

Chapter One

The Origen of Quantum theory

The Physical Foundations of Quantum Mechanics

Classical mechanics: can explain **MACROSCOPIC** phenomena such as motion of billiard balls or rockets.

Newton's mechanics (particle is particle)

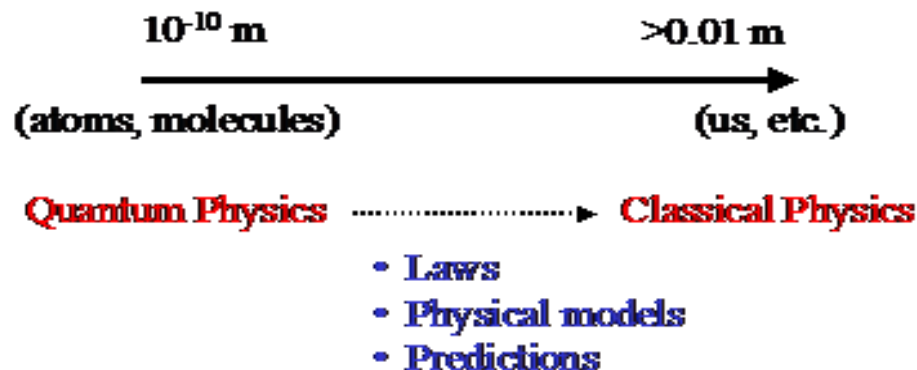
Properties (mass m , position \mathbf{r} , velocity \mathbf{v}) \Rightarrow Behaviour (collisions, momentum)

Maxwell's equations (electromagnetics theory) (wave is wave)

Properties (wavelength, frequency) \Rightarrow Behaviour (diffraction, interference)

Classical mechanics fail when we go to the atomic regime then we need to consider Quantum Mechanics.

Quantum mechanics is used to explain microscopic phenomena such as photon-atom scattering and flow of the electrons in a semiconductor.



Experimental Evidence for the Breakdown of Classical Mechanics

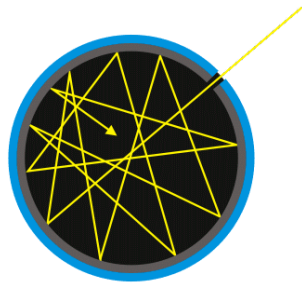
There are a lot of Experimental Evidence for the Breakdown of Classical Mechanics such as:

- 1- **Black-body radiation (1860-1901)**
- 2- **Atomic Spectroscopy (1888-)**
- 3- **Photoelectric Effect (1887-1905)**
- 4- **Compton Effect (1923).**
- 5- **Electron Diffraction Davisson and Germer (1925).**

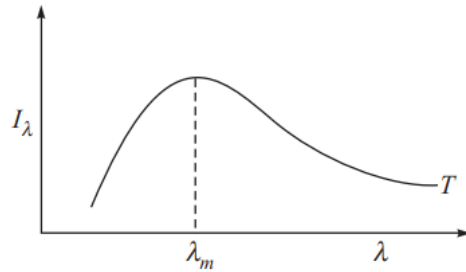
1.1 Black Body Radiation

The quantum theory had its origin in the search for an explanation of the spectral distribution of radiant energy emitted by a blackbody.

An ideal blackbody is defined as one that absorbs all electromagnetic radiation incident upon it. that such a body is also a better radiator of energy, of all frequencies, than any other body at the same temperature. *An ideal blackbody does not exist.*



Conceptual Black Body



Wien's law: Wien obtained the following semiempirical formula to explain the shape of blackbody radiation curve, known as **Wien's law:**

$$I(\lambda, T) = \frac{ae^{-b/\lambda T}}{\lambda^5}$$

where a and b are adjustable parameters. This law fitted the experimental curve fairly well except at long wavelengths.

The Rayleigh-Jeans Law was derived by applying the principles of classical physics based on the classical electrodynamics and thermodynamics.

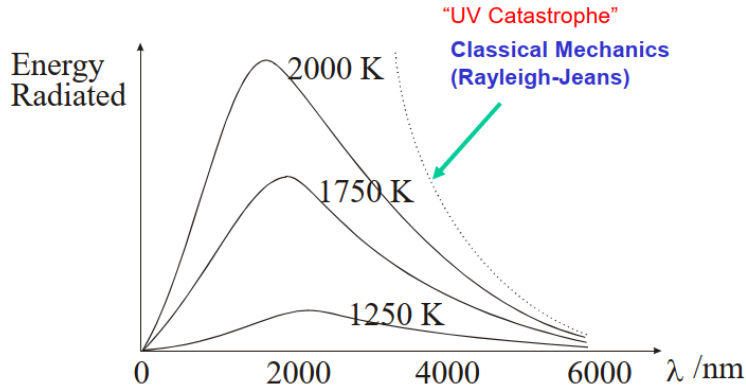
The energy density $U(\lambda, T)$ of the radiation of wave length λ in the cavity, at temperature T,

$$U(\lambda, T) = \frac{8\pi}{4\lambda^4} kT$$

The intensity $I(\lambda, T)$ of the radiation emitted by the cavity hole is;

$$I(\lambda, T) = \frac{8\pi c}{4\lambda^4} kT$$

The law was derived by applying the principles of classical physics based on the classical electrodynamics and thermodynamics.



It is found that the Rayleigh-Jeans law agrees with the experimental results in the long wavelength region. However, it diverges as the wavelength tends to zero.

Planck's Quantum Theory

Planck (1900) proposed that the light energy emitted by the black body is quantized in units of $h\nu$ (ν = frequency of light) i.e. $\Delta E = nh\nu$ ($n = 1, 2, 3, \dots$)

Planck's quantum hypothesis: *(The material oscillators (in the walls of the cavity) can have only discrete energy levels rather than a continuous range of energies as assumed in classical physics. If a particle is oscillating with frequency n , its energy can take only the values)*

$$\Delta E = nh\nu \quad (n = 1, 2, 3, \dots)$$

- High frequency light only emitted if thermal energy $KT \geq h\nu$.
- $h\nu$ a quantum of energy.
- Planck's constant $h = 6.626 \times 10^{-34} \text{Js}$
- If $h \rightarrow 0$ we regain classical mechanics.

The Planck's radiation law. In terms of the wavelength λ of the radiation,

$$U(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

Planck's law agrees very closely with the observed spectral distribution curves for all values of λ and T .

PROBLEM: Show that Planck's law reduces to Wien's law in the short wavelength limit and Rayleigh-Jeans' law in the long wavelength limit.

Solution: When λ is small, $e^{hc/\lambda kT} \gg 1$. Therefore

$$U(\lambda, T) \sim \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda k}$$

which is *Wien's law* (see Equation 2.1).

