

Quantum Mechanics

①

Imp. Wave function, ψ & physical meaning

The wavefunction, denoted by ψ is an important quantity in Quantum Mechanics. A quantity whose variations are related with matter waves called wavefunction. [Matter waves means the wave associated with particles or waves].

ψ is a mathematical function which describes the state of a particle. It is a function of position and time co-ordinates. It is generally a complex function.

$\psi^* - \psi$ star
 $\psi\psi^*$ or $|\psi|^2$ represents the probability density of the system.

The normalization condition of the wavefunction

$$\int_{-\infty}^{\infty} \psi\psi^* d\tau = 1 \quad \text{or} \quad \int_{-\infty}^{\infty} |\psi|^2 d\tau = 1$$

$d\tau$ is the volume element.

The Uncertainty principle

It is one of the most significant physical law and was formulated by Werner Heisenberg. It states that it is impossible to know both the exact position or exact momentum of an object at the same time.

It is quantitatively stated as,

$$\Delta x \Delta p_x \geq \frac{h}{2} \quad \text{where } h = \frac{h}{2\pi}$$

Similar relations can be written with the parameters like, angular displacement, θ and angular momentum, J_z .

$$\text{i, } \Delta \theta \Delta J_z \geq \frac{h}{2}$$

also, time & Energy, E

$$\text{ii, } \Delta t \Delta E \geq \frac{h}{2}$$

Applications

Q) ①. Absence of e^- in a nucleus / Can e^- remain in a nucleus / Non-existing of free e^- in the nucleus

(1a)

Normally, a nuclei have radii value of the order 10^{-14} m. For an e^- to be combined within the nucleus, the uncertainty in its position may not exceed 10^{-14} m.

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

By using the principle, $\Delta x \Delta p_x \approx \frac{h}{2\pi}$

$$\begin{aligned} \therefore \Delta p_x &\approx \frac{\frac{h}{2\pi}}{\Delta x} \\ &\approx \frac{1.054 \times 10^{-34}}{10^{-14}} \\ &\approx 1.1 \times 10^{-20} \text{ kg m/s} \end{aligned}$$

$$\begin{aligned} \frac{h}{2\pi} &= \frac{6.625 \times 10^{-34}}{2\pi} \\ &= 1.054 \times 10^{-34} \end{aligned}$$

This is the uncertainty in the momentum of e^- . The momentum itself is of the order of 1.1×10^{-20} kg m/s.

$\therefore p_x \approx 1.1 \times 10^{-20}$ kg m/s

According to k.E of e^- ,

According to relativity

$$T = p^2 c^2 + m_0^2 c^4$$

+ rest mass (neglect)

$$T = p^2 c^2$$

$T = p_x c$

$= 1.1 \times 10^{-20} \times 3 \times 10^8 \text{ J}$

$= 1.1 \times 10^{-20} \times 3 \times 10^8$

$1.6 \times 10^{-19} \text{ eV}$

$\approx 20 \text{ MeV}$

(2)
If, the K.E of the e^- must be more than 20 MeV, it to be a nuclear constituent. (e^- s, protons, neutrons etc). Experiments prove that the e^- s associated with unstable atoms never have more than a fraction of this energy. So we conclude that e^- s cannot present within the nuclei.

[Imp]

Schrodinger's Equation

Schrodinger's eqn. is the most important fundamental eqn. in Q.M. The Schrodinger eqn. has two parts - one in which the time dependent and other time independent

a) Time dependent Schrodinger equation

The diff. eqn. of a one dimensional wave associated with a particle, propagating along x-direction is.

