

A.D.M. COLLEGE FOR WOMEN (AUTONOMOUS)

(Accredited With 'A' Grade by NAAC 4th Cycle)

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NAGAPATTINAM – 611 001

PG DEPARTMENT OF PHYSICS



Course Material – Atomic and Nuclear Physics

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Unit I

Cathode and Positive Rays

Introduction

An *anode ray* (also positive ray or canal ray) is a beam of positive ions that is created by certain types of gas discharge tubes. They were first observed in Crookes tubes during experiments by the German scientist Eugen Goldstein, in 1886. Later work on anode rays by Wilhelm Wein and J.J.Thomson led to the development of mass spectroscopy. Goldstein used a gas-discharge tube which had a perforated cathode. When a high electrical potential of several thousand volts is applied between the cathode and anode, faint luminous "rays" are seen extending from the holes in the back of the cathode. These rays are beams of particles moving in a direction opposite to the "cathode rays," which are streams of electrons which move toward the anode. Goldstein called these positive rays *Kanalstrahlen*, "channel rays" or "canal rays", because they were produced by the holes or *channels* in the cathode.

In 1907 a study of how this "ray" was deflected in a magnetic field, revealed that the particles making up the ray were not all the same mass. The lightest ones, formed when there was some hydrogen gas in the tube, were calculated to be about 1840 times as massive as an electron. They were protons. The process by which anode rays are formed in a gas-discharge anode ray tube is as follows. When the high voltage is applied to the tube, its electric field accelerates the small number of ions (electrically charged atoms) always present in the gas, created by natural processes such as radioactivity. These collide with atoms of the gas, knocking electrons off of them and creating more positive ions. These ions and electrons in turn strike more atoms, creating more positive ions in a chain reaction. The positive ions are all attracted to the negative cathode, and some pass through the holes in the cathode. These are the anode rays. By the time they reach the cathode, the ions have been accelerated to a sufficient speed such that when they collide with other atoms or molecules in the gas they excite the species to a higher energy level. In returning to their former energy levels these atoms or molecules release the energy that they had gained. That energy gets emitted as light. This light-producing process, called fluorescence, causes a glow in the region where the ions emerge from the cathode.

1.1Cathode Rays

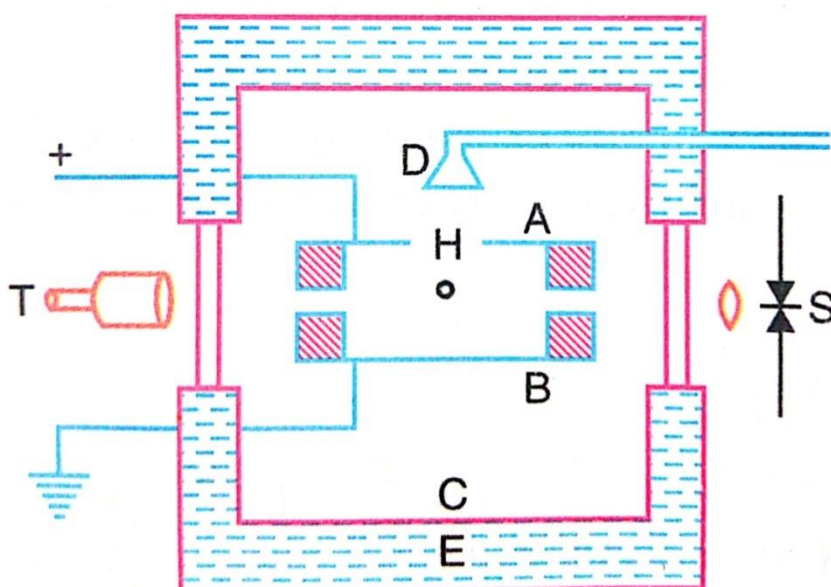
Cathode Rays-Cathode rays (electron beam or e-beam) are streams of electrons observed in vacuum tubes. If an evacuated glass tube is equipped with two electrodes and a voltage is applied, glass behind the positive electrode is observed to glow, due to electrons emitted from the cathode (the electrode connected to the negative terminal of the voltage supply).

Properties of Cathode Rays-

- (i) They travel in straight lines
- (ii) Cathode rays possess momentum and kinetic energy.
- (iii) Cathode rays produce heat, when allowed to fall on matter.
- (iv) Cathode rays produce fluorescence when they strike a number of crystals, minerals and salts.
- (v) When cathode rays strike a solid substance of large atomic weight, X-rays are produced.
- (vi) Cathode rays ionize the gas through which they pass.

- (vii) Cathode rays affect the photographic plates.
- (viii) The cathode rays are deflected from their straight line path by both electric and magnetic fields. The direction of deflection shows that they are negatively charged particles.
- (ix) Cathode rays travel with a velocity upto (1/10)th of the velocity of light.
- (x) Cathode rays comprises of electrons which are fundamental constituents of all atoms.

1.2: e/m of cathode rays-Millikan's oil drop method:



Experimental arrangement:

The apparatus consists of two optically plane parallel brass plates A and B (figure) separated by insulating rods of glass. The lower plate B is earthed. The upper plate A can be charged to a positive potential of the order of 10000 volts, from a high-tension battery. The observation chamber is situated in a bigger chamber C which is completely surrounded by a constant temperature bath of oil E. Tiny drops of a heavy non-volatile oil are sprayed into the chamber by an atomizer D. Some of the oil drops enter the space between the plates through the pinhole in the top plate A. These drops are charged, due to the frictional effect at the nozzle of the atomizer. The air between the plates can be ionized by allowing X-rays to pass through it. Then the drops may pick up additional charges. The drops are illuminated by light from an arc lamp S. The oil-drop is observed by means of a short-focus telescope T provided with a millimeter scale in the eyepiece.

Experimental procedure:

The plates are first connected together, so that the electric field action of gravity. As the drop is moving in a viscous medium (air), it will move with a constant terminal velocity v . Using the stop watch, the terminal velocity of the drop is measured. Let

v = terminal velocity of the free fall,
 a = radius of the drop,
 ρ = density of oil,
 σ = density of air,
 η = coefficient of viscosity of air,
 m = effective mass of the drop and
 g = acceleration due to gravity

Then by Stoke's law, $mg = 6 \pi \eta a v$ (1)

or $\frac{4}{3} \pi a^3 (\rho - \sigma) g = 6 \pi \eta a v$ (2)

Or $a = [9 \eta v / 2 (\rho - \sigma) g]^{1/2}$ (3)

The effective mass of the drop $m = \frac{4}{3} \pi a^3 (\rho - \sigma) = \frac{4}{3} \pi [9 \eta v / 2 (\rho - \sigma) g]^{3/2} (\rho - \sigma)$(4)

Thus, by measuring v , we can calculate the effective mass m of the chosen oil drop. Now, an electrostatic field X is applied steadily, so that the drop moves upwards with a steady velocity V_1 . If the total charge on the drop is $n_1 e$ (where n_1 is an integer), the resultant upward force on the drop $= X n_1 e - mg$. According to Stoke's law $X n_1 e - mg = 6 \pi \eta a v_1$ (5)

Dividing (5) by (1) $X n_1 e - mg / mg = v_1 / v$ (or) $X n_1 e / mg = v_1 + v / v$

$$n_1 e = mg(v_1 + v) / Xv \text{(6)}$$

Now, the air between the plates is irradiated with X-rays. X-rays ionize the air molecules. The oil drop under observation may pick up one or more ionic charges. Due to the acquisition of charges the velocity of the drop changes suddenly, when X is constant. Let the new velocity of the drop be v_2 and the corresponding charge on the drop $n_2 e$. Then,

$$n_2 e = mg(v_2 + v) / Xv \text{(7)}$$

$$(n_2 - n_1) e = mg / Xv (v_2 - v_1)$$

If $v_2 > v_1$ ($n_2 - n_1$) e is positive and if $v_2 < v_1$, ($n_2 - n_1$) e is negative. Both are possible, as both positive and negative ions are present.

Now for the same drop under the same electric field (X), mg / Xv is constant. Hence $v_2 - v_1$ is proportional to $(n_2 - n_1) e$ i.e., any change in the velocity of the drop is proportional to the quantity of the acquired charge. Millikan made thousands of observations on a single drop. He found that there was a minimum value of $(v_2 - v_1)$ and that other values of $(v_2 - v_1)$ were simple integral multiples of this $(v_2 - v_1)$ minimum. Corresponds to the addition or subtraction of one unit of charge. i.e., $(n_2 - n_1) = 1$ when $(v_2 - v_1)$ is minimum.

$$e = \pm mg / Xv (v_2 - v_1) \text{ minimum(8)}$$

Substituting the value of m from (4),

$$e = \frac{4}{3} \pi [9 \eta / 2]^{3/2} [v / (\rho - \sigma) g]^{1/2} (v_2 - v_1) \text{ minimum} / X$$

The value of electronic charge e found by Millikan was 1.591×10^{-19} C. The value of e now generally accepted is 1.602×10^{-19} C.

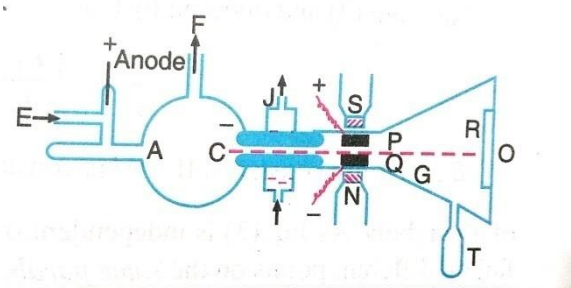
1.3 Positive Rays:

If the cathode in a discharge tube is perforated, “luminous rays” are observed behind the cathode. These rays travel in a direction opposite to the cathode rays i.e., from the anode to the cathode. These rays produce fluorescence when they strike a fluorescent screen present at the back of the cathode. They are deflected by electric and magnetic fields. The direction of deflection indicates that they are positively charged. These rays are called *positive rays* or *canal rays*.

Properties of Positive Rays

- (1) These rays affect a photographic plate, produce fluorescence and penetrate thin aluminium foils.
 - (2) They are deflected by electric and magnetic fields. The direction of deflection indicates that they are positively charged. For the same electric or magnetic field, the magnitude of deflection suffered by positive rays is much smaller than that of cathode rays. Therefore, the positive ray particles are much heavier than the electrons.
 - (3) The velocities of all the positive ray particles are not the same. The velocities of these rays range from 10^5 to 10^6 ms⁻¹.
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1.4 Positive ray analysis- Thomson’s Parabola Method



Thomson determined the charge to mass ratio of positive ions by using the apparatus shown in Figure. It consists of a discharge tube (A) in which the pressure of the gas is about 10^{-5} m of mercury. The anode is held in a side-tube. In order to ensure the supply of the gas under test, a steady stream of the gas is allowed to flow in through a capillary tube (E) and after circulating in A is pumped off at F. The cathode (C) is perforated with an extremely fine hole. The cathode is cooled by the water-jacket (J). The positive ions produced in A fly towards the cathode and those reaching it axially pass straight through the fine hole and emerge from the opposite end of the cathode as a narrow beam. This beam is then subjected to parallel electric and magnetic fields simultaneously. An electric field is applied between the plates P and Q. The electric field is perpendicular to the positive ray beam. N and S are the poles of a strong electromagnet. After passing through these fields, the beam enters a highly evacuated camera G and is received on a photographic plate R. A liquid air-trap (T) helps to keep the pressure in G quite low, even though pressure in A is comparatively large. The photographic plate, when developed, shows a series of parabolae.

Theory:

Consider a positive ion of mass M, charge E and velocity v. When no electric or magnetic field is applied, the positive ion strike the screen at O. This is called the *undeflected spot*.

Action of Electric field: Let an electric field of strength X act over a length l of the path of the ion.

Displacement of the ion in passing through the electric field = $S = \frac{1}{2} (XE/M) (l/v)^2$

After leaving the field, the ion moves in a straight line and finally strikes the plate at a distance x from O. x is proportional to s as well as to the distance between the field and the plate. Hence

$$x \propto XEl^2/2Mv^2$$

or $x = k_1 XE/Mv^2 \dots\dots\dots(1)$

Here k_1 is a constant.

Action of Magnetic Field:

Suppose a magnetic field of strength B is applied over the same direction as that of the electric field. The positive ion will now be deflected by this field in a direction at right angles to that in which it was deflected by the electric field. It will strike the plate at a distance y from O such that oy is perpendicular to ox in the plane of the plate.

Displacement of the ion just emerging from the magnetic field= $s' = 1/2 (Bev/M) (l/v)^2 = BEl^2/2Mv$

On emerging from the field, the ion moves in a straight line and finally strikes the plate at a distance y from O y is proportional to s' as well as to the distance between the field and the plate.

Hence, $y \propto BEl^2/2Mv$

or $y = k_2 BE/Mv \dots\dots\dots(2)$

Here k_2 is a constant.

Action of Combined Electric and Magnetic Fields:

The combined effect of the two fields is found by eliminating v from (1) and (2)

Squaring (2) and dividing by (1),

$$y^2/x = (k_2^2/k_1 B^2/X) E/M \dots\dots\dots(3)$$

B and X are constants. If E/M is constant, then by eq. (3), $y^2/x = \text{constant}$. This is the equation of a parabola. As eq. (3) is independent of v, particles of same E/M but of different velocities will fall on different points on the *same parabola*.

$y/x = (k_2/k_1) B/X v$. i.e., $y/x \propto v$. Thus, the position of individual particle on the parabola will depend on the velocity of the particle.

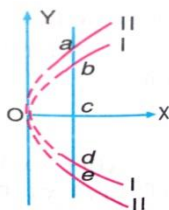
The ions having different values of E/M will lie along the different parabolas.

For one direction of the magnetic field, one half of the parabola is traced. Reversing the magnetic field, the other half is also traced. When the full parabola is traced, it is easy to draw the axis of symmetry (X- axis).

Determination of E/M:

The value of E/M can be calculated from eq.(3) by measuring the coordinates x and y for a point on the parabola, evaluating the constants k_1 and k_2 for the apparatus and knowing B and X.

Determination of Mass:



The mass of a positive ion is determined in terms of the mass M_1 of the standard hydrogen ion. A small trace of hydrogen is always present in all sample of gases. Hydrogen, being the lightest element, gives the outermost parabola. Let I and II represent the parabolic traces due to ions of the gas of mass M_2 and the hydrogen ions of mass M_1 respectively. An ordinate a, b, c, d, e is drawn. It cuts the two parabolas a, b, d, e and the X-axis at c . Let ac and bc represent the two values of y corresponding to a constant value of x on these parabolas. Let us assume that both ions have the same charge. Then from eq.(3),

$$ac^2/x = (k^2/k_1 B^2/X) E/M_1$$

and $bc^2/x = (k^2/k_1 B^2/X) E/M_2$

or $M_2/M_1 = ac^2/bc^2 = (ae/bd)^2$

The lengths ae and bd can be measured on the photograph. Hence the parabolic traces enable us to compare the masses of different ions with hydrogen used as a standard.

$$M_2 = (ae/bd)^2 M_1.$$

Discovery of Stable Isotopes: Using neon gas in his apparatus, Thomson obtained two parabolas for the gas itself a strong one corresponding to a mass 20 and a much weaker one corresponding to a mass 22. The intensity ratio of the two traces was 9:1 which gave the relative abundance of the two isotopes. Thomson, therefore, suggested that neon could exist in the form of two *isotopes*, chemically indistinguishable but with different masses 20 and 22. The actual observed atomic weight (20.2) of neon is the weighted mean of the masses of these two isotopes.

This established the existence of stable isotopes.

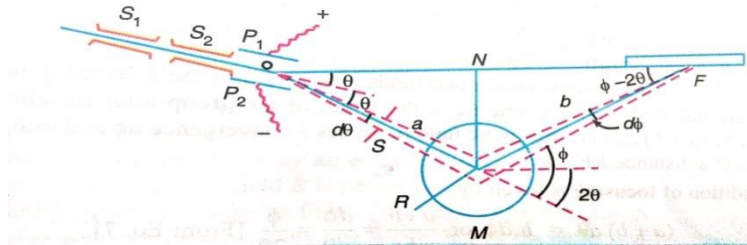
Limitations of the Parabola Method:

1. Due to the velocity dispersion, each parabolic trace is of very low intensity.
2. The traces on the photographic plate are blurred and have no definite edges. Hence accurate measurements are not possible.
3. The influence of secondary rays makes analysis difficult.

1.5 Aston's Mass Spectrograph

The apparatus used by Aston is shown in Figure. The stream of positive ions obtained from a discharge tube is rendered into a fine beam by passing it between two narrow slits S_1 and S_2 . This beam enters the electric field between the metal plates P_1 and P_2 . Due to the action of the electric field (X), all positive ions having the same value of E/M are not only deviated by an angle θ from the original path but are dispersed by an angle $d\theta$ due to their different velocities. The beam is then allowed to pass through a magnetic field M acting at right angles to the electric field so that it

produces a deflection of the beam in the same plane. The magnetic field deviates the particles by an angle ϕ and reconverges them by $d\phi$. The direction and magnitude of the field is so adjusted that it produces a deviation of the beam in the opposite direction and brings all ions having the same value of E/M , even though differing in velocities, to a focus at one point F . Ions having different values of E/M are brought to focus at different points on the photographic plate. The condition required for such a focusing may be derived as follows



Theory:

To obtain the condition of focusing. Consider a group of ions having the same value of E/M , but moving with different velocities. Let θ and ϕ be the mean angles of deviation of the group of ions in the electric and magnetic fields respectively. Let $d\theta$ be the dispersion angle due to the electric field and $d\phi$ the convergence angle due to the magnetic field.

- (i) Let X = The strength of the electric field,
- E = Charge of the ion,
- M = Mass of the ion,
- v = Velocity of the ion,
- l_1 = the length of the electric field
- d_1 = The linear displacement of an ion from its path due to the electric field

then

$$\text{The angular deviation of the beam} = \theta = d_1/l_1 = \frac{1}{2} XE/Mv^2 l_1 \dots\dots\dots (1)$$

$$\text{Angle of dispersion of the beam} = -XE l_1/M dv/v^3 \dots\dots\dots(2)$$

$$d\theta/\theta = - 2dv/v \dots\dots\dots(3)$$

(ii) Similarly, if d_2 = displacement of an ion from its path due to magnetic field of strength B , and l_2 = the length of path of the ion in the magnetic field,

$$d_2 = \frac{1}{2} Bev/M l_2^2/v^2$$

The deviation produced by the magnetic field in the opposite direction = $\phi = d_2/l_2 = \frac{1}{2} BE/Mv l_2 \dots\dots\dots(4)$

$$d\phi = -1/2 BE l_2/M dv/v^2 \dots\dots\dots(5)$$

Hence $d\phi/\phi = -dv/v \dots\dots\dots (6)$

Comparing (3) and (6), $d\theta/\theta = 2 d\phi/\phi$

$$d\phi/d\theta = \phi/2\theta \dots\dots\dots(7)$$

Let $a=OR$ = The distance between the two fields. The width of the selected group of ions at $R=a$ $d\theta$. If there had been no magnetic field, the width of the group after travelling a further distance b

would be $(a+b) d\theta$. The magnetic field produces a convergence $d\phi$ and brings the group of ions to a focus at a distance $RF = b$.

The condition of focusing is given by

$$(a+b) d\theta = b d\phi \text{ or}$$

$$a+b/b = d\phi/d\theta = \phi/2\theta \text{ (from eq.7)}$$

$$b/a = 2\theta/\phi - 2\theta \dots\dots\dots(8)$$

This expression represents a straight line drawn from O, making an angle 2θ with the direction of the beam deviated by the electric field. If $\phi = 2\theta$, the rays do not converge (since $b = \infty$). However, if $\phi = 4\theta$, $b = a$ and the convergent beam can be easily photographed. The ions are focused at F such that $OR = RF$.

Detection of isotopes:

To determine the masses of isotopes of an element, the element is mixed with a number of other elements whose atomic masses are known accurately. The traces of all of them are obtained on the same photographic plate. The distances of the traces of the known masses are measured from a given reference point on the plate. A calibration graph is drawn connecting the distances with the atomic masses. By measuring the distances of the traces of the isotopes of the element from the same reference point, their atomic masses are obtained from the calibration graph.

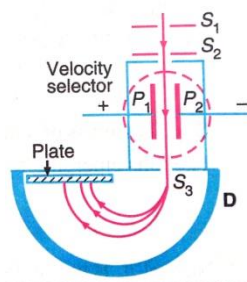
Advantages:

1. All the particles having the same value of E/M are focussed at a single point unlike Thomson's method in which they are spread out into a parabola. Hence, the intensities of the lines on the photographic plate in Aston's mass spectrograph are large, while the parabolic traces on the photographic plate in Thomson's arrangement are feeble
2. The intensity of a line in the mass spectrum is proportional to the total number of particles of that mass. Hence a rough idea of the relative abundance of various isotopes of an element can be made by this method.

Limitations:

1. The mass scale is not linear.
2. Owing to the polarisation of the electrodes of the electric field, the traces are not quite straight but slightly curved.

1.6 Bainbridge's Mass Spectrograph:



The apparatus is shown diagrammatically in Figure. The beam of positive ions produced in a discharge tube is collimated by two slits S_1 and S_2 and enter a "velocity selector". The velocity selector consists of (1) a steady electric field X maintained at right angles to the ion beam between two plane parallel plates P_1 and P_2 and (2) a magnetic field B . The magnetic field is produced by an electromagnet represented by the dotted circle. The magnetic field B is perpendicular to X and the ion beam. The electric field and magnetic field of the velocity selector are so adjusted that the deflection produced by one is nullified by the deflection produced by the other. If X and B are the electric intensity and magnetic induction, then $Xe = Bev$ or $v = X/B$

Only those ions, having this velocity v , alone pass through the entry slit S_3 , to enter the evacuated chamber D . Thus all ions entering D must have the same velocity. The positive ions which enter into D are subjected to a strong uniform magnetic field of intensity B' , perpendicular to its path. The force acting on each ion will be $B'ev$. Ions with different masses trace circular paths of different radii

$$R = Mv / B'e \quad (B'ev = Mv^2/R)$$

$$e/M = v/B'R = X/BB'R \quad (v = X/B)$$

Since v and B' are constant quantities, e/M proportional to $1/R$

After describing semicircles, the ions strike a photographic plate. Now, $M = B'e R/v$. If e is the same for all ions, then M proportional to R .

So we get a linear mass scale on the photographic plate. It will be seen that ions of different masses strike the photographic plate at different points, thus giving a typical mass spectrum.

