Wave - Particle Duality
OR Louis de Broglie Principle

De - Broglie extended the concept of dual nature of light to material particles and put forward a hypothesis -

According to De- Broglie, that every particle or quantum entity may be described as either a particle or a wave.

Every matter shows the dual nature - particle nature as well as wave nature.

⇒ De - Broglie proposed that a particle of momentum $p = mv$ has a wavelength given by

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

here λ is called as De - Broglie wave length.
h = Planck's constant = 6.6×10^{-34} J - sec.

Proof of $\lambda = \frac{h}{p}$:-

$E = mc^2$ & $E = hf$

↓ Einstein Relation

↓ Planck eqn

Equate these two eqn

$$mc^2 = hf$$

$$mc^2 = \frac{hc}{\lambda}$$

$$mc = \frac{h}{\lambda} \Rightarrow \lambda = \frac{h}{mc} \Rightarrow \boxed{\lambda = \frac{h}{p}}$$

Heisenberg Uncertainty Principle

This principle states that, it is not possible to determine the exact position and exact momentum of a particle simultaneously. If we are able to determine position, there will always be uncertainty in momentum and vice-versa.

If the uncertainty in the momentum is Δp and the uncertainty in the position is Δx, then according to Uncertainty principle

$$\boxed{\Delta x \, \Delta p \geq \frac{\hbar}{2}}$$

where $\hbar = \frac{h}{2\pi}$

⇒ Similiarly, the uncertainty in an energy measurement will be related to the uncertainty in the time at which the measurement was made by

$$\boxed{\Delta E \, . \, \Delta t \geq \frac{\hbar}{2}}$$

here ΔE is the uncertainty in energy
& Δt " " " " time

Schrodinger wave Equation

Erwin Schrodinger, in 1926, provided a formulation called wave mechanics, which incorporated the principle of quanta introduced by Planck and the wave Particle duality principle introduced by de Broglie. Based on the wave-particle duality principle, we will describe the motion of electrons in a crystal by wave theory. This wave theory is described by Schrodinger's wave equation.

wave function(ψ)

Schrodinger introduced a mathematical function associated with De-Broglie matter wave known as wave function and is denoted by ψ.

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

OR $\psi(x, t) = \cos(kx - \omega t) - j \sin(kx - \omega t)$

here k = wave vector $\Rightarrow k = 2\pi/\lambda$

Properties of wave function

wave function is $\rightarrow$ Continuous, Differentiable, finite and single valued.

and $\boxed{\int_{-\infty}^{+\infty} \psi^* \psi \, dx\, dy\, dz = 1}$

here ψ^* is a complex conjugate of ψ

Derivation of Schrodinger wave equation

The Schrodinger wave equation is derived by considering the following few basic postulates—

Basic Postulates:

1) Each particle in a physical system is described by a wave function $\psi(x, y, z, t)$. This function and its space derivative $\left(\frac{\partial \psi}{\partial x}, \frac{\partial \psi}{\partial y}, \frac{\partial \psi}{\partial z}\right)$ are continuous, finite and single valued.

2) In dealing with classical quantities such as Energy E and momentum P, we must relate these quantities with abstract quantum mechanical operators defined as follows.

Classical Variable	Quantum operator
x	x
$f(x)$	$f(x)$
P	$\frac{\hbar}{j}\frac{\partial}{\partial x}$
E	$-\frac{\hbar}{j}\frac{\partial}{\partial t}$

and similiar for other two directions

Note
Proof of $P \to \frac{\hbar}{j}\frac{\partial}{\partial x}$

$$\psi = e^{j(kx - \omega t)}$$

$$\frac{\partial \psi}{\partial x} = jk \times e^{j(kx-\omega t)}$$

$$\frac{\partial \psi}{\partial x} = jk\,\psi \quad \text{- (a)}$$

Put $k = \frac{2\pi}{\lambda} = \frac{2\pi}{h/p}$

$$k = \frac{2\pi}{h} \times P = \frac{P}{\hbar}$$

Put $k = \frac{P}{\hbar}$ in eqn (a)

$$\Rightarrow \frac{\partial \psi}{\partial x} = j\frac{P}{\hbar}\psi \Rightarrow \boxed{P = \frac{\hbar}{j}\frac{\partial}{\partial x}}$$

