Applied Physics for CSE Stream

Module - 2 : Quantum Mechanics

Wave - Particle dualism

Electromagnetic radiations & radiations in general behaves as waves in experiments like interference, diffraction, Polarisation etc. while in experiments like photo-electric effect, compton effect, Raman effect etc. the radiations behaves as particles. Thus radiation has dual nature. This led Louis de-Broglie in 1924 to propose a hypothesis that 'Since nature loves symmetry' if the radiation behaves as particle under certain circumstances & as waves under other circumstances, then material particles like protons, neutrons, electrons, photons etc. should also exhibit dual nature.

The material particles like electrons, protons, photons, neutrons etc. in motion are associated with waves known as matter waves & de-Broglie waves.

The wavelength of a matter wave & de-Broglie wave is given by

$$\lambda = \frac{h}{p}$$

where λ is de-Broglie wavelength, h is Planck's constant & P is momentum of a particle.

de-Broglie wavelength for a particle of mass 'm' moving with a velocity 'v' is given by

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad [\because P = mv]$$

de-Broglie wavelength for a particle of mass 'm' having Kinetic energy E_K is given by

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE_K}} \quad [\because P = \sqrt{2mE_K}]$$

de-Broglie wavelength of an accelerated electron

Consider an electron of mass 'm', charge 'e' which is accelerated under a potential difference of V volts.

Then

$$\text{work done} = \text{Kinetic energy}$$

$$eV = \frac{1}{2} mv^2$$

multiplying the whole equation by 2m, we get

$$2meV = m^2v^2 = p^2$$

& $P = \sqrt{2meV}$ substituting this 'P' value in $\lambda = \frac{h}{p}$ we get, $\lambda = \frac{h}{\sqrt{2meV}}$

where $h = 6.625 \times 10^{-34}$ J-s, $m = 9.1 \times 10^{-31}$ kg $e = 1.602 \times 10^{-19}$ C

substituting all these values in the above equation we get

$$\lambda = \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.602 \times 10^{-19} \times V}} = \frac{1.227\,nm}{\sqrt{V}} = \frac{12.27\,Å}{\sqrt{V}}$$

de-Broglie hypothesis of matter waves

The material particles like electrons, protons, photon & neutrons in motion are associated with waves known as matter waves & de-Broglie waves.

To obtain de-Broglie wavelength, let us consider photon as a wave of frequency ν. The energy of the photon is given by $E = h\nu$ — ①
where h is a Planck's constant.

Considering photon as a particle of mass m moving with velocity c, from Einstein's mass-energy equivalence, we have $E = mc^2$ — ②

From equations ① & ② we have,

$$h\nu = mc^2$$

$$\frac{h\cancel{c}}{\lambda} = mc^{\cancel{2}} \qquad \left[\text{Since } \nu = \frac{c}{\lambda}\right]$$

$$\frac{h}{\lambda} = mc$$

$$\frac{h}{\lambda} = P \qquad [\text{Since } P = mv]$$

$$\boxed{\lambda = \frac{h}{P}} \quad \text{— ③}$$

where P is momentum of a particle. This is called de-Broglie equation.

Heisenberg's uncertainity principle

Heisenberg's uncertainity principle states that in the simultaneous determination of the position & momentum of a particle like electron, the product of uncertainities in the position & the momentum of a particle is equal to or greater than Planck's constant.

If Δx is the uncertainity in the position of a particle & ΔP is the uncertainity in the momentum of a particle then

$$\Delta x \cdot \Delta P \geqslant \frac{h}{4\pi}$$

Similarly the uncertainity relation between energy & time and angular displacement ($\Delta\theta$) & angular momentum (ΔL) is given by

$$\Delta E \cdot \Delta t \geqslant \frac{h}{4\pi}$$

$$\Delta\theta \cdot \Delta L \geqslant \frac{h}{4\pi}$$

Physical significance of Heisenberg's uncertainity principle.

1) It signifies that one should not think about accurate values for the position and momentum of a particle. Instead one should think about only the probable values for the position & momentum.

