\pi^2}{h^2}E=k^2 \qquad \frac{8\pi^2 m}{h^2}E=k^2$ ------ 3

Then equation 2 become $\frac{d^2\psi}{dx^2}+k^2\psi=0 \qquad \frac{d^2\psi}{dx^2}+k^2\psi=0$

The solution of this 2nd order partial differential equation is:

$$\psi=C\cos kx+D\sin kx$$

------ (3)

To find the value of constants C and D

at $x=0$, $\psi=0$ because particle cannot be found at the walls

Equation 3 become, $0=C\cos k(0)+D\sin k(0)$

$$\therefore C=0$$

Also at $x=a$, $\psi=0$

$$0=C\cos ka+D\sin ka$$

$$D\sin ka=0 \qquad \because C=0$$

Since $D\neq 0 \qquad \therefore \sin ka=0 \quad \therefore ka=0,\pi,2\pi,.....$ (because if D = 0 the wave function vanishes) i.e. $\therefore ka = n\pi \qquad \Rightarrow k = \frac{n\pi}{a}$ -------- 5 where n = 0, 1, 2, 3, 4… (Quantum number)

Substituting C and k value in equation (3) to get permitted wave functions

$$\psi = D\sin\frac{n\pi}{a}x \qquad \text{------ 6}$$

To find out the value of D, normalization of the wave function is to be done.

i.e. $\int_0^a |\psi_n^2| dx = 1 \quad \int_0^a |\psi^2| dx = 1$ -------- 7

using the values of ψ from eqn (7)

$$\int_0^a D^2 \sin^2\frac{n\pi}{a}x\ dx = 1$$

$$D^2\int_0^a\left[\frac{1-\cos(2n\pi/a)x}{2}\right]dx = 1 \qquad \because \sin^2\theta = \frac{1}{2}(1-\cos 2\theta)$$

$$\frac{D^2}{2}\left[\int_0^a dx - \int_0^a \cos\frac{2n\pi}{a}x dx\right] = 1$$

$$\frac{D^2}{2}\left[x - \frac{a}{2n\pi}\sin\frac{2n\pi}{a}x\right]_0^a = 1 \quad \Rightarrow \quad \frac{D^2}{2}[a-0] = 1 \qquad \because \sin\frac{2n\pi}{a}x = 0 \text{ for the given limits}$$

$$\frac{D^2}{2}a = 1 \quad \Rightarrow \quad D = \sqrt{\frac{2}{a}}$$

Hence the normalized wave functions of a particle in one dimensional infinite potential well is:

$$\psi_n = \sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}x$$ This is eigen function

Energy Eigen values: From Eq. 6 & 3

$$\frac{8\pi^2 m}{h^2}E = k^2 = \frac{n^2\pi^2}{a^2} \quad \Rightarrow \quad \boxed{E = \frac{n^2h^2}{8ma^2}}$$ This is energy eigen value

Energy Eigen values of a free particle:

A free particle is one which has zero potential. It is not under the influence of any force or field i.e. V = 0.

The Schrodinger equation is:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}E\psi = 0 \qquad \text{or} \qquad -\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} = E\psi$$

This equation holds good for free particle in free space in which V = 0.

With the knowledge of the particle in a box or a particle in an infinite potential well V = 0 holds good over a finite width ‘a’ and outside V = ∞. By taking the width to be infinite i.e. a = ∞, the case is extended to free particle in space. The energy Eigen values for a particle in an infinite potential well is

$E = \frac{n^2h^2}{8ma^2}\ \frac{n^2h^2}{8ma^2}$ Where n =1, 2, 3, … $\Rightarrow$ $n = \frac{2a}{h}\sqrt{2mE}$

Here when ‘E’ is constant, ‘n’ depends on ‘*a*’ as a→∞ *n*→∞. It means that free particle can have any energy. That is the energy Eigen values or possible energy values are infinite in number. It follows that energy values are continuous. It means that there is no discreteness or quantization of energy. Thus a free particle is a ‘Classical entity’.