

# *Quantum Mechanics*

# Wave Velocity or Phase Velocity

When a **monochromatic wave** travels through a medium, its **velocity of advancement** in the medium is called the **wave velocity or phase velocity** ( $V_p$ ).

$$V_p = \frac{\omega}{k}$$

where  $\omega = 2\pi\nu$  is the **angular frequency**

and  $k = \frac{2\pi}{\lambda}$  is the **wave number**.

# Wave velocity/phase velocity

- ⦿ Wave motion is a form of **disturbance which travels through medium** due to the repeated motion of the particles of the medium about their mean positions, the motion being handed over from one particle to the next.
- ⦿ Every particle begins its vibrations a little later than its predecessor and there is a progressive change of phase as wave travel from one particle to the next.
- ⦿ The phase relationship of these particles that we observe as a wave and the velocity with which the plane of equal phase travels through the medium, is known as **phase velocity**.
- ⦿ Hence the velocity with which monochromatic wave propagates through medium is called the **wave velocity**.

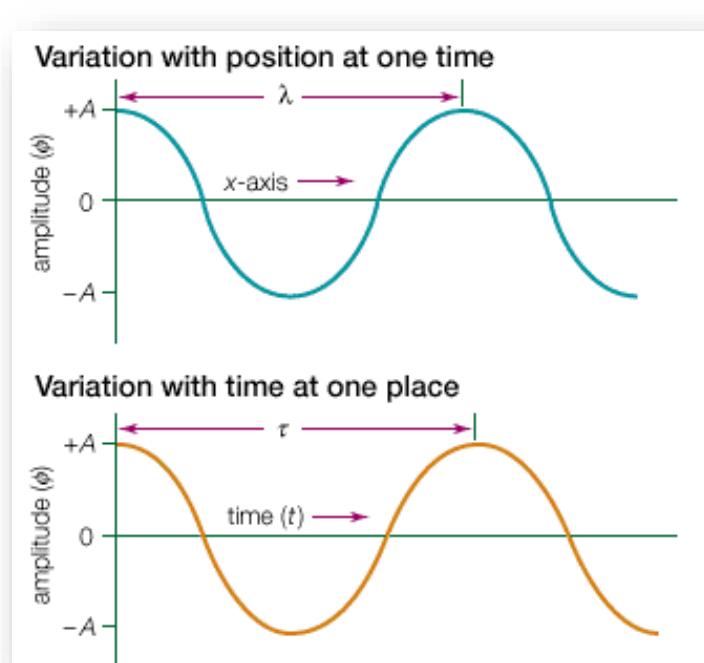
The equation of motion for a plane progressive wave is given by

$$y=A \cos (wt - kx)$$

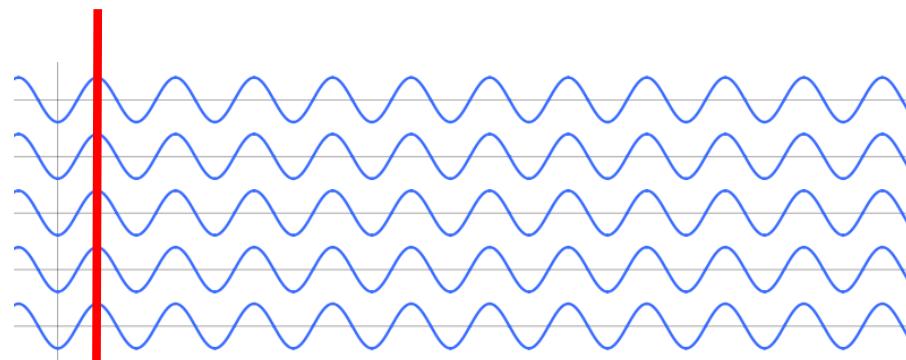
Where  $y$ = displacement of the wave depends upon space coordinate ' $x$ ' and time ' $t$ '.  $A$  is the amplitude and  $w$  is the angular frequency which is related to the frequency  $v$  by

$$w=2\pi v$$

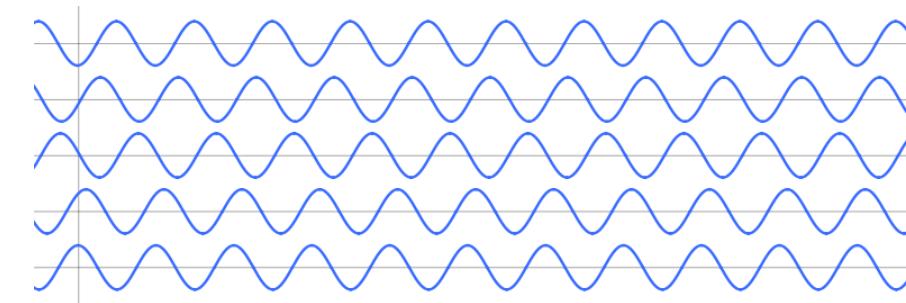
$k$  is the phase constant and given by  $k=2\pi/\lambda$



The argument of the cosine function represents the **phase** of the wave,  $\phi$ , or the fraction of a complete cycle of the wave.



In-phase waves



Out-of-phase waves

*For plane constant wave*

$$wt - kx = \text{constant}$$

*Differentiating w.r.t. t*

$$w - k \left( \frac{dx}{dt} \right)_{\phi} = 0$$

$$\left( \frac{dx}{dt} \right)_{\phi} = \left( \frac{w}{k} \right) = v_p$$

Hence, from equations we conclude that the phase velocity or wave velocity is the ratio of angular frequency 'w' to the propagation constant 'k'.

# Phase velocity of de-Broglie waves exceeds velocity of light

According to de-Broglie, a moving particle of mass  $m$  and velocity  $v$ , is associated with a single wave. The phase velocity is given by

$$v_p = \lambda v$$

$$E = hv \text{ or } v = \frac{E}{h}$$

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

$$v_p = \lambda v = \frac{h}{mv} \cdot \frac{E}{h}$$

$$\mathbf{v_p} = \frac{\mathbf{E}}{mv}$$

From Einstein's equation:  $E=mc^2$

$$v_p = \frac{mc^2}{mv} = \frac{c^2}{v}$$

By theory of relativity no particle can move with speed of light. Hence,  $c > v$

It clearly indicates that phase velocity  $v_p$  of the associated wave is greater than  $c$ , velocity of light.

