Quantum Mechanics

Introduction

There are a few phenomenon which the classical mechanics failed to explain.

1. Stability of an atom
2. Spectral series of Hydrogen atom
3. Black body radiation

Max Planck in 1900 at a meeting of German Physical Society read his paper “On the theory of the Energy distribution law of the Normal Spectrum”. This was the start of the revolution of Physics i.e. the start of **Quantum Mechanics.**

Quantum Mechanics

It is a generalization of Classical Physics that includes classical laws as special cases.

Quantum Physics extends that range to the region of small dimensions.

Just as ‘c’ the velocity of light signifies universal constant, the Planck's constant characterizes Quantum Physics.

$$h = 6.65 \times 10^{-27} \, erg.\mathrm{sec}$$

$$h = 6.625 \times 10^{-34} \, Joule.\mathrm{sec}$$

Quantum Mechanics

It is able to explain

1. Photo electric effect
2. Black body radiation
3. Compton effect
4. Emission of line spectra

The most outstanding development in modern science was the conception of Quantum Mechanics in 1925. This new approach was highly successful in explaining about the behavior of atoms, molecules and nuclei.

Photo Electric Effect

The emission of electrons from a metal plate when illuminated by light or any other radiation of any wavelength or frequency (suitable) is called photoelectric effect. The emitted electrons are called ‘photo electrons’.

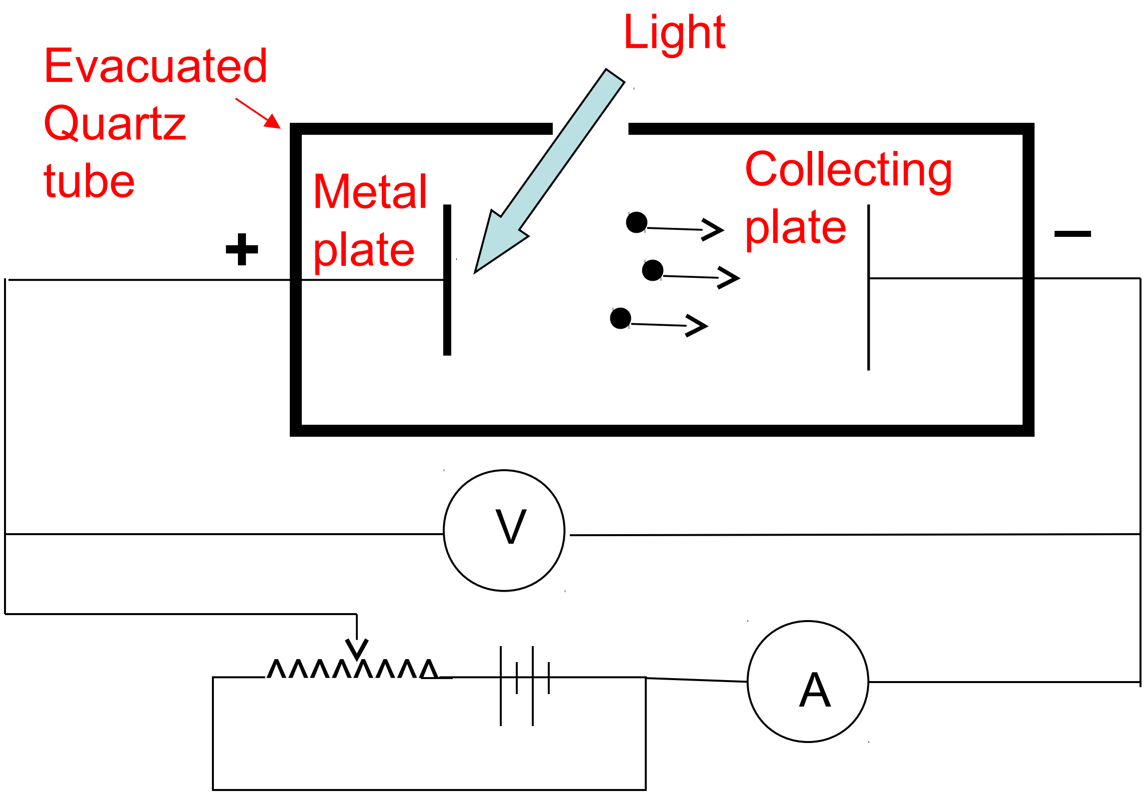


Photo Electric Effect

Experimental findings of the photoelectric effect

1. There is no time lag between the arrival of light at the metal surface and the emission of photoelectrons.
2. When the voltage is increased to a certain value say V_o, the photocurrent reduces to zero.
3. Increase in intensity increase the number of the photoelectrons but the electron energy remains the same.

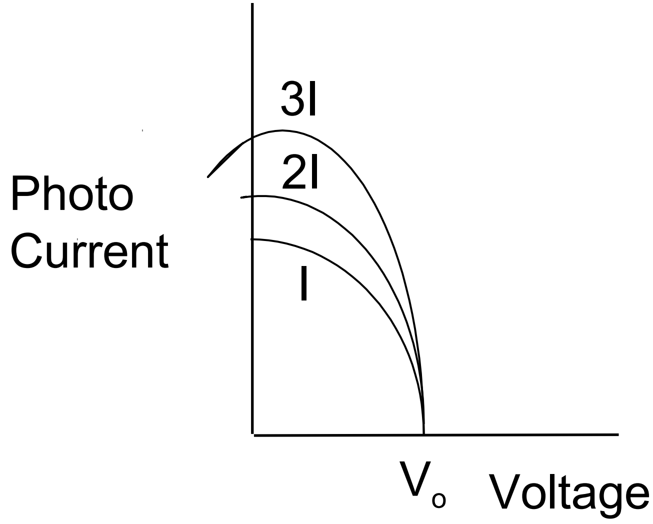
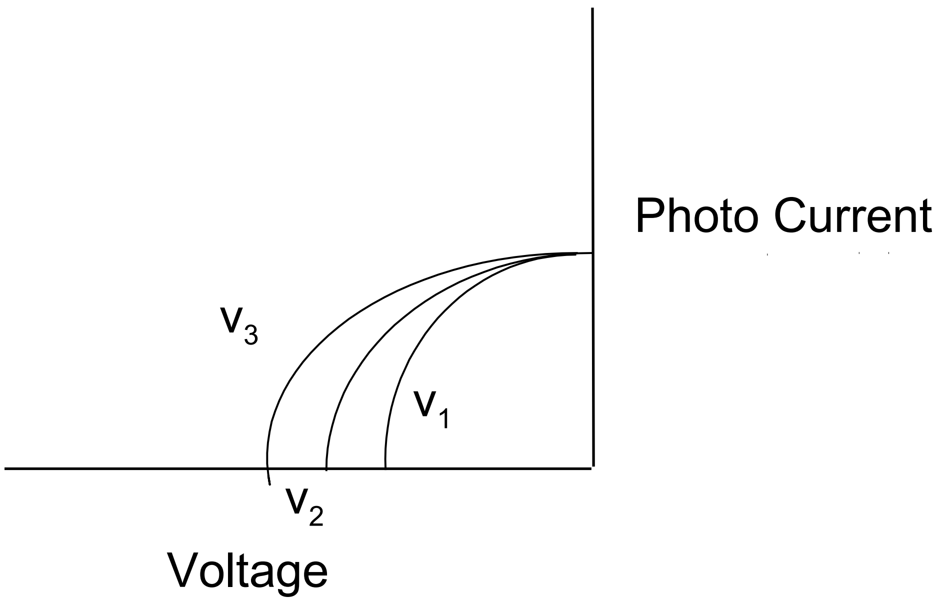


Photo Electric Effect

4. Increase in frequency of light increases the energy of the electrons. At frequencies below a certain critical frequency (characteristics of each particular metal), no electron is emitted.