Advantages :

- (1) Since a linear mass scale is obtained, accuracy of measurements is increased
- (2) The sensitivity depends on the strength of the deflecting magnetic field B' and the area of the chamber D . Bainbridge used a magnetic field of 1.5 weber/m² over a semicircle of radius 0.2m. He found a definite increase in resolving power over Aston's apparatus. The ten isotopes of tin were resolved by this instrument.

1.7 Mass Defect and Packing Fraction

“Mass defect” of a given isotope is defined as the difference between the experimentally measured mass of the isotope (M) and its mass number (A).

$$\text{Mass defect} = \Delta = M - A.$$

The packing fraction of the isotope is defined as the ratio of its mass defect ($M - A$) to its mass number (A).

$$\text{Packing fraction} = (M - A)/A.$$

Since atomic masses are measure relative to C-12, the packing fraction for this isotope is zero.

Binding Energy

Definition: When Z protons and N neutrons combine to make a nucleus, some of the mass (Δm) disappears because it is converted into an amount of energy $\Delta E = (\Delta m) c^2$. This is called the binding energy (B.E.) of the nucleus.

$$\text{B.E.} = (Zm_p + Nm_n) c^2 - M_n c^2$$

Where m_p = mass of the proton, m_n = mass of the neutron and M_n = nuclear mass.

Atomic Masses: Atomic masses refer to the masses of neutral atoms, not of bare nuclei. Thus an atomic mass always includes the masses of its Z electrons. Atomic masses are expressed in mass units (u), which are so defined that the mass of a $^{12}_6\text{C}$ atom is exactly 12u.

The value of a mass unit is

$$1\text{u} = 1.66054 \times 10^{-27} \text{ kg.}$$

The energy equivalent of a mass unit is 931.49 MeV.

Definition: The atomic mass unit (u) is defined as one twelfth of the mass of the neutral carbon C-12 atom.

Unit II

Atom Model

2.1. Introduction: VECTOR ATOM MODEL

(1) Bohr's theory was able to explain only the series spectra of the simplest hydrogen atom. It could not explain the multiple structure of spectral lines in the simplest hydrogen atom. Sommerfeld's theory was able to give an explanation of the fine structure of the spectral lines of hydrogen. However, Sommerfeld's theory could not predict the correct number of the fine structure lines. Moreover, it gave no information about the relative intensities of the lines. Sommerfeld's theory could not explain the complex spectra of alkali metals like sodium atom. (2) These older theories were inadequate to explain new discoveries like Zeeman Effect and Stark Effect in which the spectral lines could be split up under the influence of magnetic and electric fields. (3) Another drawback of the Bohr model was that it could not explain how the orbital electrons in an atom were distributed around the nucleus.

Therefore, in order to explain the complex spectra of atoms and their relation to atomic structure, the vector atom model was introduced. The two distinct features of the vector atom model are:

**the concept of spatial quantization and*

**the spinning electron hypothesis.*

***Spatial quantization:**

According to Bohr's theory, the orbits are quantised as regards their magnitude (ie., their size and form) only. But according to quantum theory, the direction or orientation of the orbits in space also should be quantized. To specify the orientation of the electron orbit in space, we need a fixed reference axis. This reference line is chosen as the direction of an external magnetic field that is applied to the atom. The different permitted orientations of an electron orbit are determined by the fact that the projections of the quantized orbits on the field direction must themselves be quantised. The idea of space quantization leads to an explanation of Zeeman effect. The Stern-Gerlach experiment provided an excellent proof of the space quantization of atom.

***Spinning electron hypothesis:**

To account for the observed fine structure of spectral lines and to explain the anomalous Zeeman effect, the concept of spinning electron was introduced by Uhlenbeck and Goudsmit in 1926. According to their hypothesis the electrons spins about its axis of its own, while it also moves round the nucleus of the atom in its orbit. The spin of the electron is analogous to the spinning of a planet about its own axis, as it moves in an elliptical orbit around the sun. In other words, the electron is endowed with a spin motion over and above the orbital motion. According to quantum theory, the spin of the electron also should be quantized. Hence a new quantum number called the *spin quantum number* (s) is introduced. Since the orbital and spin motions are both *quantized* in magnitude and direction according to the idea of spatial quantization, they are considered as *quantized vectors*. Hence the atom model based on these quantized vectors is called *vector atom model* to which vector laws apply.

2.2. VARIOUS QUANTUM NUMBERS:

(1) The Principal quantum number (n):

This is identical with the one used in Bohr-Sommerfeld theory. The serial number of the shells starting from the innermost is designated as its principal quantum number (n). It can take only integral values excluding zero. i.e., $n=1,2,3,4,\dots$

(2) The orbital quantum number (l):

This may take any integral value $0,1,2,3,4,\dots,(n-1)$. Thus, if $n=4$, l can take the four values $0,1,2,3$. By convention an electron for which $l=0$, is called s electron, if $l=1$, p electron if $l=2$, d electron, $l=3$, f electron etc. The orbital angular momentum P_l of the electron is given by $P_l = l \hbar$. According to the wave mechanics, $P_l = [l(l+1)]^{1/2} \hbar$.

(3) The spin quantum number (s):

This has only one values, $s=1/2$. The spin angular momentum $P_s = s \hbar$ where $s=1/2$. According to wave mechanics, $P_s = [s(s+1)]^{1/2} \hbar$.

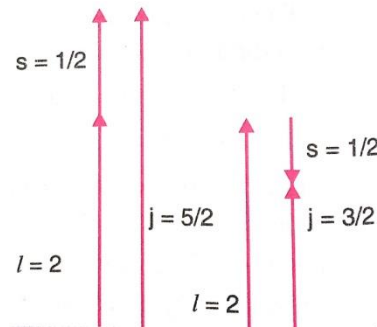
(4) Total angular momentum quantum number (j):

It represents the total angular momentum of the electron which is the sum of the orbital angular momentum and spin angular momentum. The vector j is defined as the equation $j=l + s$

with the restriction that j is positive. The spin angular momentum $s = \pm \frac{1}{2}$. $j = l \pm s$, plus sign when s is parallel to l and minus when s is anti-parallel. Thus for $l = 2$ and $s = \frac{1}{2}$ j can have the values $\frac{5}{2}$ and $\frac{3}{2}$. The total angular momentum of the electron $= P_j = j \hbar$.

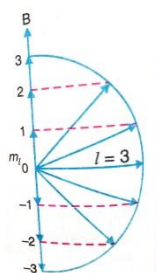
According to wave mechanics, $P_j = \sqrt{j(j+1)} \hbar$

To explain the splitting of spectral lines in a magnetic field, three more magnetic quantum numbers are introduced.



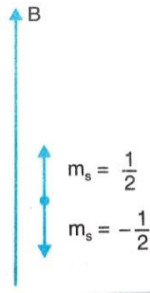
(5) Magnetic orbital quantum number (m_l):

The projection of the orbital quantum number l on the magnetic field direction is called the magnetic orbital quantum number m_l . The possible values of m_l are $l, l-1, l-2, \dots, 0, -1, -2, \dots, -l$. i.e., there are $(2l+1)$ possible values of m_l . This is illustrated in fig for $l = 3$. The angle θ between l and B is given by $\cos \theta = m_l / l$. Conversely the permitted orientations of the l vector relative to the field direction B is also $(2l+1)$. For example, if $l = 3$, the permitted orientations of l are 7, for which $m_l = 3, 2, 1, 0, -1, -2, -3$. Hence, the l vector can take only the 7 directions. l cannot be inclined to B at any other angle. This is known as “spatial quantization”.



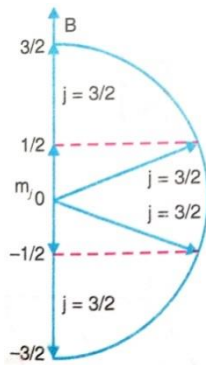
(6) Magnetic spin quantum number (m_s):

This is the projection of the spin vector s along the direction of the magnetic field. The spin angular quantum number (s) can assume only two possible positions with respect to the magnetic field, it may be parallel to it or anti-parallel. m_s can have two values $+1/2$ or $-1/2$.



(7) Magnetic total angular momentum quantum number (m_j):

This is the projection of total angular momentum vector j on the direction of the magnetic field. Since we are dealing with a single electron, j can have only odd half- integral values ($j=l\pm 1/2$). Hence, m_j must have only odd half-integral values. m_j can have only $(2j+1)$ values, from $+j$ to $-j$ zero excluded the possible values of m_j for $j=3/2$.



2.3. PAULI'S EXCLUSION PRINCIPLE:

No two electrons in an atom exist in the same quantum state. The four quantum numbers n , l , m and m_s , determine the state of an electron completely. Hence the principle may be stated as "No two electrons in an isolated atom may have the same four quantum numbers."

Explanation: The principle implies that each electron in an atom must have a different set of quantum numbers n , l , m and m_s . If two electrons have all their quantum numbers identical, then one of those two electrons would be excluded from entering into the constitution of the atom. Hence the name "exclusion principle".

Application: This principle enables us to calculate the number of electrons that can occupy a given subshell.

(1) Consider the K - shell with $n= 1, l=0$ and hence $m_l=0$. Since $s=1/2$, m_s can be either $+ 1/2$ or $-1/2$. Hence, the K-shell can have two electrons: electron 1 with quantum numbers $n =1, l=0, m_l=0, m_s= 1/2$ and electron 2 with quantum numbers $n=1, l=0, m_l=0, m_s= -1/2$. If there were a third electron, its quantum members will be identical with those of the first or second electron, which is against Pauli's exclusion principle. The K-shell is therefore completed or closed with two electrons.

(2) For the L-shell, $n = 2$ and $l=0$ or 1. For the sub shell $n=2, l=0$, m_l must be zero, $m_s=+1/2$ or $-1/2$. Hence there can be only 2 electrons in this subshell. For the subshell $n=2, l=1$, m_l can have three values $-1, 0, +1$. For each of these three values of $m_l=0$, m_s may be either $+1/2$ or $-1/2$. Hence there will be six possible set of values for the quantum numbers characterizing the electrons. Therefore, the maximum number of electrons in this sub shell is 6. The L-shell with two sub shells $[(n=2, l=0)$ and $(n=2, l=1)]$ is therefore, completed when it contains $2 + 6=8$ electrons.

(3) For the M-shell with $n=3$, there can be three sub shells with, $l= 0, 1, 2$. The first and second subshells are completed by 2 and 6 electrons as explained above. The third subshell is completed with $2(2l+ 1)$, i.e., 10 electrons since $l=2$. Hence the total number of electrons required to complete the M-shell is 18.

(4) Similarly, the N-shell can have a maximum of 32 electrons. In general, we get the two following conclusions: (i) In the n^{th} shell there are n subshells corresponding to the values $0, 1, 2, 3, (n-1)$ of l .

The maximum number of electrons in a sub-shell with a given value of l is $2(2l+ 1)$.

Orbital quantum number (l).	0	1	2	3	4
Number of possible electron state	2	6	10	14	18
Sub shell symbol	s	p	d	f	g

(ii) The number of electrons that can be accommodated in a shell. With principal quantum

number n =Sum of the electron in the constituent n sub shells.

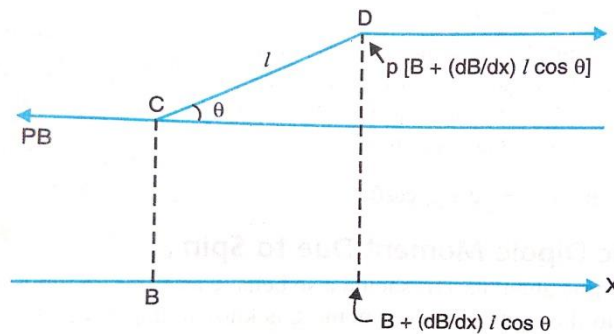
$$\begin{aligned}
 &= \sum_{l=0}^{l=n-1} 2(2l+1) = 2 \sum_{l=0}^{l=n-1} (2l+1) \\
 &= 2 [1 + 3 + 5 + 7 + \dots + \{2(n-1) + 1\}] = 2n^2
 \end{aligned}$$

The following table shows the distribution of electrons according to this scheme.

Shell symbol	K	L	M	N	O
Quantum number (n)	1	2	3	4	5
Number of electrons ($2n^2$)	2	8	18	32	50

2.4. THE STERN AND GERLACH EXPERIMENT:

We have seen that the orbital and spin motions of the electrons in atoms endow the atoms with magnetic moments. Direct evidence for the existence of magnetic moments of atoms and their space quantization is provided by the experiments of Stern and Gerlach.



PRINCIPLE:

The experiment is based on the behavior of a magnetic dipole (atomic magnet) in a non-uniform magnetic field. In a uniform magnetic field (B) the dipole experiences a torque that tends to align the dipole parallel to the field. If the dipole moves in such a field in a direction normal to the field it will trace a straight line path without any deviation. In an inhomogeneous magnetic field the dipole experiences in addition a translatory force. If the atomic magnet flies across such an inhomogeneous magnetic field normal to the field direction it will be deviated away from its rectilinear path. An expression for the deviation produced may be obtained as follows.

Let the magnetic field vary along the X -direction so that the field gradient is dB/dx and is positive. CD is the atomic magnet (of pole strength p , length l , dipole moment M) with its axis inclined at an angle θ to the field direction. If the field strength at the pole C is B , then the field strength at the other pole D will be $B + dB/dx \cdot l \cos \theta$. Hence the forces on the two poles are PB and $P(B + dB/dx \cdot l \cos \theta)$. Hence the atomic magnet experiences not only a torque ($=P/B = \mu_s B$) but also a translatory force

$$F_x = dB / dx P_l \cos \theta$$

$$F_x = dB / dx \mu_s \cos \theta \dots\dots\dots(1)$$

Let V= velocity of the atomic mass of m as it enters the field

L= length of the path of the atom in the field and

t= the time of travel of the atom through the field =L/V

The acceleration given to the atom along the field direction by the translatory force $F_x = F_x/m$

The displacement of the atom along the field direction on emerging out of the field = α

$$= \frac{1}{2} (F_x/m) t^2 = \frac{1}{2} F_x/m L^2/V^2$$

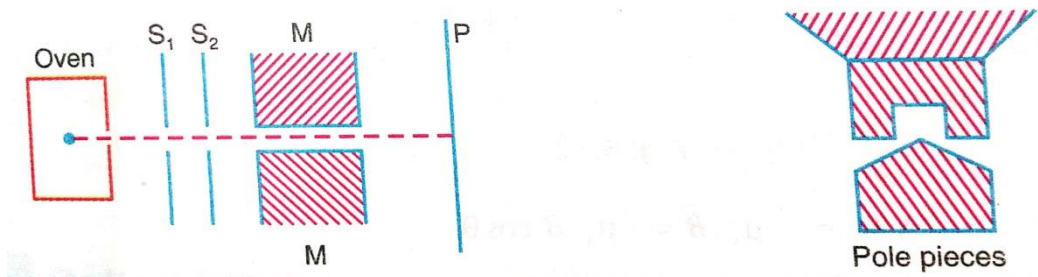
$$= \frac{1}{2} dB / dx \mu_s \cos \theta / m L^2/V^2$$

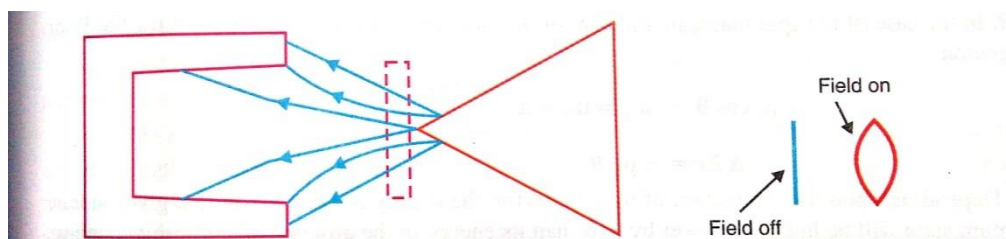
If μ is resolved component of the magnetic moment in the field direction, $\mu = \mu_s \cos \theta$

$$\alpha = \frac{1}{2} dB / dx \frac{\mu}{m} L^2/V^2$$

EXPERIMENTAL ARRANGEMENT:

Silver is boiled in an oven. Atoms of silver stream comes out from an opening in the oven. By the use of slits S₁ and S₂ a sharp linear of atoms is obtained. These atoms then pass through a very inhomogeneous magnetic field between the shaped poles of a magnet M M. A high degree of non-uniformity in the magnetic field is produced by making one of the pole-pieces of a powerful electromagnet a knife-edge. The lines of force are close together at the knife edge and the field there is much stronger than that at the other pole piece. The magnetic field is at right angles to the direction of movement of the atoms. Finally the atoms fall on a photographic plate P. The whole arrangement is enclosed in an evacuated chamber.





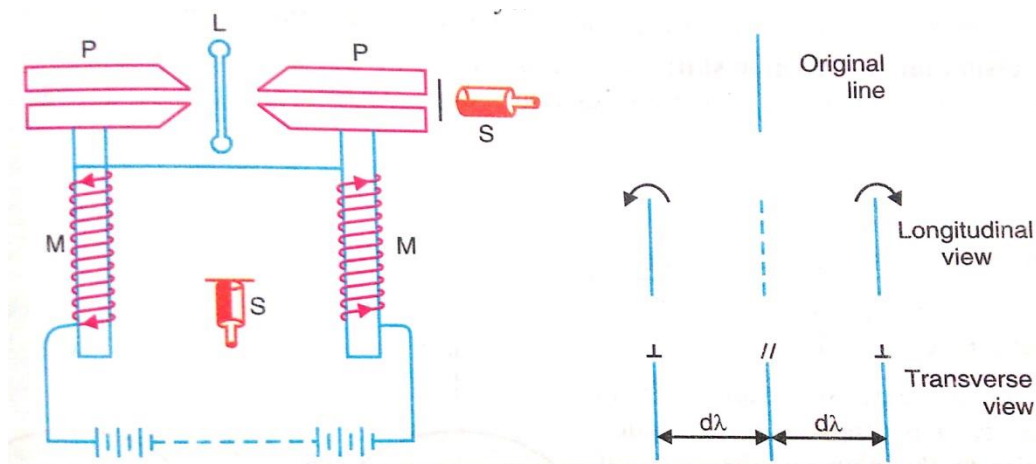
With no field the beam produces a narrow continuous line on the plate. In terms of the vector atom model those atoms with electron spins directed parallel to the magnetic field will experience a force in one direction whereas those with oppositely directed spins will experience a force in the opposite direction. According to this, the beam of atoms should split into two beams in its passage through the inhomogeneous magnetic field. This splitting of the beam into two parts of approximately equal intensity was actually observed in these experiments. On applying the inhomogeneous magnetic field it was found that the stream of silver atoms splits in two separate lines. Knowing $\frac{dB}{dx}$, L , V and α , μ was calculated. It was found that each silver atom had a magnetic moment of one BOHR MAGNETON in the direction of the field.

2.5 Zeeman Effect:

Zeeman effect is a magneto-optical phenomenon, discovered by Zeeman in 1896. He observed that if a source of light producing line spectrum is placed in a magnetic field, the spectral lines are split up into components. When the splitting occurs into two or three lines, it is called normal Zeeman effect and can be explained quantitatively by classical theory. The splitting of a spectral line into more than three components in ordinary weak magnetic fields is called anomalous Zeeman effect. This cannot be explained by classical theory.

Experimental arrangement for the normal Zeeman effect:

The arrangement is shown in figure. MM is an electromagnet capable of producing a very strong magnetic field. Its conical pole-pieces PP have longitudinal holes drilled through them. A source of light (L) emitting line spectrum (say, a sodium vapour lamp) is placed between the pole-pieces. The spectral lines are observed with the help of a spectrograph(S) of high resolving power. The Zeeman effect may be observed in two ways.



(i) The position of the spectral line is noted without applying the magnetic field. The magnetic field is now switched on and the spectral line is viewed longitudinally through the hole drilled in the pole-pieces and hence parallel to the direction of the field. It is found that the spectral line is split into two components, one slightly shorter in wavelength and the other slightly longer in wavelength than the original line. The original line is not present. The two components are found to be symmetrically situated about the position of the parent line. Analysing the two lines with a Nicol prism, both the lines are found to be circularly polarised in opposite directions. This is called normal longitudinal Zeeman effect.

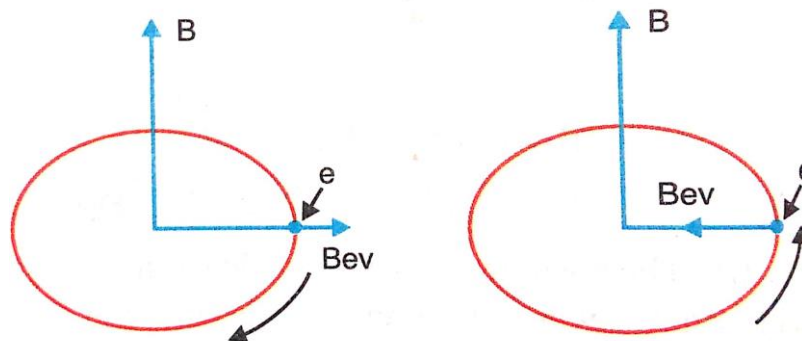
(ii) The spectral line is then viewed transversely i.e., perpendicular to the direction of the magnetic field. In this case, the single spectral line is split up into three components when the magnetic field is applied. The central line has the same wavelength as the original line and is plane polarised with vibrations parallel to the field. The outer lines are symmetrically situated on either side of the central line. The displacement of either outer line from the central line is known as the Zeeman shift. The two outer lines are also plane polarised having vibrations in a direction perpendicular to the field. This is called normal transverse Zeeman effect.

Lorentz classical theory of normal Zeeman effect:

The emission of light by a glowing gas is due to the vibratory motion of the electrons. The electrons in the atom execute simple harmonic vibration about the centre of the atom. The frequency of the spectral line is given by the frequency of vibration of the electron. Any linear motion of an electron can be resolved into three components—a linear motion along the magnetic field and two opposite circular motions perpendicular to the field. It is known that no mechanical force acts upon a charge when it moves in the direction of the field. So the linear motion along the

field is not affected by the field and hence the frequency of this component is unchanged by the magnetic field. The other two circular components are affected by the magnetic field, one being retarded and the other being accelerated. Hence the frequency of one of these circular components is increased and that of the other is decreased by the same amount. In the longitudinal view, the unaltered linear component along the field gives no light waves along the direction of observation due to the transverse nature of light vibrations. Hence the original line is not observed. The two altered circular components at right angles to the field produce circularly polarised light waves. This explains the longitudinal Zeeman pattern. In the transverse view, the unaffected linear component sends out vibrations parallel to the field and hence perpendicular to the direction of observation. This gives the central line of the triplet occupying the same position as the original line and plane polarised with vibrations parallel to the field. The two circular vibrations which are altered in frequency send out vibrations perpendicular to the field and when viewed sideways appear as plane polarised vibrations in opposite senses.