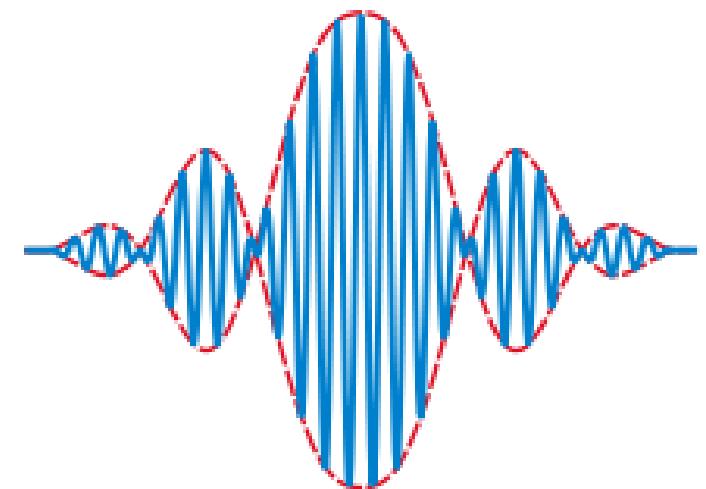
It indicates that the associated wave with the particle moves faster than the particle itself. The particle will be left far behind.

The phase velocity is a purely mathematical concept and

# Group velocity: the concept of wave packet

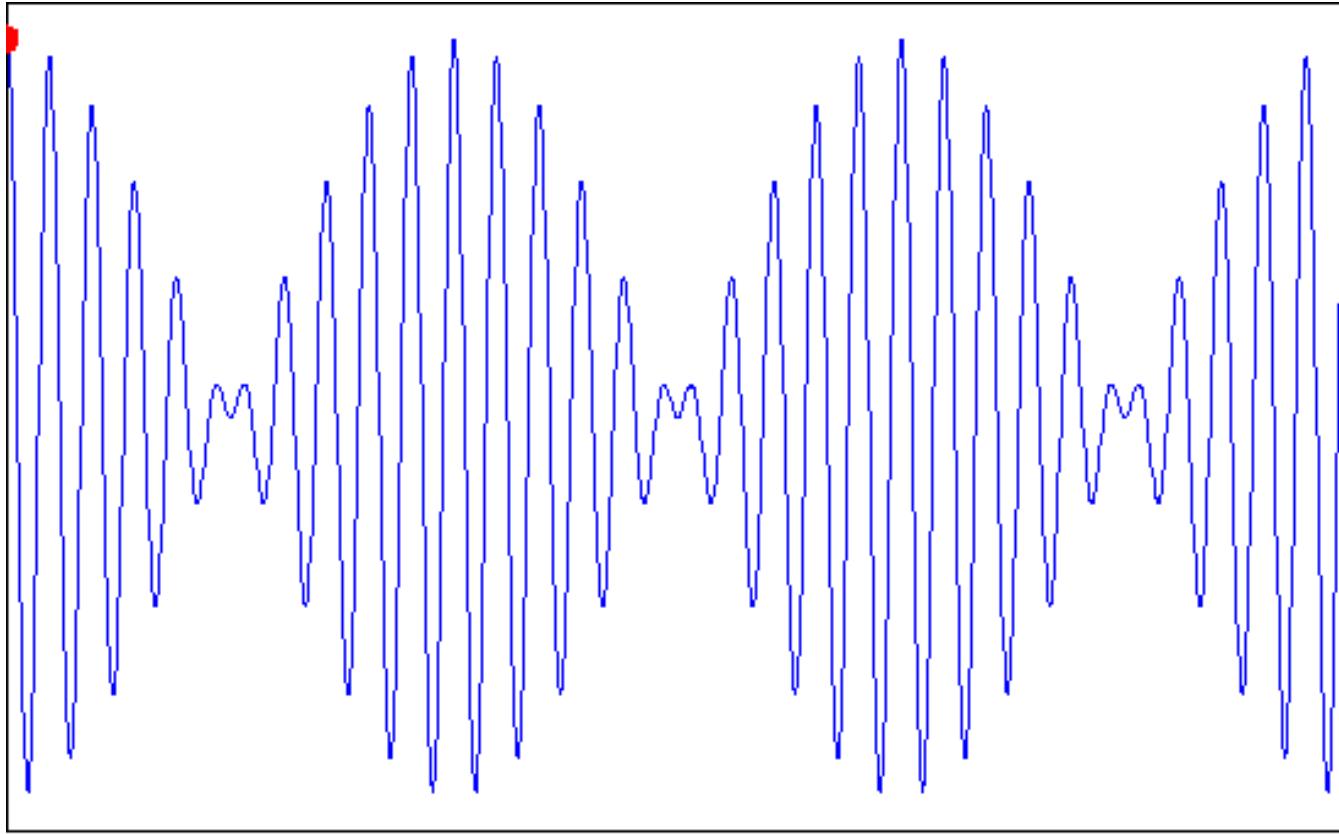
The **group velocity** of a wave is the velocity with which the overall shape of the waves' amplitudes known as the modulation or envelope of the wave propagates through space.

For example, imagine what happens if a stone is thrown into the middle of a very still pond. When the stone hits the surface of the water, a circular pattern of waves appears. It soon turns into a circular ring of waves with a quiescent center. The ever expanding ring of waves is the wave group, within which one can discern individual wavelets of differing wavelengths traveling at different speeds. The longer waves travel faster than the group as a whole, but they die out as they approach the leading edge. The shorter waves travel more slowly and they die out as they emerge from the trailing boundary of the group.