When λ is large,

$$e^{hc/\lambda kT} \sim 1 + \frac{hc}{\lambda kT}$$

Therefore,

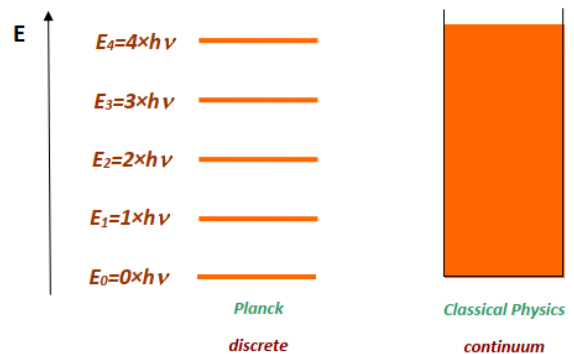
$$\begin{aligned} U(\lambda, T) &\sim \frac{8\pi hc}{\lambda^5} \frac{\lambda kT}{hc} \\ &= \frac{8\pi kT}{\lambda^4} \end{aligned}$$

which is Rayleigh-Jeans' law

Conclusions:

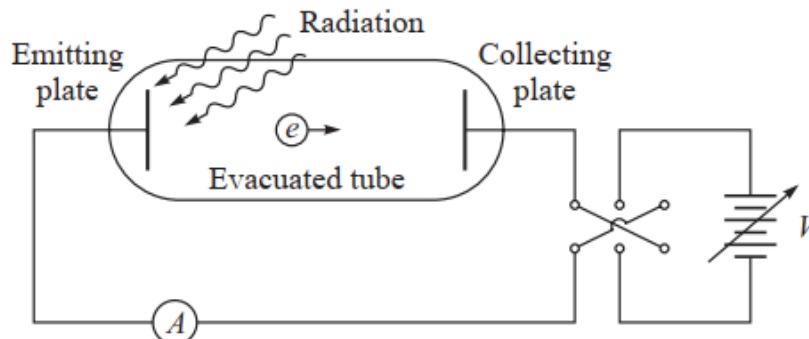
Energy is **quantized** (not continuous).

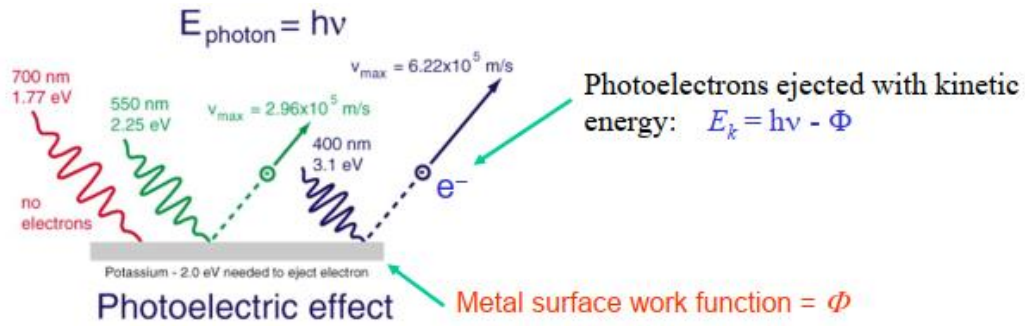
Energy can only change by well-**defined amounts**.



1.2 Photoelectric Effect (Einstein)

When electromagnetic radiation of high enough frequency is incident on a metal surface, electrons are emitted from the surface. This phenomenon is called photoelectric effect. The emitted electrons are generally called photoelectrons. This effect was discovered by Heinrich Hertz in 1887.





The following interesting results were obtained in the study:

- (1) No electrons are emitted if the incident radiation has a frequency less than a threshold value ν_0 . The value of ν_0 varies from metal to metal.
- (2) The kinetic energy of the emitted electrons varies from zero to a maximum value. The maximum value of energy depends on the frequency and not on the intensity of radiation. It varies linearly with the frequency.
- (3) The number of photoelectrons emitted per second, or the photoelectric current, is proportional to the intensity of radiation but is independent of the frequency.

Light consists of discrete packets (quanta) of energy = photons.

$$E = h\nu = E_k + \Phi$$

$$\nu = \frac{c}{\lambda} \quad \Phi = h\nu_0 \quad E_k = \frac{1}{2}mv^2$$

Photoelectrons ejected with kinetic energy:

$$E_k = h\nu - \Phi = h\nu - h\nu_0$$

Each photon has: Energy = Planks constant \times Frequency

Energy in Joules: $E = h\nu = 6.626 \times 10^{-34} (\text{J} \cdot \text{s}) \times \nu (\text{s}^{-1})$

Or,
$$E = \frac{hc}{\lambda} = \frac{1.99 \times 10^{-25} (\text{J} \cdot \text{m})}{\lambda (\text{m})}$$

Energy in (eV): $E = h\nu = 4.14 \times 10^{-15} (\text{eV} \cdot \text{s}) \times \nu (\text{s}^{-1})$

Or,
$$E = \frac{hc}{\lambda} = \frac{1.99 \times 10^{-25} (\text{J} \cdot \text{m})}{\lambda (\text{m})} = \frac{1240 (\text{eV} \cdot \text{nm})}{\lambda (\text{nm})}$$

Example:

The threshold (cutoff) frequency is $1.2 \times 10^{15} \text{ Hz}$. What is the threshold wavelength? What is the work function of tin?

$$\nu_o = 1.2 \times 10^{15} \text{ Hz}$$

$$\lambda_o = \frac{c}{\nu_o} = \frac{3 \times 10^8}{1.2 \times 10^{15}} = 2.5 \times 10^{-7} \text{ m} = 250 \text{ nm}$$

$$\Phi = h\nu_o = 6.625 \times 10^{-34} \times 1.2 \times 10^{15} = 7.95 \times 10^{-19} \text{ J}$$

$$\Phi = \frac{7.95 \times 10^{-19}}{1.6 \times 10^{-19}} = 4.97 \text{ eV}$$

Einstein's Theory—Photons

Planck had assumed that the exchange of energy between the walls of a cavity and the radiation of frequency ν takes place in quanta of magnitude $h\nu$, where h is called Planck's constant. *Einstein* suggested that the incident radiation itself acts like quanta of energy ($h\nu$). These **quanta** later came to be known as **photons**.

Therefore, the maximum kinetic energy E_{max} , and the corresponding velocity v_{max} , of the emitted electron are given by;

$$E_{max} = \frac{1}{2}mv_{max}^2 = h\nu - \Phi$$

This is called Einstein's photoelectric equation. It shows that E_{max} varies linearly with the frequency ν of the incident radiation.

ν_o is the threshold (cutoff) frequency Thus; $\Phi = h\nu_o$ then

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

Clearly, no emission is possible if $\nu \leq \nu_o$.

Stopping or cut-off Potential; For a certain value V_0 of this negative potential, the most energetic electrons are just turned back and therefore the photoelectric current becomes zero.

$$eV_0 = E_{\max}$$

$$eV_0 = h(\nu - \nu_0)$$

$$V_0 = \frac{h}{e}(\nu - \nu_0)$$

Conclusion:

An increase in the intensity of radiation results in an increase in the number of photons striking the metal per second but not in the energy of single photons.

Therefore, the number of photoelectrons emitted per second, and hence the photoelectric current, increases, but not the energy of photoelectrons.

Since the electron emission is the result of a direct collision between an electron and a photon, there is no time delay before emission starts.

PROBLEM: Find the number of photons emitted per second by a 40 W source of monochromatic light of wavelength 6000 Å.

Solution: Let the number of photons be n . Then

$$\begin{aligned}nh\nu &= E \\n &= \frac{E}{h\nu} = \frac{E\lambda}{hc} \\&= \frac{40 \times 6000 \times 10^{-10}}{6.63 \times 10^{-34} \times 3 \times 10^8} \\&= \boxed{12.06 \times 10^{19}}\end{aligned}$$

H.W

1- The work function of a metal is 3.45 eV. What is the maximum wavelength of a photon that can eject an electron from the metal?

2- A metal of work function 3.0 eV is illuminated by light of wavelength 3000 \AA . Calculate (a) the threshold frequency, (b) the maximum energy of photoelectrons, and (c) the stopping potential.