Einstein's Photo Electric Explanation

The energy of a incident photon is utilized in two ways

1. A part of energy is used to free the electron from the atom known as photoelectric workfunction (W_o).
2. Other part is used in providing kinetic energy to the emitted electron . $\left(\frac{1}{2}mv^2\right)$

$$h\nu = W_o + \frac{1}{2}mv^2$$

This is called Einstein's photoelectric equation.

$$h\nu = W_o + KE_{\max}$$

$$h\nu = h\nu_o + KE_{\max}$$

$$KE_{\max} = h(\nu - \nu_o)$$

If $\nu < \nu_o$, no photoelectric effect

$$W_o = h\nu_o = \frac{hc}{\lambda_o}$$

$$\lambda_o = \frac{hc}{W_o} = \frac{12400}{W_o(eV)} \overset{o}{A}$$

If V_o is the stopping potential, then

$$KE_{\max} = h(\nu - \nu_o)$$

$$eV_o = h\nu - h\nu_o$$

$$V_o = \frac{h\nu}{e} - \frac{h\nu_o}{e}$$

It is in form of $y = mx + c$. The graph with V_o on y-axis and ν on x-axis will be a straight line with slope h/e

Photons

Einstein postulated the existence of a particle called a photon, to explain detailed results of photoelectric experiment.

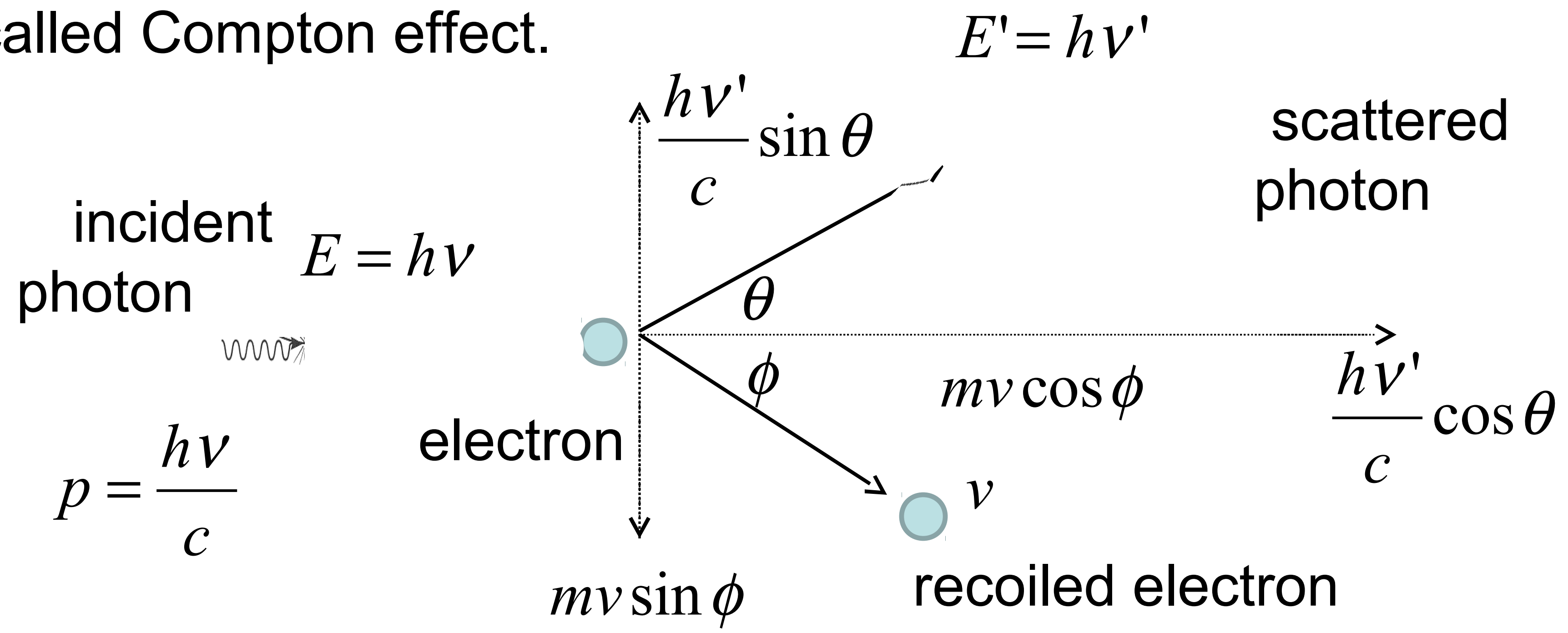
$$E_p = h\nu = \frac{hc}{\lambda}$$

Photon has zero rest mass, travels at speed of light

Explains "instantaneous" emission of electrons in photoelectric effect, frequency dependence.

Compton Effect

When a monochromatic beam of X-rays is scattered from a material then both the wavelength of primary radiation (unmodified radiation) and the radiation of higher wavelength (modified radiation) are found to be present in the scattered radiation. Presence of modified radiation in scattered X-rays is called Compton effect.



From Theory of Relativity, total energy of the recoiled electron with v ~ c is

$$E = mc^2 = K + m_o c^2$$

$$K = mc^2 - m_o c^2$$

$$K = \frac{m_o c^2}{\sqrt{1 - v^2/c^2}} - m_o c^2$$

$$K = m_o c^2 \left[\frac{1}{\sqrt{1 - v^2/c^2}} - 1 \right]$$

Similarly, momentum of recoiled electron is

$$mv = \frac{m_o v}{\sqrt{1 - v^2/c^2}}$$

Now from Energy Conversation

$$h\nu = h\nu' + m_o c^2 \left[\frac{1}{\sqrt{1 - v^2/c^2}} - 1 \right] \qquad \text{(i)}$$

From Momentum Conversation

$$\frac{h\nu}{c} = \frac{h\nu'}{c}\cos\theta + \frac{m_o v}{\sqrt{1 - v^2/c^2}}\cos\phi \qquad \text{(ii)}$$

along x-axis

and

$$0 = \frac{h\nu'}{c}\sin\theta - \frac{m_o v}{\sqrt{1 - v^2/c^2}}\sin\phi \qquad \text{(iii)}$$

along y-axis

Rearranging (ii) and squaring both sides

$$\left(\frac{h\nu}{c} - \frac{h\nu'}{c}\cos\theta\right)^2 = \frac{m_o^2 v^2}{1 - v^2/c^2}\cos^2\phi \qquad \text{(iv)}$$

Rearranging (iii) and squaring both sides

$$\left(\frac{h\nu'}{c}\sin\theta\right)^2 = \frac{m_o^2 v^2}{1 - v^2/c^2}\sin^2\phi \qquad \text{(v)}$$

Adding (iv) and (v)

$$\left(\frac{h\nu}{c}\right)^2 + \left(\frac{h\nu'}{c}\right)^2 - \frac{2h^2\nu\nu'}{c^2}\cos\theta = \frac{m_o^2 v^2}{1 - v^2/c^2} \qquad \text{(vi)}$$