Proof of $E \rightarrow -\frac{\hbar}{j}\frac{\partial}{\partial t}$

$$\psi = e^{j(kx-\omega t)}$$

$$\frac{\partial \psi}{\partial t} = -j\omega e^{j(kx-\omega t)} = -j\omega\psi \quad -(b)$$

Now $E = hf = h\frac{\omega}{2\pi} = \frac{h}{2\pi}\omega = \hbar\omega$

$E = \hbar\omega \Rightarrow \omega = \frac{E}{\hbar}$

Put $\omega = E/\hbar$ in eqn (b)

$$\Rightarrow \frac{\partial\psi}{\partial t} = -j\frac{E}{\hbar}\psi \Rightarrow \boxed{E = -\frac{\hbar}{j}\frac{\partial}{\partial t}}$$

3) The Probability of finding a particle with wave function ψ in the volume $dx\,dy\,dz$ is $\psi^*\psi\,dx\,dy\,dz$. The product $\psi^*\psi$ is normalized according to

$$\int_{-\infty}^{+\infty}\psi^*\psi\,dx\,dy\,dz = 1 \quad -(c)$$

Note : the probability density function is $= \psi^*\psi = |\psi|^2$.

$\Rightarrow$ The Classical equation for the energy of a particle can be written:

Kinetic Energy + Potential energy = Total Energy

$$\frac{1}{2}mv^2 + V = E$$

OR

$$\Rightarrow \frac{p^2}{2m} + V = E \quad -(1)$$

In quantum mechanics we use the operator form for these variable (Postulate 2), the operators are allowed to operate on the wave function ψ.

For a one-dimensional problem, eq^n ① becomes -

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\psi(x,t) = -\frac{\hbar}{j}\frac{\partial \psi(x,t)}{\partial t}} \quad -②$$

This is the Schrodinger wave eq^n in one-dimension.

⇒ In three dimension the eq^n is

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = -\frac{\hbar}{j}\frac{\partial \psi}{\partial t}} \quad - ③$$

Where $\nabla^2\psi$ is $\frac{\partial^2\psi}{\partial x} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$

The wave function ψ in eq^n ② and ③ includes both space and time dependencies.

here ψ = wave function, V = Potential Energy

m = mass of particle

$\hbar = \frac{h}{2\pi}$ = Modified Planck's Constant

⇒ we may determine the time dependent equation and position dependent (OR time independent) eq^n by using the technique of seperation of variables.

let the wave function is written as -

$$\psi(x,t) = \varphi(x)\,\phi(t)$$

here $\varphi(x)$ is the function of position only and $\phi(t)$ is the function of time only

Substituting $\Psi(x,t) = \psi(x)\,\phi(t)$ in eq^n (2), we obtain –

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}\phi(t) + V(x)\,\psi(x)\,\phi(t) = -\frac{\hbar}{j}\,\psi(x)\,\frac{\partial\phi(t)}{\partial t}$$

OR $$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}\phi(t) + V(x)\,\psi(x)\,\phi(t) = j\hbar\,\psi(x)\,\frac{\partial\phi(t)}{\partial t}$$

dividi by total wave function $\Psi(x,t) = \psi(x)\,\phi(t)$ in both side

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} + V(x) = j\hbar\frac{1}{\phi(t)}\frac{\partial\phi(t)}{\partial t} \quad -(4)$$

the left side of above eq^n is a function of x only and the right side of the equation is a function of time t only. Each side of this equation must be equal to a constant. We will denote this sepration of variables constant say η.