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{1}{v^2} \frac{\partial^2 \psi}{\partial t^2}$$

It's separable exponential solution is ③

$$\psi = a e^{-i/t} [Et - Px]$$

$$\psi = a e^{-i/t} [Et - Px] \quad \text{--- --- ①}$$

Also soln. is
 $\psi = A \sin k(x - vt)$
 then, substituting k
 then with eq. from

partial Differentiating ① w.r to t

$$\frac{\partial \psi}{\partial t} = a e^{-i/t} [Et - Px] \cdot \frac{-iE}{t}$$

$$= \psi \cdot \frac{-iE}{t}$$

$$= \frac{-iE}{t} \psi$$

then, $E\psi = i t \frac{\partial \psi}{\partial t}$ --- ②

$$\frac{\partial \psi}{\partial t} = \frac{-iE\psi}{t}$$

$$\partial \psi \cdot t = -iE \partial t \psi$$

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

$$= \frac{\partial \psi}{\partial t} \cdot t \cdot i$$

$$= i t \frac{\partial \psi}{\partial t}$$

partial Diff ① w.r to x, twice

$$\frac{\partial^2 \psi}{\partial x^2} = a e^{-i/t} [Et - Px] \cdot \frac{i^2}{t} P$$

then, $\frac{\partial^2 \psi}{\partial x^2} = a e^{-i/t} [Et - Px] \cdot \left(\frac{i^2}{t} P\right)^2$

$$= -\psi \cdot \frac{P^2}{t^2}$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{-2}{t^2} \psi$$

$$\partial x^2 > \frac{-2}{t^2}$$

$$i^2 = -1$$

∴ $P^2 \psi = -t^2 \frac{\partial^2 \psi}{\partial x^2}$ --- ③ $P^2 \psi = -t^2 \frac{\partial^2 \psi}{\partial x^2}$

(4)

The total energy, E of the particle is the sum of kinetic + potential energies.

$$i, E = \frac{p^2}{2m} + V$$

multiplying both sides by ψ

$$i, E\psi = \frac{p^2\psi}{2m} + V\psi$$

Substituting the values of $E\psi$ and $p^2\psi$ from (2) & (3)

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

This is the one dimensional time-dependent Schrödinger equation.

then, 3D is,

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

$$E = K.E + P.E$$

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

$$= \frac{1}{2} \frac{m \times m v^2}{m} + V$$

$$= \frac{1}{2} m^2 v^2 + V$$

$$\text{if } mv = p$$

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

(5)

Time independent Schrodinger equation

Here, the wavefunction as a product of function of position, x is, $\psi(x)$ and a function of time, t is, $\phi(t)$.

$$\text{Let, } \Psi(x,t) = \psi(x)\phi(t) \text{ --- (1)}$$

Differentiating eqn. (1) w.r to x twice,

$$\frac{\partial^2 \Psi}{\partial x^2} = \phi(t) \cdot \frac{\partial^2 \psi}{\partial x^2} \text{ --- (2)}$$

Differentiating partially eqn (1) w.r to t ,

$$\frac{\partial \Psi}{\partial t} = \psi(x) \frac{\partial \phi}{\partial t} \text{ --- (3)}$$

Substituting (2) and (3) in time dependent Schrodinger eqn.

$$\text{Let, } i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi$$

[$\Psi = \psi(x)\phi(t)$]

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



Dividing throughout by $\psi(x)\psi(t)$

$$\rho h \frac{1}{\psi(t)} \frac{\partial \psi}{\partial t} = -\frac{\rho^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi}{\partial x^2} + V \quad \text{--- (4)}$$

LHS of this eqn is a function of t alone and RHS function of x . For the eqn. to be consistent, each side must be equal to same constant, k .

i, equalizing the LHS of eqn (4) with k ,

$$\rho h \frac{1}{\psi(t)} \frac{\partial \psi}{\partial t} = k$$

$$\text{then, } \frac{\partial \psi}{\psi} = \frac{-i k}{\rho h} dt$$

Integrating,

$$\int \frac{\partial \psi}{\psi} = \frac{-i k}{\rho h} \int dt$$

$$\int \frac{1}{\psi} \partial \psi = \frac{-i k}{\rho h} \int dt$$

$$\log |\psi| = \frac{-i k}{\rho h} \cdot t$$

$$\begin{aligned} \rho h \frac{\partial \psi}{\psi} &= k \\ \rho h \partial \psi &= k \psi dt \\ \frac{\partial \psi}{\psi} &= \frac{k dt}{\rho h} \\ \int \frac{\partial \psi}{\psi} &= \frac{-i k dt}{\rho h} \end{aligned}$$