From equation (i)

$$\frac{h\nu}{c} - \frac{h\nu'}{c} + m_o c = \frac{m_o c}{\sqrt{1 - v^2/c^2}}$$

On squaring, we get

$$\left(\frac{h\nu}{c}\right)^2+\left(\frac{h\nu'}{c}\right)^2+m_o^2c^2-\frac{2h^2\nu\nu'}{c^2}+2hm_o(\nu-\nu')=\frac{m_o^2c^2}{1-v^2/c^2}$$

(vii)

Subtracting (vi) from (vii)

$$-\frac{2h^2\nu\nu'}{c^2}(1-\cos\theta)+2hm_o(\nu-\nu')=0$$

$$2hm_o(\nu-\nu')=\frac{2h^2\nu\nu'}{c^2}(1-\cos\theta)$$

$$m_o(\nu-\nu')=\frac{h\nu\nu'}{c^2}(1-\cos\theta)$$

But $\nu = \dfrac{c}{\lambda}$ and $\nu' = \dfrac{c}{\lambda'}$ So,

$$m_o c\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right) = \frac{h}{\lambda\lambda'}(1-\cos\theta)$$

$$m_o c\left(\frac{\lambda' - \lambda}{\lambda\lambda'}\right) = \frac{h}{\lambda\lambda'}(1-\cos\theta)$$

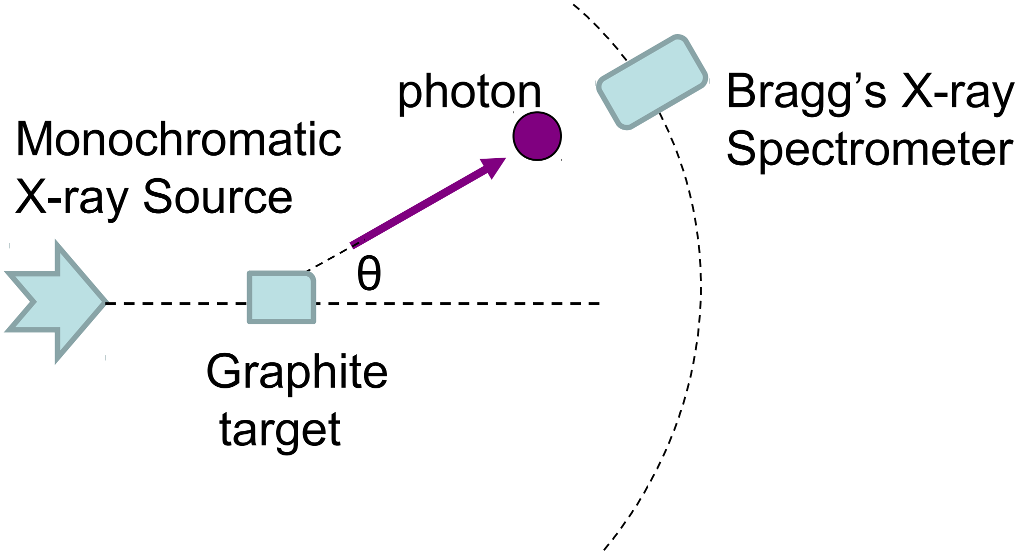
$$\lambda' - \lambda = \Delta\lambda = \frac{h}{m_o c}(1-\cos\theta)$$

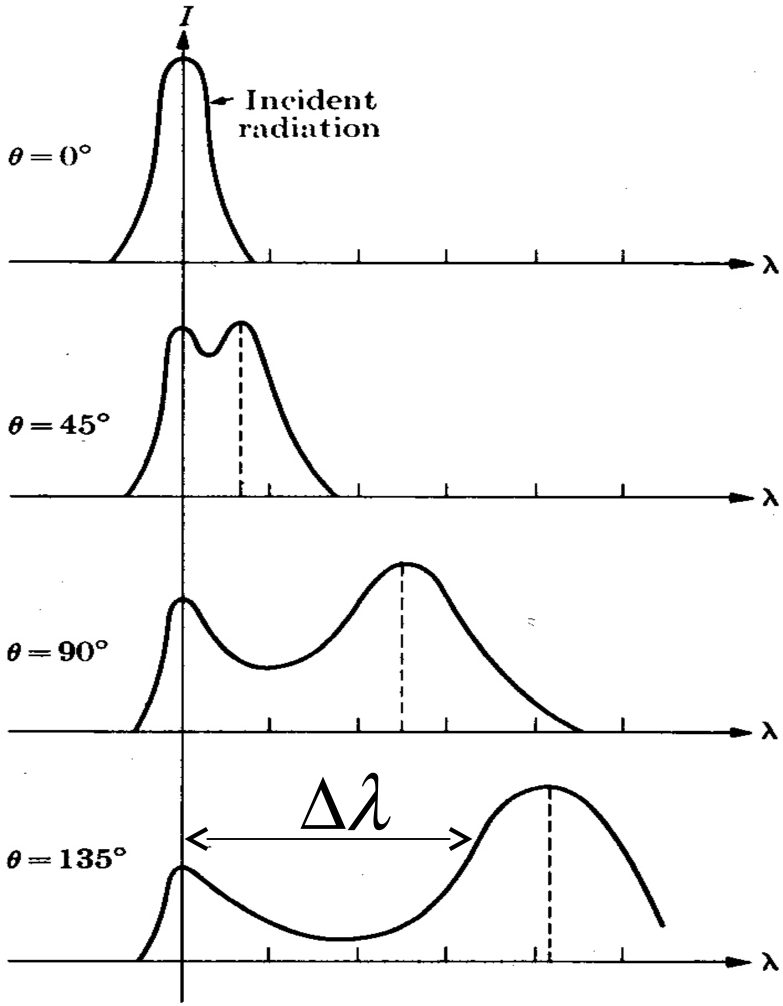
$\Delta\lambda$ is the Compton Shift.

It neither depends on the incident wavelength nor on the scattering material. It only on the scattering angle i.e. θ

$\dfrac{h}{m_o c}$ is called the Compton wavelength of the electron and its value is 0.0243 Å.

Experimental Verification





1. One peak is found at same position. This is unmodified radiation

2. Other peak is found at higher wavelength. This is modified signal of low energy.

3. $\Delta\lambda$ increases with increase in θ.

Compton effect can't observed in Visible Light

$$\Delta\lambda = \frac{h}{m_o c}(1-\cos\theta) = 0.0243\ (1-\cos\theta)\ \text{Å}$$

$\Delta\lambda$ is maximum when (1- cosθ) is maximum i.e. 2.

$$\Delta\lambda_{\max} = 0.05\ \text{Å}$$

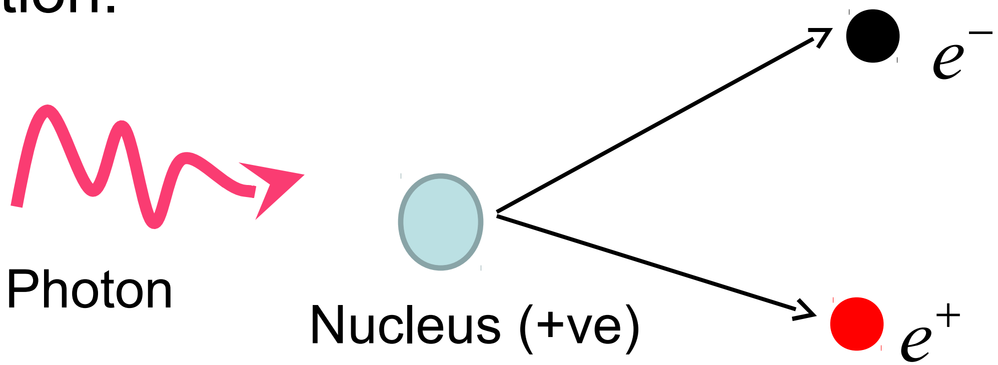
So Compton effect can be observed only for radiation having wavelength of few Å.