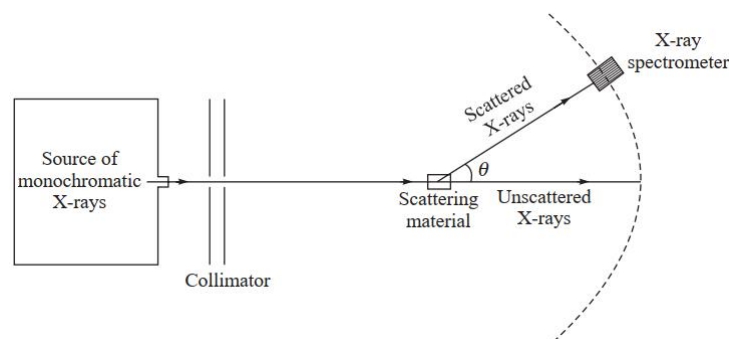
3- (a) A stopping potential of 0.82 V is required to stop the emission of photoelectrons from the surface of a metal by light of wavelength 4000 \AA . For light of wavelength 3000 \AA , the stopping potential is 1.85 V . Find the value of Planck's constant.

(b) At stopping potential, if the wavelength of the incident light is kept fixed at 4000 \AA but the intensity of light is increased two times, will photoelectric current be obtained? Give reasons for your answer.

4- Light of wavelength 4560 \AA and power 1 mW is incident on a Caesium surface. Calculate the photoelectric current, assuming a quantum efficiency of 0.5% . Work function of Caesium $= 1.93 \text{ eV}$.

1.3 The Compton Effect :

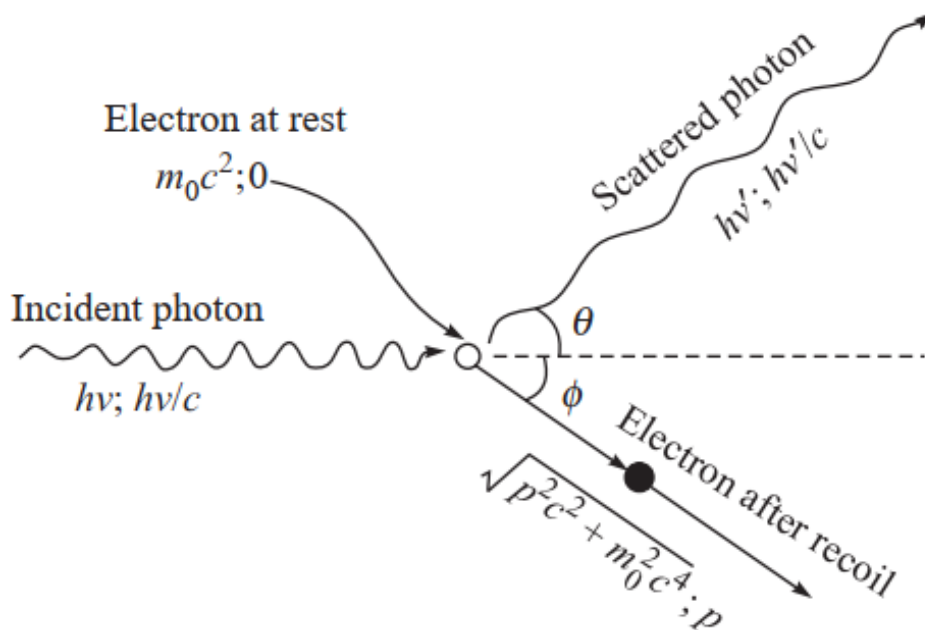
When a monochromatic beam of X-rays is scattered by an element of low atomic weight (for example carbon), it is observed that the scattered X-rays, at all angles, have maximum intensities at two wavelengths, one at the original wavelength and the other at a slightly longer wavelength. The wavelength shift is independent of the wavelength of the incident beam and the scattering material; it depends only on the scattering angle. *This phenomenon is called the Compton effect.*



the original wavelength (λ_0) and the other due to the modified wavelength (λ). The wavelength shift ($\Delta\lambda$) increases with the increase of scattering angle θ .

Compton's Explanation

Compton was able to explain this phenomenon using the quantum theory of radiation, developed by Planck and Einstein. He considered the incident X-rays as a stream of photons, each of energy $h\nu$ and momentum $h\nu/c$. The scattering process is treated as an elastic collision between a photon and a "free" electron, which is initially at rest. In the collision, a part of the photon energy is transferred to the electron which recoils. Therefore, the scattered photon has a smaller energy and hence a lower frequency (higher wavelength).



If λ and λ' are the wavelengths of the incident and scattered photons, then

$$\nu' = \frac{c}{\lambda'} \quad \text{and} \quad \nu = \frac{c}{\lambda}$$

Therefore, (2.17) can be expressed as

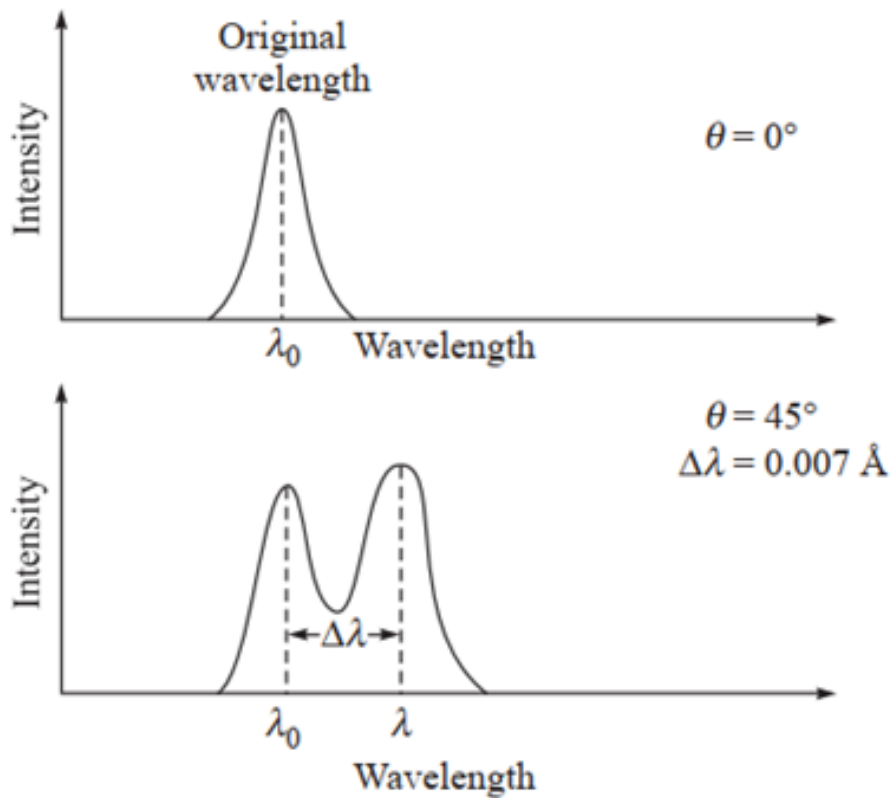
$$\lambda' - \lambda = \Delta\lambda = \frac{h}{m_0 c} (1 - \cos\theta) \quad (2.18)$$