Expression for the Zeeman shift: Consider an electron in the atom moving in a circular orbit of radius r with a linear velocity v and angular velocity ω . Let e be the charge of the electron and m its mass.



The centripetal force on the electron towards the centre in the absence of the magnetic field $= F = mv^2/r = m \omega^2 r$ (1)

Now let an external magnetic field of flux density B be applied in a direction perpendicular to the plane of the orbits of the two circular components and directed towards the reader. Then an additional radial force of magnitude Bev acts on the electron. The direction of this force will be outwards from the centre for clockwise motion but inwards towards the centre for anticlockwise motion. The resulting complex motion of the electron subjected to an additional radial force is called Larmor precession. This produces a change in the angular velocity without any change in the form of the orbit.

Let $\delta\omega$ be the change in angular velocity caused by the field. For the circular motion in the clockwise direction, the additional radial force is directed away from the centre.

$$F - Bev = m(\omega + \delta\omega)^2 r \dots\dots\dots(2)$$

$$m\omega^2 r - m(\omega + \delta\omega)^2 r = Be\omega r$$

$$\text{or } -2mr\delta\omega = Be\omega r$$

$$\text{or } \delta\omega = -Be/2m \dots\dots\dots(3)$$

For the circular motion in the anticlockwise direction, the additional radial force is directed towards the centre.

$$F + Bev = m(\omega + \delta\omega)^2 r$$

$$\delta\omega = +Be/2m \dots\dots\dots(4)$$

The two cases can be combined into the equation

$$\delta\omega = \pm Be/2m \dots\dots\dots(5)$$

If ν = frequency of vibration of the electron

$$\omega = 2\pi\nu ; \delta\omega = 2\pi\delta\nu \text{ or } \delta\nu = \delta\omega/2\pi$$

$$\text{Change in frequency of the spectral line} = \delta\nu = \pm Be/4\pi m \dots\dots\dots (6)$$

If ν and λ are the frequency and wavelength of the original line,

$$\nu = c/\lambda \text{ or } \delta\nu = -c/\lambda^2 \delta\lambda$$

$$\text{The Zeeman shift} = \delta\lambda = \pm Be \lambda^2 / 4\pi mc \dots\dots\dots(7)$$

2.6 Larmor's Theorem Statement :

The effect of a magnetic field on an electron moving in an orbit is to superimpose on the orbital motion a precessional motion of the entire orbit about the direction of the magnetic field with angular velocity ω given by $\omega = Be/2m$.

Explanation:

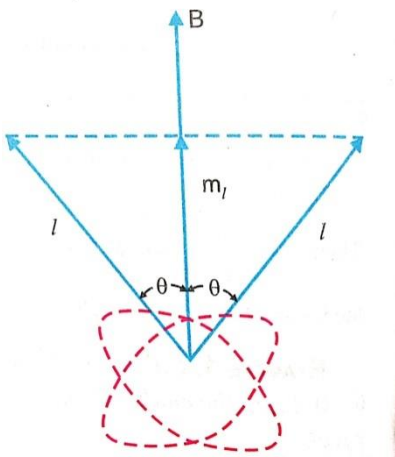
Figure shows two positions of the vector l as it precesses about the magnetic field at constant inclination and the corresponding positions of the electronic orbit. Just as mechanical top precesses in a gravitational field, an electron in an orbit precesses in a magnetic field. This is called Larmor precession.

Change in K.E. due to Larmor precession:

In the magnetic field, the angular velocity of the atomic system changes by an amount $Be/2m$. Let ω_0 be the original angular velocity. Then change in K.E.

$$\begin{aligned}
 &= \frac{1}{2} m r^2 (\omega_0 + Be/2m)^2 - \frac{1}{2} m r^2 \omega_0^2 \\
 &= \frac{1}{2} m r^2 \omega_0^2 (1 + Be/2m \omega_0)^2 - \frac{1}{2} m r^2 \omega_0^2 \\
 &= \frac{1}{2} m r^2 \omega_0^2 (1 + Be/m\omega_0) - \frac{1}{2} m r^2 \omega_0^2 \\
 &= m r^2 \omega_0^2 Be/m\omega_0 = L Be/2m
 \end{aligned}$$

Where $L =$ original angular momentum $= m r^2 \omega_0$



2.7 Quantum Mechanical Explanation of the Normal Zeeman Effect:

Debye explained the normal Zeeman effect without taking into account the concept of electron spin. If we neglect the spin motion of the electron, then,

The orbital angular momentum of the electron = $L = l h/2\pi$ (1)

And magnetic moment = $\mu_l = l h/2\pi e/2m = e/2m L$ (2)

the presence of an external magnetic field of flux density B. the vector l precesses around the direction of the magnetic field on axis.

The frequency of Larmor precession = $\omega = Be/2m$ (3)

Figure shows two positions of the vector l , as it precesses about the magnetic field at constant inclination and the corresponding positions of the electronic orbit. The additional energy of the electron due to this precessional motion

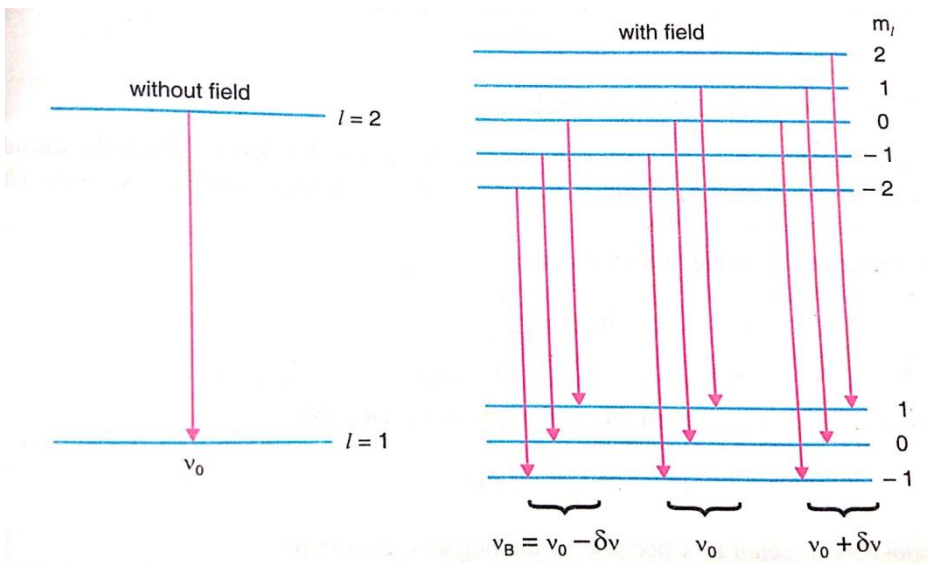
$$\Delta E = \mu_l B \cos\Theta = (l h/2\pi e/2m) B \cos\Theta \quad (\text{where } \mu_l = l h/2\pi e/2m)$$

$$= h/2\pi Be/2m l \cos\Theta$$

But $Be/2m = \omega$ and $l \cos\Theta = \text{projection of } l \text{ on } B = ml$

$$\Delta E = ml eh/4\pi m B = ml \omega h/2\pi \dots\dots\dots(4)$$

Now, ml can have $(2l + 1)$ values from $+l$ to $-l$. Therefore, an external magnetic field will split a single energy level into $(2l + 1)$ levels. The d-state ($l=2$) is split into 5 sub-levels and the p-state ($l=1$) is split into 3 sublevels.



Let E_0' represent the energy of the level $l=1$ in the magnetic field and E_0 represent the energy of this level in the presence of magnetic field. Then,

$$E_0' = E_0 + \Delta E' = E_0 + m'l' eh/4\pi m B \dots\dots\dots(5)$$

Similarly, if E_0'' and E_0 represent the energies of the level $l= 2$ in the absence of the magnetic field and E_0' represent the energy of this level in the presence of magnetic field. Then,

$$E_0'' = E_0 + \Delta E'' = E_0 + m'l'' eh/4\pi m B \dots\dots\dots(6)$$

The quantity of energy radiated in the presence of magnetic field is

$$E_{B''} - E_{B'} = (E_{0''} - E_{0'}) + (m_{l''} - m_{l'}) \frac{eh}{4\pi m} B$$

$$h\nu = h\nu_0 + \Delta m_l \frac{eh}{4\pi m} B$$

$$\nu = \nu_0 + \Delta m_l \frac{eh}{4\pi m} \dots\dots\dots (7)$$

where ν = frequency of the radiation emitted with the magnetic field and ν_0 = frequency of the radiation in the absence of the magnetic field. The selection rule for m_l is $\Delta m_l = 0$ or ± 1 .

Hence we have three possible lines,

$$\nu_1 = \nu_0 \text{ for } \Delta m_l = 0 \dots\dots\dots(8)$$

$$\nu_2 = \nu_0 + \frac{eB}{4\pi m} \text{ for } \Delta m_l = +1 \dots\dots\dots(9)$$

$$\nu_3 = \nu_0 - \frac{eB}{4\pi m} \text{ for } \Delta m_l = -1 \dots\dots\dots(10)$$

Figure represents the normal Zeeman effect. Although there are nine possible transitions, they are grouped into only three different frequency components as indicated by equations (8), (9) and (10). For three transitions in a bracket, change in the value of Δm_l is the same and hence they represent same change of energy and a single line.

2.8 Anomalous Zeeman effect:

This can be explained only by using the idea of the spin of the electron. With the introduction of spin, we have two angular momentum vectors l and s associated with each electron.

The total angular momentum vector

$$j = l + s \dots\dots\dots (1)$$

The magnetic moment due to orbital motion

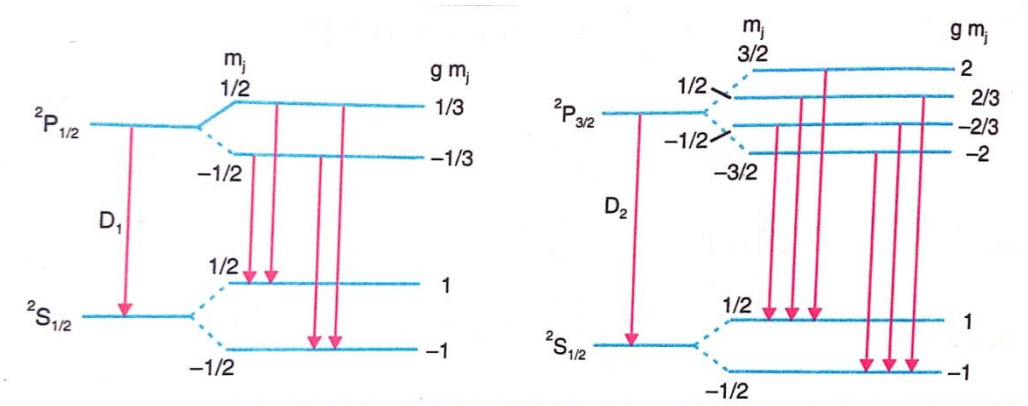
$$= \mu_l = l \frac{eh}{4\pi m} \dots\dots\dots(2)$$

μ_l is directed oppositely to l because of the negative charge of the electron.

Similarly, the magnetic moment due to spin of the electron

$$= \mu_s = 2s \frac{eh}{4\pi m} \dots\dots\dots(3)$$

μ_s is oppositely directed to S because of the negative charge of the electron. The relationships between the magnetic moments and the angular momenta are shown in Figure.



The resultant magnetic moment is not along j . Since l and s precess about j , μ_l , μ_s and μ_j must also precess about j . To find out the resultant magnetic moment of the electron, each of these vectors μ_l and μ_s is resolved into two components, one along j and the other perpendicular to it. The value of the perpendicular component of each vector, averaged over a period of the motion will be zero, since it is constantly changing direction. The effective magnetic moment of the electron will be

$$\begin{aligned} \mu_j &= \text{component of } \mu_l \text{, along the direction of } j + \text{component of } \mu_s \text{, along the direction of } j \\ &= \frac{eh}{4\pi m} l \cos(\angle l, j) + \frac{eh}{4\pi m} 2s \cos(\angle s, j) \\ &= \frac{eh}{4\pi m} [l \cos(\angle l, j) + 2s \cos(\angle s, j)] \end{aligned}$$

But according to cosine law,

$$\cos(\angle l, j) = \frac{l^2 + j^2 - s^2}{2lj}$$

and $\cos(\angle s, j) = \frac{s^2 + j^2 - l^2}{2lj}$

Hence,

$$\begin{aligned} \mu_j &= \frac{eh}{4\pi m} \left[\frac{l^2 + j^2 - s^2}{2lj} + \frac{s^2 + j^2 - l^2}{2lj} \right] \\ &= \frac{eh}{4\pi m} [3j^2 + s^2 - l^2 / 2j] \\ &= \frac{eh}{4\pi m} j [1 + j^2 + s^2 - l^2 / 2j^2] \end{aligned}$$

Writing $j^2 = j(j+1)$ and so on

$$\mu_j = \frac{eh}{4\pi m} j [1 + j(j+1) + s(s+1) - l(l+1) / 2j(j+1)]$$

The quantity $\mu_j = \frac{eh}{4\pi m} j [1+j(j+1)+s(s+1)-l(l+1)]/2j(j+1) = g$ is called the Lande g factor.

Hence $\mu_j = \frac{eh}{4\pi m} jg$.

If the atom is placed in a weak magnetic field, the total angular momentum vector j precesses along the direction of the magnetic field as axis.

The additional energy ΔE due to the action of the magnetic field on this atomic magnet is

$$\Delta E = \mu_j B \cos(j,B) = \frac{eh}{4\pi m} g jB \cos(j,B)$$

But $j \cos(j,B)$ = the projection of the vector j on the direction of the magnetic field on this atomic magnet is

Hence, $\Delta E = \frac{eh}{4\pi m} B g m_j$

The quantity $\frac{eh}{4\pi m} B$ is called a Lorentz unit. It is a unit of energy used for expressing the splitting of the energy levels in a magnetic field.

Since m_j has $(2j + 1)$ values, a given energy level is split up into $(2j + 1)$ sublevels with the application of magnetic field. When this m_j is subjected to the selection rule $\Delta m = 0$ or ± 1 , we get the transitions shown in figure for the sodium D-lines. The ground state $^2S_{1/2}$ splits into two sublevels.

Here $l = 0, s=1/2, j=1/2$

hence $g=1+[1/2+ 3/2 +1/2 \times 3/2 / 2 \times 1/2 \times 3/2] =2$

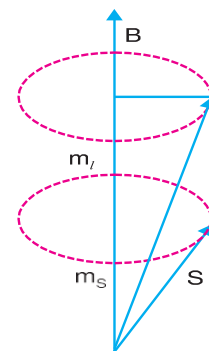
State	l	s	j	g	m_j	$m_j g$
$^2S_{1/2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	2	$\frac{1}{2}, -\frac{1}{2}$	1, -1
$^2P_{1/2}$	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{3}, -\frac{1}{3}$
$^2P_{3/2}$	1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{4}{3}$	$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$	$2, \frac{2}{3}, -\frac{2}{3}, -2$

Since m_j can have the values $\frac{1}{2}$ and $-\frac{1}{2}$ g_{mj} can have the values $+1$ and -1 . The following table gives the values for the quantum numbers necessary for the determination of the splitting factor g_{mj} for each energy levels of the sodium D-lines.

The longer wavelength component ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$ splits into four lines. The shorter wavelength component ${}^2P_{3/2} \rightarrow {}^2S_{1/2}$ splits into six lines. Thus the introduction of electron spin has led to complete agreement between the experimental results and the theory splitting factor g_{mj} , for each of the energy levels of the sodium D-lines. Component of the anomalous Zeeman effect.

2.9 Paschen-Back Effect

Paschen and Back found that whatever be the anomalous Zeeman pattern of a given line in a weak magnetic field, the pattern always approximates the normal Zeeman triplet as the field strength is progressively increased. This reduction may occur either through the coalescence of lines or through the disappearance of certain lines. This transition phenomenon is called Paschen-Back effect.



Explanation. In a strong magnetic field, the coupling between l and s breaks down, and j loses its significance. l and s are quantised separately. l and s precess separately about the external magnetic field B independent of each other (Fig. 6.40). The energy change due to the presence of the field will then be made up of two parts, one arising from the precession of l about B and the other from the precession of s about B .

Hence

$$\begin{aligned} \Delta E &= (\Delta E)_l + (\Delta E)_s \\ &= B \frac{eh}{4\pi m} [l \cos(l, B) + 2s \cos(s, B)] \\ &= \frac{eh}{4\pi m} B(m_l + 2m_s) \end{aligned}$$

In terms of frequency change,

$$\Delta \nu = \frac{eB}{4\pi m} \Delta(m_l + 2m_s)$$

The quantity $(m_l + 2m_s)$ is known as the strong field quantum number and is evidently an integer. Now since $\Delta m_l = 0$ or ± 1 , $\Delta m_s = 0$, $\Delta(m_l + 2m_s) = 0$ or ± 1 .

Hence in a strong magnetic field, a given spectral line will split into three components only and this is the usual characteristic of the normal Zeeman effect.

2.10 Stark Effect

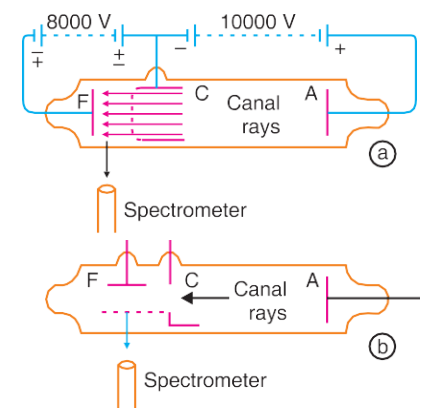
The Stark effect is the electrical analogue of the Zeeman effect. The Stark effect is the splitting of spectral lines due to the action of an external electric field on the radiating substance. Even very strong external electric fields are weak compared to the interatomic fields. Hence the action of electric field on the motion of the atomic electrons can be regarded as small perturbations. Consequently, the Stark line splitting is very minute and can be observed only with instruments having a high resolving power. The lines are split into a series of components (satellites) located, in case of hydrogen, symmetrically on both sides of the original line.

Experimental study. Here the hydrogen atoms emitting spectral lines are subjected to a powerful electric field. The arrangement used by Stark is shown in Fig. 6.41. The canal rays are produced in an ordinary glass discharge tube provided with a perforated cathode C. When the pressure in the tube is not very low, discharge takes place between the anode A and cathode C maintained at a suitable P.D. The canal rays stream through the perforations in the cathode and

form behind the cathode narrow cylindrical bundles of luminous rays. An auxiliary electrode F is placed parallel and close to C at a distance of a few millimetres. A very strong electric field of several thousand volts per metre is maintained between F and C. The effect produced can be studied both transversely [Fig. 6.41 (a)] and longitudinally [Fig. 6.41 (b)]. Stark observed that the lines in the spectrum emitted by the canal rays of hydrogen were split up into numerous sharp components under the action of the electric field.

Results. The results obtained with the lines of the Balmer series of the hydrogen spectrum are given below:

- (i) Every line is split up into a number of sharp components. All hydrogen lines form symmetrical patterns. The pattern depends markedly on the quantum number n of the term involved. The number of lines and the total width of the pattern increases with n . Thus, the number of components of H_β line is greater than that of the H_α line; similarly, the number of components of H_γ , is greater than that of H_β .
- (ii) Observation perpendicular to the direction of the electric field (transverse view) shows that the components are polarised, some parallel to the direction of the field and others perpendicular to it.
- (iii) Upto fields of about 10^7 V/m, the resolution increases in proportion to the field strength (E). In this region, we have *linear* or *first order* Stark effect. When E exceeds 10^7 V/m, there are shifts in the line patterns which are proportional to E^2 and we speak of



Unit-III

X-Rays

3.1 Introduction

X-rays were discovered by Roentgen in 1895. X-rays are electromagnetic waves of short wavelengths in the range of 10 \AA to 0.5 \AA . The longer wavelength end of the spectrum is known as the “soft X-rays” and the shorter wavelength end is known as “hard X-rays.”

Production of X-rays

The Coolidge tube: X-rays are produced when fast moving electrons are suddenly stopped by a solid target. A Coolidge tube is shown in Fig. 3.1.1 The tube is exhausted to the best possible vacuum of the order of $10\text{--}5 \text{ mm}$ of mercury.

The cathode consists of a tungsten filament (F) heated by a low tension battery. Thermionic electrons emitted by the filament are accelerated towards the target (T) by a high P.D. maintained between F and T.

The filament is placed inside a metal cup G to focus the electrons on to the target. The target must be cooled to remove the heat generated in it by continuous electron-bombardment. The usual method is to mount the target material on a hollow copper tube through which cold water is continuously circulated. The target is made of a metal like tungsten or molybdenum having a high melting point and a high atomic number. Metals with high atomic number give more energetic and intense rays when used as targets.

In the Coolidge tube, the intensity and frequency of X-rays can be easily controlled.

1. The intensity of X-rays depends on the number of electrons striking the target per second. The number of electrons given out by the filament is proportional to its temperature, which can be adjusted by varying the current in the filament circuit. Therefore, the intensity of X-rays varies with the filament current.
2. The frequency of X-rays emitted depends on the voltage between the cathode and the anode (target). Let V be the accelerating potential across the tube. If e is the charge on the electron, the work done on the electron in moving from the cathode to the anticathode = eV . The electron thus acquires K.E. which is converted into X-rays, when the electron

strikes the target. If V_{\max} is the maximum frequency of the X-rays produced, then $h \nu_{\max} = eV$.

The minimum wavelength produced by an X-ray tube = $\lambda_{\min} = \frac{c}{\nu_{\max}} = \frac{hc}{eV}$

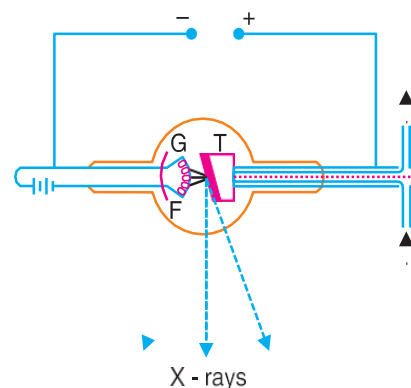


Fig. 3.1.1

3.2 Bragg's Law

When monochromatic X-rays impinge upon the atoms in a crystal lattice, each atom acts as a source of scattering radiation of the same wavelength. The crystal acts as a series of parallel reflecting planes. The intensity of the reflected beam at certain angles will be maximum when the path difference between two reflected waves from two different planes is an integral multiple of λ .