2. The estimation of such probabilities are made by mathematical functions named probability density functions.

Application of Heisenberg's uncertainity principle

Non existence of electron in the nucleus

The kinetic energy of a body & a particle is given by

$$E = \frac{p^2}{2m} \quad — ①$$

$p \rightarrow$ momentum of a body

$m \rightarrow$ mass of a body

According to Heisenberg's uncertainity principle

$$\Delta x . \Delta P \geq \frac{h}{4\pi} \quad — ②$$

We know that the typical value of diameter of nucleus is of the order of 10^{-14} m. If the electron exists inside the nucleus, it can be anywhere with in this size of the nucleus. Therefore the maximum uncertainity Δx in the position of the electron must not exceed this value.

$$\therefore \Delta x \leq 10^{-14} m$$

using this in eqn ② we have

$$\Delta P \geq \frac{h}{4\pi \times \Delta x}$$

$$\Delta P \geq \frac{6.625 \times 10^{-34}}{4 \times \pi \times 10^{-14}}$$

$\Delta P \geq 0.5 \times 10^{-20}$ kgm/s is the uncertainty in the momentum of the electron. But since the momentum of the electron must atleast be equal to the uncertainity in the momentum,

$$P \geq 0.5 \times 10^{-20} \ kgm/s$$

Substituting this in eqn ① we get

$$E \geq \frac{P^2}{2m} \geq \frac{(0.5 \times 10^{-20})^2}{2 \times 9.11 \times 10^{-31}}$$

$$E \geq 1.372 \times 10^{-11} J$$

$$E \geq \frac{1.372 \times 10^{-11}}{1.6 \times 10^{-19}} \quad \text{expressing in eV}$$

$$E \geq 85 \ MeV$$

Thus if an electron exists inside the nucleus, its energy must be greater than or equal to 85 MeV. But experimental investigations on β-decay emission reveal that, the kinetic energy of the β-particles (same as electrons) is of the order of 3 to 4 MeV. This large difference between theoritical and experimental results disfavours the electron to exist inside the nucleus.

Time independent Schrodinger's wave equation

Schrodinger's equation is the fundamental wave equation in quantum mechanics which explains properties of a quantum mechanical particle.

According to de-Broglie theory, for a particle of mass 'm' moving with a velocity 'v', the de-Broglie wave length is given by $\lambda = \frac{h}{p} = \frac{h}{mv}$ -- ①

The de-Broglie wave equation is a differential equation involving wave function 'ψ' with respect to time & position. For motion in one-dimension

$$\psi = A e^{-i(\omega t - kx)} \quad \text{—} \ ②$$

where A is a constant & ω is the angular frequency.

differentiating eq^n ② with respect to time, we get,

$$\frac{d\psi}{dt} = A e^{-i(\omega t - kx)} \cdot (-i\omega)$$

Again differentiating,

$$\frac{d^2\psi}{dt^2} = A e^{-i(\omega t - kx)} (-i\omega) \cdot (-i\omega)$$

$$\frac{d^2\psi}{dt^2} = -\omega^2 \psi \quad \text{—} \ ③ \qquad \left[\because i^2 = -1 \ \& \ \psi = A e^{-i(\omega t - kx)}\right]$$

We have the equation for a travelling wave as

$$\frac{d^2 y}{dx^2} = \frac{1}{V^2} \frac{d^2 y}{dt^2} \quad \text{—} \ ④$$

where y is the displacement & v is the velocity of the wave.

By analogy, we can write the wave equation for a de-Broglie wave as

$$\frac{d^2\psi}{dx^2} = \frac{1}{V^2} \frac{d^2\psi}{dt^2} \quad \text{—} \ ⑤$$

Substituting eq^n ③ in ⑤ we get

$$\frac{d^2\psi}{dx^2} = -\frac{\omega^2}{V^2} \psi$$

We know $\omega = 2\pi\nu$ & $v = \nu\lambda$. Substituting these values in the above equation we get,

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2\cancel{\nu^2}\psi}{\cancel{\nu^2}\lambda^2} = -\frac{4\pi^2\psi}{\lambda^2}$$

or $$\frac{1}{\lambda^2} = -\frac{1}{4\pi^2\psi}\cdot\frac{d^2\psi}{dx^2} \quad — ⑥$$

The total energy 'E' of a particle is the sum of the kinetic energy $\frac{p^2}{2m}$ & its potential energy V.

$$\therefore \quad E = \frac{p^2}{2m} + V$$

or $$E - V = \frac{p^2}{2m}$$

$$2m(E-V) = p^2$$

$$p^2 = \frac{h^2}{\lambda^2} = 2m(E-V) \qquad \left[\because p = \frac{h}{\lambda}\right]$$

$$\frac{1}{\lambda^2} = \frac{2m(E-V)}{h^2} \quad — ⑦$$

From eqn ⑥ & ⑦ we have

$$-\frac{1}{4\pi^2\psi}\cdot\frac{d^2\psi}{dx^2} = \frac{2m(E-V)}{h^2}$$

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

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

This is the time independent Schrodinger's wave equation in one-dimension.

Physical interpretation of wavefunction ψ

The wavefunction ψ is a complex quantity with both real & imaginary parts. Although the wavefunction ψ describes a particle-wave associated with a de-Broglie wavelength $\lambda = \frac{h}{mv}$ in space. This does not mean that the particle itself is spread out. Therefore ψ itself has no physical meaning. $|\psi|^2$; the absolute value of the wavefunction is always a real quantity. Max Born proposed that $|\psi|^2$ at any point as the probability that the particle will be at that point.