For $\lambda =$ 1Å $\quad \Delta\lambda$ ~ 1%

For $\lambda =$ 5000Å $\quad \Delta\lambda$ ~ 0.001% (undetectable)

Pair Production

When a photon (electromagnetic energy) of sufficient energy passes near the field of nucleus, it materializes into an electron and positron. This phenomenon is known as pair production.



In this process charge, energy and momentum remains conserved prior and after the production of pair.

The rest mass energy of an electron or positron is 0.51 MeV (according to $E = mc^2$).

The minimum energy required for pair production is 1.02 MeV.

Any additional photon energy becomes the kinetic energy of the electron and positron.

The corresponding maximum photon wavelength is 1.2 pm. Electromagnetic waves with such wavelengths are called gamma rays (γ).

Pair Annihilation

When an electron and positron interact with each other due to their opposite charge, both the particle can annihilate converting their mass into electromagnetic energy in the form of two γ - rays photon.

$$e^{-} + e^{+} \rightarrow \gamma + \gamma$$

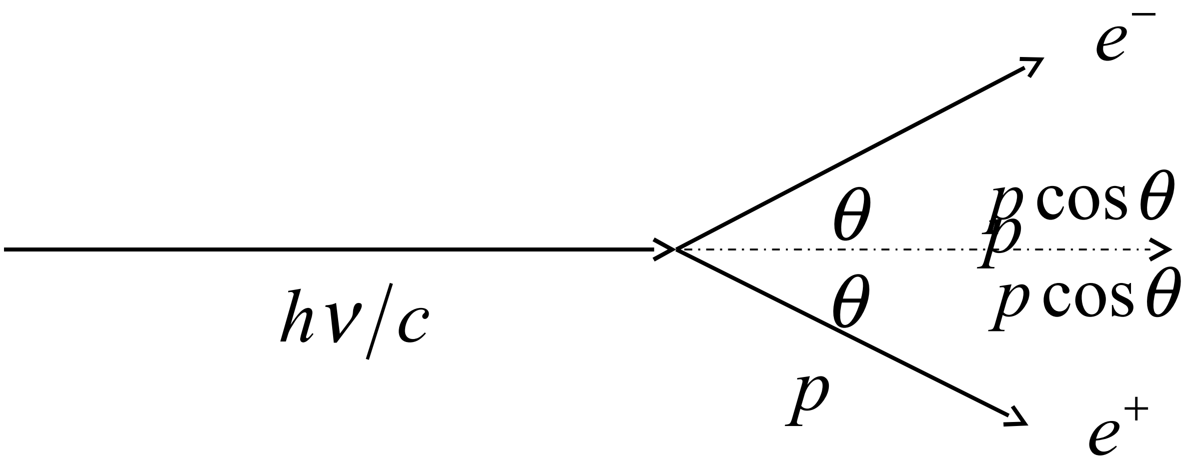
Charge, energy and momentum are again conversed. Two γ - photons are produced (each of energy 0.51 MeV plus half the K.E. of the particles) to conserve the momentum.

Pair production cannot occur in empty space

From conservation of energy

$$h\nu = 2m_o c^2 \gamma$$

here m_o is the rest mass and $\gamma = 1 \big/ \sqrt{1 - v^2/c^2}$



In the direction of motion of the photon, the momentum is conserved if

$$\frac{h\nu}{c} = 2p\cos\theta$$

$$h\nu = 2cp\cos\theta \qquad \text{(i)}$$

Momentum of electron and positron is

$$p = m_o v\gamma$$

Equation (i) now becomes

$$h\nu = 2m_o cv\gamma\cos\theta$$

$$h\nu = 2m_o c^2\gamma\left(\frac{v}{c}\right)\cos\theta$$

But $\quad {}^{v}\!/_{c} < 1 \quad$ and $\quad \cos\theta \le 1$

$$h\nu < 2m_o c^2\gamma$$

But conservation of energy requires that

$$h\nu = 2m_o c^2 \gamma$$

Hence it is impossible for pair production to conserve both the energy and momentum unless some other object is involved in the process to carry away part of the initial photon momentum. Therefore pair production cannot occur in empty space.

Wave Particle Duality

Light can exhibit both kind of nature of waves and particles so the light shows wave-particle dual nature.

In some cases like interference, diffraction and polarization it behaves as wave while in other cases like photoelectric and compton effect it behaves as particles (photon).

De Broglie Waves

Not only the light but every materialistic particle such as electron, proton or even the heavier object exhibits wave-particle dual nature.

De-Broglie proposed that a moving particle, whatever its nature, has waves associated with it. These waves are called “**matter waves**”.

Energy of a photon is

$$E = h\nu$$

For a particle, say photon of mass, m

$$E = mc^2$$

$$mc^2 = hv$$

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

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

Suppose a particle of mass, m is moving with velocity, v then the wavelength associated with it can be given by

$$\lambda = \frac{h}{mv} \quad \text{or} \quad \lambda = \frac{h}{p}$$

(i) If $v = 0 \Rightarrow \lambda = \infty$ means that waves are associated with **moving** material particles only.

(ii) De-Broglie wave does not depend on whether the moving particle is charged or uncharged. It means matter waves are not electromagnetic in nature.

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.

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 and Group Velocity

$$V_g = \frac{d\omega}{dk} \qquad = \frac{d}{dk}(kV_p)$$

$$V_g = V_p + k\frac{dV_p}{dk}$$

$$V_g = V_p + \frac{2\pi}{\lambda}\frac{dV_p}{d\left(2\pi/\lambda\right)}$$

$$V_g = V_p + \frac{1}{\lambda}\frac{dV_p}{d\left(1/\lambda\right)}$$

$$V_g = V_p + \frac{1}{\lambda}\frac{dV_p}{\left(-\frac{1}{\lambda^2}d\lambda\right)}$$

$$V_g = V_p - \lambda\frac{dV_p}{d\lambda}$$

In a Dispersive medium V_p depends on frequency

i.e. $\frac{\omega}{k} \neq$ constant

So, $\lambda\frac{dV_p}{d\lambda}$ is positive generally (not always).

$\Rightarrow V_g < V_p$ generally

$$V_g = V_p - \lambda \frac{dV_p}{d\lambda}$$

In a non-dispersive medium (such as empty space)

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

$$\Rightarrow \frac{dV_p}{d\lambda} = 0$$

$$\Rightarrow V_g = V_p$$

Phase Velocity of De-Broglie's waves

According to De-Broglie's hypothesis of matter waves

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

wave number $$k = \frac{2\pi}{\lambda} = \frac{2\pi mv}{h} \qquad \text{(i)}$$

If a particle has energy E, then corresponding wave will have frequency

$$\nu = \frac{E}{h}$$

then angular frequency will be $$\omega = 2\pi\nu = \frac{2\pi E}{h}$$

$$\omega = \frac{2\pi mc^2}{h} \qquad \text{(ii)}$$

Dividing (ii) by (i)

$$\frac{\omega}{k} = \frac{2\pi mc^2}{h} \times \frac{h}{2\pi mv}$$

$$V_p = \frac{c^2}{v}$$

But v is always < c (velocity of light)

(i) Velocity of De-Broglie's waves $V_p > c$ (not acceptable)

(ii) De-Broglie's waves (V_p) will move faster than the particle velocity (v) and hence the waves would left the particle behind.