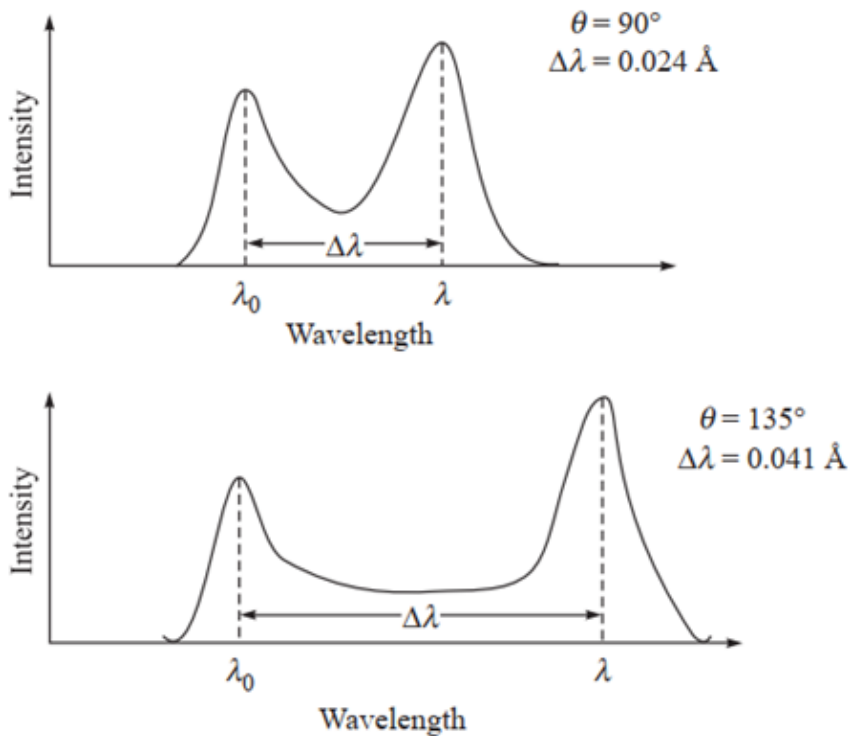
or, equivalently,

$$\Delta\lambda = \frac{2h}{m_0 c} \sin^2 \frac{\theta}{2} \quad (2.19)$$

The above equation shows that the **Compton shift** in wavelength is independent of the wavelength (or energy) of the incident photon and depends only on the angle of scattering.

The quantity $(h/m_0 c)$ is called the *Compton wavelength* of the electron. Its value is 0.0242 \AA .





Variation of the shifted line with scattering angle. The peak at λ_0 is due to the incident beam.

Conclusion: Compton's work established the existence of photons as real particles having momentum as well as energy.

PROBLEM: X-rays of wavelength 2.0 \AA are scattered from a carbon block. The scattered photons are observed at right angles to the direction of the incident beam. Calculate (a) the wavelength of the scattered photon, (b) the energy of the recoil electron.

Solution: (a) If λ and λ' are the wavelengths of the incident and the scattered photons, respectively, and θ is the scattering angle, then

$$\begin{aligned} \Delta\lambda = \lambda' - \lambda &= \frac{h}{m_0c} (1 - \cos\theta) \\ &= \frac{6.6 \times 10^{-34}}{9.1 \times 10^{-31} \times 3 \times 10^8} (1 - \cos 90^\circ) \\ &= 2.4 \times 10^{-12} \text{ m} \\ &= 0.024 \text{ \AA} \end{aligned}$$

Therefore,

$$\lambda' = \lambda + \Delta\lambda = \boxed{2.024 \text{ \AA}}$$

(b) Neglecting the binding energy of the electron, its recoil energy is given by

$$\begin{aligned} E &= h(\nu - \nu') \\ &= hc\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right) \\ &= \frac{hc(\lambda' - \lambda)}{\lambda\lambda'} \\ &= \frac{6.6 \times 10^{-34} \times 3 \times 10^8 \times 0.024 \times 10^{-10}}{2.0 \times 10^{-10} \times 2.024 \times 10^{-10}} \\ &= \boxed{1.17 \times 10^{-17} \text{ J}} \end{aligned}$$

Kinetic Energy of the Recoil Electron

The kinetic energy of the recoil electron is

$$E = h\nu - h\nu'$$

From equation of Compton shift

$$\lambda' - \lambda = \Delta\lambda = \frac{h}{m_0c}(1 - \cos\theta)$$

or
$$\frac{1}{\nu'} - \frac{1}{\nu} = \frac{h}{m_0c^2}(1 - \cos\theta)$$

We get
$$\frac{\nu}{\nu'} = 1 + \alpha(1 - \cos\theta) \quad \text{where } \alpha = h\nu/m_0c^2.$$

$$\nu' = \frac{\nu}{1 + \alpha(1 - \cos\theta)} \quad \dots(1.17)$$

Therefore,

$$E = h\nu \left[1 - \frac{1}{1 + \alpha(1 - \cos\theta)} \right]$$

or
$$\boxed{E = h\nu \frac{\alpha(1 - \cos\theta)}{1 + \alpha(1 - \cos\theta)}} \quad \dots(1.18)$$

H.W.

1- In a Compton scattering experiment, the incident radiation has wavelength 2 \AA while the wavelength of the radiation scattered through 180° is 2.048 \AA . Calculate (a) the wavelength of the radiation scattered at an angle of 60° to the direction of incidence, and (b) the energy of the recoil electron which scatters the radiation through 60° .

2- A photon of energy 0.9 MeV is scattered through 120° by a free electron. Calculate the energy of the scattered photon.

Dual Nature of Radiation

In order to explain several phenomena like *interference*, *diffraction* and *polarization*, it is necessary to assume that electromagnetic *radiation has wave nature*.

To explain the observed results connected with the interaction of radiation with matter, such as the *blackbody radiation*, the *photoelectric effect* and the *Compton effect*, it becomes necessary to assume that *radiation has particle nature*—it is emitted or absorbed in the form of discrete quanta called photons. Thus, we have to accept the paradoxical situation that ***radiation has dual nature***.

1.4 Atomic Spectra

- All elements in atomic state emit line spectra.
- A line spectrum consists of narrow bright lines separated by dark intervals.
- It is characteristic of the atoms of the element which emits it.
- This makes spectroscopy a very important tool of chemical analysis because measurement of the wavelengths emitted by a material allows us to identify the elements present in it, even in very small amounts.

- It was found that the wavelengths present in the atomic spectrum of an element fall into sets which exhibit some definite pattern. Such a set is called a *spectral series*.
- In 1885, Johann Balmer showed that the wavelengths of all the spectral lines of the hydrogen atom known till then could be expressed by the formula

$$\frac{1}{\lambda} = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad n = 3, 4, 5, \dots$$

The constant R is known as the Rydberg constant. Its value is $1.097 \times 10^7 m^{-1}$. This set of lines lies in the visible part of the electromagnetic spectrum and is called the ***Balmer series***.

Other series of lines were discovered for the hydrogen atom in different regions of the electromagnetic spectrum.

Lyman Series: Ultraviolet Region

$$\frac{1}{\lambda} = R \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \quad n = 2, 3, 4, \dots$$

Paschen Series: Infrared Region

$$\frac{1}{\lambda} = R \left(\frac{1}{3^2} - \frac{1}{n^2} \right) \quad n = 4, 5, 6, \dots$$

Brackett Series : Infrared Region

$$\frac{1}{\lambda} = R \left(\frac{1}{4^2} - \frac{1}{n^2} \right) \quad n = 5, 6, 7, \dots$$

Pfund Series : Infrared Region

$$\frac{1}{\lambda} = R \left(\frac{1}{5^2} - \frac{1}{n^2} \right) \quad n = 6, 7, 8, \dots$$

All the above formulae are special cases of the general formula

$$\left| \frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \right| \quad \dots(1.19)$$

where n_1 and n_2 are positive integers with $n_1 < n_2$ and $n_2 = n_1 + 1, n_1 + 2, \dots$. This is known as the **Rydberg-Ritz formula**.