The time-dependent portion of eq^n (4) is then written as –

$$\eta = j\hbar\frac{1}{\phi(t)}\frac{\partial\phi(t)}{\partial t}$$

OR $$\eta = j\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}$$

$$\frac{d\phi(t)}{dt} = \frac{\eta}{j\hbar}\,\phi(t)$$

OR $$\frac{d\phi(t)}{dt} = -\frac{j\eta}{\hbar}\,\phi(t) \Rightarrow \frac{d\phi(t)}{dt} + \frac{j\eta}{\hbar}\,\phi(t) = 0$$

$-(5)$

here η = seperation constant. the solⁿ of eqⁿ (5) can be written in the form

$$\phi(t) = e^{-j(\eta/\hbar)t}$$

the form of this solⁿ is the classical exponential form of a sinusoidal wave function, where $\eta/\hbar$ is radian freq ω.

$$\Rightarrow \omega = \frac{\eta}{\hbar}$$

But $E = hf = \frac{h\omega}{2\pi} = \omega\hbar \Rightarrow \omega = \frac{E}{\hbar}$

$$\Rightarrow \frac{\eta}{\hbar} = \frac{E}{\hbar} \Rightarrow E = \eta$$

So the seperation constant η is same as the total Energy E of the particle so put $\eta = E$ in eqⁿ (5)

$$\boxed{\frac{d\phi(t)}{dt} + j\frac{E}{\hbar}\phi(t) = 0}$$

→ Time dependent Schrodinger Equation — (6)

The time-independent portion of the wave eqⁿ is obtained by putting left side of eqⁿ (4) equal to seperation constant E.

$$-\frac{\hbar^2}{2m}\cdot\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x) = E$$

$$\boxed{\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}\left[E - V(x)\right]\psi(x) = 0} \quad -(7)$$

↓

Time independent Schrodinger eqⁿ.

Application of Schrodinger's wave equation

1) Electron in free space :-

Consider the motion of an electron in free space. If there is no force acting on the particle, then the potential function $V(x)$ will be constant and we must have $E > V(x)$. Assume for simplicity, that the potential function $V(x) = 0$ for all x. Then the time-independent wave equation can be written

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2mE}{\hbar^2} \psi(x) = 0 \qquad -①$$

The soluation of this differential equation will be

$$\psi(x) = A \exp\left[\frac{jx\sqrt{2mE}}{\hbar}\right] + B \exp\left[\frac{-jx\sqrt{2mE}}{\hbar}\right] \qquad -②$$

& the time dependent portion of the solu^n is

$$\phi(t) = e^{-j(E/\hbar)t}$$

Then the total solution for the wave eq^n

$$\Psi(x,t) = \psi(x)\,\phi(t) \qquad -③$$

$$\Psi(x,t) = A \exp\left[\frac{j}{\hbar}\left(x\sqrt{2mE} - Et\right)\right] + B \exp\left[\frac{-j}{\hbar}\left(x\sqrt{2mE} + Et\right)\right] \qquad -④$$

This wave function (eq^n 4) is a traveling wave, which means that a particle moving in free space is represented by traveling wave. The first term with

Co-efficient A_f is a wave travelling in the $+x$ direction, while the second term, with the co-efficient B is a wave travelling in the $-x$ direction.

Assume, for a moment, that we have a particle traveling in the $+x$ direction, then the wave eq^n is written by setting $B=0$

$$\Psi(x,t) = A \exp\left[\frac{j}{\hbar}\left(x\sqrt{2mE} - Et\right)\right]$$

OR $$\Psi(x,t) = A \exp\left[j(kx - \omega t)\right]$$

Where k is a wave Number

$$k = \frac{\sqrt{2mE}}{\hbar}$$

but $$k = \frac{2\pi}{\lambda}$$

On comparing $$\frac{\sqrt{2mE}}{\hbar} = \frac{2\pi}{\lambda} \Rightarrow \lambda = \frac{2\pi \times \hbar}{\sqrt{2mE}}$$

$$\lambda = \frac{2\pi \times \frac{h}{2\pi}}{\sqrt{2mE}} \Rightarrow \boxed{\lambda = \frac{h}{\sqrt{2mE}}}$$

From De-broglie's wave particle duality principle, the wavelength $\lambda = \frac{h}{p}$

$$\Rightarrow \boxed{p = \sqrt{2mE}}$$

$\Rightarrow$ Thus a free particle with a well defined Energy E will also have a well-defined wavelength & Momentum.