Solid line: A wave packet. Dashed line: The envelope of the wave packet. The envelope moves at the group velocity.

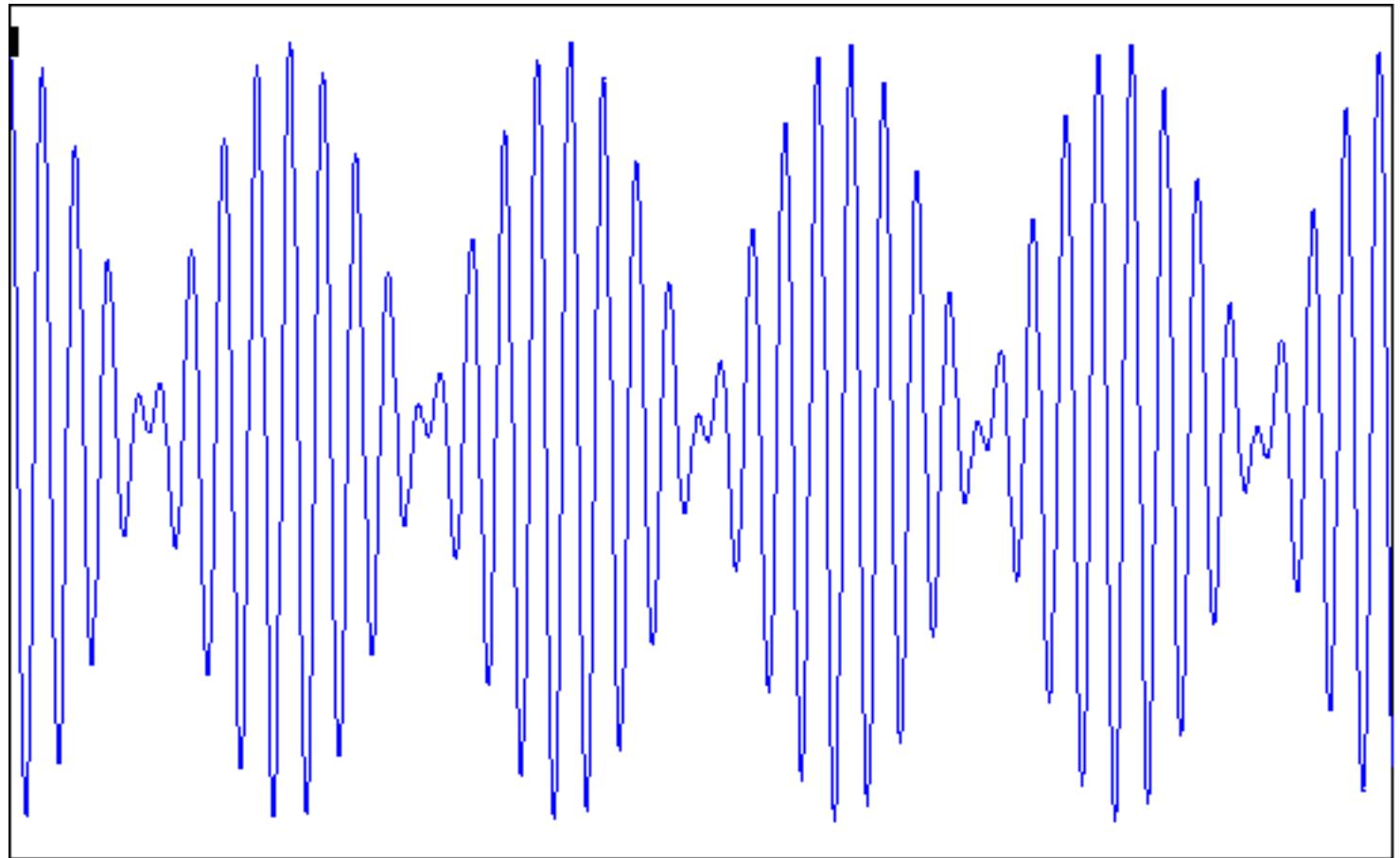
# *The Group Velocity*



This is the velocity at which the overall shape of the wave's amplitudes, or the wave 'envelope', propagates. (= signal velocity)

Here, phase velocity = group velocity (the medium is **non-dispersive**)

## *Dispersion: phase/group velocity depends on frequency*



Black dot moves at phase velocity. Red dot moves at group velocity.  
This is *normal dispersion* (refractive index decreases with increasing  $\lambda$ )

# *Expression for group velocity and wave velocity*

Let the wave packet is formed by the superimposition of two waves of equal amplitude 'A' but of slightly different frequency  $w$  and  $w+dw$  and propagation constants  $k$  and  $k+dk$ . Displacement  $y_1$  and  $y_2$  of two waves

$$y_1 = A \cos(wt - kx)$$

$$y_2 = A \cos[(w+dw)t - (k+dk)x]$$

The resultant displacement  $y = y_1 + y_2$

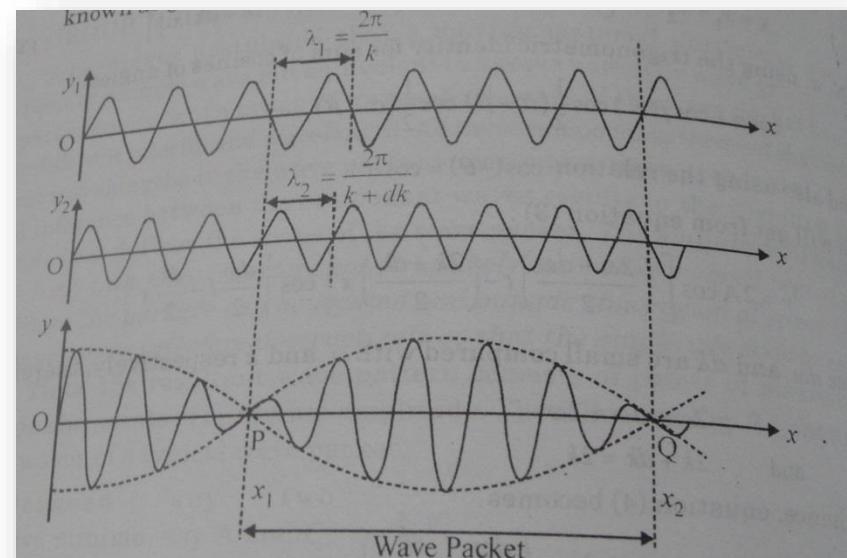
$$y = A \{ \cos(wt - kx) + \cos[(w+dw)t - (k+dk)x] \}$$

$$y = 2A \cos \left[ \left( \frac{2w+dw}{2} \right) t - \left( \frac{2k+dk}{2} \right) x \right] \cos \left( \frac{dw}{2} t - \frac{dk}{2} x \right)$$