It may be noted that the above formula expresses the wave number ($1/\lambda$) of any line as the difference of two terms of the type

$$T_n = \frac{R}{n^2} \quad n = 1, 2, \dots$$

1.5 Bohr Model of Hydrogenic Atoms

In 1913, a major step forward was taken by Niels Bohr.. He combined Rutherford's nuclear model with the quantum idea of Planck and Einstein to develop a theory of hydrogenic atoms. These are also called hydrogen-like atoms. The theory was remarkably successful in explaining the observed spectrum of hydrogen.

The Bohr model is based on the following **postulates**:

1. The electron can revolve around the nucleus only in certain allowed circular orbits of definite energy and in these orbits it does not radiate. These orbits are called **stationary orbits**.
2. The angular momentum of the electron in a stationary orbit is an integral multiple of $\hbar (= h/2\pi)$, h being Planck's constant:

$$l = mvr = n\hbar$$

where m is the mass of the electron, v is its speed, r is the radius of the orbit and n is a positive integer.

3. The electron can make a transition from one orbit to another. The emission of radiation takes place as a single photon when an electron "jumps" from a higher orbit to a lower orbit. The frequency of the photon is

$$\nu = \frac{E_2 - E_1}{h}$$

where E_2 and E_1 are the energies of the electron in the higher and lower orbits, respectively. Conversely, an electron in the lower orbit can jump to the higher orbit by absorbing a photon of this frequency.

Let Z be the atomic number of the nucleus. If e is the electronic charge, then the charge of the nucleus is Ze . The centripetal acceleration for circular motion is provided by the Coulomb attraction between the electron and the nucleus. Therefore,

$$\frac{mv^2}{r} = \frac{k(Ze)e}{r^2}$$
$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2}$$

The expressions for the radius of the n th Bohr orbit and the speed of the electron in this orbit, respectively, as

$$r_n = \frac{(4\pi\epsilon_0)\hbar^2 n^2}{Ze^2 m}$$

and

$$v_n = \frac{Ze^2}{(4\pi\epsilon_0)\hbar n}$$

The integer n is called the *quantum number*. Substituting the values of ϵ_0 , \hbar , e , and m ,

For the first Bohr orbit, also called the *ground state*, of hydrogen, $Z = 1$, $n = 1$. Therefore, the radius and the speed are 0.53 \AA and $2.18 \times 10^6 \text{ m/s}$, respectively. The first Bohr radius of hydrogen is generally denoted by the symbol a_0 :

Energy of the Electron in the n th Bohr Orbit

The total energy E_n of the electron is the sum of the kinetic and potential energies:

$$\begin{aligned} E_n &= \frac{1}{2} m v_n^2 - \frac{Z e^2}{(4\pi\epsilon_0)r_n} \\ &= \frac{m}{2\hbar^2} \left(\frac{Z e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} - \frac{m}{\hbar^2} \left(\frac{Z e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} \end{aligned}$$

or

$$E_n = -\frac{m}{2\hbar^2} \left(\frac{Z e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2}$$

Sometimes it is convenient to express the energy in terms of the *Bohr radius*

$$E_n = -\frac{\hbar^2}{2m a_0^2} \frac{Z^2}{n^2}$$

Substituting the values of the constants,

$$E_n = -2.2 \times 10^{-18} \frac{Z^2}{n^2} \text{ J} = -13.6 \frac{Z^2}{n^2} \text{ eV}$$

This shows that the energy of the ground state of hydrogen is (-13.6 eV).

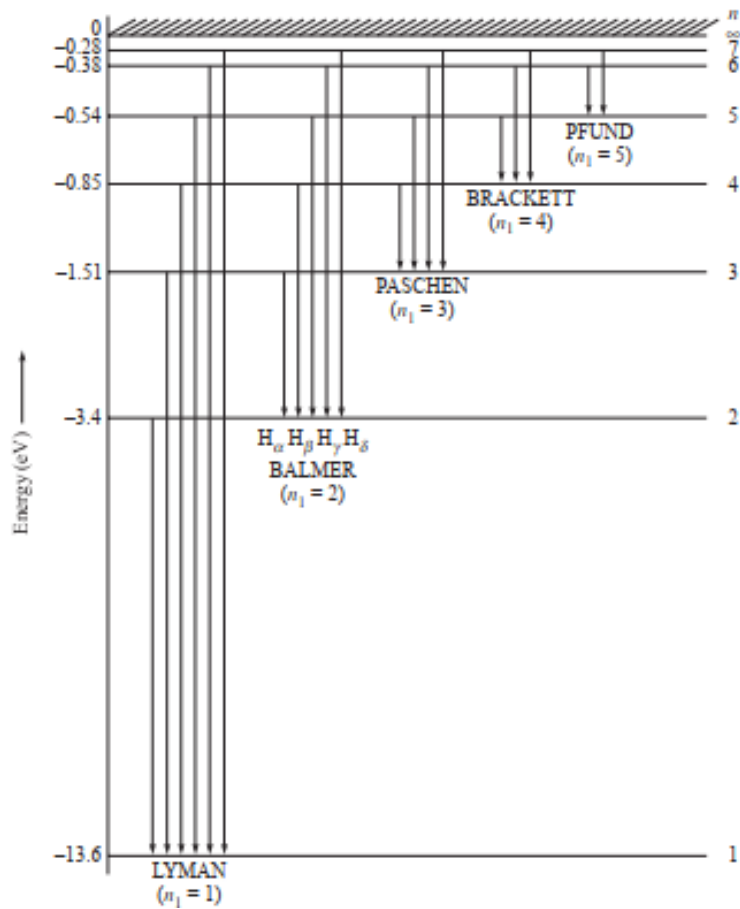
The negative sign indicates that the electron is bound.

1.6 Explanation of the Hydrogen Spectrum

If we put $z = 1$, $n_1 = 1$ and $n_2 = 2, 3, 4, \dots$ in formula of wave number

$$\bar{\nu} = \frac{1}{\lambda} = R_\infty Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

We find that the values of λ so obtained agree with the experimentally observed wavelengths.



Energy level diagram for hydrogen atom

PROBLEM: The energy of an excited hydrogen atom is -3.4 eV. Calculate the angular momentum of the electron according to Bohr theory.

Solution: The energy of the electron in the n th orbit is

$$E_n = -\frac{13.6}{n^2} \text{ eV}$$

Therefore,

$$n^2 = \frac{-13.6}{E_n} = \frac{-13.6}{-3.4} = 4$$

or

$$n = 2$$

$$\begin{aligned}\text{Angular momentum} &= \frac{nh}{2\pi} \\ &= \frac{2 \times 6.63 \times 10^{-34}}{2 \times 3.14} \\ &= \boxed{2.11 \times 10^{-34} \text{ Js}}\end{aligned}$$

H.W.

1. The energy of the ground state of hydrogen atom is -13.6 eV. Find the energy of the photon emitted in the transition from $n = 4$ to $n = 2$.
2. The H line of Balmer series is obtained from the transition $n = 3$ (energy = -1.5 eV) to $n = 2$ (energy = -3.4 eV). Calculate the wavelength for this line.