$$\psi, \Phi_{\text{time}} = e^{-\frac{i}{\hbar} K t}$$

then, eqn. (1) \Rightarrow

$$\Psi(x,t) = \psi(x) e^{-\frac{i}{\hbar} K t} \quad \text{--- (5)}$$

Partial Differentiating (5) w.r.t to t ,

$$\frac{\partial \Psi}{\partial t} = \psi(x) e^{-\frac{i}{\hbar} K t} \cdot \frac{-i K}{\hbar}$$

$$= \frac{-i K}{\hbar} \Psi_{\text{time}}$$

$$K \Psi = \frac{\hbar}{i} \frac{\partial \Psi}{\partial t}$$

which is similar to $E \Psi$

\therefore , K is identical with E .

then equating the RHS of eqn. (6) to E , we get,

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \Psi}{\partial x^2} + V = E$$

multiplying by $\psi(x)$

$$\therefore, -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V \Psi = E \Psi$$

$$\begin{aligned} \frac{\partial \Psi}{\partial t} &= \frac{-i K \Psi}{\hbar} \\ -i K \cdot \partial t &= E \partial \Psi \\ K \Psi &= \frac{\hbar}{-i} \frac{\partial \Psi}{\partial t} \\ \frac{1}{i} &= -i \\ K \Psi &= +i \frac{\hbar}{1} \frac{\partial \Psi}{\partial t} \end{aligned}$$



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Department of Technical Education

Rajiv Gandhi Institute of Technology, Govt. Engineering College, Kottayam

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or,
$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0.$$

ii, Dividing throughout by $-\frac{\hbar^2}{2m}$

iii,
$$\frac{\partial^2 \psi}{\partial x^2} + -\frac{2m}{\hbar^2} V \psi + \frac{2m}{\hbar^2} E \psi = 0$$

iii,
$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0.$$

This is the Schrodinger's time independent equation in 1D. or steady state eqn.

In 3D,
$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

Characteristics of wavefunction

① The solution of the wavefunction should be finite and

② $\psi(x)$ should be single valued.

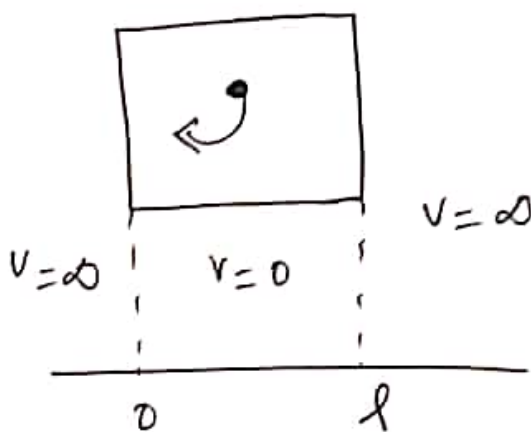
②

③ $\varphi(x)$, $\frac{\partial \varphi}{\partial x}$, $\frac{\delta \varphi}{\delta x^2}$ should be continuous.



Particle in a Box

Consider a free particle [means a particle that is not subjected to any forces, their p.e. is constant, $V=0$] moving inside a box. The particle is bouncing back & forth b/w the walls of the box. If 'l' is the length (width) of the box. The p.e, V of the particle is infinite on both sides of the box.



i, $V=0$ if $0 < x < l$

$V=\infty$ if $x \leq 0, x \geq l$.

Within the box, the time independent Schrodinger eqn. is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0$$

[for a free particle, $v = 0$] (2)

then,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0 \quad [\because k = \sqrt{\frac{2mE}{\hbar^2}}]$$

$$\therefore \frac{d^2\psi}{dx^2} + k^2\psi = 0$$

The general solution of this eqn. is

$$\psi = A \sin kx + B \cos kx. \quad \text{--- (a)}$$

Applying boundary conditions,

$$\psi = 0 \quad \text{at } x = 0 \quad \text{--- (1)}$$

$$\psi = 0 \quad \text{at } x = l \quad \text{--- (2)}$$

When applying (1) condition, then $B = 0$.