⇒ The Probability density function $\psi(x,t)\,\psi^*(x,t) = A^2$, which is a constant independent of position. Thus a free particle with a well-defined momentum can be found anywhere with equal probability. This result is in agreement with the Heisenberg Uncertainty Principle in that a precise momentum implies an undefined Position.

2) Potential well problem

OR

The infinite Potential Well

The problem of a particle in the infinite potential well is a classic ~~exp~~ example of a bound particle. The potential V(x) as a function of position is shown in below fig. The particle is assumed to exist in Region II so the particle is contained within a finite region of space. ~~The~~

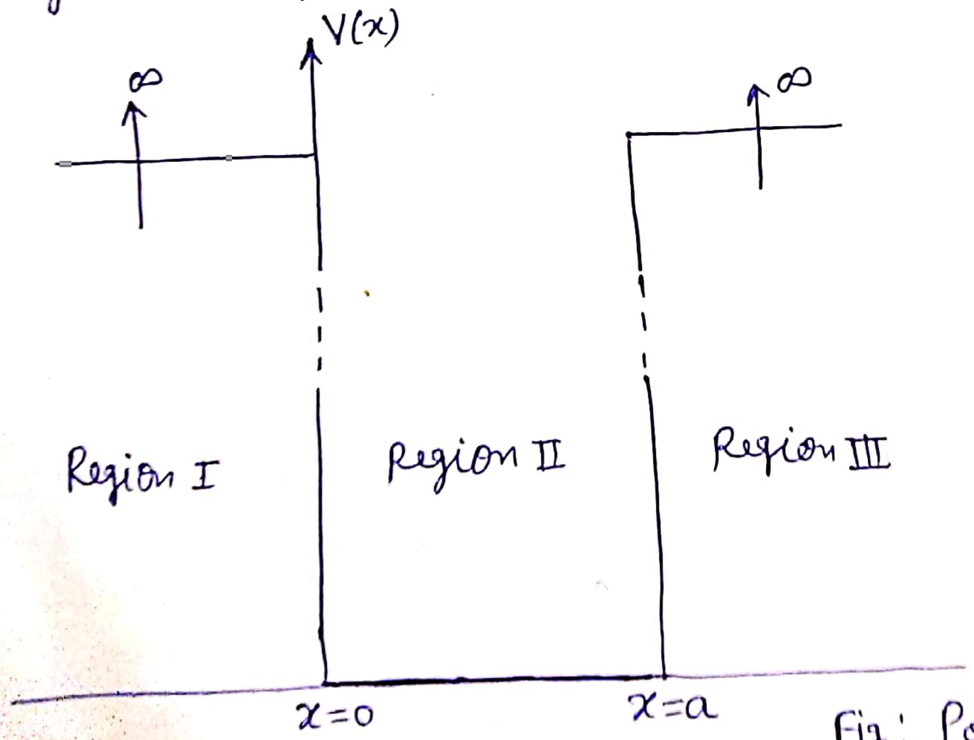

Fig: Potential function of the infinite potential well.

The time-independent Schrodinger's wave equation is given by -

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{h^2}\left[E - V(x)\right]\psi(x) = 0 \qquad -(1)$$

Where E is the total energy of the particle. If E is finite, the wave function must be zero in both region I and III. A particle can not penetrate these infinite potential barrier, so the probability of finding the particle in region I & III is zero.