Specifically if dv is the volume element in space located at a point whose co-ordinates are x, y, z at an instant of time 't' then $|\psi|^2 dv$ is the probability of finding the partice in space.

The probability of finding the particle, that is somewhere in space must be equal to unity.

i.e., $\int_{-\infty}^{+\infty} |\psi|^2 dv = 1$

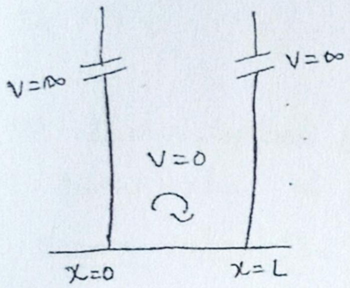
This is called normalization condition.

Properties of wavefunction ψ

1. The wave function ψ is single valued everywhere.
2. ψ is finite everywhere.
3. ψ and its first order derivatives with respect to its variable are continuous everywhere.

For bound states, ψ must vanish at infinity. If ψ is a complex function, then $\psi\psi^*$ must vanish at ∞.

Particle in one-dimensional box [Potential well] of infinite depth
[Eigen values & Eigen functions]



$V = 0$ for $0 < x < L$

$V = \infty$ for $x < 0$ & $x > L$

Consider a free particle in 1-dimensional box.
A particle of mass m is moving along x-direction. The range of the particle is $0 < x < L$.
The general schrodinger wave equation is given by

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m(E-V)\psi}{h^2} = 0 \quad \text{--- (1)}$$

For a free particle $V = 0$ for $0 < x < L$.
Also the wave function vanishes at $x = 0$ & $x = L$
∴ eq^n (1) can be written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 mE}{h^2}\psi = 0 \quad \text{--- (2)} \quad \text{for } 0 < x < L$$

eq^n (2) is similar to an equation of harmonic oscillator.

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \text{--- (3)}$$

Comparing eq^n ② & ③ we get,

$$K^2 = \frac{8\pi^2 mE}{h^2} \quad — ④$$

The general solution for eq^n ③ is given by

$$\psi(x) = A\sin kx + B\cos kx \quad — ⑤$$

The boundary conditions are

$$\psi(0) = 0 \quad \text{at } x = 0 \quad — ⑥$$

$$\psi(L) = 0 \quad \text{at } x = L \quad — ⑦$$

using boundary condition ⑥ in ⑤ we get,

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

$$0 = 0 + B \qquad [\because \cos 0 = 1]$$

$$\Rightarrow B = 0$$

Using boundary condition ⑦ in ⑤ we get,

$$\psi(L) = A\sin kL + B\cos kL$$

$$0 = A\sin kL + 0 \qquad [\because B = 0]$$

$$\therefore A\sin kL = 0$$

Since $A \neq 0$, $\sin kL = 0$

This is true only when $kL = n\pi$ & $k = \frac{n\pi}{L}$

where $n = 0, 1, 2, 3 \ldots$ is called quantum number which is either zero or a +ve integer.

Using the value of B & K in eq^n ⑤ we get

$$\psi_n(x) = A\sin\left(\frac{n\pi}{L}\right)x \quad — ⑧$$

Using the value of k in eq^n ④ we get,

$$\frac{n^2\pi^2}{L^2} = \frac{8\pi^2 mE}{h^2}$$

$$E_n = \frac{n^2 h^2}{8mL^2} \quad \text{—— (9)}$$

If $n=1$, $E_1 = \frac{h^2}{8mL^2}$ [Zero point energy or ground state energy]

If $n=2$, $E_2 = \frac{4h^2}{8mL^2} = 4E_1$ [First Excited State]

If $n=3$, $E_3 = \frac{9h^2}{8mL^2} = 9E_1$ [Second Excited state]

It shows that E_n depends on the value of n.

$\therefore$ each value of E_n i.e., E_1, E_2, E_3 ---- are called Eigen values.

We know the normalization condition given by

$$\int_0^L |\psi_n(x)|^2 dx = 1 \quad \text{—— (10)}$$

Using eq^n (8) in eq^n (10) we get

$$\int_0^L \left| A \sin\left(\frac{n\pi}{L}\right)x \right|^2 dx = 1$$

$$A^2 \int_0^L \sin^2\left(\frac{n\pi}{L}\right)x \, dx = 1$$

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

on integrating we get

$$\frac{A^2 L}{2} = 1 \quad \& \quad A = \sqrt{\frac{2}{L}}$$

Now eq^n (8) becomes

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

If $n=1$, $\psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi}{L}\right) x$ ..