Applying (2) condition, $0 = A \sin kx + 0$

$$\therefore A \sin kl = 0.$$

$$\therefore kl = n\pi, \text{ where}$$

$$\therefore k = \frac{n\pi}{l}, \quad n = 1, 2, 3, \dots$$

Substituting the value of k in the eqn. (a)

$$\psi_n(x) = A \sin \frac{n\pi}{l} x, \text{ where } n = 1, 2, 3, \dots$$

We know, $k^2 = \frac{2mE}{\hbar^2}$

$$E = \frac{k^2 \hbar^2}{2m} \quad \left[\text{since } k = \frac{n\pi}{l}, \quad \hbar = \frac{h}{2\pi} \right]$$

$$\therefore \psi \neq \frac{k^2 \hbar^2}{2m}$$

$$\therefore E = \frac{\left(\frac{n\pi}{l}\right)^2 \left(\frac{h}{2\pi}\right)^2}{2m}$$

$$= \frac{n^2 \pi^2 \hbar^2}{l^2 \times 2m \times 4\pi^2} = \frac{n^2 \hbar^2}{8ml^2}, \quad n = 1, 2, 3, \dots$$

Here $\psi_n(x) = A \sin \frac{n\pi x}{l}$, where $n = 1, 2, 3, \dots$

is the eigen function and its corresponding eigen value is

$$E_n = \frac{n^2 \hbar^2}{8ml^2}, \quad n = 1, 2, 3, \dots \quad \text{--- (b)}$$

To find the constant A in the eigen function we apply the normalization condition of wavefunctions.

$$n, \quad \int_{-l}^l |\psi|^2 dx = 1.$$

$$n, \quad \int_0^l \left| A \sin \frac{n\pi x}{l} \right|^2 dx = 1$$

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

$$\frac{A^2}{2} \int_0^l (1 - \cos \frac{2n\pi x}{l}) dx = 1$$

$$\frac{A^2}{2} \left[x - \sin \frac{2n\pi x}{l} \cdot \frac{l}{2n\pi} \right]_0^l = 1$$

$$\frac{A^2 l}{2} \left[1 - \sin \frac{2n\pi x}{l} \cdot \frac{l}{2n\pi} \right] = 1$$

$$ii) \frac{A^2 l}{2} [1 - 0] = 1 \quad \left(\begin{array}{l} n\pi = 0 \\ \sin 2n\pi = 0 \end{array} \right)$$

$$\frac{A^2 l}{2} = 1$$

$$\therefore A^2 = \frac{2}{l}$$

$$\therefore A = \sqrt{\frac{2}{l}}$$

\therefore The eigen function, $\psi_n(x) = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$,

where $n = 1, 2, 3, \dots$

Eqn. (b) represents the stationary energy states possible to the particle in a box.

The energy of the particle in a box in the ground state is obtained by putting $n=1$

in eqn. (b).

$$n, E_n = \frac{h^2}{8ml^2}$$

(5)

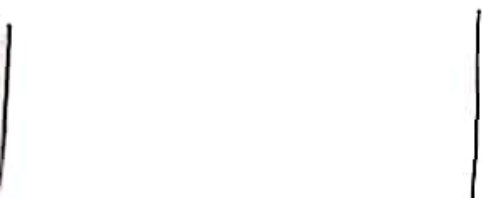
$$\left[\begin{array}{l} n, E_n = \frac{n^2 h^2}{8ml^2} \\ n=1 \\ \text{then, } E_1 = \frac{h^2}{8ml^2} \end{array} \right.$$