⇒ The time-independent Schrodinger's wave equation in region II, where V = 0, becomes -

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2mE}{h^2}\psi(x) = 0 \qquad -(2)$$

the soluation of the above eqn is

$$\psi(x) = A_1 \cos kx + A_2 \sin kx \qquad -(3)$$

where $K = \frac{\sqrt{2mE}}{\hbar}$ $\qquad -(4)$

The boundary conditions are -

$\psi(x=0) = 0$ & $\psi(x=a) = 0$

Applying the boundary condition at $x=0$.

$$0 = A_1 \cos k\cdot 0 + A_2 \sin k\cdot 0$$

$$0 = A_1 \Rightarrow \boxed{A_1 = 0} \qquad -(5)$$

At $x = a$, $\psi(x=a) = 0$

$$0 = A_1 \cos ka + A_2 \sin ka$$

$$0 = 0 \times \cos ka + A_2 \sin ka$$

$$\Rightarrow A_2 \sin ka = 0$$

$A_2 \sin ka = 0$

since $A_2 \neq 0$

$\Rightarrow \sin ka = 0$

$\sin ka = \sin n\pi$

$ka = n\pi \Rightarrow \boxed{k = \frac{n\pi}{a}}$ — (6)

The co-efficient A_2 can be found from the normalized boundary condition.

$$\int_{-\infty}^{+\infty} \psi(x)\, \psi^*(x)\, dx = 1$$

If we assume wave f^n $\psi(x)$ is a real number then $\psi(x) = \psi^*(x)$

$$\int_{-\infty}^{+\infty} \psi(x) \times \psi(x)\, dx = 1$$

$$\int_{-\infty}^{+\infty} A_2^2 \sin^2 kx\, dx = 1$$

$$\int_{-\infty}^{+\infty} A_2^2 \left(\frac{1 - \cos 2kx}{2}\right) dx = 1$$

Put the integral limit 0 to a

$$A_2^2 \int_0^a \left(\frac{1}{2} - \frac{\cos 2kx}{2}\right) dx = 1$$

$A_2^2 \times \frac{1}{2} a = 1 \Rightarrow \boxed{A_2 = \sqrt{\frac{2}{a}}}$ — (7)

Finally the time-independent wave solution is given by -

$$\boxed{\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right), \quad \text{where } n = 1, 2, 3} \quad (8)$$

This solution represent the electrons in the infinite Potential well and is a standing wave solution

⇒ The parameter K in the wave ~~eq~~ solution was described by eqn (4) & eqn (6). Equating these two expressions for K, we obtain

$$\frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{a}$$

$$\Rightarrow \frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{a^2}$$

$$\Rightarrow \boxed{E = E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2}} \quad - (9)$$

⇒ Thus for each allowable value of n, the particle energy is described by eqn (9). We notice that the energy is quantized. Only certain values of energy are allowed. Then ~~one~~ integer n is called a quantum number.

The first three allowable energy ~~state~~ levels, wave function and probability density function $\psi\psi^* = |\psi|^2$ is shown in next fig.