Since  $dw$  and  $dk$  are small compared with  $w$  and  $k$

$$y = 2A \cos [wt - kx] \cos \left( \frac{dw}{2} t - \frac{dk}{2} x \right)$$

This equation represent a wave of angular frequency  $w$  and wave number  $k$  which has been modulated by a wave of angular frequency  $dw/2$  and wave number  $dk/2$ . *The effect of modulation is to produce successive wave packets.*



Wave packet produced by superimposition of two waves with slightly different frequency

# Group Velocity

In practice, we came across pulses rather than monochromatic waves. A **pulse** consists of a **number of waves** differing slightly from one another in frequency.

The **observed velocity** is, however, the velocity with which the maximum amplitude of the group advances in a medium.

So, the **group velocity** is the velocity with which the energy in the group is transmitted ( $V_g$ ).

The individual waves travel “inside” the group with their phase velocities.

$$V_g = \frac{d\omega}{dk}$$

# *Relation between phase velocity and group velocity*

- Phase velocity

$$v_p = \frac{w}{k} \text{ means, } w=v_p k$$

- Group velocity

$$v_g = \frac{dw}{dk} = \frac{d(v_p k)}{dk} = v_p + k \frac{dv_p}{dk}$$

$$v_g = v_p + k \frac{dv_p}{d\lambda} \cdot \frac{d\lambda}{dk}$$

$$\frac{d\lambda}{dk} = - \frac{\lambda^2}{2\pi}$$

$$\text{Therefore, } v_g = v_p + k \frac{dv_p}{d\lambda} \cdot \left( - \frac{\lambda^2}{2\pi} \right)$$

$$v_g = v_p - \lambda \frac{dv_p}{d\lambda}$$

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- A medium in which the waves varies with wavelength is known as **dispersive medium**. Hence,  $\frac{dv_p}{d\lambda} \neq 0$  so the waves of different frequencies propagate with different velocities through the medium. Therefore, when the medium is dispersive  $v_g$  is less than  $v_p$
- In **non-dispersive media** all waves of all wavelengths travel with the same speed so  $\frac{dv_p}{d\lambda} = 0$  and  $v_g = v_p$ . This is **true** for electromagnetic waves in vacuum and elastic waves in homogeneous medium.

# Group Velocity of De-Broglie's waves

The discrepancy is resolved by postulating that **a moving particle** is associated with **a “wave packet” or “wave group”, rather than a single wave-train.**

A **wave group** having wavelength  $\lambda$  is composed of a **number of component waves with slightly different wavelengths** in the neighborhood of  $\lambda$ .

Suppose a particle of rest mass  $m_o$  moving with velocity  $v$  then associated matter wave will have

$$\omega = \frac{2\pi mc^2}{h} \quad \text{and} \quad k = \frac{2\pi mv}{h}$$

$$\text{where } m = \frac{m_o}{\sqrt{1 - v^2/c^2}}$$

$$\omega = \frac{2\pi m_o c^2}{h\sqrt{1-v^2/c^2}} \quad \text{and}$$

$$k = \frac{2\pi m_o v}{h\sqrt{1-v^2/c^2}}$$

On differentiating w.r.t. velocity, v

$$\frac{d\omega}{dv} = \frac{2\pi m_o v}{h(1-v^2/c^2)^{3/2}} \quad (\text{i})$$

$$\frac{dk}{dv} = \frac{2\pi m_o}{h(1-v^2/c^2)^{3/2}} \quad (\text{ii})$$

Dividing (i) by (ii)

$$\frac{d\omega}{dv} \cdot \frac{dv}{dk} = \frac{2\pi m_o v}{2\pi m_o}$$

$$\frac{d\omega}{dk} = v = V_g$$

**Wave group** associated with a moving particle also moves with the velocity of the particle.

Moving particle  $\equiv$  wave packet or wave group

# Heisenberg Uncertainty Principle

It states that only one of the “**position**” or “**momentum**” can be measured accurately at a single moment within the instrumental limit.

or

It is impossible to measure both the **position** and **momentum** simultaneously with unlimited accuracy.

$\Delta x \rightarrow$  uncertainty in position

$\Delta p_x \rightarrow$  uncertainty in momentum

then

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

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

The product of  $\Delta x$  &  $\Delta p_x$  of an object is greater than or equal to  $\frac{\hbar}{2}$

If  $\Delta x$  is measured accurately i.e.  $\Delta x \rightarrow 0 \Rightarrow \Delta p_x \rightarrow \infty$

The principle applies to all **canonically conjugate pairs** of quantities in which measurement of one quantity affects the capacity to measure the other.

Like, **energy E** and **time t**.