Putting $n=2$,

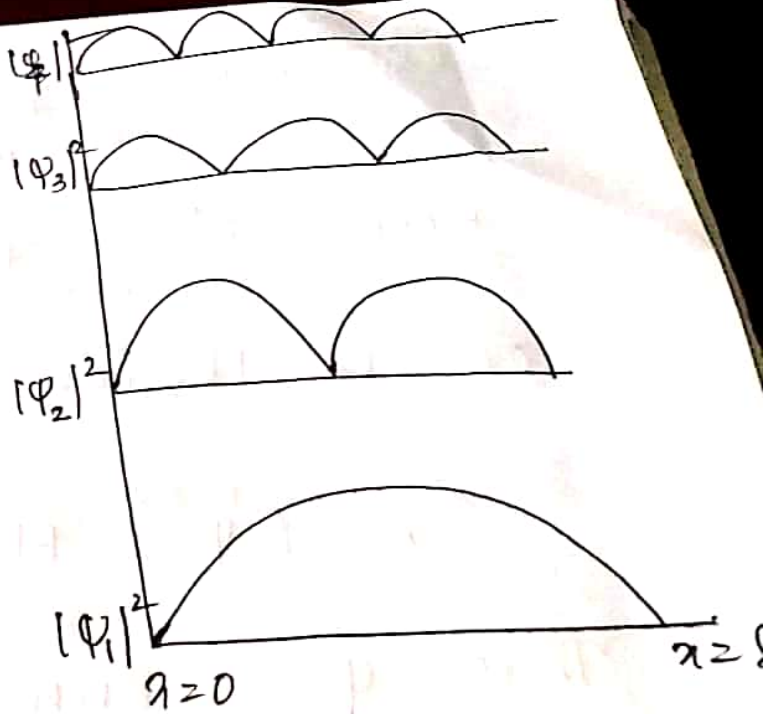
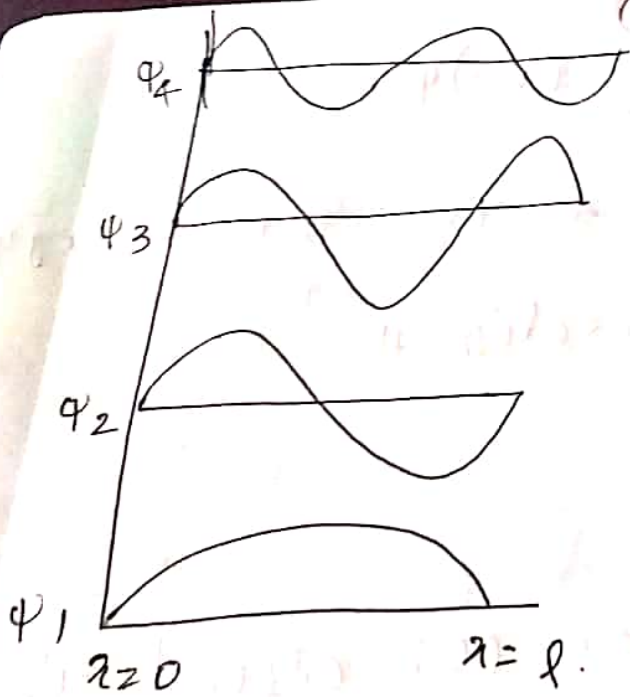
$$E_2 = \frac{4h^2}{8ml^2} = \frac{h^2}{2ml^2} \text{ and so on.}$$

Thus, a particle confined to a box cannot have any arbitrary or continuous value of Energy.

The following fig. represents the wavefunction (ψ) & probability density $|\psi|^2$ for a single particle in a box.



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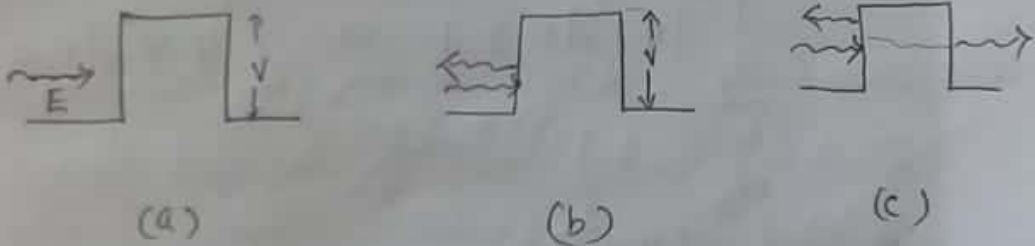


(7)

Quantum mechanical Tunnelling

Consider a plane wave through a rectangular barrier. The transmission is based on tunnel effect. If a particle is impinging on a barrier with energy less than the height of the potential barrier, it will not be totally reflected by the barrier but there is always a probability that it may cross the barrier and continue its motion.