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 λ is composed of a number of component waves with slightly different wavelengths in the neighborhood of λ.

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

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

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

On differentiating w.r.t. velocity, v

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

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

Dividing (i) by (ii)

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

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

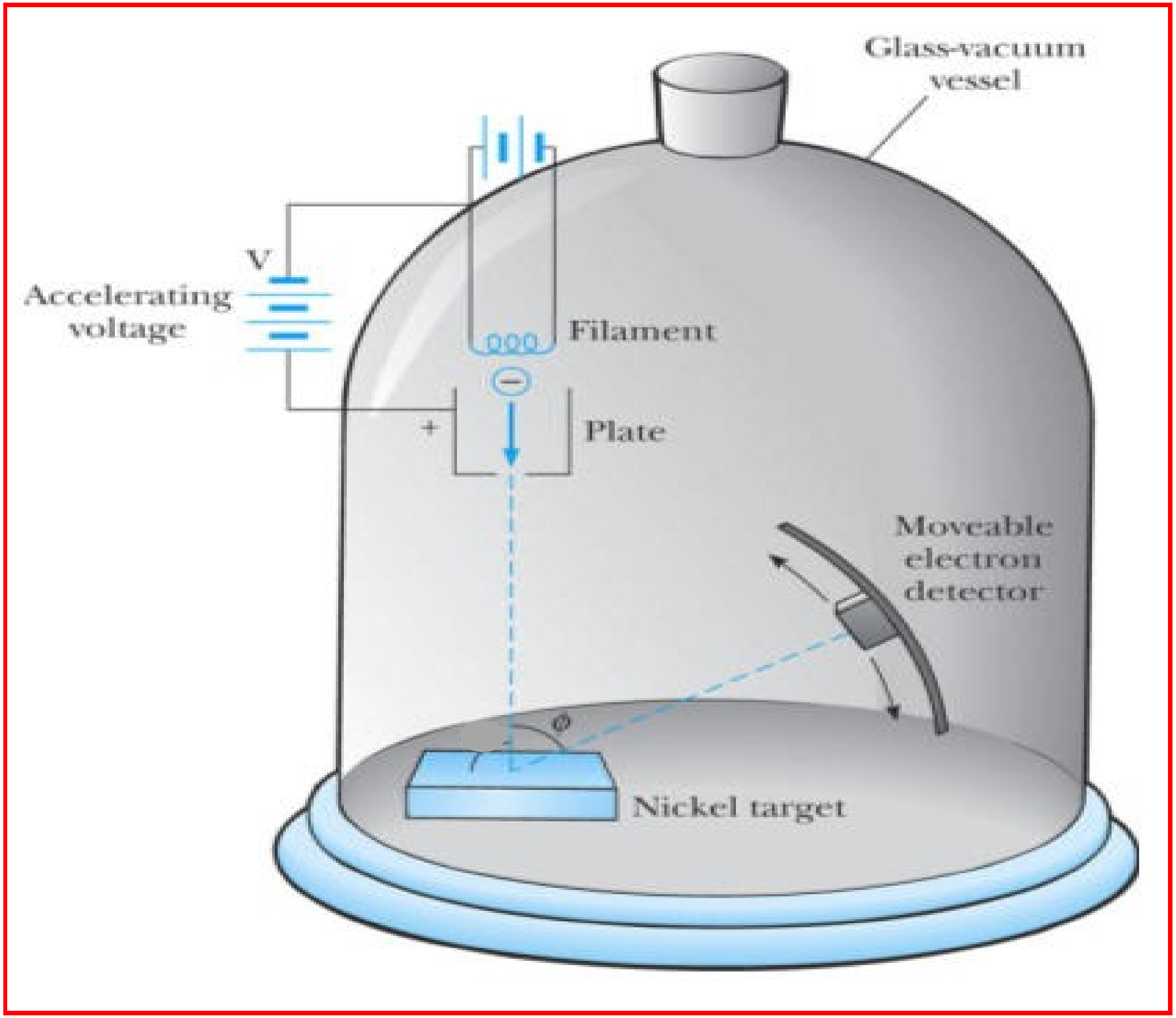
Wave group associated with a moving particle also moves with the velocity of the particle.

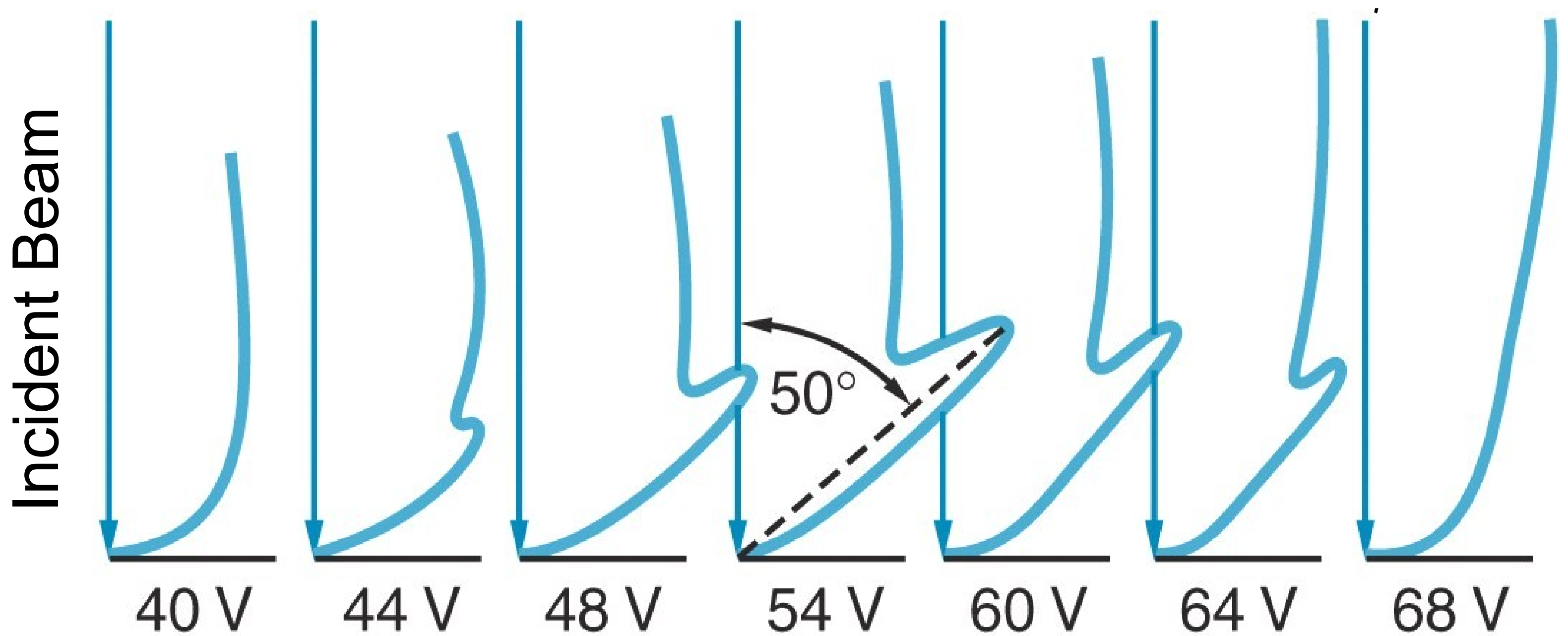
Moving particle $\equiv$ wave packet or wave group