$n=2$, $\psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi}{L}\right) x$

$n=3$, $\psi_3(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi}{L}\right) x$

Since $\psi_n(x)$ depends on the value of n, each value of $\psi_n(x)$ i.e., $\psi_1(x)$, $\psi_2(x)$, $\psi_3(x)$ ----- are called Eigen functions.

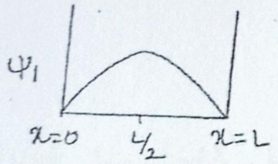
Wave functions, Probability densities & energy levels for a particle in a box

Case-1 :- $n=1$. This is the ground state & the particle is normally found in this state.

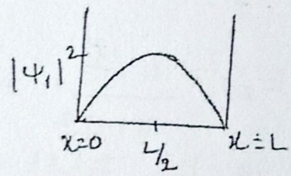
The eigen function & wave function is

$$\psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi}{L}\right) x$$

A plot of ψ_1 versus x is as shown in fig (a).



(a)



(b)

A plot of probability density $|\psi_1|^2$ versus x is as shown in fig (b). The probability of finding the particle is zero at $x=0$ & $x=L$. It is maximum at $x = L/2$. This means that in the ground state, the probability of finding the particle is maximum at the centre of the box.

The energy of the particle in the ground state is given by

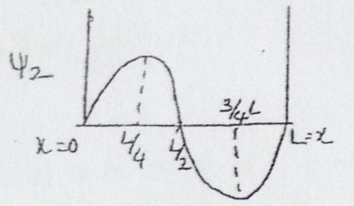
$$E_1 = \frac{h^2}{8mL^2}$$

Case-2 :. This is the first excited state. The eigen function associated for this state is

$n = 2$.

$$\psi_2 = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi}{L}\right) x$$

A plot of ψ_2 versus x is as shown in fig (c)



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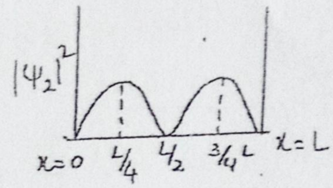


ⓓ

A probability density $|\psi_2|^2$ versus x plot is as shown in fig ⓓ. $|\psi_2|^2 = 0$ at $x = 0, L/2$ & L, this means in the first excited state the particle cannot be found either at the walls or at the center.

The energy of the particle in the first excited state is

$$E_2 = \frac{4h^2}{8mL^2} = 4E_1$$

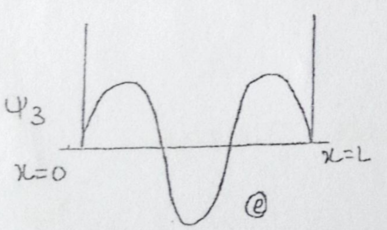
Thus energy in the first excited state is four times the ground state energy.

Case-3 :- This is the second excited state. $n=3$.

The eigen function for this state is

$$\psi_3 = \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi}{L}\right)x$$

A plot of ψ_3 versus x & a plot of $|\psi_3|^2$ versus x is shown in fig ⓔ & ⓕ.



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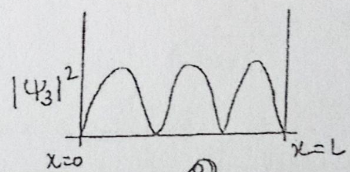

ⓕ

$|\psi_3|^2$ is maximum at $x = L/6, L/2$ & $5L/6$ which also imply the locations at which the particle is most likely to be found.

The energy of the particle in the second excited state is

$$E_3 = \frac{9h^2}{8mL^2} = 9E_1$$

Thus energy of the particle in the second excited state is 9 times the ground state energy.

Expectation value

In Quantum mechanics the expectation value is the probabilistic value. ~~is the proba~~ of the result of an experiment. It can be thought of as an average of all the possible outcomes of a measurement as weighted by their likelihood.

Expectation value as such it is not the most probable value of a measurement in the real sense the expectation value may have zero probability of occuring. Let us consider a particle moving along x-axis.

The result of measurement of the position x is a conitinuous random variable. Consider a wave function $\psi(x,t)$. The $[\psi(x,t)]^2$ value is probability density for the position observable and $[\psi(x,t)]^2 dx$ is the probability of finding the particle between x & $x+dx$ at time t.

Possible outcomes are possible and expectation value of these out comes is, according to the following equation.

$$\langle x \rangle = \int_{-\infty}^{\infty} x \, [\psi(x+)]^2 \, dx$$

Principle of complementarity

According to this all the objects in atomic dimension requires description ~~dimension requires~~ of both wave and particle properties for complete knowledge about it, however particle and wave behaviour are mutually exclusive.. this dialecticism in quantum system is principle of complementarity.