$E \rightarrow$ particle energy
 $V \rightarrow$ height of the barrier



- (a) A particle with energy $E < V$ approaching a potential barrier
- (b) From classical mechanics, the particle must be reflected by the barrier.
- (c) In Q.M, the particle are ~~partly~~ partly reflected & partly transmitted i.e., the particle has the probability to penetrating the barrier.

problems

3) The wavefunction of a particle is $\psi = A \cos^2 x$ for the interval $-\pi/2$ to $\pi/2$. Find the value of A ?

$$\psi = A \cos^2 x \quad \text{for } -\pi/2 \text{ to } \pi/2$$

The Normalization condition of wave

$$\int_{-\infty}^{\infty} |\psi|^2 dv = 1 \quad \text{or} \quad \int_{-\infty}^{\infty} \psi \psi^* dv = 1$$

$$\therefore \int_{-\pi/2}^{\pi/2} |\psi|^2 dx = 1$$

$$\int_{-\pi/2}^{\pi/2} |A \cos^2 x|^2 dx = 1$$

$$A^2 \int_{-\pi/2}^{\pi/2} \cos^4 x dx = 1$$

$$2A^2 \int_0^{\pi/2} \cos^4 x dx = 1$$

Integrating the function ⁽⁹⁾

$$\text{then, } 2A^2 \frac{3\pi}{16} = 1$$

$$\therefore \underline{\underline{A = \sqrt{\frac{8}{3\pi}}}}$$

- ② Calculate the separation b/w the two lowest energy levels of an electron in a 1D box of width 4 \AA^0 in joules. Given $m_e = 9.1 \times 10^{-31} \text{ kg}$, $h = 6.625 \times 10^{-34} \text{ Js}$.

We know, the eqn. of Energy in a particle in a box,

$$E_n = \frac{n^2 h^2}{8ml^2}$$

First to calculate, E_1 in, $n=1$.

$$E_1 = \frac{(6.625 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (4 \times 10^{-10})^2}$$

$l = 4 \text{ \AA}^0$
 $= 4 \times 10^{-10}$

$$= \underline{\underline{0.0376 \times 10^{-17} \text{ J}}}$$

E_2 if

then, $n=2$.

$$\begin{aligned}
 \therefore E_2 &= \frac{2^2 \times (6.625 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (4 \times 10^{-10})^2} \\
 &= \underline{\underline{0.1507 \times 10^{-17} \text{ J}}}
 \end{aligned}$$

then, $E_2 - E_1 = \underline{\underline{0.1131 \times 10^{-17} \text{ J}}}$

③ Estimate the de Broglie wavelength of an electron moving with a kinetic energy of 100 eV.

$$K.E = 100 \text{ eV} = 100 \times 1.6 \times 10^{-19} \text{ J}$$

$$\begin{aligned}
 \text{We know, } K.E &= \frac{1}{2} m v^2 \\
 &= \frac{m \times m \times v \times v}{2m} = \frac{m^2 v^2}{2m}
 \end{aligned}$$

$$K.E = \frac{p^2}{2m}$$

$$[\because p = mv]$$

$$\therefore p = \sqrt{2m K.E}$$

(11)
de Broglie's wavelength, $\lambda = \frac{h}{p}$

$$= \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 100 \times 1.6 \times 10^{19}}}$$

$m = 9.1 \times 10^{-31}$
~~KE~~ $K.E = 100 \times 1.6 \times 10^{19}$

$$= \underline{\underline{1.22 \times 10^{-10} \text{ m}}}$$

① Operators in Quantum Mechanics

An operator transforms one function into another.