PROBLEM: The ionization energy of a hydrogen-like atom is 4 rydberg. Find the wavelength of the radiation emitted when the electron jumps from the first excited state to the ground state.

$$1 \text{ rydberg} = 2.2 \times 10^{-18} \text{ J}; h = 6.6 \times 10^{-34} \text{ Js.}$$

Solution: Ionization energy = $4 \times 2.2 \times 10^{-18}$
 $= 8.8 \times 10^{-18} \text{ J}$

Energy of the electron in the ground state ($n = 1$)

$$E_1 = -8.8 \times 10^{-18} \text{ J}$$

Energy of the electron in the first excited state ($n = 2$)

$$E_2 = \frac{E_1}{(2)^2} = -2.2 \times 10^{-18} \text{ J}$$

If λ is the wavelength of the radiation emitted in the transition $n = 2 \rightarrow n = 1$, then

$$\frac{hc}{\lambda} = E_2 - E_1$$

or

$$\begin{aligned}\lambda &= \frac{hc}{E_2 - E_1} \\ &= \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{(8.8 - 2.2) \times 10^{-18}} \\ &= 3.0 \times 10^{-8} \text{ m} \\ &= \boxed{300 \text{ \AA}}\end{aligned}$$

The Need for Wave Function

1.7 DE BROGLIE'S HYPOTHESIS

- After the work of Planck, Einstein and Compton, it was established that **radiation has dual nature**. That is, it acts like a **wave** in some situations and as a **particle** in some other situations.
- In 1924, Louis **de Broglie** extended this **wave-particle duality to material particles**.

Nature has two entities matter and radiation. Therefore, if radiation has particle-like properties, then material particles (electron, proton, neutron etc.) should possess wave-like properties.

We have seen that a photon of frequency ν has energy

$$E = h\nu$$

and momentum

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

In terms of wavelength this can be written as

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

De Broglie proposed that this relation applies to material particles as well as photons. Thus, de Broglie postulated that *with every material particle a wave is associated, having wavelength*

$$\lambda = \frac{h}{p} \quad \text{(De Broglie wavelength)}$$

For a particle of mass m , moving with a speed v , this becomes

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

This is called **de Broglie's hypothesis** and λ is called the *de Broglie wavelength*.

de Broglie's hypothesis, when proposed, had no supporting experimental evidence. Such evidence came three years later in 1927.

However, **de Broglie** attempted to explain the stationary Bohr orbits by fitting a standing wave around the circumference of an orbit.

If λ is the wavelength associated with the n th orbit and r is its radius, then it must be required that, postulate

$$2\pi r = n\lambda$$

Combining this with the Bohr postulate

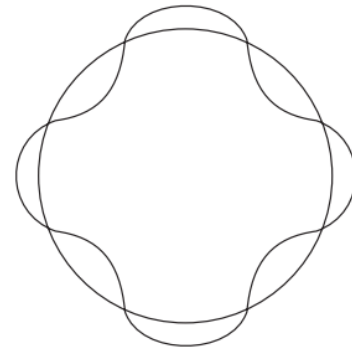
$$mvr = \frac{nh}{2\pi}$$

We get;

$$n\lambda = 2\pi \left(\frac{nh}{2\pi mv} \right)$$

or

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



De Broglie wave for $n = 4$ Bohr orbit.

We may write

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

where $k = 2\pi/\lambda$. Thus, the two basic relations of quantum theory are

and

$$\begin{aligned} E &= \hbar\omega \\ \mathbf{p} &= \hbar\mathbf{k} \end{aligned}$$

(Basic relations of quantum theory)

PROBLEM: A ball of mass 10 g is moving with a speed of 1 m/s . Calculate the de Broglie wavelength associated with it. Can the effect of this wavelength be observed experimentally?

Solution:

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

$$= \frac{6.63 \times 10^{-34}}{10 \times 10^{-3} \times 1}$$

$$= \boxed{6.63 \times 10^{-32} \text{ m}}$$

This wavelength is negligible compared to the dimensions of the ball. Therefore its effect cannot be observed.

PROBLEM: Find the de Broglie wavelength of electrons moving with a kinetic energy of 100 eV .

Solution:

In terms of Kinetic Energy:

For a nonrelativistic particle of mass m having kinetic energy K ,

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

or
$$p = \sqrt{2mK}$$

Therefore, the de Broglie wavelength can be expressed as

$$\lambda = \frac{h}{\sqrt{2mK}}$$

$$\lambda = \frac{h}{\sqrt{2mK}} = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 100 \times 1.6 \times 10^{-19}}}$$

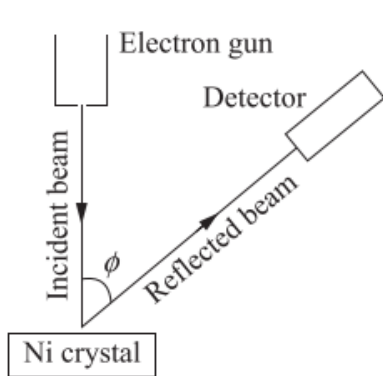
$$= \boxed{1.2 \times 10^{-10} \text{ m}}$$

1.8 Experimental Verification of De Broglie Hypothesis

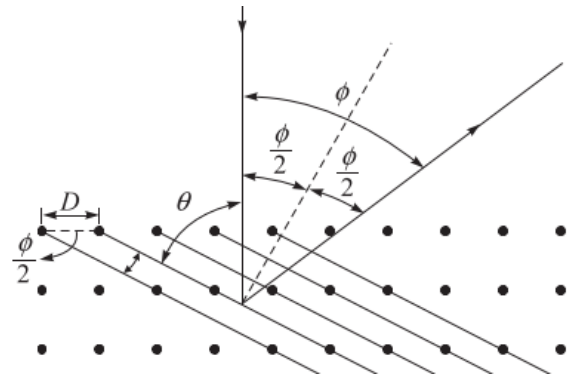
Davisson-Germer Experiment

A narrow beam of electrons, accelerated through a potential difference V , was directed normally towards the surface of Nickel crystal. The electrons were scattered in all directions by the atoms in the crystal.

This fact suggests that the existence of matter waves may be demonstrated by using crystals as diffraction for electrons in manner similar to X-ray diffraction by crystals.



Schematic diagram of Davisson-Germer experiment



Diffraction of electron waves by a crystal

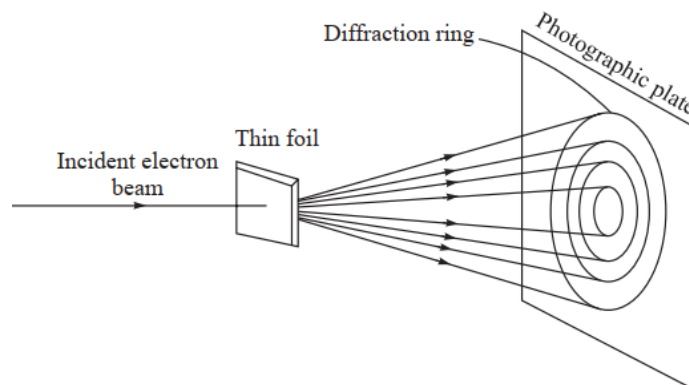
The Bragg condition for constructive interference is

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

where d is the spacing between the adjacent Bragg planes and n is an integer.