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

and

**angular momentum L** and **angular position θ**

$$\Delta L \Delta \theta \geq \frac{\hbar}{2}$$

# *Applications of Heisenberg Uncertainty Principle*

## (i) Non-existence of electron in nucleus

Order of diameter of a nucleus  $\sim 5 \times 10^{-15} \text{ m}$

If electron exist in the nucleus then

$$(\Delta x)_{\max} = 5 \times 10^{-15} \text{ m}$$

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

$$(\Delta x)_{\max} (\Delta p_x)_{\min} = \frac{\hbar}{2}$$

$$(\Delta p_x)_{\min} = \frac{\hbar}{2 \Delta x} = 1.1 \times 10^{-20} \text{ kg.m.s}^{-1}$$

then

$$E = 20 \text{ MeV}$$

$\therefore$  relativistic

- Thus the **kinetic energy** of an electron must be greater than **20 MeV** to be a part of nucleus
- Experiments** show that the electrons emitted by certain unstable nuclei **don't have energy greater than 3-4 MeV.**
- Thus we can conclude that the **electrons cannot be present within nuclei.**

# *Concept of Bohr Orbit violates Uncertainty Principle*

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$$

But  $E = \frac{p^2}{2m}$

$$\Delta E = \frac{p \Delta p}{m} = \frac{mv \Delta p}{m} = \frac{\Delta x}{\Delta t} \Delta p$$

$$\Delta E \cdot \Delta t = \Delta x \cdot \Delta p$$

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$$

According to the concept of Bohr orbit, ***energy of an electron in a orbit is constant*** i.e.  $\Delta E = 0$ .

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$$

$$\Rightarrow \Delta t \rightarrow \infty$$

It means that all energy states of the atom must have an infinite life-time.

**But** the excited states of the atom have life-time  $\sim 10^{-8} \text{ sec}$ .

The finite life-time  $\Delta t$  gives a finite width (uncertainty) to the energy levels.

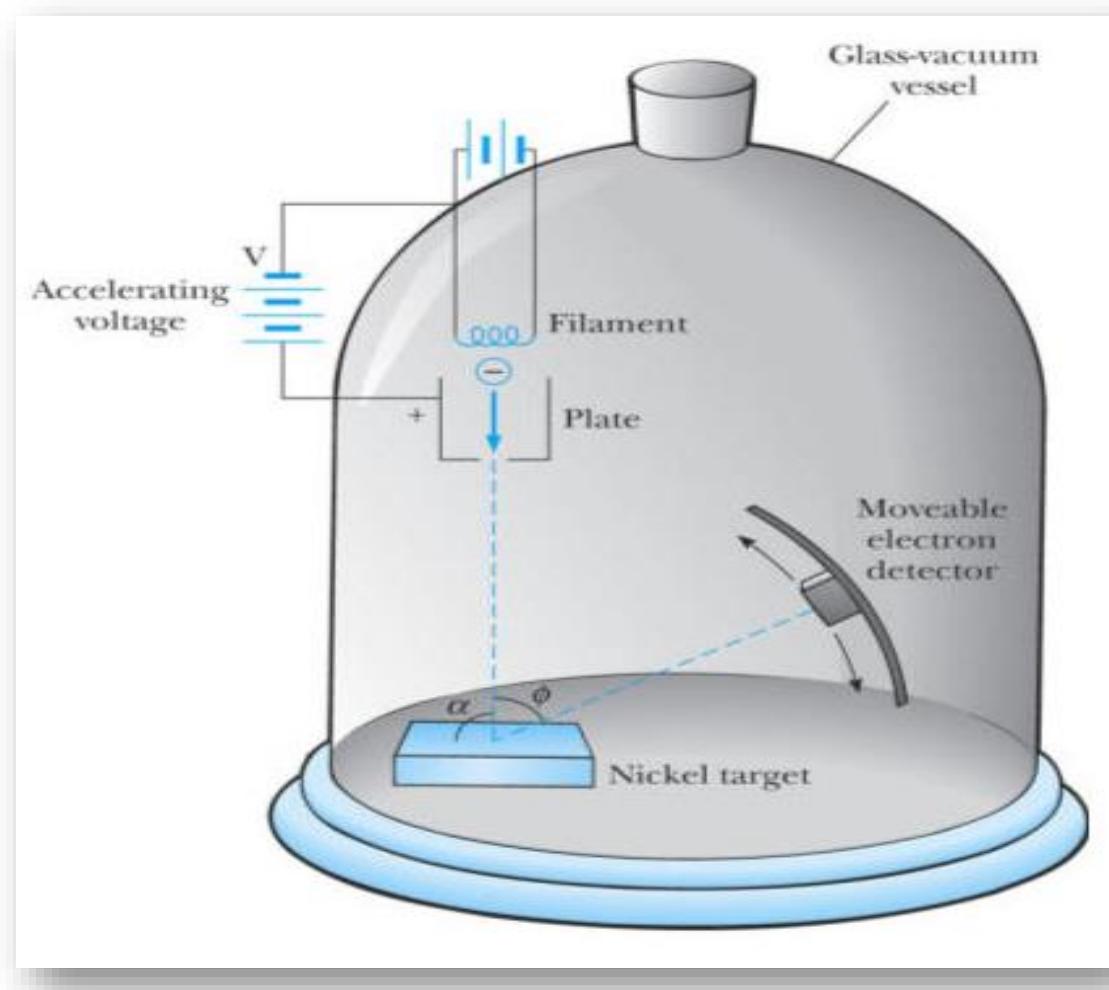
# *Davisson & Germer experiment of electron diffraction*