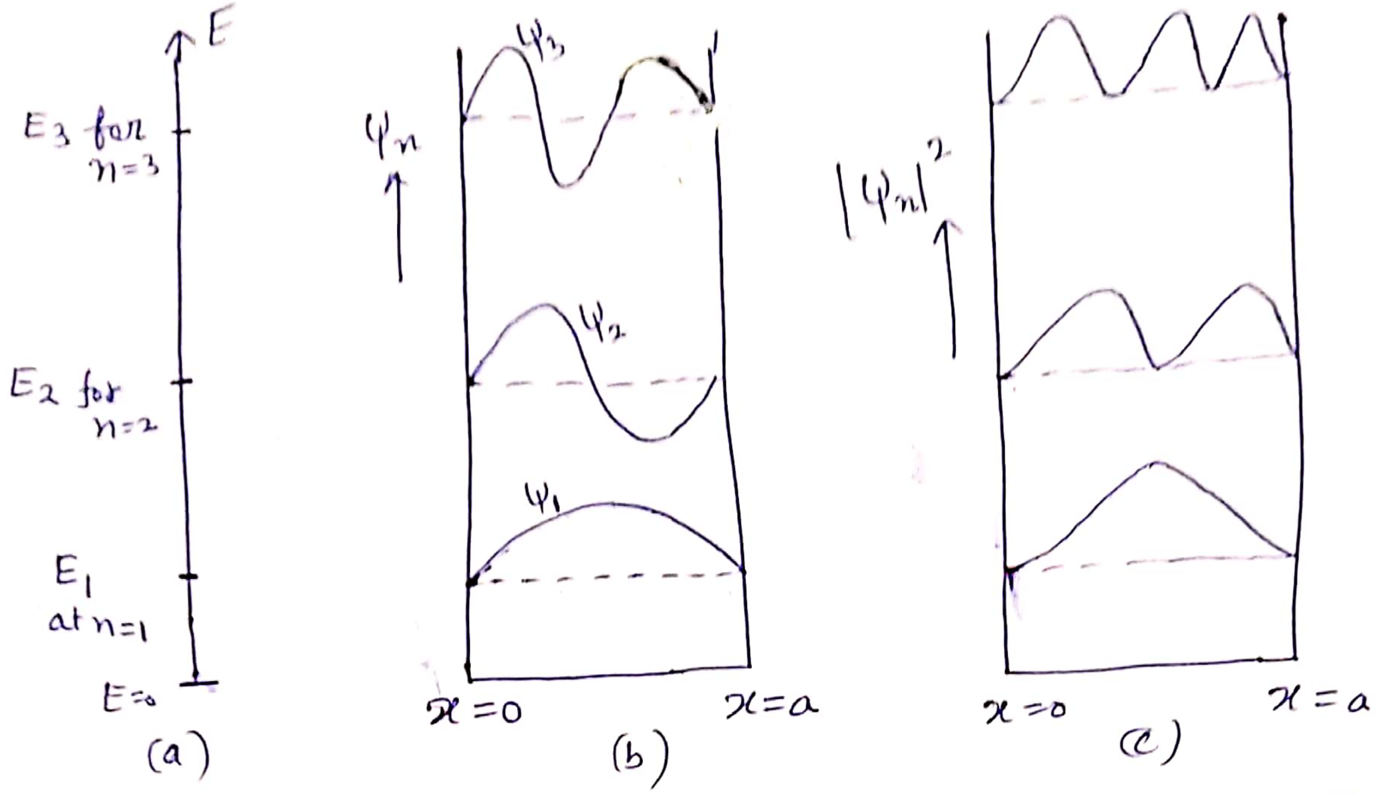

Fig: Particle in an infinite potential well
(a) Three Lowest energy levels (b) corresponding wave function (c) corresponding probability fn.

Q Calculate the first three energy levels of an electron in an infinite potential well. Consider an e^- in an ∞ potential well of width 5 A°

Soln $a = 5\,A^\circ = 5 \times 10^{-10}$ meter

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2} = \frac{\left(\frac{6.6 \times 10^{-34}}{2\pi}\right)^2 \times \pi^2 \times n^2}{(2 \times 9.1 \times 10^{-31}) \times (5 \times 10^{-10})^2}$$

$$E_n = n^2 \times (2.41 \times 10^{-19}) \text{ Joule}$$

$$\text{or } E_n = \frac{n^2 (2.41 \times 10^{-19})}{1.6 \times 10^{-19}} = n^2 \times 1.51 \text{ eV}$$

Then $\boxed{E_1 = 1.51 \text{ eV}}$, $E_2 = (2)^2 \times 1.51 \text{ eV} = 6.04 \text{ eV}$

$E_3 = (3)^2 \times 1.51 \text{ eV} = 13.59 \text{ eV}$