Eg. The differential operator $\frac{d}{dx}$ which applied to a function $f(x)$, we get the differential coefficient of $f(x)$, denoted by $f'(x)$.

$$\text{i.e., } \frac{d}{dx} [f(x)] = f'(x)$$

Here, $\frac{d}{dx}$ is the operator and $f(x)$ is the operand.

In Q.M, we represent the operator by a bold letter **A**.

Operators in Q.M are linear, i.e. **A** is linear if it satisfies the condition,

$$\mathbf{A} [\psi_1 + \psi_2] = \mathbf{A}\psi_1 + \mathbf{A}\psi_2$$

$$\mathbf{A} [C\psi_1] = C\mathbf{A}\psi_1, \quad C \text{ is a const.}$$

Energy and Momentum Operators

Consider the wavefunction for a free particle

$$\Psi(x,t) = A e^{-\frac{i}{\hbar} [Et - Px]}$$

Diff. w.r to x & t .

$$\frac{\partial \Psi}{\partial x} = A e^{-\frac{i}{\hbar} [Et - Px]} \cdot \frac{i}{\hbar} P$$

$$= \frac{Pi}{\hbar} \Psi \quad \text{--- (1)}$$

$$\frac{\partial \Psi}{\partial t} = A e^{-\frac{i}{\hbar} [Et - Px]} \cdot \frac{-i}{\hbar} E$$

$$= -\frac{iE}{\hbar} \Psi \quad \text{--- (2)}$$

From (1),

$$\therefore P\Psi = -i\hbar \frac{\partial \Psi}{\partial x}$$

$$E\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

\therefore The momentum and Energy operators are,

$$\boxed{\begin{aligned} P_x &= -i\hbar \frac{\partial}{\partial x} \\ E &= i\hbar \frac{\partial}{\partial t} \end{aligned}}$$

Kinetic Energy Operator

We know, the k.E, $E_k = \frac{p^2}{2m}$

$$\begin{aligned}
 E_k &= \frac{1}{2} m v^2 \\
 &= \frac{1}{2} \frac{m^2 v^2}{m} \\
 &= \frac{p^2}{2m}
 \end{aligned}$$

We have, $P_x = -i\hbar \frac{\partial}{\partial x}$, the momentum operator,

then, ① \Rightarrow $E_k = \frac{(-i\hbar \frac{\partial}{\partial x})^2}{2m}$

$$E_k = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

k.E depends on 1D.

In classical mechanics,

In 3D,

$$E_k = \frac{-\hbar^2}{2m} \nabla^2$$

Total Energy (Hamiltonian) operator

The classical expression for the Hamiltonian function for 1D motion which is equal to the total energy of the particle,

$$i, H = \frac{p_x^2}{2m} + V(x)$$

$V(x) \rightarrow$ P.E of the particle

Total Energy = k.E + P.E
This total energy is Hamiltonian

Substituting the operator P_x

$$\text{then, } H = \frac{1}{2m} P_x^2 + V(x)$$

$$= \frac{1}{2m} \left[-i\hbar \frac{\partial}{\partial x} \right]^2 + V(x)$$

$$\boxed{H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)}$$

Hamiltonian
or total
energy operator
in 1D

$$\text{In 3D, } \boxed{H = -\frac{\hbar^2}{2m} \nabla^2 + V}$$

③ Eigen values and Eigen functions of Operators

An operator A operating on a function ψ is to multiply ψ by a constant factor, λ .

$$\text{is, } A\psi = \lambda\psi$$

Here ψ is an eigen function of A and corresponding eigen value is λ .

We know the time dependent Schrodinger eqn.

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

$$i, E\psi = \left(\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \right) \psi \quad (6)$$

Here $\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V$ is the total energy

or Hamiltonian operator, H

$$i, E\psi = H\psi$$

Thus, ψ is known as the eigen function
and E is eigen value.