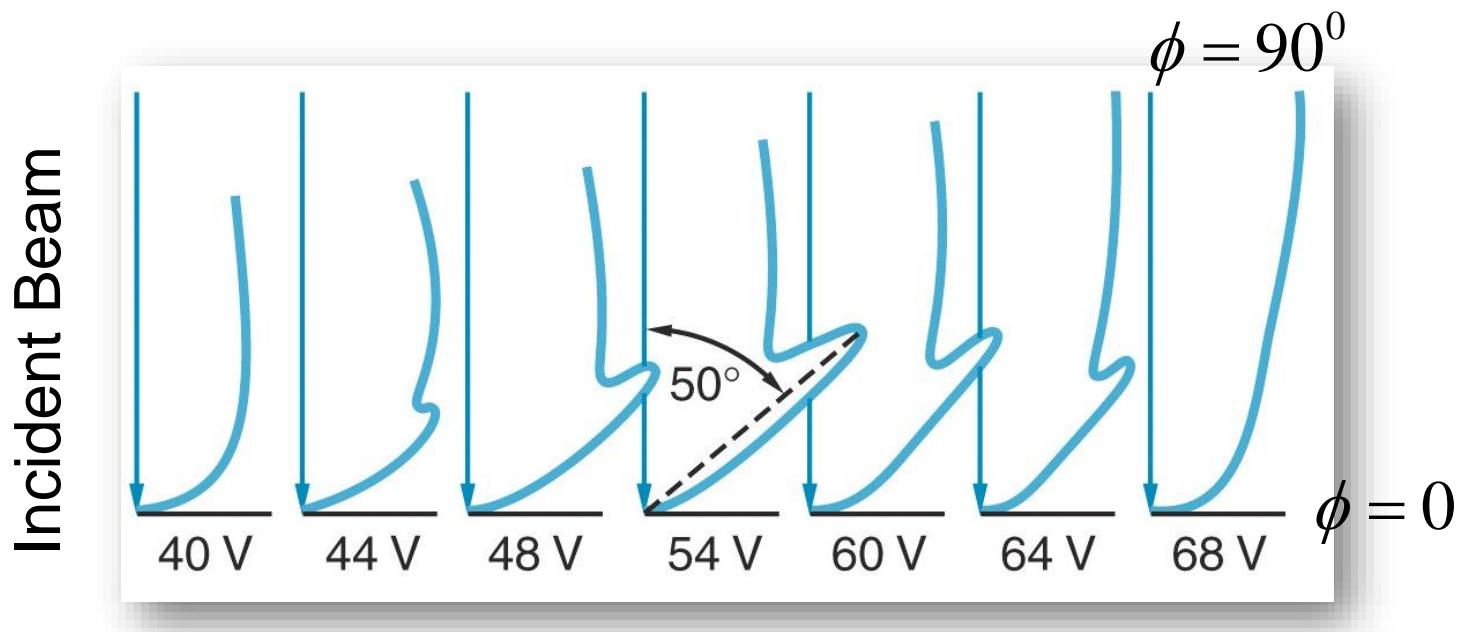
- ⦿ If particles have a **wave nature**, then under appropriate conditions, they **should exhibit diffraction**.
- ⦿ **Davisson & Germer** measured the **wavelength of electrons**
- ⦿ This provided **experimental confirmation** of the **matter waves** proposed by de Broglie

# Davisson and Germer Experiment

Electrons exhibit diffraction when they are scattered from crystals whose atoms are spaced appropriately.

The apparatus had facility to vary the energy of the electrons in the primary beam, the angle at which they are incident upon the target and the position of the detector.





**Current vs accelerating voltage** has a **maximum** (a bump or kink noticed in the graph), i.e. the highest number of electrons is scattered in a specific direction.

**The bump becomes most prominent for 54 V at  $\phi \sim 50^\circ$**

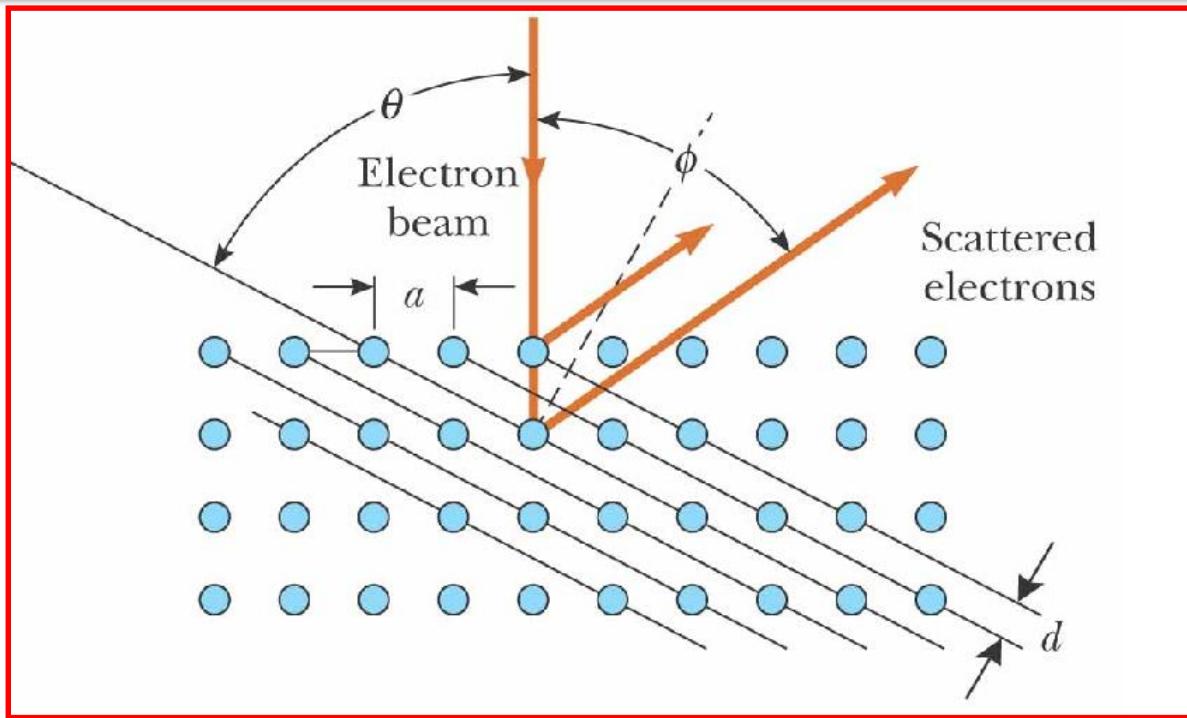
According to de Broglie, the wavelength associated with an electron accelerated through  $V$  volts is

$$\lambda = \frac{12.28}{\sqrt{V}} \text{ } \text{\AA}$$

Hence the wavelength for 54 V electron

$$\lambda = \frac{12.28}{\sqrt{54}} = 1.67 \text{ } \text{\AA}$$

From X-ray analysis we know that the nickel crystal acts as a plane diffraction grating with grating space  $d = 0.91 \text{ \AA}$