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





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 φ ~ 50°

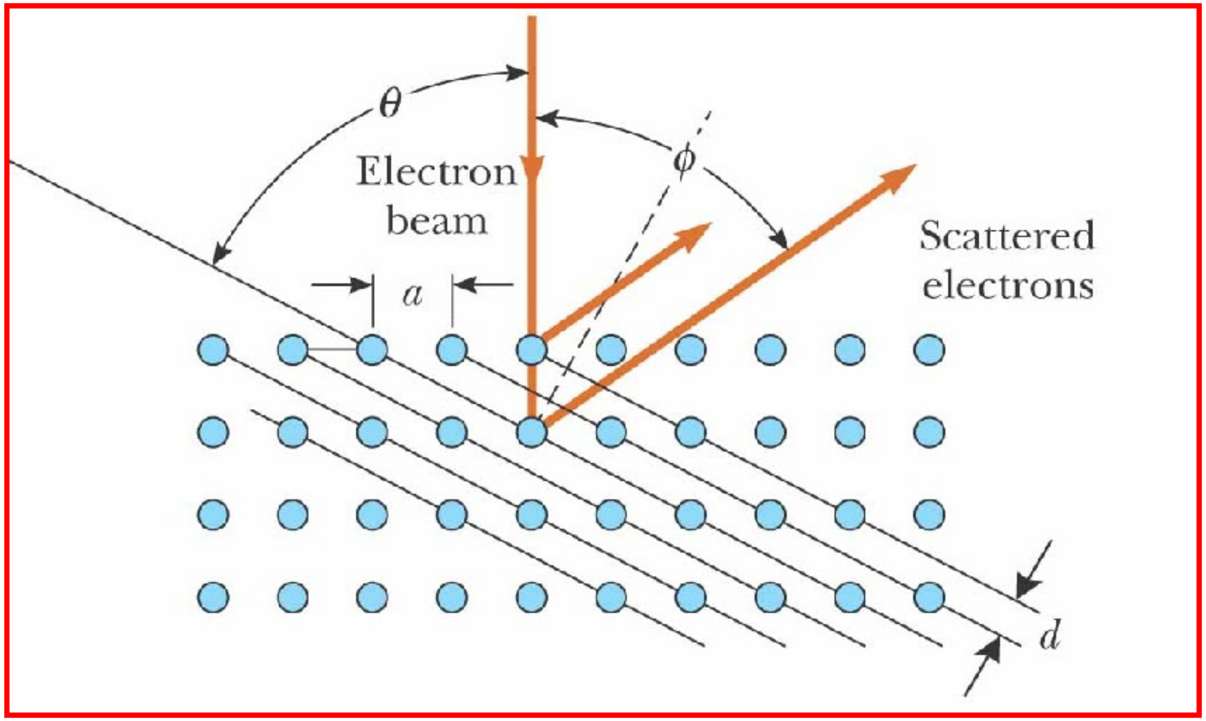
According to de Broglie, the wavelength associated with an electron accelerated through V volts is

$$\lambda = \frac{12.28}{\sqrt{V}} \overset{o}{A}$$

Hence the wavelength for 54 V electron

$$\lambda = \frac{12.28}{\sqrt{54}} = 1.67 \overset{o}{A}$$

From X-ray analysis we know that the nickel crystal acts as a plane diffraction grating with grating space d = 0.91 Å



Here the diffraction angle, $\varphi \sim 50°$

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

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

From the Bragg's equation

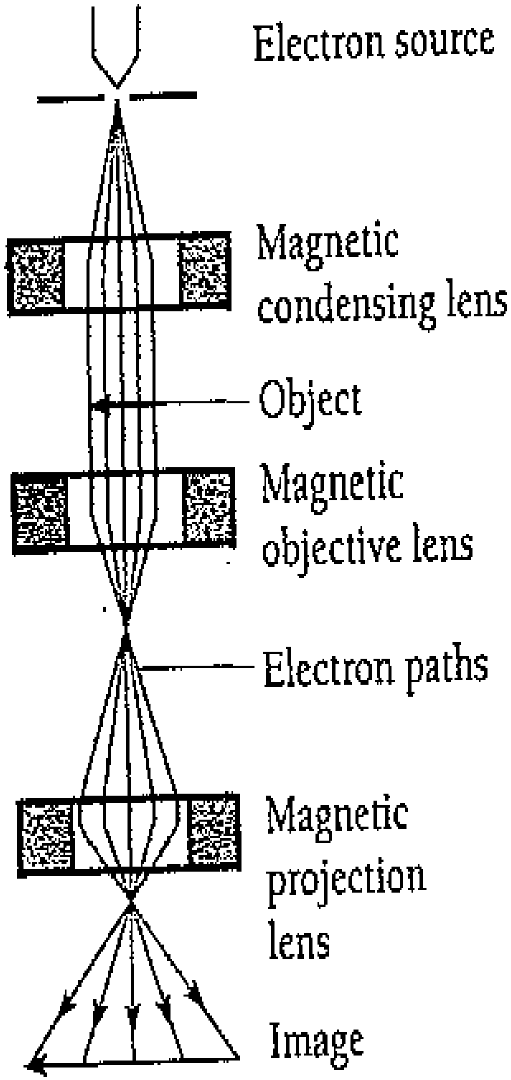
$$\lambda = 2d \sin\theta$$

$$\lambda = 2 \times (0.91 \overset{o}{A}) \times \sin 65^o = 1.65 \overset{o}{A}$$

which is equivalent to the λ calculated by de-Broglie's hypothesis.

It confirms the wavelike nature of electrons

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/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/magnification 1,000,000x can be achieved in an Electron Microscope.

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 $$\Delta x \Delta p_x \geq \frac{\hbar}{2} \qquad \therefore \hbar = \frac{h}{2\pi}$$

The product of Δx & Δp_x of an object is greater than or equal to $\frac{\hbar}{2}$

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

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

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

Determination of the position of a particle by a microscope

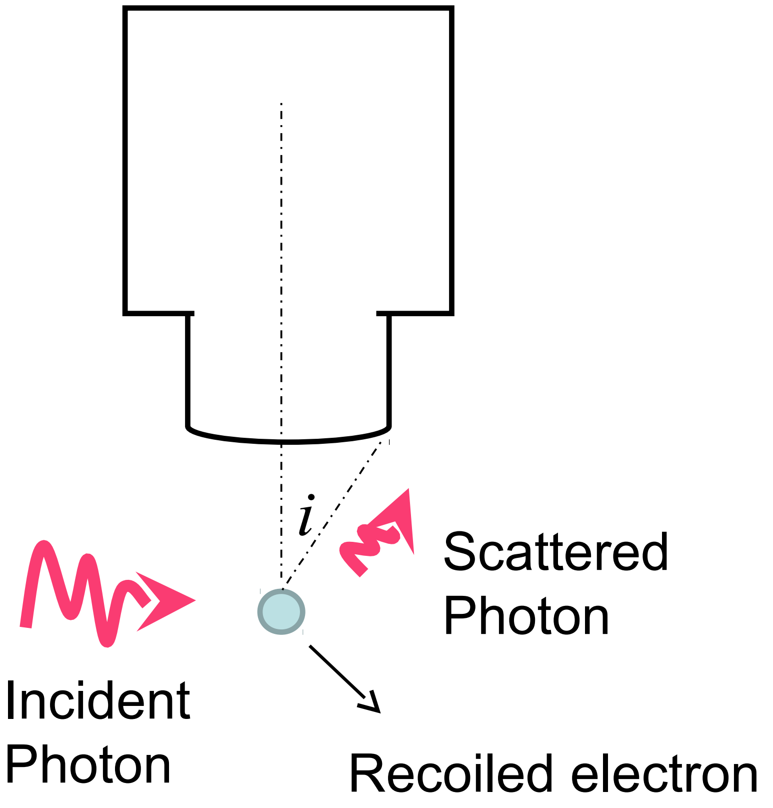
Suppose we want to determine accurately the position and momentum of an electron along x-axis using an ideal microscope free from all mechanical and optical defects.