The electron diffraction observed in good agreement with De Broglie's hypothesis.

G.P. Thomson s Experiment

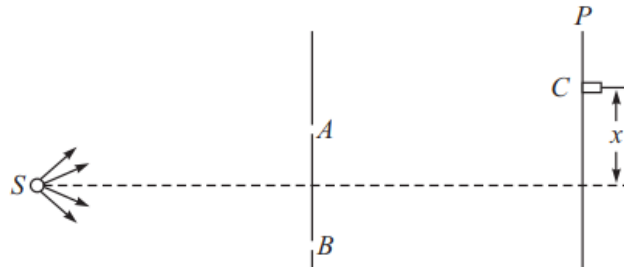


Thomson obtained the wavelength of the electrons from the de Broglie formula. and then calculated the spacing d between atomic planes using Bragg's equation. It was found that the value of d is same as that obtained from X-ray experiments.

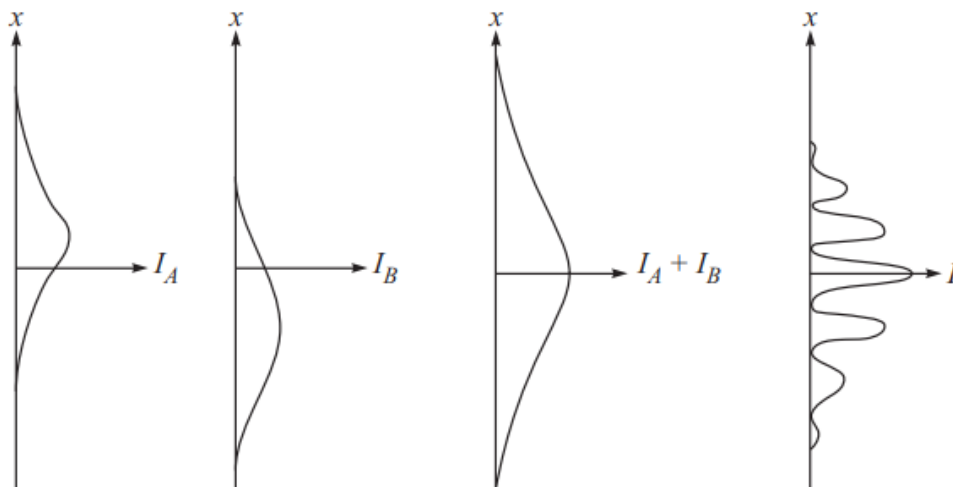
The Double-Slit Experiment with Particles

The double-slit experiment is an excellent way of demonstrating the wave-particle duality of radiation. A similar experiment can be performed using material particles instead of electromagnetic radiation.

The results of the double-slit experiment lead to that “each particle interferes with itself in some way”.



Double-slit experiment with electrons



Variation of intensity (I) with the position on the screen (x)

1.9 The Need For A Wave Function

From the classical theory of waves. We know that waves are characterized by an amplitude function such that the intensity of the wave at any point is determined by the square of the amplitude.

Assuming that associated with each particle a **wave function $\Psi(x, t)$** such that the **absolute square of this function** gives the intensity I :

$$I = |\Psi(x, t)|^2 = \Psi^*(x, t) \Psi(x, t)$$

where * denotes complex-conjugation.

For simplicity, we have taken

- One-dimensional wave function but the treatment can be easily generalized to 3D.
- $|\Psi(x, t)|$ is taken because the wave function is, in general, a complex quantity.
- The intensity I , is a real, positive quantity.

In the case of the double-slit experiment with particles,

At some point on the screen let,

Ψ_1 the wave function corresponding to the waves spreading from slit 1 with $I_1 = |\Psi_1|^2$

Ψ_2 the wave function corresponding to the waves spreading from slit 2 with $I_2 = |\Psi_2|^2$

I_1, I_2 : The corresponding intensities on the screen when **only one slit is open**.

When **both the slits are open**, the resultant amplitude:

$$\Psi = \Psi_1 + \Psi_2$$

The resultant intensity is, therefore

$$I = |\Psi|^2 = |\Psi_1 + \Psi_2|^2$$

Let us write

$$\Psi_1 = |\Psi_1|e^{i\alpha_1}, \quad \Psi_2 = |\Psi_2|e^{i\alpha_2}$$

where $|\Psi_1|, |\Psi_2|$ are the absolute values and α_1, α_2 are the phases of the two wave functions, respectively. Then

$$|\Psi_1|^2 = \Psi_1^* \Psi_1 \quad \text{and} \quad |\Psi_2|^2 = \Psi_2^* \Psi_2$$

This gives

$$\begin{aligned} I &= (\Psi_1 + \Psi_2)^* (\Psi_1 + \Psi_2) \\ &= \Psi_1^* \Psi_1 + \Psi_2^* \Psi_1 + \Psi_1^* \Psi_2 + \Psi_2^* \Psi_2 \\ &= |\Psi_1|^2 + |\Psi_2|^2 + \Psi_1^* \Psi_2 + \Psi_2^* \Psi_1 \\ &= |\Psi_1|^2 + |\Psi_2|^2 + |\Psi_1| |\Psi_2| (e^{-i(\alpha_1 - \alpha_2)} + e^{i(\alpha_1 - \alpha_2)}) \\ &= I_1 + I_2 + 2\sqrt{I_1 I_2} \cos(\alpha_1 - \alpha_2) \end{aligned}$$

This shows that $I \neq I_1 + I_2$,

$2\sqrt{I_1 I_2} \cos(\alpha_1 - \alpha_2)$ is the *interference* term.

We shall see in later that the wave function satisfies a linear equation which is known as the *Schrödinger equation*.

The quantum mechanical wave function $\Psi(x, t)$ is an abstract quantity.

Max Born, in 1926, suggested that the wave function must be **interpreted statistically**.as follows:

If a particle is described by a wave function $\Psi(x, t)$, then the probability $P(x) dx$ of finding the particle within an element dx about the point x at time t is;

$$P(x) dx = |\Psi(x, t)|^2 dx$$

The quantity

$$P(x) = |\Psi(x, t)|^2 = \Psi^*(x, t)\Psi(x, t)$$

is, naturally, called the **position probability density**.

Since the probability of finding the particle somewhere must be unity, the wave function should be **normalized** so that

$$\int_{-\infty}^{\infty} \Psi^* \Psi dx = 1$$

That is, the wave function should be **square integrable**.

1.10 Wave Packet and the Uncertainty Principle

From the de Broglie relation; $p = \frac{h}{\lambda} = \hbar k$

where $k = 2\pi/\lambda = \text{propagation constant}$ or the **wave number**.

E is the energy of the particle

ν is the frequency of the associated wave

$E = h\nu = \hbar\omega$ is the **Planck-Einstein relation**

$\omega = 2\pi\nu$ is the angular frequency of the wave.

Let us consider a plane, monochromatic wave as a wave function to be associated with a particle,

$$\Psi(x, t) = Ae^{i(kx - \omega t)}$$

this represents a simple harmonic disturbance of wavelength λ and frequency ν , travelling towards the positive x -direction with velocity, $v_{ph} = \frac{\omega}{k} = \text{phase velocity}$.

The plane wave $\Psi(x, t)$ represents a particle having a momentum $p = \hbar k$.

The probability density (the amplitude A is constant)

$$P = |\Psi(x, t)|^2 = A^2$$

P is independent of position. Thus, the particle has equal probability of being found anywhere.