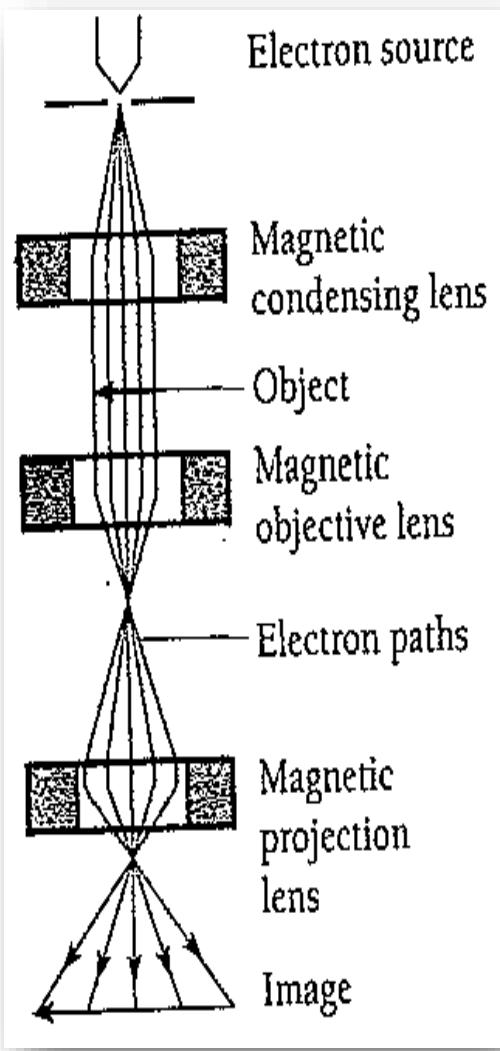


Here the diffraction angle,  $\varphi \sim 50^\circ$

The angle of incidence relative to the family of Bragg's plane

$$\theta = \left( \frac{180^\circ - 50^\circ}{2} \right) = 65^\circ$$

# *Electron Microscope: Instrumental Application of Matter Waves*



- ⦿ Resolving power of any optical instrument is **proportional** to the **wavelength** of whatever (**radiation or particle**) is used to illuminate the sample.
- ⦿ An **optical microscope** uses visible light and gives **500x** magnification and **200 nm resolution**.
- ⦿ Fast electron in **electron microscope**, however, have much shorter wavelength than those of visible light and hence a **resolution of ~0.1 nm** and a magnification of **1,000,000x** can be achieved in an Electron Microscope.

# Wave function

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

Wave function,  $\psi$  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.

$$|\psi|^2 = \psi^* \psi \quad \psi \text{ is the probability amplitude.}$$

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

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

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

# *Properties of wave function*

## **1. It must be finite everywhere.**

If  $\psi$  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  $\psi$  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

$$\psi = A \sin \frac{2\pi x}{\lambda} \quad (\text{i})$$

where

$\psi$  is the wave amplitude for a given  $x$ .

$A$  is the maximum amplitude.

$\lambda$  is the wavelength

From (i)

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

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

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

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

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

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

Equation (ii) now becomes

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

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

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

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

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

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

$$\psi = A e^{\frac{-i}{\hbar}(Et - px)} \quad (i)$$

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

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

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

Differentiating (i) w.r.t. t

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

For non-relativistic case

$$E = \text{K.E.} + \text{Potential Energy}$$

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

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

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  $\psi_1$  and  $\psi_2$  are two solutions of any Schrodinger equation of a system, then linear combination of  $\psi_1$  and  $\psi_2$  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)  $\psi_1$  and  $\psi_2$  follow the superposition principle

If  $P_1$  is the probability density corresponding to  $\psi_1$  and  $P_2$  is the probability density corresponding to  $\psi_2$

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

Total probability will be

$$\begin{aligned} P &= |\psi|^2 = |\psi_1 + \psi_2|^2 \\ &= (\psi_1 + \psi_2)^*(\psi_1 + \psi_2) \\ &= (\psi_1^* + \psi_2^*)(\psi_1 + \psi_2) \\ &= \psi_1^*\psi_1 + \psi_2^*\psi_2 + \psi_1^*\psi_2 + \psi_2^*\psi_1 \\ P &= P_1 + P_2 + \psi_1^*\psi_2 + \psi_2^*\psi_1 \\ P &\neq P_1 + P_2 \end{aligned}$$

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

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} f(x) |\psi|^2 dx \quad \text{for normalized } \psi$$

Thus expectation value for position 'x' is

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\psi|^2 dx$$

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  $\psi = ax$  between  $x = 0$  &  $1$ ,  $\psi = 0$  elsewhere.

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Solution

$$\langle x \rangle = \int_0^1 x |\psi|^2 dx = a^2 \int_0^1 x^3 dx$$

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

$$\langle x \rangle = \frac{a^2}{4}$$

# 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

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

Then

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

Here

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

is called the momentum operator

Similarly

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

Here

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

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

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

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

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

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

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 ( $\psi$ ) is operated by an operator ‘ $\alpha$ ’ 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

$\psi$  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

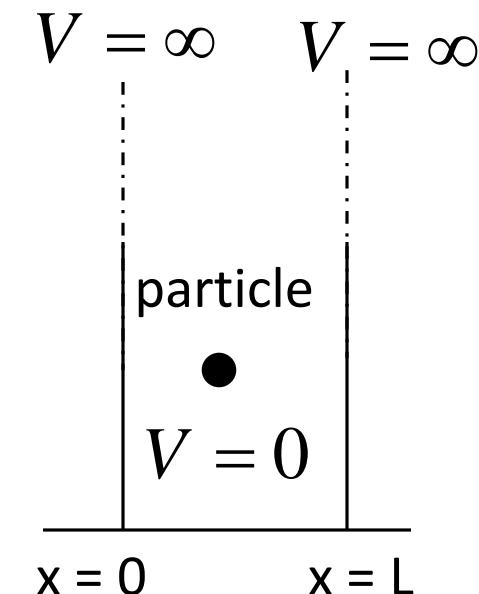
Consider a particle of rest mass  $m_o$  enclosed in a one-dimensional box (infinite potential well).