Derivation of Bragg's law: Consider a set of parallel planes of atom points at a spacing d between two successive planes. Let a narrow monochromatic X-ray beam of wavelength λ be incident on the first plane at a glancing angle θ (Fig. 3.2.1). Consider the ray PQ incident on the first plane.

The corresponding reflected ray QR must also be inclined at the same angle θ to the plane. Since X-rays are much more penetrating than ordinary light, there is only partial reflection at each plane. The complete absorption takes place only after penetrating several layers. Consider two parallel rays PQR and P'Q'R' in the beam, which are reflected by two atoms Q and Q'. Q' is vertically below Q. The ray P'Q'R' has a longer path than the ray PQR. To compute the path-difference between the two rays, from Q draw normals QT and QS on P'Q' and Q'R' respectively.

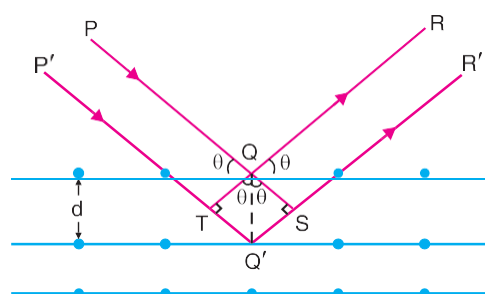


Fig.3.2.1

Then the path-difference = $TQ' + Q'S$

$$= d \sin \theta + d \sin \theta = 2d \sin \theta.$$

Hence the two rays will reinforce each other and produce maximum intensity, if

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

where $n = 1, 2, 3, \dots$. The integer n gives the order of the scattered beam, λ is the wavelength of the X-rays used. This equation is called Bragg's law.

3.3 The Bragg X-ray Spectrometer

The essential parts of a Bragg spectrometer are shown in Fig. 3.3.1 It is similar in construction to an optical spectrometer. It consists of three parts. (1) a source of X-rays (2) a crystal held on a circular table which is graduated and provided with vernier and (3) a detector (ionisation chamber). X-rays from an X-ray tube, limited by two narrow lead slits S_1 and S_2 , are allowed to fall upon the crystal C . The crystal is mounted on the circular table T , which can rotate about a vertical axis and its position can be determined by the vernier V . The table is provided with a radial arm (R) which carries an ionisation chamber (I). This arm also can be rotated about the same vertical axis as the crystal. The position of this arm can be determined by a second vernier (not shown in the figure). The ionisation chamber is connected to an electrometer (E) to measure the ionisation current. Hence we can measure the intensity of the diffracted beam of X-rays, diffracted in the direction of the ionisation chamber. S_3 is a lead slit, to limit the width of the diffracted beam. In practice, the crystal table is geared to the

ionisation chamber so that the chamber turns through 2θ when the crystal is turned through θ .

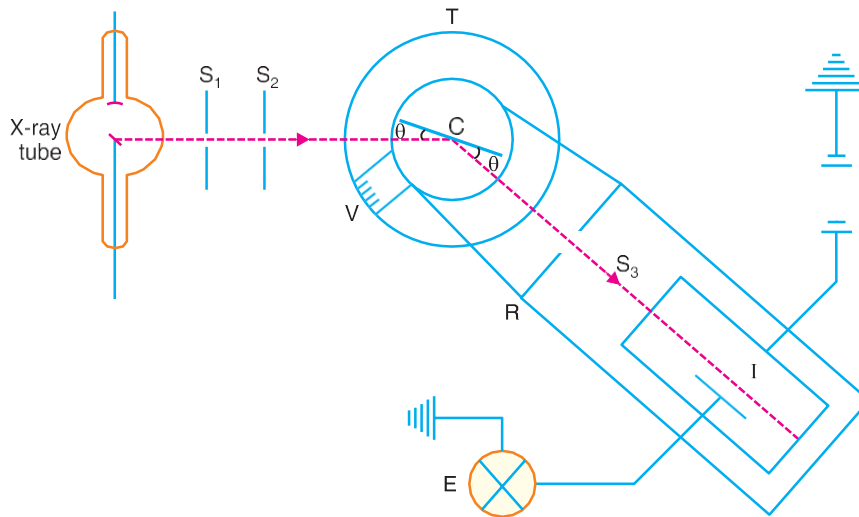


Fig.3.3.1

Working: To begin with, the glancing angle θ for the incident beam is kept very small. The ionisation chamber is adjusted to receive the reflected beam till the rate of deflection is maximum. The glancing angle (θ) and the intensity of the diffracted beam (I) are measured. The glancing angle is next increased in equal steps, by rotating the crystal table. The ionisation current is noted for different glancing angles. The graph of ionisation current against glancing angle is drawn. The graph obtained is as in Fig. 3.3.2

and is called an X-ray spectrum. The prominent peaks A_1, A_2, A_3 refer to X-rays of wavelength λ . The glancing angles $\theta_1, \theta_2, \theta_3$ corresponding to the peaks A_1, A_2, A_3 are obtained from the graph. It is found that $\sin \theta_1 : \sin \theta_2 : \sin \theta_3 = 1 : 2 : 3$. This shows that A_1, A_2, A_3 , refer to the first, second and third order reflections of the same wavelength. B_1, B_2, B_3 are such peaks for the first, second and third order for another wavelength (λ_2). Thus Bragg experimentally verified the relation

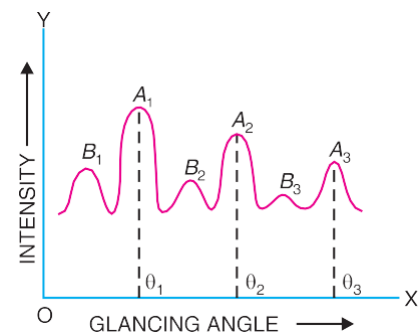


Fig.3.3.2

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

The wavelength of X-rays is determined by using the equation $2d \sin \theta = n\lambda$. The glancing angle θ is experimentally determined as explained already for a known order. If d is known, λ can be calculated.

Calculation of d : Rocksalt (NaCl) possesses a cubic structure with sodium ions and chlorine ions situated alternately at corners of a cube. If d is the distance between two neighbouring ions and ρ is the density of the crystal, then mass of the unit cube = ρd^3 .

Now each corner ion is shared by 8 neighbour cubes. This is illustrated by the ion indicated by an asterisk in Fig. 3.3.3. Hence each ion contributes only 1/8 th of its mass to the cube. The unit cube is made up of 4 sodium ions and 4 chlorine ions.

Hence, the mass of each cube = the mass of 1/2 NaCl molecule. If M is the molecular weight of NaCl and N_A the Avogadro's No.,

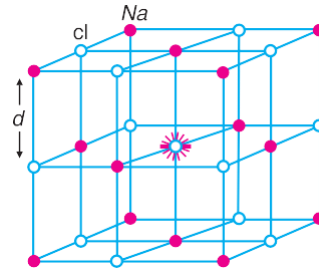


Fig. 3.3.3

$$\text{Mass of } \frac{1}{2} \text{ NaCl molecule} = M/2N_A$$

$$\therefore \rho d^3 = \frac{M}{2N_A} \text{ or } d = 3 \sqrt{\frac{M}{2N_A \rho}}$$

Knowing M , N_A and ρ , d can be found.

For NaCl, $M = 58.45 \text{ kg}$; $\rho = 2170 \text{ kg m}^{-3}$ and $N_A = 6.06 \times 10^{26}$.

$$\therefore d = 3 \sqrt{\frac{58.45}{2 \times (6.06 \times 10^{26}) \times 2170}} = 2.81 \times 10^{-10} \text{ m.}$$

3.4 Laue's experiment

Laue showed that if X-rays are allowed to pass through a crystal, a diffraction pattern is obtained. T is a source of X-rays. This source gives white X-rays, i.e., X-ray beam of continuous range of wavelengths. A narrow beam of X-rays from the X-ray tube is collimated by two slits S₁ and S₂ and is allowed to pass through a thin crystal of zinc blende (ZnS). The transmitted beam is received on a photographic plate P [Fig. 3.4.1 (i)]. After an exposure of many hours, the plate is developed. The Laue photograph obtained on the photographic plate is shown in Fig. 3.4.1 (ii). The photograph consists of a central spot which arises due to the direct beam. The central spot is surrounded by many other fainter spots arranged in a definite pattern around O. This indicates that the incident X-ray beam has been diffracted from the various crystal planes. These spots are known as Laue spots. These spots are arranged according to different geometrical patterns for different crystals, depending on their structure. This experiment proved: (1) that X-rays are electromagnetic waves and (2) that the atoms of a crystal are arranged in a regular three-dimensional lattice.

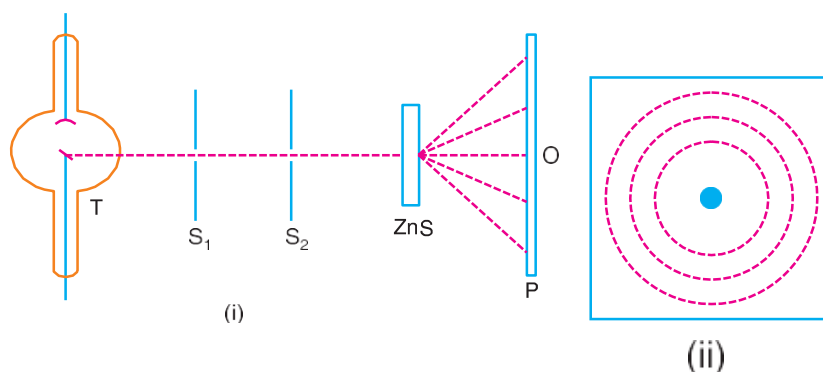


Fig. 3.4.1

Bragg gave a simple interpretation of the pattern. The regular repetition of atomic, ionic or molecular units in three dimensions is called the “lattice”.

Many planes can be imagined in the lattice, containing these atoms. Some planes will be richer in atoms than others. This can be easily seen by considering two dimensional lattice. Fig. 3.4.2(iii) represents a two-dimensional lattice, indicating lines of atom distribution. Line AB contains greater concentration of atoms, line AC less and line AD still less.

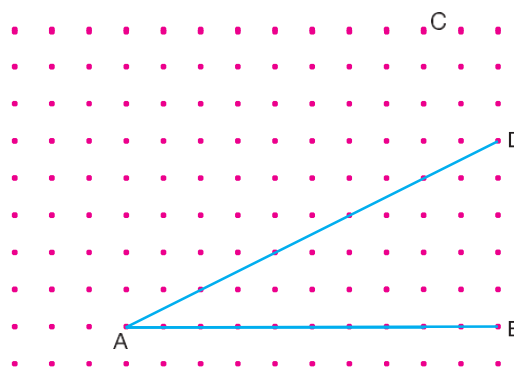


Fig. 3.4.2

These lines of atoms in two-dimensional lattice are analogous to planes of atoms in a three-dimensional lattice.

If now a beam of X-rays is incident in the vertically downward direction, at each plane of atoms there is a partial reflection of X-rays. These reflected beams give rise to the Laue diffraction pattern. The condition to be satisfied so that X-rays reflected from a set of lattice planes may produce an intense spot in the diffraction pattern may be derived. This is known as Bragg's law.

3.5 The Powder Crystal Method

The Laue's and Bragg's techniques for the investigation of crystal structures can be applied only if single crystals of reasonable size are available. But, in general, large crystals, without fault are difficult to obtain. Therefore, Debye and Scherrer adopted a different technique. The specimen was taken in the form of a well powdered sample of the crystal in a thin glass capsule. The experimental arrangement is shown in Fig. 3.5.1. The X-rays from the source are made approximately monochromatic by the filter F. A narrow beam of these monochromatic X-rays, suitably collimated by two lead slits S₁ and S₂, falls on the powdered specimen S. The specimen is suspended vertically on the axis of a cylindrical camera. The photographic film is mounted round the inner surface of the camera, covering nearly the whole circumference in order to receive the beams diffracted upto 180°.

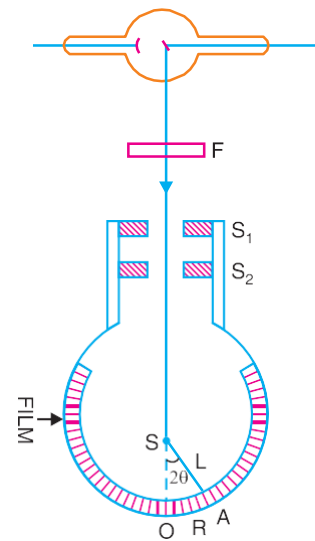


Fig. 3.5.1

The photographic film is mounted round the inner surface of the camera, covering nearly the whole circumference in order to receive the beams diffracted upto 180°.

The powder specimen of the crystal can be imagined to be a collection of random oriented tiny crystals, presenting all values of glancing angles to the incident beam. For a given wavelength and a given value of d , there can be only one value of θ (the glancing angle) which satisfies the equation $2d \sin \theta = n\lambda$, where $n = 1$. Such reflected beams emerge out from the specimen in all directions inclined at an angle 2θ with the direction of the incident beam, because millions of tiny crystals

in the specimen are random oriented. The reflected rays will be on the surface of a cone, vertex at the specimen, base on the photographic film and having a semi-vertical angle 2θ . The traces obtained on the photographic film will be as in Fig. 3.5.2. Let L be the radius of the cylindrical camera. The direct beam strikes the film at O .



Fig. 3.5.1

Suppose a spectrum with glancing angle θ is found at A which is at a distance R from O . Then $\theta = R / 2L$. Using this value of θ in the Bragg's equation and knowing the value of λ , d (spacing of the plane involved) can be calculated.

The powder method has been employed in the study of microcrystalline substances like metals, alloys, carbons, fluorescent powders and other forms where single crystals are not available.

3.6 Rotating-Crystal Method

In this method, a single crystal is rotated about a fixed axis (usually vertical), in a beam of monoenergetic X-rays. The variation in the angle θ brings different atomic planes into position for reflection. The experimental arrangement is shown in Fig. 3.6.1. The crystal is usually about 1 mm in diameter and is mounted on a spindle which can be rotated. A photographic film is placed on the inner side of a cylinder concentric with the axis of rotation.

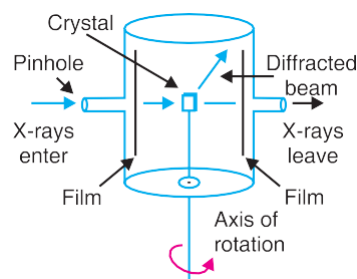


Fig. 3.6.1

The incident X-ray beam is monochromatised by a filter or by reflection from an earlier crystal. The incident beam is diffracted from a given crystal plane whenever in course of rotation the value of θ satisfies the Bragg equation. Beams from all planes parallel to the vertical rotation axis will lie in the horizontal plane. Planes with other orientations will reflect in layers above and below the horizontal plane. However, there will be no reflected beams from a plane which always contains the incident beam during the whole rotation and from ones whose spacing is so small that

$\lambda/2d > 1$. The reflected spots on the film form parallel lines. Since λ is known, the spacing d may be

calculated from $2d \sin \theta = n\lambda$.

3.7 Characteristic X-ray Spectrum

There are two methods of producing characteristic X-rays.

(1) The characteristic X-rays of an element can be excited by using the element as the target in the X-ray tube and thus subjecting it to direct bombardment by electrons. For each target there is a minimum potential below which the line spectra do not appear. This critical P.D. below which the line spectra do not appear, is different for different targets. Molybdenum shows up the line spectra only if the P.D. is above 35 kV.

(2) Characteristic X-rays of an element can also be excited by allowing primary X-rays from a hard X-ray tube to fall on the element. The primary X-rays must be harder than the characteristic X-rays to be produced. The peaks obtained in the X-ray spectrum give the line spectrum which is characteristic of the element used in the target. The group of lines of shortest wavelength is called the K-series. Usually two lines of this series are detected. These lines are termed as $K\alpha$ and $K\beta$ lines in the order of decreasing wavelengths. The next group is called the L-series of longer wavelengths ($L\alpha$, $L\beta$, $L\gamma$, etc.). For heavier elements a third series, called the M-series has been detected.

Origin of characteristic X-rays. This can be understood in terms of Bohr's theory. Suppose an atom in the target of an X-ray tube is bombarded by a high-speed electron and a K-electron is removed. A vacancy is created in the K-shell. This vacancy can be filled up by an electron from either of L, M or N shells or a free electron. These possible transitions can result in the $K\alpha$, $K\beta$ lines and the limiting line. Similarly, the longer wavelength L-series originates when an L electron is knocked out of the atom, the M-series when an M electron is knocked out and so on (Fig. 3.7.1).

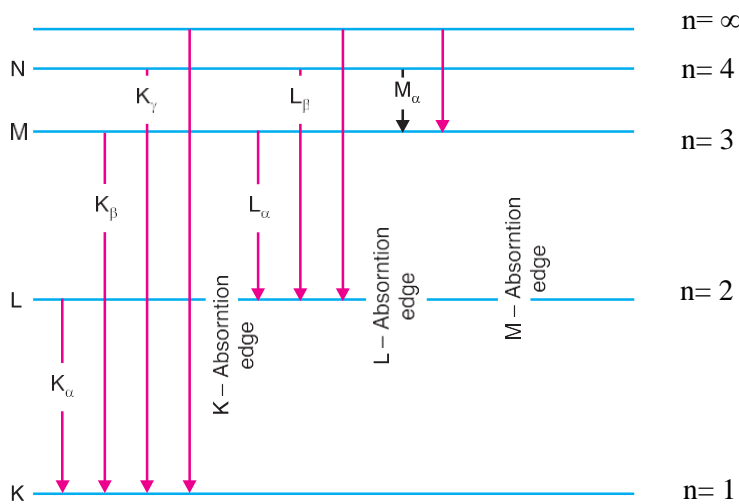


Fig. 3.7.1

3.8 Moseley's Law

Moseley plotted the square root of the frequencies ($\sqrt{\nu}$) of a given line (say $K\alpha$) against the atomic numbers (Z) of the elements emitting that line. Moseley obtained a straight line as shown in Fig. 3.8.1. The same linear relation was found to hold good for any line in any series. He concluded, therefore, that atomic number (and not atomic weight) is the fundamental property of elements.

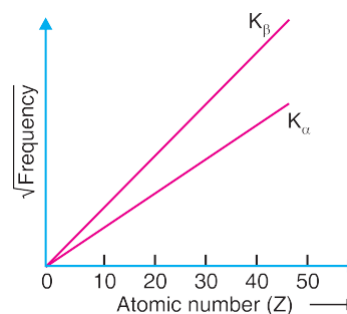


Fig. 3.8.1

Moseley's law: statement. The frequency of a spectral line in X-ray spectrum, varies as the square of the atomic number of the element emitting it, or $\nu \propto Z^2$. Moseley's law may be written as

$\sqrt{\nu} = a(Z - b)$. Here, Z is the atomic number of the element and a and b are constants depending upon the particular line.

Explanation, according to Bohr's theory. Bohr's theory of hydrogen spectrum gives the

frequency of a spectral line as $\nu = Z^2 R c \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$ where R is Rydberg's constant and c the velocity of light. Considering the K_α line, we can regard it as originating from the transition of electron from second to first orbit. Now, $n_1 = 1$ and $n_2 = 2$.

$$\text{So frequency of } k_\alpha \text{ line} = \nu = Z^2 R c \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} c R Z^2$$

This approximately corresponds to Moseley's law.

Importance of Moseley's law.

(1) According to this law, it is the atomic number and not atomic weight of an element which determines its characteristic properties, both physical and chemical. Therefore, the atoms must be arranged in the periodic table according to their atomic numbers and not according to their atomic weights. This would remove some discrepancies in the order of certain elements from the point of view of their atomic weights. For example, argon $18\text{Ar}40$ comes before potassium $(19\text{K}39)$, cobalt $(27\text{Co}58.9)$ comes before nickel $(28\text{Ni}58.7)$, etc. So the arrangement is correct in the order of atomic number.

(2) Moseley's work has also helped to perfect the periodic table by (i) the discovery of new elements, e.g., hafnium (72), illinium (61), masurium (43), rhenium (75), etc., and (ii) the determination of the atomic numbers of rare-earths and fixing their positions in the periodic table.

3.9.Compton Scattering

The Compton Effect. Compton discovered that when X-rays of a sharply defined frequency were incident on a material of low atomic number like carbon, they suffered a change of frequency on scattering. The scattered beam contains two wavelengths. In addition to the expected incident wavelength, there exists a line of longer wavelength. The change of wavelength is due to loss of energy of the incident X-rays. This elastic interaction is known as Compton Effect.

In the case of incoherent scattering, a scattered beam undergoes not only deviation in its direction but also change of wavelength occurs. In Compton effect, there is a change in wavelength of the scattered beam along with the change in its direction. Hence Compton effect is an incoherent scattering.

This effect was explained by Compton on the basis of quantum theory of radiation. The whole process is treated as a particle collision event between X-ray photon and a loosely bound electron of the scatterer. In this process, both momentum and energy are conserved. In the photon-electron collision, a portion of the energy of the photon is transferred to the electron. As a result, the X-ray proceeds with less than the original energy (and therefore has a lower frequency or a higher wavelength). The incident photon with an energy $h\nu$ and momentum $h\nu/c$ strikes an electron at rest.

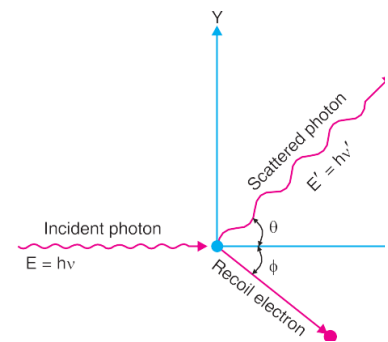


Fig. 3.9.1

The initial momentum of the electron is zero and its initial energy is only the rest mass energy, m_0c^2 . The scattered photon of energy $h\nu'$ and momentum $h\nu'/c$ moves off in a direction inclined at an angle θ to the original direction. The electron acquires a momentum mv and moves at an angle ϕ to the original direction. The energy of the recoil electron is mc^2 (Fig. 3.9.1).