The limit of resolution of the microscope is

$$\Delta x = \frac{\lambda}{2\sin i}$$

here *i* is semi-vertex angle of the cone of rays entering the objective lens of the microscope.

Δx is the order of uncertainty in the x-component of the position of the electron.



We can’t measure the momentum of the electron prior to illumination. So there is uncertainty in the measurement of momentum of the electron.

The scattered photon can enter the microscope anywhere between the angular range +*i* to –*i*.

The momentum of the scattered photon is (according to de-Broglie)

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

Its x-component can be given as

$$\Delta p_x = \frac{2h}{\lambda}\sin i$$

The x-component of the momentum of the recoiling electron has the same uncertainty, Δp_x (conservation of momentum)

The product of the uncertainties in the x-components of position and momentum for the electron is

$$\Delta x.\Delta p_x = \frac{\lambda}{2\sin i} \times \frac{2h}{\lambda} \sin i$$

$$\Delta x.\Delta p_x = h > \frac{\hbar}{2}$$

This is in agreement with the uncertainty relation.

Applications of Heisenberg Uncertainty Principle

(i) Non-existence of electron in nucleus

Order of radius of an atom ~ 5 x10^{-15} m

If electron exist in the nucleus then $(\Delta x)_{\max} = 5\times10^{-15}\, m$

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

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

$$(\Delta p_x)_{\min} = \frac{\hbar}{2\Delta x} = 1.1\times10^{-20}\, kg.m.s^{-1}$$

then

$$E = pc = 20 MeV \qquad \therefore \quad \text{relativistic}$$

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

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

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

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

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

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

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

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

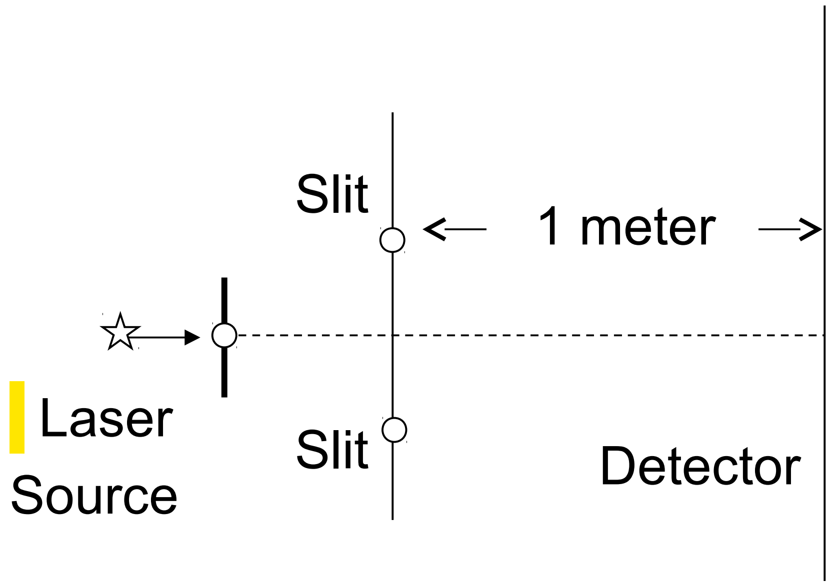
$$\Rightarrow \Delta t \rightarrow \infty$$

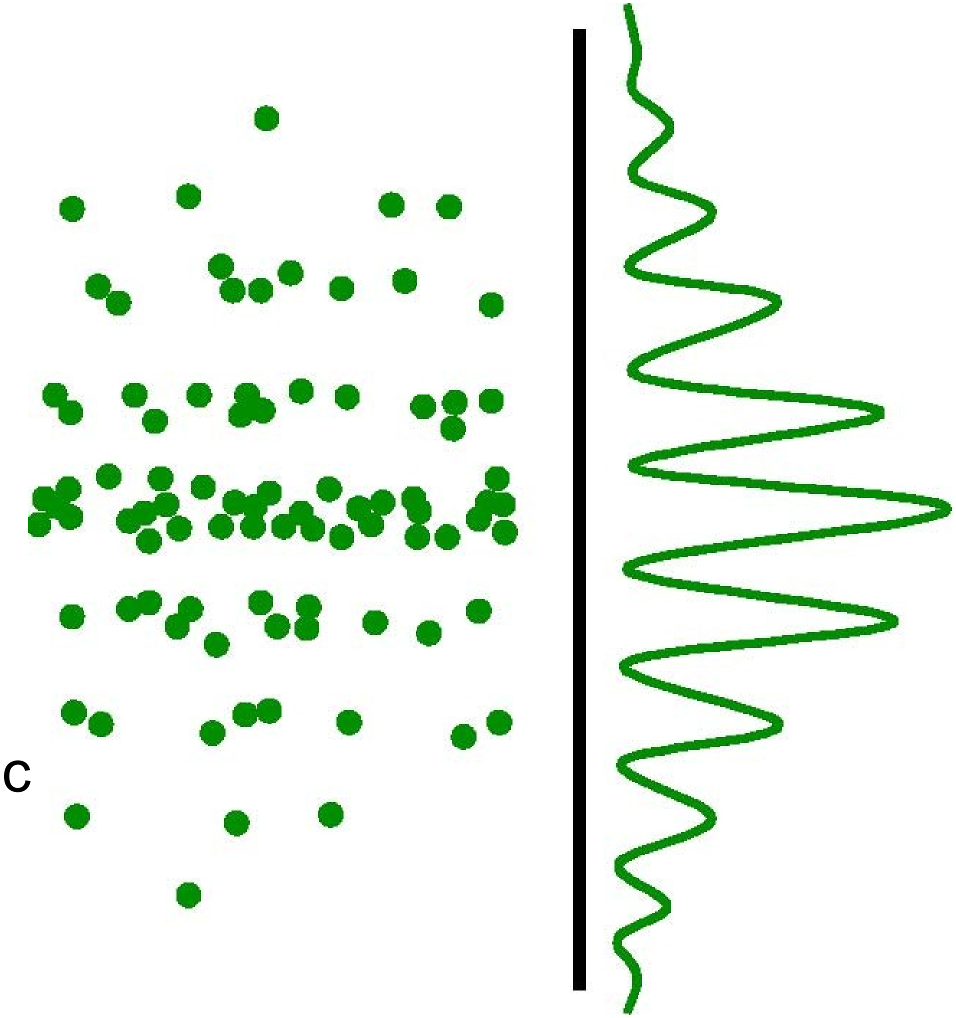
All energy states of the atom must have an infinite life-time.

But the excited states of the atom have life–time ~ 10^{-8} sec.

The finite life-time Δt gives a finite width (uncertainty) to the energy levels.