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  $\psi$

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



Thus for a particle inside the box Schrodinger equation is

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

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

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

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

Equation (i) becomes

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

General solution of equation (iii) is

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

Boundary condition says  $\psi = 0$  when  $x = 0$

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

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

Equation (iv) reduces to

$$\psi(x) = A \sin kx \quad (v)$$

Boundary condition says  $\psi = 0$  when  $x = L$

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

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

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

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

$$kL = n\pi$$

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

Put this in Equation (v)

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

Where  $n \neq 0$  i.e.  $n = 1, 2, 3, \dots$ , because  $n=0$  gives  $\psi = 0$  everywhere.

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

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

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

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

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

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  $n = 1$

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

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

$$\Rightarrow \Delta x \rightarrow \infty$$

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

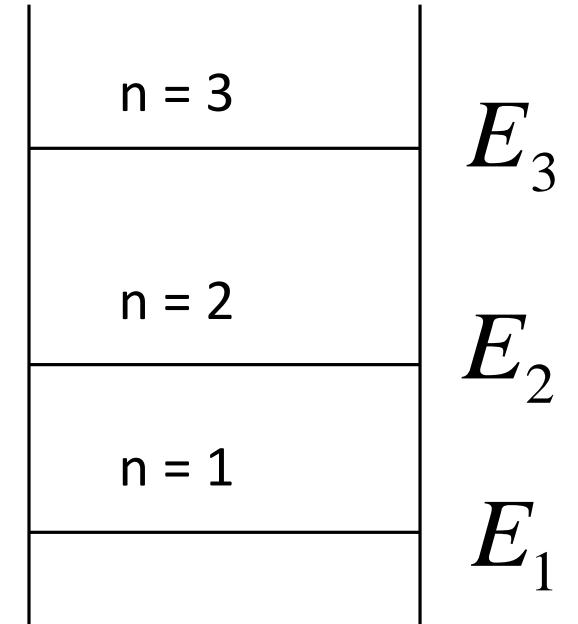
Thus zero value of zero point energy violates the Heisenberg's uncertainty principle and hence zero value is not acceptable.

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

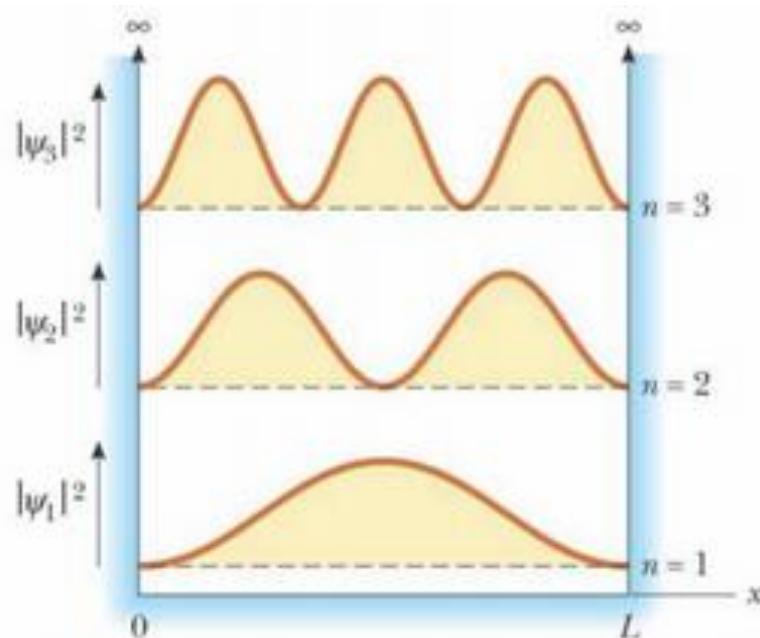
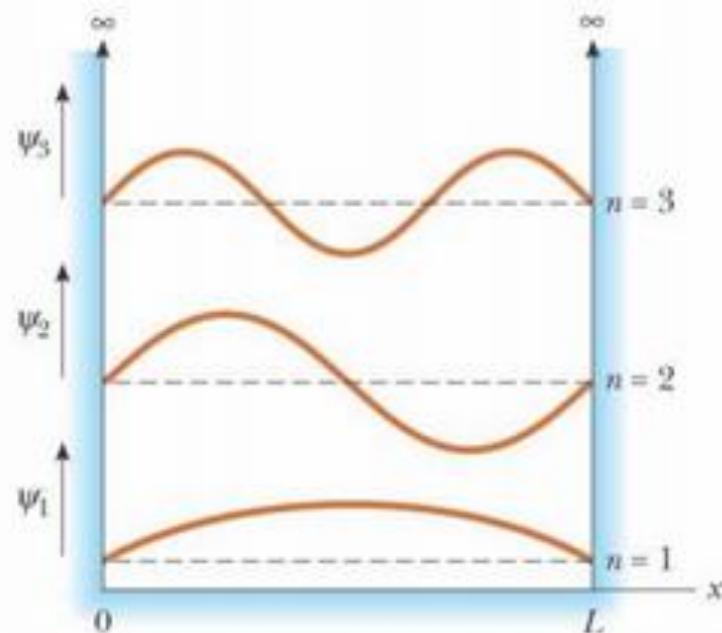
$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

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 at  $L/2$ .



## Particle in a Three Dimensional Box

Eigen energy

$$E = E_x + E_y + E_z$$

$$E = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8mL^2}$$

Eigen function

$$\psi = \psi_x \psi_y \psi_z$$

$$\psi = A_x A_y A_z \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L}$$

$$\psi = \left( \sqrt{\frac{2}{L}} \right)^3 \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L}$$