According to the principle of conservation of energy,

$$h\nu + m_0c^2 = h\nu' + mc^2 \dots(1)$$

Considering the x and y components of the momentum and applying the principle of conservation of momentum,

$$\frac{h\nu}{c} = \frac{h\nu'}{c} \cos \theta + mv \cos \phi \dots(2)$$

and

$$0 = \frac{h\nu'}{c} \sin \theta - mv \sin \phi \dots(3)$$

From (2), $mv \cos \phi = h(\nu - \nu' \cos \theta) \dots(4)$

From (3), $mv \sin \phi = h\nu' \sin \theta \dots(5)$

Squaring and adding (4) and (5),

$$\begin{aligned} m^2 v^2 c^2 &= h^2 v^2 - 2vv' \cos \theta + v'^2 \cos^2 \theta + h^2 v'^2 \sin^2 \theta \\ &= h^2 (v^2 - 2vv' \cos \theta) + h^2 v'^2 = h^2 (v^2 - 2vv' \cos \theta + v'^2) \dots(6) \end{aligned}$$

From (1), $mc^2 = h(v - v') + m_0 c^2$

$$m^2 c^4 = h^2 (v^2 - 2vv' + v'^2) + 2h(v - v') m_0 c^2 + m_0^2 c^4 \dots(7)$$

Subtracting (6) from (7),

$$m^2 c^2 (c^2 - v^2) = -2h^2 vv' (1 - \cos \theta) + 2h(v - v') m_0 c^2 + m_0^2 c^4 \dots(8)$$

The value of $m^2 c^2 (c^2 - v^2)$ can be obtained from the relativistic formula

$$m = \frac{m_0}{\sqrt{(1 - v^2 / c^2)}}. \text{ Squaring,}$$

$$m^2 = \frac{m_0^2}{1 - v^2 / c^2} = \frac{m_0^2 c^2}{c^2 - v^2}$$

$$\therefore m^2 c^2 (c^2 - v^2) = m_0^2 c^4 \dots(9)$$

From (8) and (9),

$$m_0^2 c^4 = -2h^2 vv' (1 - \cos \theta) + 2h(v - v') m_0 c^2 + m_0^2 c^4$$

$$\therefore 2h(v - v') m_0 c^2 = 2h^2 vv' (1 - \cos \theta)$$

$$\text{or } \frac{v - v'}{vv'} = \frac{h}{m_0 c^2} (1 - \cos \theta) \text{ or } \frac{1}{v'} - \frac{1}{v} = \frac{h}{m_0 c^2} (1 - \cos \theta)$$

$$\text{or } \frac{c}{v'} - \frac{c}{v} = \frac{h}{m_0 c} (1 - \cos \theta)$$

$$\text{or } \lambda' - \lambda = \frac{h}{m_0 c} (1 - \cos \theta) \dots(10)$$

$$\therefore \text{The change in wavelength} = d\lambda = \frac{h}{m_0 c} (1 - \cos \theta)$$

This relation shows that $d\lambda$ is independent of the wavelength of the incident radiations as well as the nature of the scattering substance. $d\lambda$ depends upon the angle of scattering only.

Case 1. When $\theta = 0$, $\cos \theta = 1$ and hence $d\lambda = 0$

Case 2. When $\theta = 90^\circ$, $\cos \theta = 0$ and hence

$$d\lambda = \frac{h}{m_0 c} = \frac{6.63 \times 10^{-34}}{(9.11 \times 10^{-31}) \times (3 \times 10^8)} m = 0.0243 \text{ \AA}$$

This is known as Compton wavelength.

Case 3. When $\theta = 180^\circ$, $\cos \theta = -1$ and hence $d\lambda = 2h/m_0c = 0.0485 \text{ \AA}$. $d\lambda$ has the maximum value at $\theta = 180^\circ$.

Experimental verification. Monochromatic X-rays of wavelength λ are allowed to fall on a scattering material like a small block of carbon (Fig. 3.9.2). The scattered X-rays are received by a Bragg spectrometer and their wavelength is determined. The spectrometer can freely swing in an arc about the scatterer. The wavelength of the scattered X-rays is measured for different values of the scattering angle. The experimental results obtained by Compton are shown in Fig. 3.9.3. In the scattered radiation in addition to the incident wavelength (λ), there exists a line of longer wavelength (λ'). The “Compton shift” $d\lambda$ is found to vary with the angle at which the scattered rays are observed.

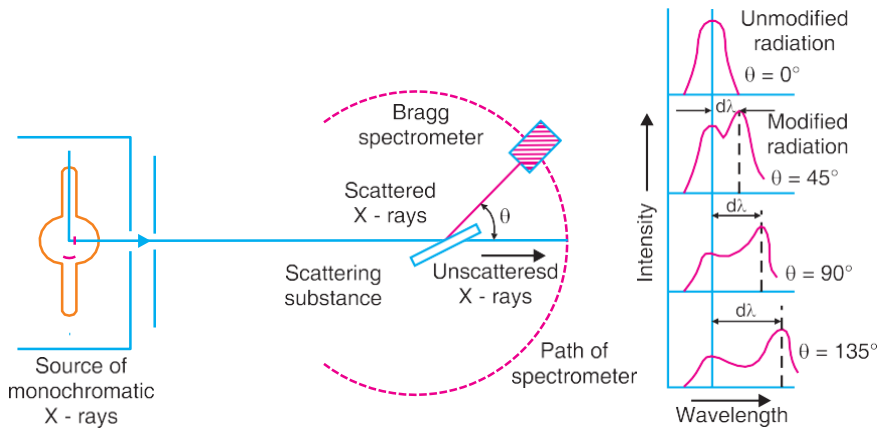


Fig. 3.9.2

Fig. 3.9.3

Direction of Recoil electron. Dividing Eq. (5) by Eq. (4), we get

$$\tan \phi = \frac{h\nu' \sin \theta}{h(\nu - \nu' \cos \theta)} = \frac{\nu' \sin \theta}{(\nu - \nu' \cos \theta)} \quad \dots(12)$$

Using Eq. (10), we get

$$\frac{1}{\nu'} = \frac{1}{\nu} + \frac{h}{m_0 c^2} (1 - \cos \theta) = \frac{1}{\nu} + \frac{h}{m_0 c^2} \cdot 2 \sin^2 \frac{\theta}{2}$$

or

$$\nu' = \frac{\nu}{1 + \left(\frac{h\nu}{m_0 c^2} \right) 2 \sin^2 \frac{\theta}{2}} = \frac{\nu}{1 + 2\beta \sin^2 \left(\frac{\theta}{2} \right)} \quad \text{where } \beta = \frac{h\nu}{m_0 c^2} \quad \dots(13)$$

Substituting this value of ν' in Eq. (12), we get

$$\tan \phi = \frac{\nu \sin \theta / \left[1 + 2\beta \sin^2 \left(\frac{\theta}{2} \right) \right]}{\left[\nu - \left\{ \nu \cos \theta / \left(1 + 2\beta \sin^2 \frac{\theta}{2} \right) \right\} \right]} = \frac{\cot \left(\frac{\theta}{2} \right)}{(1 + \beta)}$$

\therefore

$$\tan \phi = \frac{\cot \left(\frac{\theta}{2} \right)}{1 + \left(\frac{h\nu}{m_0 c^2} \right)} \quad \dots(14)$$

Kinetic Energy of Recoil electron. The K.E. of recoil electron is the difference between the energies of incident and scattered photons, *i.e.*,

$$\text{K.E.} = h\nu - h\nu'$$

$$\text{K.E.} = h\nu - h \left[\frac{\nu}{1 + 2\beta \sin^2 (\theta/2)} \right] = h\nu \left[\frac{2\beta \sin^2 (\theta/2)}{1 + 2\beta \sin^2 (\theta/2)} \right] \quad \dots (15)$$

where $\beta = h\nu / m_0 c^2$

3.10 Symmetry Operations

A symmetry operation is one which leaves the crystal invariant. Symmetry operations may be grouped into three classes:

1. Translation operations
2. Point operations
3. Hybrid operations

1. Translation Operation. A translation operation is defined as the displacement of a crystal parallel to itself by a crystal translation vector defined by $T = n_1 a + n_2 b$.

2. Point operations

- (i) **The mirror reflection:** In this operation, the reflection of a structure at a

mirror plane m passing through a lattice point leaves the crystal unchanged. Fig. 3.10.1 shows two mirror planes in a two-dimensional crystal.

(ii) **Inversion:** A crystal structure has an inversion symmetry if for every lattice point of position vector r , there is a corresponding lattice point at the position $-r$ [Fig. 3.10.2]. The origin about which the position vector r is chosen is called the *centre of inversion* and is represented by i .

(iii) **Rotation:** A structure is said to possess rotational symmetry about an axis if rotation of the structure about this axis by an angle ϕ gives an unchanged configuration of the original structure. The angle ϕ which satisfies this condition is given by

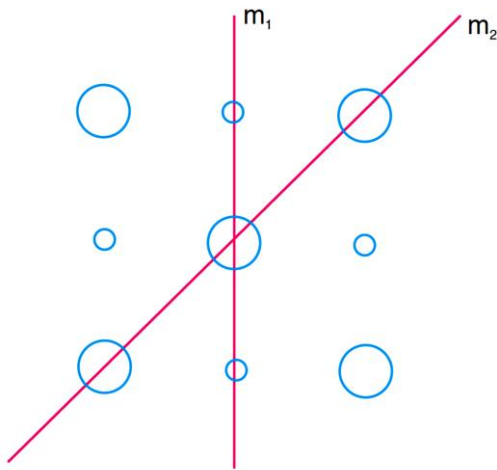


Fig. 3.10.1

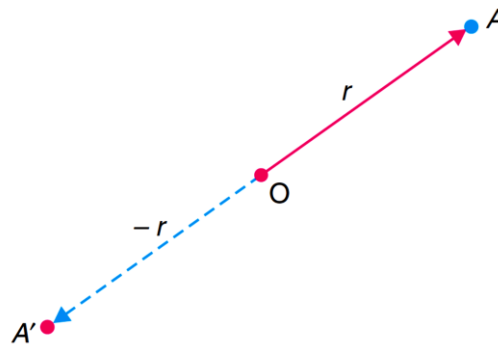


Fig. 3.10.2

$$\phi = \frac{2\pi}{n}; n = 1, 2, 3, \dots$$

where the rotation axis is n -fold. In a crystal lattice only one, two, three, four, and six-fold rotation axes of symmetry are possible. Fig. 3.10.3 shows a 6-fold axis of rotation.

3. Hybrid Operations

(i) **Rotoreflexion:** It is the combination of an n -fold rotation followed by a reflection in a plane perpendicular to the rotation axis. It is denoted by n/m , where $n = 1, 2, 3, 4, 6$.

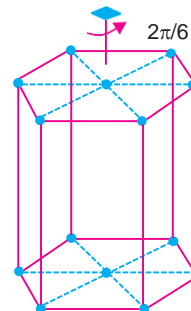


Fig.3.10.3

(ii) **Rotoinversion:** This is the combination of an n -fold rotation followed by an inversion and is denoted by \bar{n} with $n= 1, 2, 3, 4, 6$.

The axis of rotation in roto-reflection and roto-inversion is referred to as improper axis.

(iii) **Screw translation:** In this the n -fold rotation axis is coupled with the translation parallel to rotation axis. The new symmetry element is called a *screw axis* and is denoted by n_m .

(iv) **Glide reflection:** We can combine a reflection with a translation parallel to the reflection plane to achieve congruence in some crystals. This combination is called a glide reflection. The translation component of a glide reflection is expressed as the combination of translations by fractions of repeat distances in a crystal. For example, the translation in a diagonal glide may be written as

$$t = \frac{1}{2}a + \frac{1}{2}b, \quad \frac{1}{2}b + \frac{1}{2}c \text{ or } \frac{1}{2}c + \frac{1}{2}a$$

The list of symmetry operations is not without a very special symmetry operation, known as the *identity operation*. This operation means doing no operation on the crystal or keeping the crystal undisturbed. Thus every crystal has the identity operation. It is generally denoted by the symbol I .

Close-packed Crystal Structures. There are two ways of arranging equivalent spheres in a regular array to minimise the interstitial volume. One has hexagonal symmetry and is called the hexagonal close-packed structure. The other has cubic symmetry and is called the face-centred cubic structure.

Spheres may be arranged in a single closest-packed layer by placing each sphere in contact with six others (Fig. 3.10.4). The centres of the spheres are at points marked A . A second and identical layer of spheres can be placed over this, with centres over the points marked B (or equivalently C). If the second layer goes in over B , there are two nonequivalent choices for a third layer. It can go in over A or over C . If the third layer goes in over A , the sequence is $ABABAB$ and the structure is hcp (Fig. 3.10.5). Examples of elements which have this structure are Cd, Mg, Ti, Zn, etc.

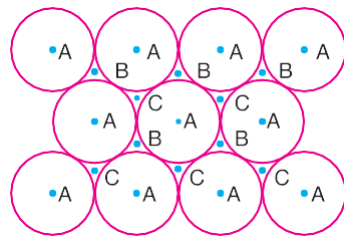


Fig. 3.10.4

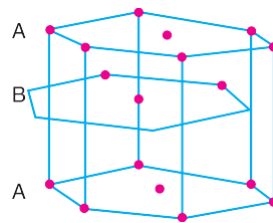


Fig. 3.10.5

If the third layer goes in over *C*, the sequence is *ABCABCABC* and the structure is fcc (Fig. 3.10.6). Elements having fcc structure are Cu, Ag, Au, Al, Pd, Pt, etc. In either structure, each atom has 12 nearest neighbors. So the *coordination number* is 12. The packing fraction is 0.74 for both the fcc and hcp structures.

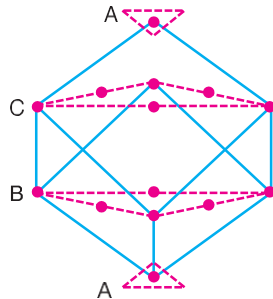


Fig. 3.10.6

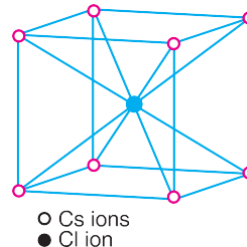


Fig. 3.10.7

The Cesium Chloride Structure. The structure of CsCl is shown in Fig 3.10.7 The Cs^+ ions form an sc lattice interlocked with another sc lattice formed by the Cl^- ions. There is one molecule per primitive cell with ions at the corners 000 and body centred positions of the simple cubic space lattice. Each ion is at the centre of a cube of ions of the opposite kind, so that the coordination number is 8. TlBr, TlI, NH_4Cl , CuPd, CuZn (β -brass), AgMg, LiHg, AlNi, BeCu are representative crystals having the CsCl arrangement.

3.11 Elements of Symmetry

What is meant by a symmetry? Formally, we might say that a symmetry of a particular kind exists, when a certain operation leaves something unchanged. A candle is symmetric about a vertical axis because it can be rotated about that axis without changing in appearance or any other feature.

Crystals possess different symmetries. The symmetry operations of a crystal carry the crystal structure into itself. Symmetry operations performed about a point or line are called point-group symmetry. The point-group symmetry elements possessed by a crystal are :

(1) **Plane of symmetry.** A crystal is said to have a *plane of symmetry*, when it is divided by an imaginary plane into two halves, such that one is the mirror image of the other. For example, a cube has nine planes of symmetry. Fig. 3.11.1 represents a plane of symmetry parallel to the faces of a cube. There are three such planes. Fig. 3.11.2 represents one of the six diagonal planes of symmetry.

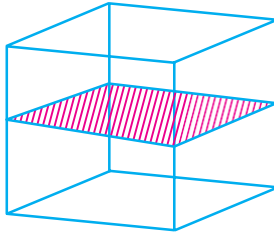


Fig. 3.11.1

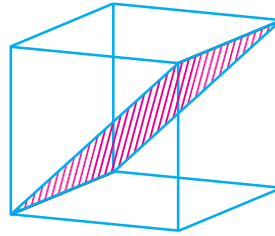


Fig. 3.11.2

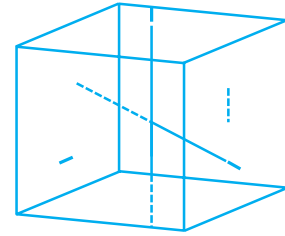


Fig. 3.11.3

(2) **Axis of symmetry.** This is an axis such that, if the crystal is rotated around it through some angle, the crystal remains invariant. The axis is called n -fold if the angle of rotation is $360/n$.

Example. If equivalent configuration occurs after rotation of 180° , 120° and 90° , the axes of rotation are known as two-fold, three-fold and four-fold, axes of symmetry respectively. For example, Fig. 3.11.3 shows the three tetrad (four-fold) axes of a cube.

(3) **Centre of symmetry.** It is a point such that any line drawn through it will meet the surface of the crystal at equal distances on either side. It is important to mention here that a crystal may possess a number of planes or axes of symmetry but it can have only one centre of symmetry. *Example.* A cube has a single centre of symmetry at the centre of the cube.

Point Group. A lattice point group is defined as the collection of the symmetry operations which, when applied about a lattice point, leave the lattice invariant. 32 such groups are possible. Every known crystal can be assigned to one of these 32 crystal classes.

Space Groups. When identical objects are placed at the lattice points of a *space lattice* a regular special array is obtained, which has, perhaps, *symmetry elements* over and above those of the *point group* of the original lattice. Thus, because of some symmetry property of the identical objects (*i.e.*, of the *unit cells* in a crystal), there may exist *glide* (= reflection + translation) *planes* and *screw* (= rotation + translation) *axes* which define operations turning the structure into itself. It has been shown that there are only 230 different types of symmetry possible for such a system. Thus 230 three dimensional space groups or “structures” exist in total.

Two-Dimensional Lattice Types. There are five Bravais lattices in two-dimensions (Fig. 3.11.4). These are listed in Table 3.11.

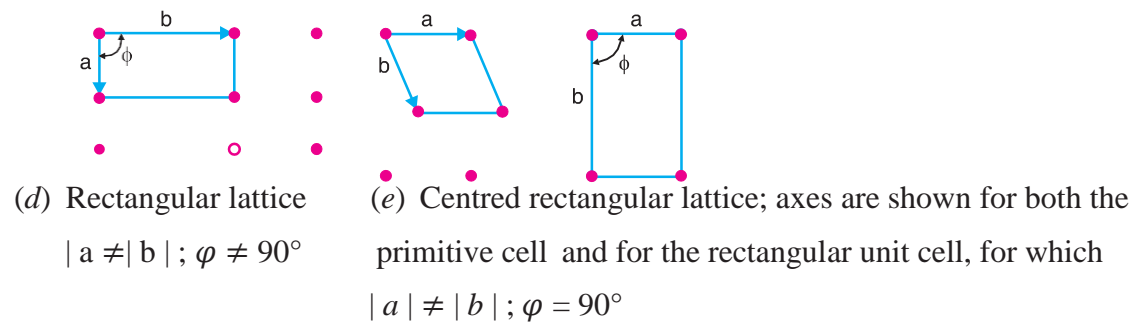
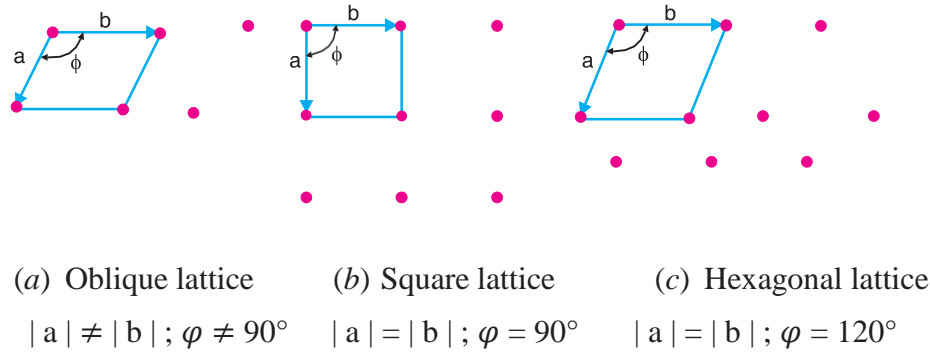


Fig. 3.11.4

TABLE 3.11.1. The five two-dimensional lattice types (The notation mm means that two mirror lines are present)

<i>Lattice</i>	<i>Conventional unit cell</i>	<i>Axes of conventional unit cell</i>	<i>Point-group symmetry of lattice about lattice points</i>
Oblique	Parallelogram	$a \neq b$ $\varphi \neq 90^\circ$	2
Square	Square	$a = b$ $\varphi = 90^\circ$	4 mm
Hexagonal	60° rhombus	$a = b$ $\varphi = 120^\circ$	6 mm
Primitive rectangular	Rectangle	$a \neq b$ $\varphi = 90^\circ$	2 mm
Centred rectangular	Rectangle	$a \neq b$ $\varphi = 90^\circ$	2 mm

Unit IV

Photoelectric Effect and free Electron theory of metals

4.1 Photo electric effect:

Whenever light or electromagnetic radiations (such as X-rays, Ultraviolet rays) fall on a metal surface, it emits electrons. This process of emission of electrons from a metal plate, when illuminated by light of suitable wavelength, is called the photoelectric effect. The electrons emitted are known as the photoelectrons. In the case of alkali metals photoelectric emission occurs even under the action of visible light. Zinc, cadmium etc., are sensitive to only ultraviolet light.

Laws of photoelectric emission:

- (1) For every metal, there is a particular minimum frequency of the incident light, below which there is no photoelectric emission, whatever be the intensity of the radiation. This minimum frequency, which can cause photoelectric emission, is called the threshold frequency.
- (2) The strength of the photoelectric current is directly proportional to the intensity of the incident light, provided the frequency is greater than the threshold frequency.
- (3) The velocity and hence the energy of the emitted photoelectrons is independent of the intensity of light and depends only on the frequency of the incident light and the nature of the metal.
- (4) Photoelectric emission is an instantaneous process. The time lag, if any, between incidence of radiation and emission of the electrons, is never more than 3×10^{-9} sec.