Two-slit Interference Experiment





Rate of photon arrival = 2 x 10^6/sec

Time lag = 0.5 x 10^{-6} sec

Spatial separation between photons = 0.5 x 10^{-6} c = 150 m

- Taylor’s experiment (1908): double slit experiment with very dim light: interference pattern emerged after waiting for few weeks
- interference cannot be due to interaction between photons, i.e. cannot be outcome of destructive or constructive combination of photons

  ⇒ interference pattern is due to some inherent property of each photon - it “interferes with itself” while passing from source to screen
- photons don’t “split” –

  light detectors always show signals of same intensity
- slits open alternatingly: get two overlapping single-slit diffraction patterns – no two-slit interference
- add detector to determine through which slit photon goes:

  ⇒ no interference
- interference pattern only appears when experiment provides no means of determining through which slit photon passes

Double slit experiment – QM interpretation

- patterns on screen are result of distribution of photons
- no way of anticipating where particular photon will strike
- impossible to tell which path photon took – cannot assign specific trajectory to photon
- cannot suppose that half went through one slit and half through other
- can only predict how photons will be distributed on screen (or over detector(s))
- interference and diffraction are statistical phenomena associated with probability that, in a given experimental setup, a photon will strike a certain point
- high probability $\Rightarrow$ bright fringes
- low probability $\Rightarrow$ dark fringes

Double slit expt. -- wave vs quantum

wave theory

- pattern of fringes:
  - Intensity bands due to variations in square of amplitude, A^2, of resultant wave on each point on screen
- role of the slits:
  - to provide two coherent sources of the secondary waves that interfere on the screen

quantum theory

- pattern of fringes:
  - Intensity bands due to variations in probability, P, of a photon striking points on screen
- role of the slits:
  - to present two potential routes by which photon can pass from source to screen

Wave function

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

Wave function, ψ 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.

$$|\psi|^2 = \psi^* \psi$$

ψ 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

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

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

Properties of wave function

1. It must be finite everywhere.

   If ψ 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 ψ 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.

   $$\frac{\partial\psi}{\partial x}, \frac{\partial\psi}{\partial y}, \frac{\partial\psi}{\partial z}$$ 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

$$\psi(x,t) = Ae^{\frac{-i}{\hbar}(Et-px)} \text{ and } \psi(x,t=0) = Ae^{\frac{2\pi i}{\lambda}(x)}$$

where

ψ is the wave amplitude for a given x.

A is the maximum amplitude.

λ is the wavelength

From (i)

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

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

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

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

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

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

Equation (ii) now becomes

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

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

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

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

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

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

$$\psi = Ae^{\frac{-i}{\hbar}(Et - px)} \qquad \text{(i)}$$

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

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

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

Differentiating (i) w.r.t. t

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

For non-relativistic case

E = K.E. + Potential Energy

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

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

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 ψ_1 and ψ_2 are two solutions of any Schrodinger equation of a system, then linear combination of ψ_1 and ψ_2 will also be a solution of the equation..

$$\psi = a_1\psi_1 + a_2\psi_2$$ is also a solution

Here $a_1 \,\&\, a_2$ are constants

Above equation suggests:

(i) The linear property of Schrodinger equation

(ii) ψ_1 and ψ_2 follow the superposition principle

If P_1 is the probability density corresponding to ψ_1 and P_2 is the probability density corresponding to ψ_2

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

Total probability will be

$$P = |\psi|^2 = |\psi_1 + \psi_2|^2$$

$$= (\psi_1 + \psi_2)^* (\psi_1 + \psi_2)$$

$$= (\psi_1^* + \psi_2^*)(\psi_1 + \psi_2)$$

$$= \psi_1^* \psi_1 + \psi_2^* \psi_2 + \psi_1^* \psi_2 + \psi_2^* \psi_1$$

$$P = P_1 + P_2 + \psi_1^* \psi_2 + \psi_2^* \psi_1$$

$$P \neq P_1 + P_2$$

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

$$< f(x) > = \int_{-\infty}^{\infty} f(x) |\psi|^2 dx$$

for normalized ψ

Thus expectation value for position ‘x’ is

$$< x > = \int_{-\infty}^{\infty} x |\psi|^2 dx$$

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 ψ = ax between x = 0 & 1, ψ = 0 elsewhere.

Solution

$$< x > = \int_0^1 x\,|\psi|^2 dx \quad = a^2 \int_0^1 x^3 dx$$

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

$$< x > = \frac{a^2}{4}$$

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

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

Then

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

Here

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

is called the momentum operator

Similarly

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

Here

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

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

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

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

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

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

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 (ψ) is operated by an operator 'α' 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

ψ 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.

$$\hat{G} = \frac{d^2}{dx^2}$$

$$\hat{G}\psi = \frac{d^2\psi}{dx^2} = \frac{d^2}{dx^2}(e^{2x})$$

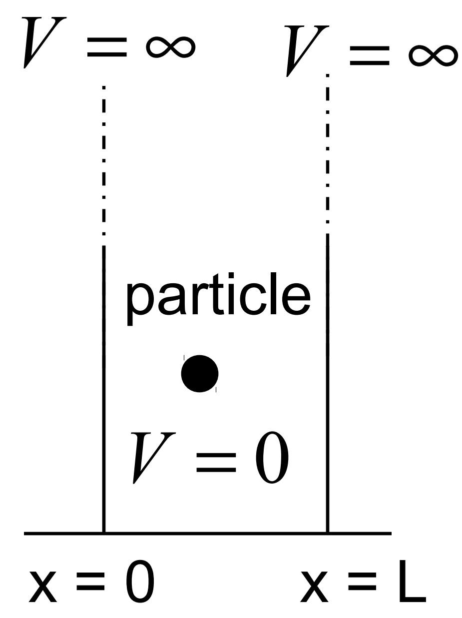
$$\hat{G}\psi = 4e^{2x}$$

$$\hat{G}\psi = 4\psi$$

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 ψ

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

Thus for a particle inside the box Schrodinger equation is

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

$\therefore V = 0$ inside

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

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

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

Equation (i) becomes

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

General solution of equation (iii) is

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

Boundary condition says ψ = 0 when x = 0

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

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

Equation (iv) reduces to

$$\psi(x) = A\sin kx \qquad \text{(v)}$$

Boundary condition says ψ = 0 when x = L

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

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

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

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

$$kL = n\pi$$

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

Put this in Equation (v)

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

When n # 0 i.e. n = 1, 2, 3…., this gives ψ = 0 everywhere.

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

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

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

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

Where n = 1, 2, 3….

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

$$E_1 = \frac{h^2}{8m_o L^2}$$ **(Zero Point Energy)**

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

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

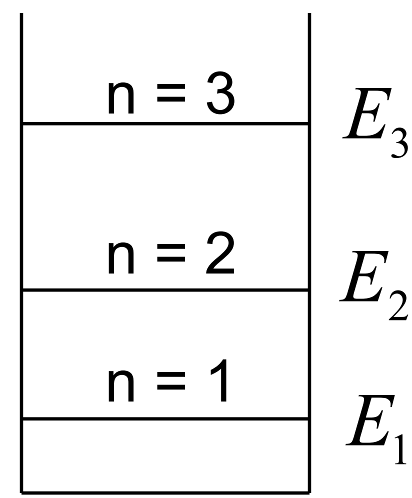
But $\Delta x_{\max} = L$ since the particle is confined in the box of dimension L.

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

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

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

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

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