So, the question is: *how to construct a wave function that can look like a particle?*

A particle can be represented by a **wave packet**.

A wave packet can be formed by superposing plane waves of different wave numbers in such a way that they interfere with each other destructively outside of a given region of space.

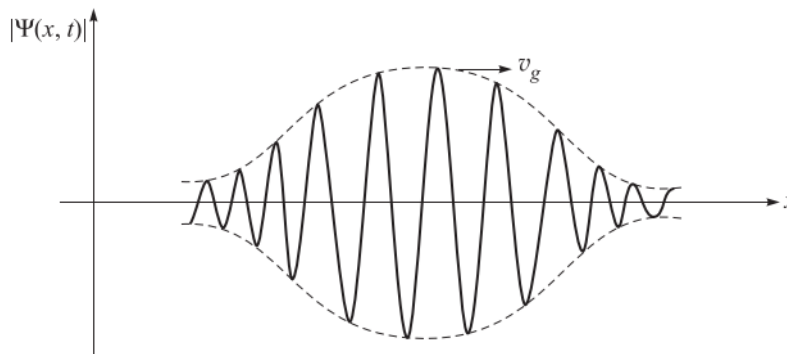
Let $\Psi(x, t)$ be a one-dimensional wave packet formed by of plane waves:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i(kx - \omega t)} dk$$

where the amplitude A and the angular frequency ω depend on k .

a **wave packet** which moves with the *group velocity*

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



A wave packet propagating along the x-axis.

If Δx is the spatial extent of a wave packet and Δk is its wave number range, then it always happens that $\Delta x \Delta k \geq 1$ **Heisenberg's uncertainty principle**

Heisenberg's Uncertainty Principle

- In classical mechanics,

The position x and the momentum p of a particle are independent of each other and can be simultaneously measured precisely.

- In quantum mechanics,

A particle is represented by a wave packet. The particle may be found anywhere within the region where the amplitude of the wave function $\Psi(x)$ is nonzero.

How precisely we can determine the position and the momentum of a particle simultaneously?

By using the relation $\Delta x \Delta k \geq 1$ and $p = \hbar k$ we obtain $\Delta x \Delta p \geq \hbar$

This is **Heisenberg's uncertainty relation for position and momentum**. It states that *it is not possible to specify both the position and the momentum of a particle simultaneously with arbitrary precision; the product of the uncertainties in the position and the momentum is always greater than a quantity of order \hbar .*

It is important to note that there is no uncertainty relation between one cartesian component of the position vector of a particle and a different cartesian component of the momentum.

$\Delta x \Delta p_x \geq \hbar$
$\Delta y \Delta p_y \geq \hbar$
$\Delta z \Delta p_z \geq \hbar$

Energy-Time Uncertainty Relation

The energy E of a free particle of mass m and momentum p is

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

If Δp is the uncertainty in momentum then the uncertainty in energy is

$$\Delta E = \frac{2p}{2m} \Delta p = \frac{p}{m} \Delta p = v \Delta p$$

where v is the velocity of the particle.

The uncertainty in time $\Delta t = \frac{\Delta x}{v}$

Multiplying the two,

$$\Delta E \Delta t = (v \Delta p) \left(\frac{\Delta x}{v} \right) = \Delta x \Delta p \geq \hbar$$

or $\Delta E \Delta t \geq \hbar$

PROBLEM: Calculate the uncertainty in the momentum of a proton confined in a nucleus of radius $10^{-14}m$. From this result, estimate the kinetic energy of the proton.

Solution: If the proton is confined within a nucleus of radius r_0 , then the uncertainty in its momentum is

$$\Delta p \approx \frac{\hbar}{r_0} = \frac{1.054 \times 10^{-34}}{10^{-14}} = \boxed{1.054 \times 10^{-20} \text{ kg m/s}}$$

Taking the momentum p to be of order Δp , the kinetic energy of the proton is given by

$$E = \frac{p^2}{2m} \approx \frac{\hbar^2}{2mr_0^2}$$

where m is the mass of the proton. Substituting the values,

$$\begin{aligned} E &\approx \frac{(1.054 \times 10^{-34})^2}{2 \times 1.67 \times 10^{-27} \times (10^{-14})^2} \\ &= 0.3326 \times 10^{-13} \text{ J} \\ &= \frac{0.3326 \times 10^{-13}}{1.6 \times 10^{-13}} \text{ MeV} \\ &= \boxed{0.21 \text{ MeV}} \end{aligned}$$

PROBLEM: The lifetime of a nucleus in an excited state is $10^{-12}s$. Calculate the probable uncertainty in the energy and frequency of a γ -ray photon emitted by it.

Solution: The energy-time uncertainty relation is

$$\Delta E \Delta t \approx \hbar$$

Therefore, the uncertainty in energy is

$$\Delta E \approx \frac{\hbar}{\Delta t} = \frac{1.054 \times 10^{-34}}{10^{-12}} = \boxed{1.054 \times 10^{-22} \text{ J}}$$

The uncertainty in frequency is

$$\Delta \nu = \frac{\Delta E}{h} = \frac{1.054 \times 10^{-22}}{6.625 \times 10^{-34}} = \boxed{1.59 \times 10^{11} \text{ Hz}}$$

PROBLEM: Using the uncertainty principle, show that an alpha particle can exist inside a nucleus.

Solution: The radius of a typical nucleus is of the order of 10^{-14} m. If a particle is to exist within the nucleus, then the uncertainty in its position must be of this order:

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

Therefore, the uncertainty in the momentum of the particle must be

$$\begin{aligned} \Delta p &\approx \frac{\hbar}{\Delta x} = \frac{1.054 \times 10^{-34}}{10^{-14}} \\ &= 1.054 \times 10^{-20} \text{ kg m/s} \end{aligned}$$

The momentum of the particle is at least of this order.

The rest mass of an α -particle is approximately four times the mass of a proton:

$$m = 4 \times 1.67 \times 10^{-27} \text{ kg}$$

The speed of the α -particle would be

$$v = \frac{1.054 \times 10^{-20}}{4 \times 1.67 \times 10^{-27}} = 1.58 \times 10^6 \text{ m/s}$$

With this speed the motion can be considered nonrelativistic. Therefore, the kinetic energy of the particle is at least

$$\begin{aligned} K &= \frac{p^2}{2m} = \frac{(1.054 \times 10^{-20})^2}{2 \times 4 \times 1.67 \times 10^{-27}} \\ &= 8.3 \times 10^{-15} \text{ J} \\ &= \boxed{52 \text{ keV}} \end{aligned}$$

Interpretation of the Wavefunction

In Quantum Mechanics, a “particle” (e.g. an electron) does not follow a definite trajectory $\mathbf{r}(t)$, $\mathbf{p}(t)$ but rather it is best described as being distributed through space like a wave.

Wavefunction $\Psi(x)$: is a wave representing the spatial distribution of a “particle”.

- e.g. electrons in an atom are described by a wavefunction centred on the nucleus.

$\Psi(x)$: is a function of the coordinates defining the position of the classical particle

One-dimension (1D) time independent $\Psi(x)$

Three-dimension (3D) time independent $\Psi(\mathbf{r}) = \Psi(x, y, z) = \Psi(r, \theta, \phi)$ (e.g. atoms)

Ψ may be time dependent e.g. $\Psi(x, t)$ and $\Psi(\mathbf{r}, t) = \Psi(x, y, z, t) = \Psi(r, \theta, \phi, t)$