Einstein's photoelectric equation:

According to Einstein, light of frequency ν consists of a shower of corpuscles or photons each of energy $h\nu$. When a photon of light of frequency ν is incident on a metal, the energy is completely transferred to a free electron in the metal. A part of the energy acquired by the electron is used to pull out the electron from the surface of the metal and the rest of it is utilized in imparting K.E. to the emitted electron. Let Φ be the energy spent in extracting the electron from emitter to which it is bound (photoelectric work function) and $\frac{1}{2}mv^2$ the K.E. of the photoelectron.

$$\text{Then } h\nu = \Phi + \frac{1}{2}mv^2 \dots\dots\dots(1)$$

This relation is known as the Einstein's Photoelectric equation. If ν_0 is the threshold frequency which just ejects an electron from the metal without any velocity then $\Phi = h\nu_0$.

$$h\nu = h\nu_0 + mv_{\max}^2 \dots\dots\dots(2)$$

where v_{\max} is the maximum velocity acquired by the electron.

$$\text{(or) } \frac{1}{2}mv_{\max}^2 = h(\nu - \nu_0) \dots\dots\dots(3)$$

4.2 Lenard's method to determine e/m for Photoelectrons

The apparatus used is shown in Fig. 4.2.1. It consists of a glass tube G which can be evacuated through the side tube T . Ultraviolet light passes through a quartz window W and falls on an aluminium cathode C enclosed in G . An earthed metal screen A with a small central hole forms the anode. The cathode (C) can be maintained at a desired potential, positive or negative relative to the anode A . P_1 and P_2 are small metal electrodes connected to electrometers E_1 and E_2 .

When C is raised to a negative potential and illuminated, negatively charged particles are produced and accelerated towards the anode. A few particles pass through the hole in A and proceed with uniform velocity to P_1 . Their arrival at P_1 is indicated by E_1 . By applying a uniform magnetic field B (represented by the dotted circle) perpendicular to the plane of the figure and directed towards the reader, the photoelectrons can be deflected towards P_2 . Their arrival at P_2 is indicated by the deflection they produce in E_2 .

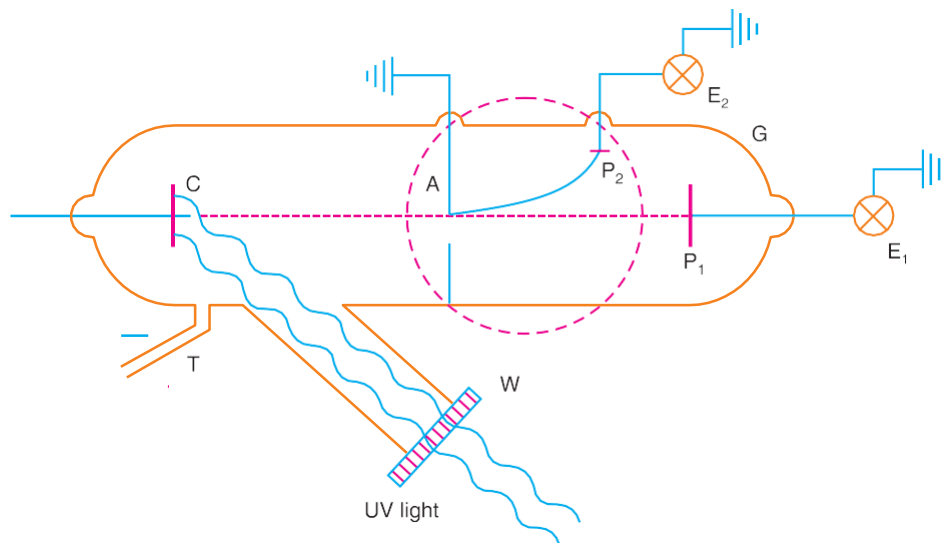


Fig. 4.2.1

Lenard first studied the relation between current and the potential applied to C . When the cathode potential was several volts positive, the current was zero. When V was +2 volts, there was a feeble current showing that a few particles possessed enough velocity to overcome the retarding potential of 2 volts. When the potential was further decreased, the current increased and reached a saturation value for -20 volts. Fig. 4.2.2 shows the variation of photoelectric current with cathode potential

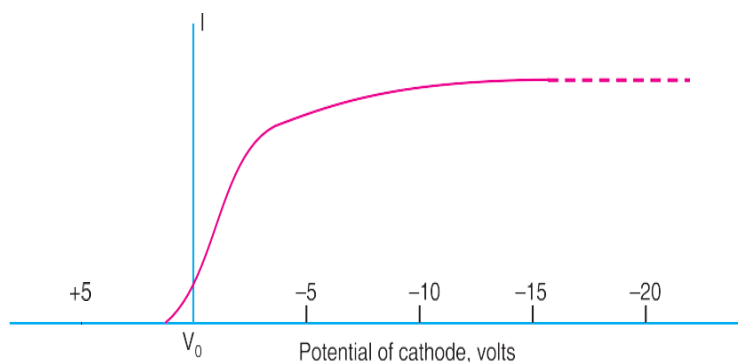


Fig.4.2.2

After this preliminary investigation, Lenard applied to C a negative potential V , very large compared to the potential of 2 volts. The velocity imparted by the accelerating potential is so large that the velocity of the particles in the act of emission is negligible in comparison to it. Let V be the accelerating potential and v the velocity acquired by the photoelectrons. Then,

$$\frac{1}{2}mv^2 = eV \quad \dots(1)$$

where e is the charge and m the mass of the photoelectron.

Let R be the radius of the circular path described by the photoelectrons in the region of uniform magnetic field of strength B .

Then
$$\frac{mv^2}{R} = Bev.$$

\therefore
$$v = \frac{BeR}{m} \quad \dots(2)$$

Substituting this value of v in eqn. (1), $\frac{1}{2}m (BeR / m)^2 = eV$

\therefore
$$\frac{e}{m} = \frac{2V}{B^2 R^2} \quad \dots(3)$$

Knowing V , B and R , e/m is calculated. Lenard found the value of e/m to be the same as that for electrons. *This clearly shows that the photoparticles are nothing but electrons.*

4.3 Richardson and Compton Experiment

The apparatus used by them is shown in Fig. 4.3.1. The emitter of photoelectrons (C) is a small strip of the metal under study and is kept at the centre of a spherical glass bulb B . B is silvered on the inner side and can be evacuated through the tube T . The silver coating on the inside of the bulb serves as the anode A and is connected to an electrometer E which measures the photoelectric current. Monochromatic light L is made to pass through a quartz window W and fall on C . C can be maintained at any desired potential V , relative to A and this potential can be read with a voltmeter.

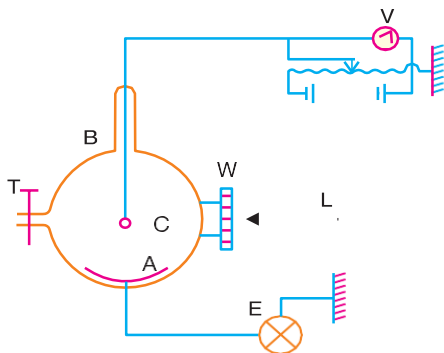


Fig. 4.3.1

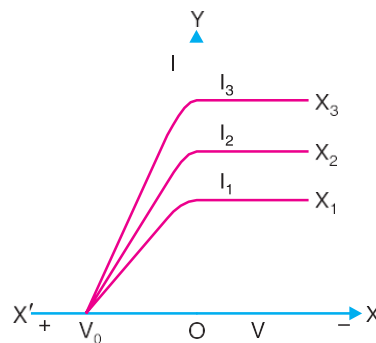


Fig. 4.3.2

(i) Relation between photoelectric current and retarding potential.

They first studied the relation between the photoelectric current I and the retarding potential V . Irradiating the cathode C with monochromatic light of a given intensity, the cathode potential (V) was varied from a few volts positive upto zero and negative values. The photoelectric current I was measured for different values of V . The observations were repeated with the intensity of illumination (X) doubled, trebled, etc. The relation between I and V is shown in Fig. 4.3.2. For a given intensity of illumination (X_1), there is no photoelectric current when the positive potential on the cathode is greater than a critical value $+V_0$. At potentials just less than $+V_0$, a small current is produced. As the potential decreases to zero, the current rapidly increases and reaches a maximum value when $V = 0$. No further increases in current are observed when V becomes negative. Hence I_1 is the maximum current due to illumination of intensity X_1 . When the intensity is doubled (X_2) as in (2), the maximum current I_2 is double I_1 : But the critical potential V_0 is the same as before. When the intensity of illumination is increased three fold (X_3), the corresponding maximum current increases proportionately, but the critical potential remains unchanged. Thus, the maximum current I_m is proportional to the intensity of illumination X , i.e., $I_m \propto X$. The critical potential V_0 is independent of the intensity.

Relation between velocity of photoelectrons and the frequency of light.

Several monochromatic radiations of wavelengths $\lambda_1, \lambda_2, \lambda_3$, etc., are allowed to fall on the emitter. The intensity of illumination for each wavelength is adjusted to give the same value of I_m in each case. In each case, the photoelectric current I for different values of V is determined. Fig. 4.3.3 represents the nature of the curves. It is seen from the curves that if $\lambda_1 > \lambda_2 > \lambda_3$ the critical potentials are $V_1 < V_2 < V_3$. Hence, as the wavelength of light increases, the critical retarding potential decreases. This means that the maximum K.E. of the photoelectrons

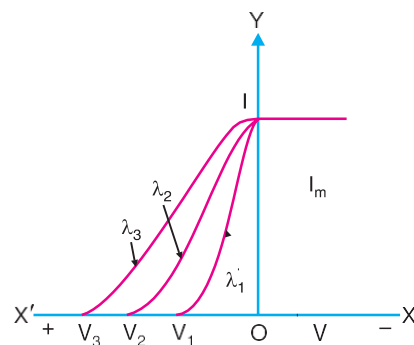


Fig. 4.3.3

(given by $\frac{1}{2} m v_m^2 = eV_0$)

frequency of light. Since V_0 is independent of the intensity of illumination, we conclude that the velocity and K.E. of photoelectrons are independent of the intensity of illumination, but dependent on the frequency of the incident light

A linear relation is found to exist between the maximum energy of emission (eV_0) and the frequency (ν) of the light. If eV_0 is plotted against ν , we get, for any emitting surface a straight line (Fig. 4.3.4), whose intercept on the frequency axis gives the threshold frequency $\nu_0 = c/\lambda_0$ for this surface. The slope of the straight line is the same for all emitting surfaces and is found to be equal to h . The value of ν_0 however, depends on the emitting surface. ν_0 is called the threshold frequency, as it represents the beginning of the photoelectric activity of the emitter.

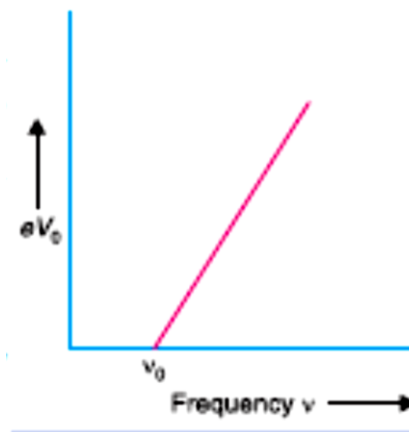


Fig. 4.3.4

Threshold frequency is defined as the minimum value of frequency of incident light below which the photo-electric emission stops completely, howsoever high the intensity of light may be. At threshold frequency, the kinetic energy of emitted photo-electrons is just zero.

4.4 Experimental Investigations on the Photoelectric Effect

Photoelectric effect can be studied in detail with the help of the apparatus shown in Fig. 4.4.1.

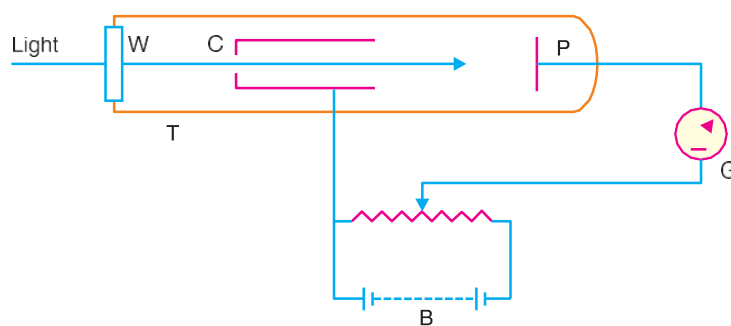


Fig.4.4.1

It consists of an evacuated glass tube T with a quartz window W . P is a photoelectrically sensitive plate. C is a hollow cylinder and it has a small hole that permits the incident light to fall on the plate

P . P is connected to the negative end. C is connected to the positive terminal of a battery B . When light from some source falls on the plate P , the photoelectrons are ejected out of the plate P . These photoelectrons are attracted by the positively charged cylinder C .

Hence a photoelectric current flows from P to C in the bulb and from C to P outside the bulb. This current can be measured from the deflection produced in the galvanometer G . It is found that the strength of the photoelectric current increases as the potential of C is more and more positive with respect to P . The deflection in G decreases when the potential of C is negative with respect to P . The results obtained can be summarised into four statements, which are known as the laws of photoelectric emission.

Laws of photoelectric emission.

- (i) For every metal, there is a particular minimum frequency of the incident light, below which there is no photoelectric emission, whatever be the intensity of the radiation. This minimum frequency, which can cause photoelectric emission, is called the threshold frequency.
- (ii) The strength of the photoelectric current is directly proportional to the intensity of the incident light, provided the frequency is greater than the threshold frequency.
- (iii) The velocity and hence the energy of the emitted photoelectrons is independent of the intensity of light and depends only on the frequency of the incident light and the nature of the metal.
- (iv) Photoelectric emission is an instantaneous process. The time lag, if any, between incidence of radiation and emission of the electrons, is never more than 3×10^{-9} sec.

Failure of the electromagnetic theory. The above experimental facts could not be explained on the basis of the electromagnetic theory of light.

1. Calculations showed that it would require about 500 days to dislodge a photoelectron from sodium by exposure to violet light of wavelength 4000 \AA . Experimentally, however, we observe that electron ejection commences without delay.
2. According to the classical theory, light of greater intensity should impart greater K.E. to the liberated electrons. But, this does not happen. Also, the velocity of the emitted electron should not depend on the frequency of the incident light. But it does.

The phenomenon was adequately explained by Einstein on the basis of Planck's Quantum theory of radiation.

Quantum theory. According to Planck, the energy of a monochromatic wave with frequency ν can only assume those values which are integral multiples of energy $h\nu$. *i.e.*, $E_n = nh\nu$, where n is an integer referring to the number of "Photons". Thus the energy of a single *PHOTON* of frequency

ν is $E = h\nu$.

4.5 Einstein's Photoelectric Equation

According to Einstein, light of frequency ν consists of a shower of corpuscles or photons each of energy $h\nu$. When a photon of light of frequency ν is incident on a metal, the energy is completely transferred to a free electron in the metal. A part of the energy acquired by the electron is used to pull out the electron from the surface of the metal and the rest of it is utilised in imparting K.E. to the emitted electron. Let ϕ be the energy spent in extracting the electron from the emitter to which it is bound (photoelectric work function) and $\frac{1}{2}mv^2$ the K.E. of the photoelectron.

Then
$$h\nu = \phi + \frac{1}{2} m v^2 \quad \dots(1)$$

This relation is known as the *Einstein's Photoelectric equation*. If ν_0 is the threshold frequency which just ejects an electron from the metal without any velocity then, $\phi = h\nu_0$.

\therefore
$$h\nu = h\nu_0 + \frac{1}{2} m v_{\max}^2 \quad \dots(2)$$

where v_{\max} is the maximum velocity acquired by the electron.

or
$$\frac{1}{2} m v_{\max}^2 = h(\nu - \nu_0) \quad \dots(3)$$

Experimental verification of Einstein's Photoelectric Equation—Millikan's Experiment.

Theory. Millikan's experiment is based on what is known as the "stopping potential". The stopping potential is the necessary retarding potential difference required in order to just halt the most energetic photoelectron emitted.

The K.E. of a photoelectron leaving the surface of a metal irradiated with light of frequency ν $\left. \vphantom{\begin{matrix} \text{The K.E. of a photoelectron leaving} \\ \text{the surface of a metal irradiated with} \\ \text{light of frequency } \nu \end{matrix}} \right\} = \frac{1}{2} m v_{\max}^2 = h\nu - \phi.$

Let V be the P.D. which is applied between the emitter and a collecting electrode in order to prevent the photoelectron from just leaving the emitter, the emitter being maintained at a positive potential with respect to the collector. Then,

$$eV = \frac{1}{2} m v_{\max}^2$$

\therefore
$$eV = h\nu - \phi$$

or
$$V = \frac{h}{e} \nu - \frac{\phi}{e} \quad \dots(1)$$

ϕ is constant for a given metal; h and e are also constants.

Hence, Equation (1) represents a straight line. V is measured for different values of ν . A graph is then plotted between the stopping potential (V) taken along the Y-axis and the frequency of light (ν) taken along the X-axis. The graph is a straight line

The slope of the straight line

$$\tan \theta = \frac{h}{e}$$

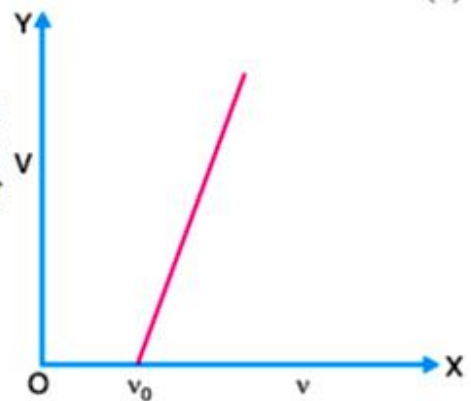


Fig. 4.5.1

$$\therefore h = e \tan \theta \dots(2)$$

Hence the value of h (Planck's constant) can be calculated. The intercept on the X-axis gives the threshold frequency ν_0 for the given emitter. From this, photoelectric work function $\phi = h \nu_0$ can be calculated.

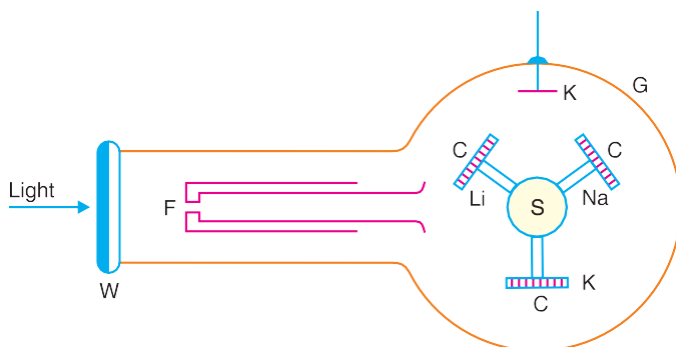


Fig.4.5.2

Experiment.

Millikan's apparatus is shown in Fig. 4.5.2. Alkali metals are employed as emitters, since they readily exhibit photoelectric emission even with visible light. Cylindrical blocks (C) of sodium, potassium or lithium are mounted on a spindle S at the centre of the glass flask G. The flask is evacuated to a very high vacuum to free the metals from all absorbed gases and to prevent their oxidation. The spindle can be rotated from outside by an electromagnet. As each metal block passes by the adjustable sharp edge K, a thin layer of it is removed, thus exposing a fresh surface of the metal to the irradiating light entering the flask through a quartz window W. Monochromatic light provided by a spectroscope is used to illuminate the fresh metal surfaces. The photoelectrons are collected by a Faraday cylinder F. The Faraday cylinder is made of copper oxide which is not photosensitive. The photocurrent is measured by an



Robert Andrews Millikan
(1868–1953)

As a Scientist, Millikan made numerous discoveries, chiefly in the fields of electricity, optics, and molecular physics. His earliest major success was the accurate determination of the charge carried by an electron, using the elegant "falling-drop method"; he also proved that this quantity was a constant for all electrons (1910), thus demonstrating the atomic structure of electricity. Next, he verified experimentally Einstein's all-important photoelectric equation, and made the first direct photoelectric determination of Planck's constant h (1912-1915).

The stopping potential of the liberated photoelectrons is measured by raising the emitter surface to a positive potential, just sufficient to prevent any of the electrons from reaching the collector (F). The

stopping potential is the positive potential applied to the emitter, which corresponds to zero current in the electrometer. The stopping potential (V) is determined for different wavelengths of the incident light. The value of V should be corrected for any contact potential between the metal (C) and Faraday cylinder (F). On plotting V against ν , we get a straight line. Measuring the slope of the straight line, the value of h/e is obtained. Then substituting the known value of e , h is calculated. The value of h calculated in this way agrees fairly well with the value obtained by other methods. Thus the Einstein's equation can be verified experimentally.

4.6 Millikan's Experiment:

Theory: Millikan's experiment is based on what is known as the "stopping potential". The stopping potential is the necessary retarding potential difference required in order to just halt the most energetic photoelectron emitted.

The K.E. of a photoelectron leaving the surface of a metal irradiated with light of frequency ν
 $= \frac{1}{2} m v_{\max}^2 = h\nu - \Phi$

Let V be the P.D. which is applied between the emitter and a collecting electrode in order to prevent the photoelectron from just leaving the emitter, the emitter being maintained at a positive potential with respect to the collector. Then,

$$eV = \frac{1}{2} m v_{\max}^2$$

$$eV = h\nu - \Phi \quad \text{or}$$

$$V = \frac{h}{e} \nu - \frac{\Phi}{e} \dots\dots\dots(1)$$

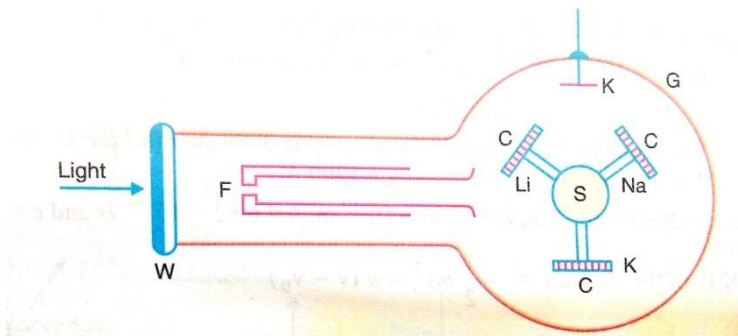
Φ is constant for a given metal; h and e are also constants.

Hence, Equation (1) represents a straight line. V is measured for different values of ν . A graph is then plotted between the stopping potential (V) taken along the Y-axis and the frequency of light (ν) taken along x-axis. The graph is a straight line. The slope of the straight line

$$\tan \theta = \frac{h}{e}$$

$$h = e \tan \theta$$

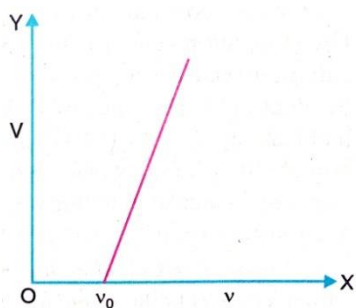
Hence the value of h (plank's constant) can be calculated. The intercept on the x-axis gives the threshold frequency ν_0 for the given emitter. From this, photoelectric work function $= \Phi = h\nu_0$ be calculated.



Experiment:

Millikan's apparatus is shown in figure. Alkali metals are employed as emitters since they readily exhibit photoelectric emission even with visible light. Cylindrical blocks(C) of sodium, potassium or lithium are mounted on a spindle S at the centre of the glass flask G. The flask is evacuated to a very high vacuum to free the metals from all absorbed gases and to prevent their oxidation. The spindle can be rotated from outside by an electromagnet. As each metal block passes by the adjustable sharp edge K, a thin layer of it is removed, thus exposing a fresh surface of the metal to the irradiating light entering the flask through a quartz window W. Monochromatic light provided by a spectroscope is used to illuminate the fresh metal surfaces. The photoelectrons are collected by a Faraday cylinder is made of copper oxide which is not photosensitive. The photocurrent is measured by an electrometer connected to the Faraday cylinder.

The stopping potential of the liberated photoelectrons is measured by raising the emitter surface to a positive potential, just sufficient to prevent any of the electrons from reaching the collector (F). The stopping potential is the positive potential applied to the emitter which corresponds to zero current in the electrometer. The stopping potential (V) is determined for different wavelength of the incident light. The value of V should be corrected for any contact potential between the metal(C) and Faraday cylinder (F). On plotting V against ν , we get a straight line. Measuring the slope of the straight line, the value of h/e is obtained. Then substituting the known value e, h is calculated. The value of h calculated in this way agrees fairly well with the value obtained by other methods. Thus the Einstein's equation can be verified experimentally.



4.7 Photoelectric Cells

Photoelectric cell is an arrangement to convert light energy into electrical energy. There are three types of photocells, photoemissive, photovoltaic and photoconductive.

1. **Photo-emissive Cell.** This consists of a glass or quartz bulb (*B*) according as it is to be used with visible or ultraviolet light (Fig. 4.7.1). *C* is the silver cathode in the form of a semi-cylindrical plate. The anode (*A*) is a rod mounted vertically at the centre of the bulb and parallel to its axis. A positive potential of about 100 volts is applied to the anode, the negative being connected to the cathode through a galvanometer *G*. When light falls on the cathode *C*, electrons are ejected from the cathode. A small current flows through the cell and can be measured by the galvanometer. The photoemissive cell is used for reproduction of sound from photo-films.

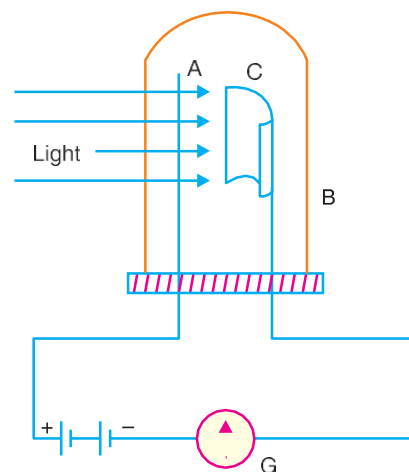


Fig. 4.7.1

2. **Photo-voltaic cell.** It consists of a layer of semiconductor material spread over a metallic surface by heat treatment. In one type of the photovoltaic cell, the metal plate is made of copper and the semiconductor is cuprous oxide (Cu_2O). On the other side of the semiconductor, there is a very thin layer of a translucent deposit which allows the semiconductor to be illuminated by radiations (Fig.4.7.2). Light falling on the surface film (of gold or silver) penetrates into it and ejects photoelectrons from the semiconductor layer.

These electrons travel in a direction opposite to the direction of the incident light. The conventional current, therefore, flows in the direction of the incident light. For small values of the resistance of the galvanometer, the current is directly proportional to the intensity of light. No external battery is required to operate a photovoltaic cell as the cell itself generates an e.m.f.

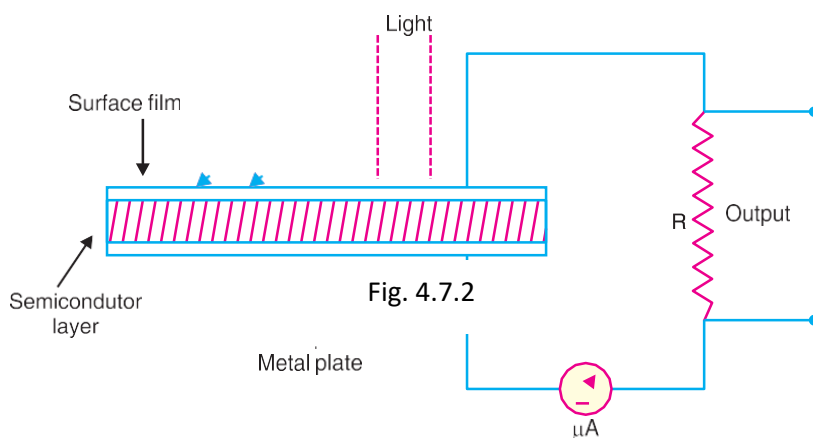


Fig. 4.7.2

Unit-V

Molecular physics

5.1 Theory of the Origin of Pure Rotational Spectrum of a Molecule

We may picture a diatomic molecule as consisting of atoms of masses m_1 and m_2 a distance R apart. The diatomic molecule can rotate about its centre of mass as shown in Fig.5.1.1

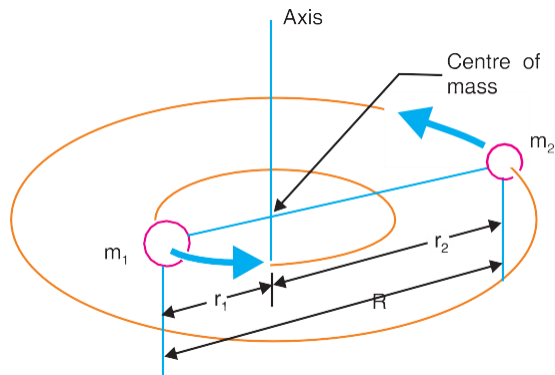


Fig.5.1.1

The moment of inertia of this molecule about an axis passing through its centre of mass and perpendicular to a line joining the atoms is

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \dots(1)$$

where r_1 and r_2 are the distances of m_1 and m_2 , respectively from the centre of mass.

From the definition of centre of mass

$$m_1 r_1 = m_2 r_2 \quad \dots(2)$$

Further $R = r_1 + r_2 \quad \dots(3)$

From equations (2) and (3)

$$r_1 = \frac{m_2}{m_1 + m_2} R \text{ and } r_2 = \frac{m_1}{m_1 + m_2} R.$$

Putting these values of r_1 and r_2 in Eq. (1),

$$I = \frac{m_1 m_2^2}{(m_1 + m_2)^2} R^2 + \frac{m_2 m_1^2}{(m_1 + m_2)^2} R^2 = \frac{m_1 m_2}{(m_1 + m_2)} R^2$$

or $I = m' R^2 \quad \dots(4)$

where the reduced mass m' is defined as

$$m' = \frac{m_1 m_2}{(m_1 + m_2)} \quad \dots(5)$$

The angular momentum L of the molecule has the magnitude $L = I\omega$

The angular momentum of the rotating diatomic molecule is quantised according to

$$L = \sqrt{J(J+1)} \hbar \quad J = 0, 1, 2, 3, \dots \quad \dots(6)$$

J is called the rotational quantum number.

The rotational kinetic energy of a diatomic molecule is $\frac{1}{2}I\omega^2$.

$$\therefore E_J = \frac{1}{2} I\omega^2 = \frac{L^2}{2I} = \frac{J(J+1)\hbar^2}{2I} \quad \dots(7)$$

Rotational transitions occur only in those molecules which possess a permanent electric dipole moment. For this reason nonpolar diatomic molecules such as H_2 and symmetric polyatomic molecules such as CO_2 and CH_4 do not exhibit rotational spectra.

The selection rule for rotational transitions is $\Delta J = \pm 1$

Rotational spectra are always obtained in absorption. Hence for a transition from some initial state of quantum number J to the next higher state of quantum number $J+1$, the frequency of the absorbed photon is

$$\nu_{J \rightarrow J+1} = \frac{\Delta E}{h} = \frac{E_{J+1} - E_J}{h} = \frac{\hbar}{2\pi I} (J+1) \quad \dots(9)$$

The spectrum of a rigid molecule therefore consists of equally spaced lines (Fig. 5.1.2).

Importance of the pure rotational spectrum for determining the properties of a molecule: The frequency difference between two successive lines in the pure rotational spectrum of a diatomic molecule is given by

$$\Delta\nu = \nu_{J+1 \rightarrow J+2} - \nu_{J \rightarrow J+1} = \frac{\hbar}{2\pi I}$$

By measuring $\Delta\nu$, the moment of inertia I of the molecule can be calculated. Now,

$$I = m' R^2 = \left\{ \frac{m_1 m_2}{(m_1 + m_2)} \right\} R^2$$

Thus the distance R between the nuclei can be calculated. This gives the length of the chemical bond between the atoms.

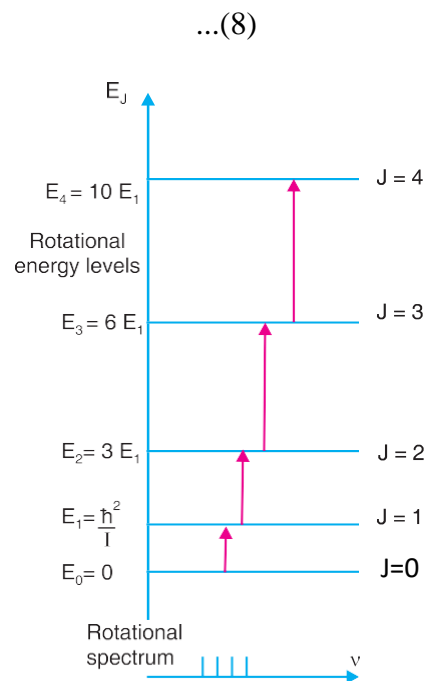


Fig. 5.1.2

5.2 Theory of the Origin of the Vibration-rotation Spectrum of a Molecule

When sufficiently excited, a molecule can vibrate as well as rotate. We shall consider only diatomic molecules. Fig. 5.2.1 shows how the potential energy of a diatomic molecule varies with

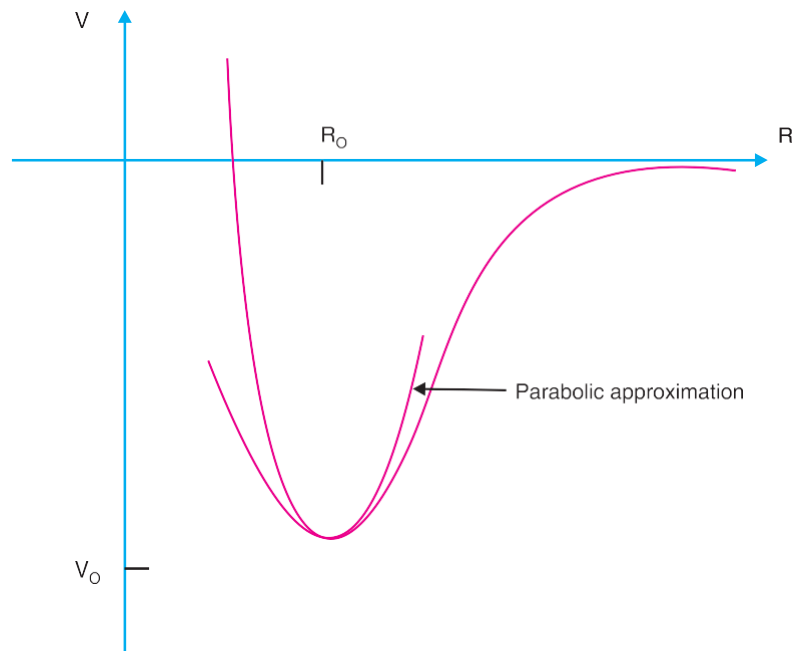


Fig. 5.2.1

the internuclear distance R . In the neighbourhood of the minimum of this curve, which corresponds to the normal configuration of the molecule, the shape of the curve is very nearly a parabola. In this region, then

$$V = V_0 + \frac{1}{2}k(R - R_0)^2 \quad \dots(1)$$

where R_0 is the equilibrium separation of the atoms.

The interatomic force that gives rise to this potential energy

$$F = -dV/dR = -k(R - R_0) \quad \dots(2)$$

The force is just the restoring force that a stretched or compressed spring exerts and, as with a spring, a molecule suitably excited can undergo simple harmonic oscillations. Classically, the frequency of a vibrating body of mass m connected to a spring of force constant k is

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \dots(3)$$

In the diatomic molecule we have two bodies of masses m_1 and m_2 joined by a spring. The use of the “reduced mass” reduces the problem of two particles m_1 and m_2 vibrating about their common centre of

mass to the problem of a single mass m' vibrating about a fixed point (Fig. 5.2.2).

The frequency of oscillation of such a two-body oscillator is

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m'}} \quad \dots(4)$$

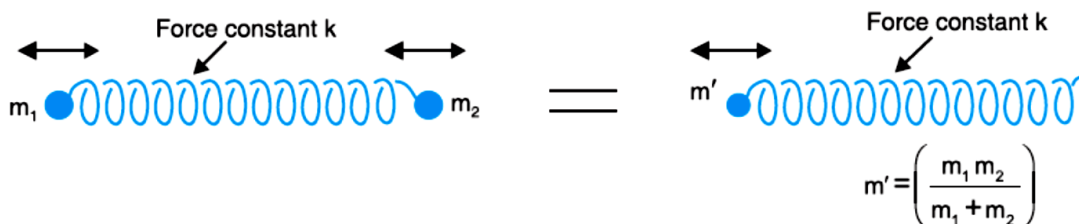


Fig. 5.2.2

When the harmonic oscillator problem is solved quantum mechanically, the energy of the oscillator is found to be restricted to the values

$$E_\nu = \left(\nu + \frac{1}{2} \right) h\nu_0 \quad \dots(5)$$

Here ν is the vibrational quantum number. It may have the values $\nu = 0, 1, 2, 3, \dots$ Substituting the value of ν_0 from Eq. (4),

$$E_\nu = \left(\nu + \frac{1}{2} \right) \hbar \sqrt{\frac{k}{m'}} \quad \dots(6)$$

These levels are sketched on Fig. 5.2.3.

For *large*-amplitude vibrations, the parabola does not fit the actual energy curve. Eq. (6) no longer holds. The energy well is wider than the parabola for the higher E_ν 's, and therefore these energy levels are closer together than the lower E_ν 's. This diagram also shows the fine structure in the vibrational levels caused by the simultaneous excitation of rotational levels.

The selection rule for transitions between vibrational states is

$$\Delta\nu = \pm 1 \quad \dots(7)$$

Pure vibrational spectra are observed only in liquids. This is because interactions between neighbouring molecules prevent their rotational motion.

The vibrations and rotations of a molecule take place independently of each other. Under these circumstances the energy levels of a diatomic molecule are specified by

$$E_{\nu, J} = \left(\nu + \frac{1}{2} \right) \hbar \sqrt{\frac{k}{m'}} + J(J+1) \frac{\hbar^2}{2I} \quad \dots(8)$$

E_ν is very much larger than E_r . Even at high temperatures only the vibrational states corresponding to $\nu = 0$ and $\nu = 1$ are excited. Fig. 5.2.4 shows the $J = 0, 1, 2, 3$ and 4 levels of a diatomic molecule for the $\nu = 0$ and $\nu = 1$ vibrational states. It also shows the spectral lines in absorption. The selection rules are $\Delta\nu = 1$ and $\Delta J = \pm 1$. The transition with $\Delta J = 0$ is not allowed.

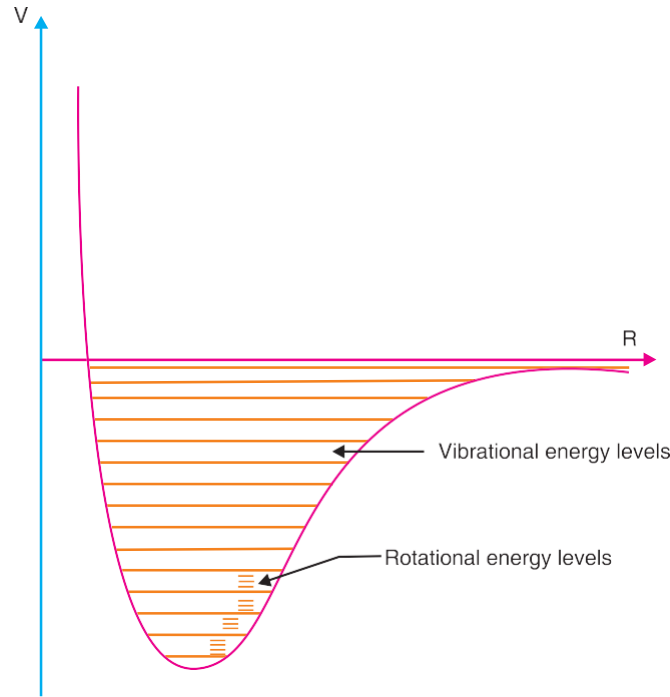


Fig. 5.2.3

The $v = 0 \rightarrow v = 1$ transitions fall into two categories :

(i) *P Branch*: Here, $\Delta J = -1$ (i.e., $J \rightarrow J - 1$).

From Eq. (8) the frequencies of the spectral lines in the *P* branch are given by

$$\nu_p = \frac{E_{1,J-1} - E_{0,J}}{h} = \frac{1}{2\pi} \sqrt{\frac{k}{m'}} + [(J-1) J - J (J+1)] \frac{\hbar}{4\pi I}$$

or
$$\nu_p = \nu_0 - J \frac{\hbar}{2\pi I} \quad J = 1, 2, 3, \dots \quad \dots(9)$$

(ii) *R Branch*: Here, $\Delta J = +1$ (i.e., $J \rightarrow J + 1$)

$$\nu_R = \frac{E_{1,J+1} - E_{0,J}}{h} = \frac{1}{2\pi} \sqrt{\frac{k}{m'}} + [(J+1) (J+2) - J (J+1)] \frac{\hbar}{4\pi I}$$

or
$$\nu_R = \nu_0 + (J+1) \frac{\hbar}{2\pi I} \quad J = 0, 1, 2, 3, \dots \quad \dots(10)$$

There is no line at $\nu = \nu_0$ (the *Q* branch) because transitions for which $\Delta J = 0$ are forbidden in diatomic molecules.

The spacing between the lines in both the *P* and the *R* branch is $\Delta\nu = \frac{\hbar}{2\pi I}$.

Hence, by measuring the frequencies of these lines, the moment of inertia of the molecule and the length of the chemical bond can be calculated.

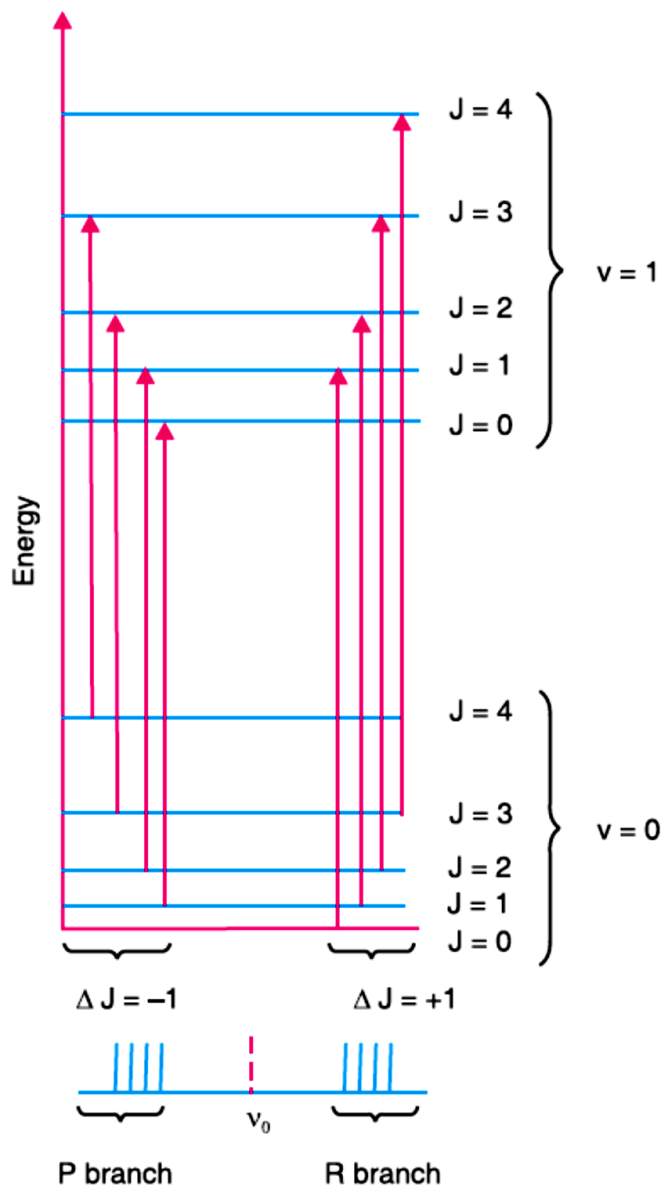


Fig. 5.2.4

Fig. 5.2.5 shows a typical vibration-rotation molecular spectrum of HBr . It is made by sending radiation from a source of continuous infrared wavelengths through a cell containing HBr and recording the absorption spectra.

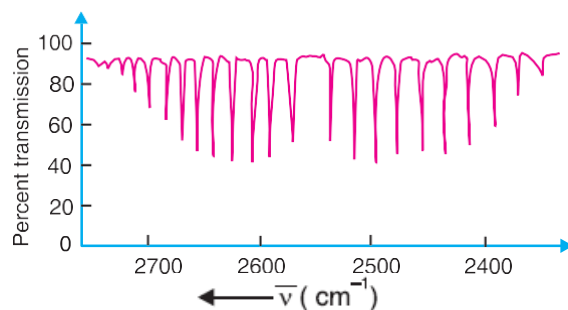


Fig.5.2.5

5.3 Electronic Spectra of Molecules

When there is enough available energy, the electronic states of the molecules can be excited. This gives rise to the most general type of transitions, rotation-vibration-electronic transitions. These produce photons of frequency

$$\nu = \frac{E_{e1} - E_{e2}}{h} + \frac{E_{v1} - E_{v2}}{h} + \frac{E_{rot1} - E_{rot2}}{h} .$$

It is the outermost electrons of the atoms composing the molecules that are involved. These transitions are energetic enough that they produce *electronic bands* in the visible and ultraviolet regions. All molecules exhibit electronic spectra, since a dipole moment change always accompanies a change in the electronic configuration of a molecule. In molecular spectra, as in atomic spectra, radiative transitions between electronic states of different total spin are forbidden.

5.4 Molecular Orbital Theory of Hydrogen Molecule Ion H_2^+

The hydrogen molecule ion H_2^+ consists of two hydrogen nuclei and one electron (Fig. 5.4.1). R is internuclear distance, r_a and r_b are distances of electron from nuclei a and b respectively.

The electron when in the neighbourhood of a is described by the atomic orbital Ψ_a centred on a . The electron when in the neighbourhood of b is described by the atomic orbital Ψ_b centred on b .

Ψ_a and Ψ_b are 1s atomic orbitals given by

$$\Psi_a = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-r_a/a_0}, \quad \Psi_b = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-r_b/a_0} \quad \dots(1)$$

a_0 is radius of Bohr's orbit.

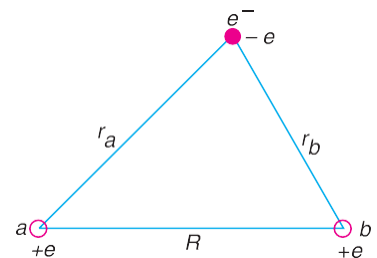


Fig. 5.4.1

A reasonable molecular orbital is a linear combination of Ψ_a and Ψ_b , i.e.,

$$\Psi = c_1\Psi_a + c_2\Psi_b \quad \dots(2)$$

Here, c_1 and c_2 are constants.

This particular form of a linear combination of atomic ‘orbitals’ making a molecular orbital is called LCAO – MO for short.

The energy E of the system is given by the Schrodinger equation

$$H\Psi = E\Psi, \quad E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \quad \dots(3)$$

The Hamiltonian of the system is given by

$$H = \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} + \frac{e^2}{4\pi\epsilon_0 R} \quad \dots(4)$$

Here, m is the mass of the electron.

Substituting the value of Ψ in Eq. (3), we get

$$E = \frac{\langle(c_1\Psi_a + c_2\Psi_b)|H|(c_1\Psi_a + c_2\Psi_b)\rangle}{\langle(c_1\Psi_a + c_2\Psi_b)|(c_1\Psi_a + c_2\Psi_b)\rangle}$$

Since the atomic orbitals Ψ_a and Ψ_b are normalized,

$$E = \frac{|c_1|^2 \langle\Psi_a|H|\Psi_a\rangle + c_1^*c_2 \langle\Psi_a|H|\Psi_b\rangle + c_2^*c_1 \langle\Psi_b|H|\Psi_a\rangle + |c_2|^2 \langle\Psi_b|H|\Psi_b\rangle}{|c_1|^2 + |c_2|^2 + c_1^*c_2 \langle\Psi_a|\Psi_b\rangle + c_2^*c_1 \langle\Psi_b|\Psi_a\rangle} \quad \dots(5)$$

The integrals,

$$\langle\Psi_a|H|\Psi_a\rangle = H_{aa}, \quad \langle\Psi_b|H|\Psi_b\rangle = H_{bb} \quad \dots(6a)$$

are known as **Coulomb integrals**.

H_{aa} and H_{bb} are the energies of the atomic orbitals Ψ_a and Ψ_b in the molecular skeleton.

$$\text{The integrals } \langle\Psi_a|H|\Psi_b\rangle = H_{ab}, \quad \langle\Psi_b|H|\Psi_a\rangle = H_{ba} \quad \dots(6b)$$

are known as **resonance or exchange integrals** and $H_{ab} = H_{ba}^*$.

$$\text{The integral } \langle\Psi_a|\Psi_b\rangle = \langle\Psi_b|\Psi_a\rangle = S \quad \dots(6c)$$

is known as **overlap integral**.

Since the selection of the wave function Ψ is arbitrary, according to the variational theorem

$$E \geq E_0 \quad \dots(7)$$

Here, E_0 is the exact ground state energy of the system.

Assuming the atomic orbitals Ψ_a and Ψ_b to be real, from Eq. (5),

$$E(c_1^2 + c_2^2 + 2c_1c_2S) = c_1^2H_{aa} + c_2^2H_{bb} + 2c_1c_2H_{ab} \quad \dots(8)$$

In order to minimise E with respect to c_1 and c_2 , it is necessary that

$$\frac{\partial E}{\partial c_1} = 0, \quad \text{and} \quad \frac{\partial E}{\partial c_2} = 0.$$

Applying the condition $\partial E/\partial c_1 = 0$ in Eq. (8), we get

$$(H_{aa} - E)c_1 + (H_{ab} - ES)c_2 = 0 \quad \dots(9)$$

The condition $\partial E/\partial c_2 = 0$ gives

$$(H_{ab} - ES)c_1 + (H_{bb} - ES)c_2 = 0 \quad \dots(10)$$

Equations (9) and (10) are known together as the **secular equations**.

These simultaneous homogeneous equations in c_1 and c_2 have non-trivial solutions only if

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES \\ H_{ab} - ES & H_{bb} - E \end{vmatrix} = 0 \quad \dots(11)$$

$$\text{or} \quad (H_{aa} - E)(H_{bb} - E) - (H_{ab} - ES)^2 = 0 \quad \dots(12)$$

Since $H_{aa} = H_{bb}$, we get

$$H_{aa} - E = \pm (H_{ab} - ES) \quad \dots(13)$$

The two roots for E are the allowed energy values of the system.

$$E_1 = \frac{H_{aa} + H_{ab}}{1 + S}, \quad E_2 = \frac{H_{aa} - H_{ab}}{1 - S} \quad \dots(14)$$

Combining Eqs. (9) and (13), we get

$$\pm (H_{ab} - ES)c_1 + (H_{ab} - ES)c_2 = 0 \quad \dots(15)$$

From Eq. (15), $c_1 = c_2$ for energy E_1 and $c_1 = -c_2$ for the energy E_2 .

The wave functions, corresponding to energies E_1 and E_2 are respectively,

$$\Psi_1 = c_1(\Psi_a + \Psi_b) \quad \text{and} \quad \Psi_2 = c_2(\Psi_a - \Psi_b) \quad \dots(16)$$

Normalization gives

$$\Psi_1 = \frac{\Psi_a + \Psi_b}{\sqrt{2 + 2S}}, \quad \Psi_2 = \frac{\Psi_a - \Psi_b}{\sqrt{2 - 2S}} \quad \dots(17)$$

The Coulomb integral

$$H_{aa} = \left\langle \Psi_a \left| \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} \right| \Psi_a \right\rangle - \left\langle \Psi_a \left| \frac{e^2}{4\pi\epsilon_0 r_b} \right| \Psi_a \right\rangle + \left\langle \Psi_a \left| \frac{e^2}{4\pi\epsilon_0 R} \right| \Psi_a \right\rangle \quad \dots(18)$$

The first term on the right is simply the ground state energy of the hydrogen atom E_H since the operator in it is the hydrogen atom Hamiltonian and Ψ_a is the one electron wave function.

The nuclear repulsion term $\frac{e^2}{4\pi\epsilon_0 R}$, is independent of the electronic coordinates.

$$\text{Let} \quad V_{aa} = \left\langle \Psi_a \left| \frac{e^2}{4\pi\epsilon_0 r_b} \right| \Psi_a \right\rangle \quad \text{and} \quad V_{ab} = \left\langle \Psi_a \left| \frac{e^2}{4\pi\epsilon_0 r_a} \right| \Psi_b \right\rangle \quad \dots(19)$$

$$H_{aa} = E_H - V_{aa} + \frac{e^2}{4\pi\epsilon_0 R} \quad \dots(20)$$

$$H_{ab} = E_H S - V_{ab} + \frac{e^2}{4\pi\epsilon_0 R} S \quad \dots(21)$$

The value of the quantities V_{aa} , V_{ab} , S and the nuclear repulsion energy $\frac{e^2}{4\pi\epsilon_0 R}$ depend on the internuclear distance R and are always positive. The overlap $S = 0$, if the two nuclei are infinitely separated and $S = 1$ if they are together.

Substituting Eqs. (20) and (21) in Eq. (14), we get

$$E_1 = E_H - \frac{V_{aa} + V_{ab}}{1 + S} + \frac{e^2}{4\pi\epsilon_0 R} \quad \dots(22)$$

and

$$E_2 = E_H - \frac{V_{aa} - V_{ab}}{1 - S} + \frac{e^2}{4\pi\epsilon_0 R} \quad \dots(23)$$

Fig. 5.4.2 shows the relative energies of molecular orbitals and their constituent atomic orbitals. The original energy state of two hydrogen atoms possess the same energy E_H . But in H^+ ion they split into two new energy states, one of lower energy (symmetric molecular state) and the other of higher energy (anti symmetric molecular state) than the original $1 - S$ state. These two states are sometimes referred to as *bonding* and *antibonding* states of the hydrogen-molecule ion.

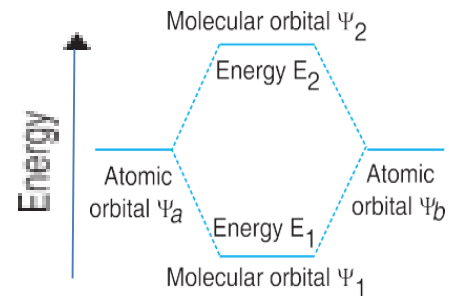


Fig. 5.4.2

Fig. 5.4.3 shows the probability density for the bonding and antibonding states.

Fig. 5.4.3(a) shows the probability density functions. Full lines represent Ψ_1^2 or Ψ_2^2 . Broken lines represent Ψ_a^2 or Ψ_b^2 .

Fig. 5.4.3(b) shows contours of equal electron density for Ψ_1^2 and Ψ_2^2

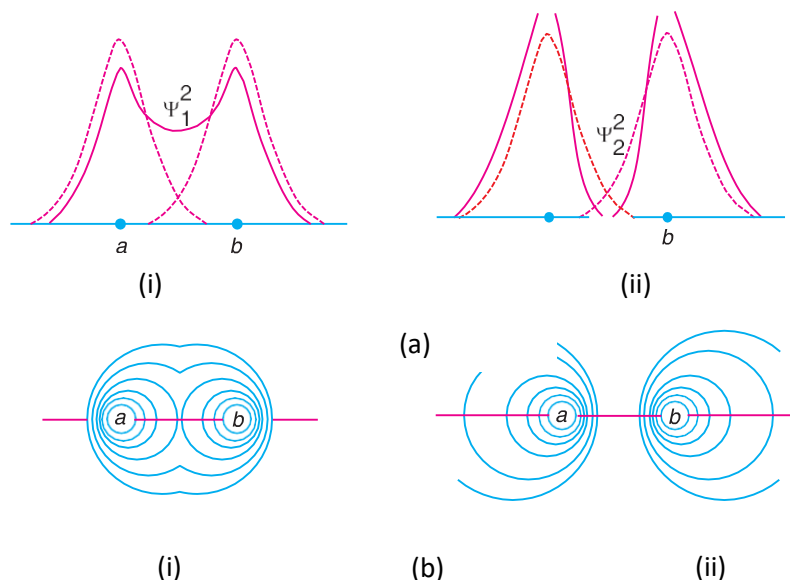


Fig. 5.4.3

Fig. 5.4.4 shows the binding (potential) energy of H_2^+ ion as a function of internuclear distance R . Antisymmetric orbital leads to an *unstable repulsive state*. Symmetric orbitals give the binding energy curve with a minimum which indicates the formation of a *stable state*. The minimum in the symmetric curve corresponds to the equilibrium distance of H^+ and H , $R=2.5 a_0$. This is the internuclear distance at which H_2^+ is most stable. The dissociation energy of H_2^+ ion is 1.77 eV. The experimental value for dissociation energy is 2.789 eV. A better agreement between theory and experiment is obtained by introducing a variational parameter in the trial wave function

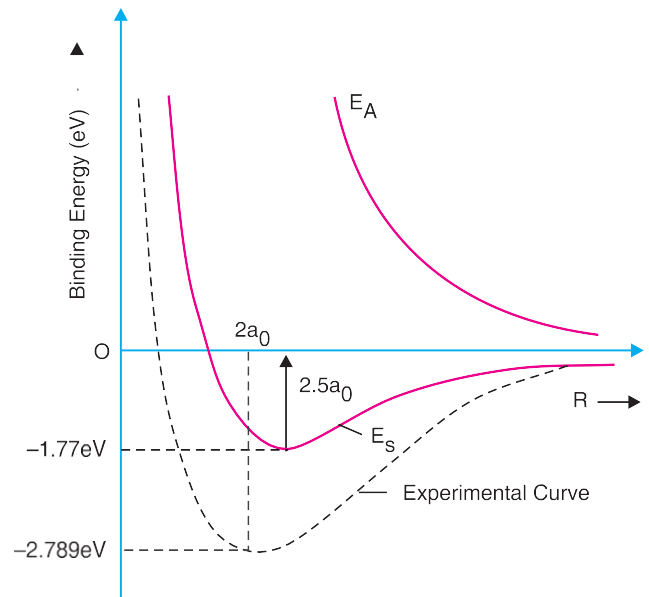


Fig. 5.4.4

5.5 Heitler-London Theory of Hydrogen Molecule

Fig. 19.28 shows the Hydrogen molecule system. It consists of two positively charged hydrogen nuclei a and b and two electrons whose coordinates are denoted by symbols 1, 2. r_{12} is the distance between two electrons 1 and 2. R is the internuclear distance. When R is large, the system may be regarded as consisting of two separated hydrogen atoms.

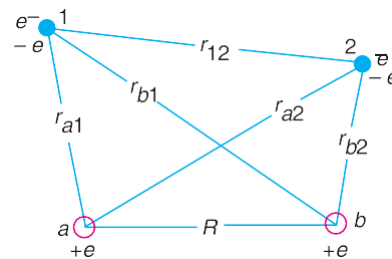


Fig. 5.5.1

The Schrodinger equations are

$$H_a(1) \Psi_a(1) = E_a \Psi_a(1) \quad H_b(2) \Psi_b(2) = E_b \Psi_b(2) \dots(1)$$

Here, $E_a = E_b = E_H$, the ground state energy of the hydrogen atoms and $\Psi_a(1)$ and $\Psi_b(2)$ are the 1s hydrogenic wave functions.

$$H_a(1) = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 r_{a1}}, \quad H_b(2) = -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{b2}} \dots(2)$$

2

When the two atoms are brought closer and if there is no interaction between the two, the total Hamiltonian of the system.

$$H = H_a(1) + H_b(2) \dots(3)$$

It amounts to assuming that electron 1 is moving about proton a and electron 2 is moving about proton b .

$$\begin{aligned} [H_a(1) + H_b(2)] \Psi_a(1) \Psi_b(2) &= H_a(1) \Psi_a(1) \Psi_b(2) + H_b(2) \Psi_a(1) \Psi_b(2) \\ &= E_a \Psi_a(1) \Psi_b(2) + E_b \Psi_a(1) \Psi_b(2) \\ &= (E_a + E_b) \Psi_a(1) \Psi_b(2) \end{aligned} \quad \dots(4)$$

So this system of two hydrogen atoms can be described by the wave function

$$\Psi_1(1,2) = \Psi_a(1) \Psi_b(2) \quad \dots(5)$$

with energy eigenvalue $E_a + E_b$.

If the electron 1 is associated with atom b and electron 2 is associated with atom a , an equally good wave function with the same energy is

$$\Psi_2(2,1) = \Psi_a(2) \Psi_b(1) \quad \dots(6)$$

$\Psi_1(1,2)$ and $\Psi_2(2,1)$ are eigen functions of the Hamiltonian ($H_a + H_b$) with eigenvalue ($E_a + E_b$). The two functions differ only in the interchange of the two electrons between the orbitals. Hence, this degeneracy is called the **exchange degeneracy**. The wave functions of the two electron system, must be a linear combination of $\Psi_1(1,2)$ and $\Psi_2(2,1)$.

The Hamiltonian operator for the hydrogen molecule is

$$\begin{aligned} H = \left(-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 r_{a1}} - \frac{e^2}{4\pi\epsilon_0 r_{b1}} \right) + \left(-\frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{b2}} - \frac{e^2}{4\pi\epsilon_0 r_{a2}} \right) \\ + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R} \end{aligned} \quad \dots(7)$$

or
$$H = H_a(1) + H_b(2) + H' + \frac{e^2}{4\pi\epsilon_0 R} \quad \dots(8)$$

Here,
$$H' = -\frac{e^2}{4\pi\epsilon_0 r_{b1}} - \frac{e^2}{4\pi\epsilon_0 r_{a2}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad \dots(9)$$

An exchange of the two electrons leaves the Hamiltonian H unchanged. So the wave functions must either be symmetric or antisymmetric with respect to such an exchange.

The symmetric Ψ_s and antisymmetric Ψ_{as} combinations are

$$\Psi_s = N_s [\Psi_a(1) \Psi_b(2) + \Psi_a(2) \Psi_b(1)] \quad \dots(10)$$

$$\Psi_{as} = N_a [\Psi_a(1) \Psi_b(2) - \Psi_a(2) \Psi_b(1)] \quad \dots(11)$$

Here, N_s and N_a are normalization constants.

Normalization condition gives

$$N_s^2 = \frac{1}{2(1+S^2)}, \quad N_a^2 = \frac{1}{2(1-S^2)} \quad \dots(12)$$

Here, $S = \langle \Psi_a | \Psi_b \rangle = \langle \Psi_b | \Psi_a \rangle \quad \dots(13)$

The inclusion of electron spin and Pauli's principle leads to the Heitler-London wave functions

$$N_s[\Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad \dots(14)$$

$$N_a[\Psi_a(1)\Psi_b(2) - \Psi_a(2)\Psi_b(1)] \begin{cases} \alpha(1)\alpha(2) \\ \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)] \\ \beta(1)\beta(2) \end{cases} \quad \dots(15)$$

The first one corresponds to a singlet ($S = 0$) and the second one to a triplet ($S = 1$). As the Hamiltonian does not contain spin terms, the energy is not affected by the inclusion of spin part. The space parts alone can then be taken as the unperturbed wave functions for the evaluation of energy.

A perturbation calculation is then carried out with H' (Eq. 9) as perturbation. The first order correction to the energy E' is the diagonal matrix element of the perturbing Hamiltonian corresponding to the unperturbed wave functions. Then

$$\begin{aligned} E'_1 &= N_s^2 \langle \Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1) | H' | (\Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1)) \rangle \\ &= \frac{(2J + 2K)}{2(1 + S^2)} = \frac{J + K}{1 + S^2} \quad \dots(16) \end{aligned}$$

Here, $J = \langle \Psi_a(1)\Psi_b(2) | H' | \Psi_a(1)\Psi_b(2) \rangle \quad \dots(17)$

J is called *coulomb integral*.

$$K = \langle \Psi_a(1)\Psi_b(2) | H' | \Psi_a(2)\Psi_b(1) \rangle \quad \dots(18)$$

K is called *exchange integral*.

The energy of the singlet state corrected to first order

$$E_s = 2E_H + \frac{J + K}{1 + S^2} + \frac{e^2}{4\pi\epsilon_0 R} \quad \dots(19)$$

Singlet state is the *stable state*.

The first order correction to the triplet state

$$E'_2 = \frac{J - K}{1 - S^2} \quad \dots(20)$$

The energy of the triplet state

$$E_a = 2E_H + \frac{J - K}{1 - S^2} + \frac{e^2}{4\pi\epsilon_0 R} \quad \dots(21)$$

Experimental and theoretical results :

Fig. 5.5.2 shows the plots of energies E_1' and E_2' against internuclear distance R . The equilibrium internuclear distance r_0 is the one corresponding to the minimum of the Ψ_S curve. The theoretical value of 0.085 nm for r_0 is high compared to the experimental value of 0.074 nm.

The state characterised by the Ψ_{as} combination corresponds to repulsion for all values of R .

Fig. 5.5.3. shows distribution of charge density of electron cloud in (a) stable and (b) unstable States of a hydrogen molecule.

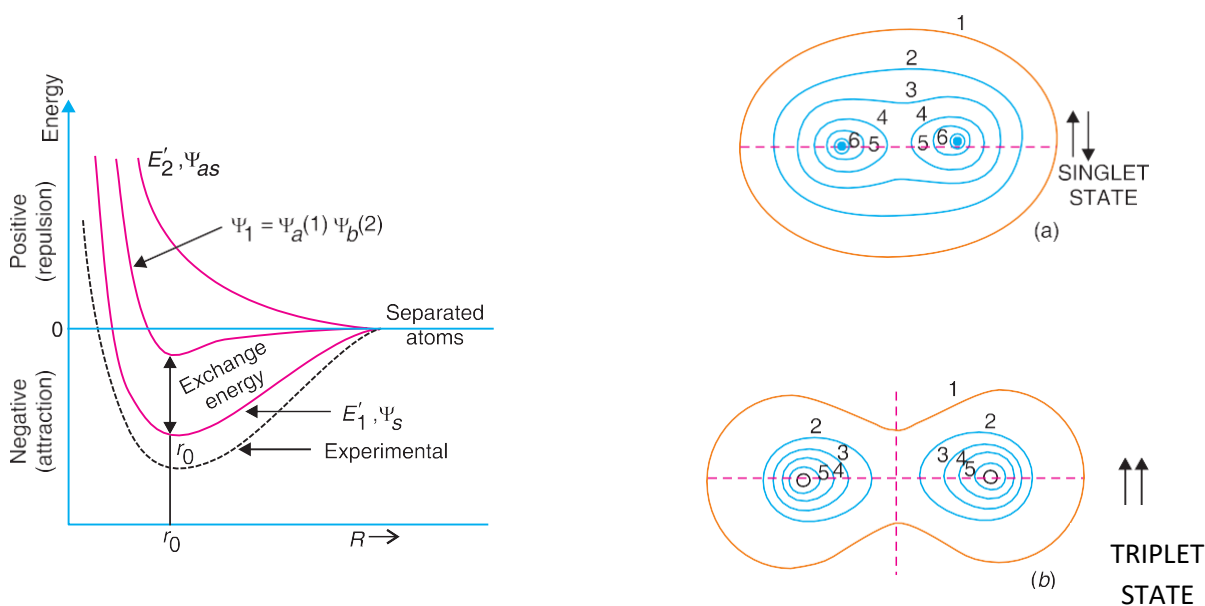


Fig. 5.5.2

Fig. 5.5.3