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SCHOOL OF SCIENCE AND HUMANITIES

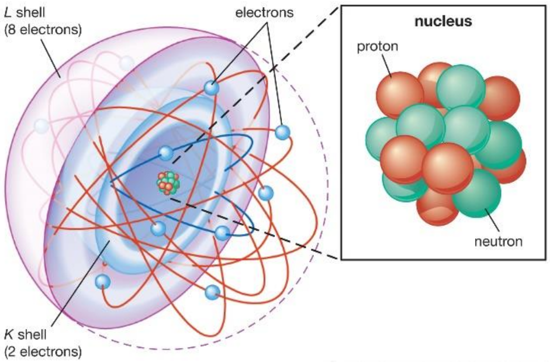
DEPARTMENT OF PHYSICS

UNIT – I – Concept of the Atom – SPH1311

1.1 Brief introduction to history of atom

Introduction

Atoms are very tiny. They could not be seen before scanning tunnelling microscopes were invented in 1981. However, the idea of atoms goes back to ancient Greece. That's where this brief history of the atom begins.



Democritus: (460 – 370 BC)

Democritus was a Greek philosopher who was the first person to use the term atom (atomos: meaning indivisible). He thought that if you take a piece of matter and divide it and continue to divide it you will eventually come to a point where you could not divide it any more. This fundamental or basic unit was what Democritus called an atom.

He called this the theory of the universe:

- **All matter consists of atoms, which are bits of matter too small to be seen.**
- **There is an empty space between atoms**
- **Atoms are completely solid**
- **Atoms have no internal structure**
- **Each atom (of a different substance) is different in size, weight and shape**

John Dalton: (1766-1844)

John Dalton was the first to adapt Democritus' theory into the first modern atomic model.

John Dalton's Atomic Model:

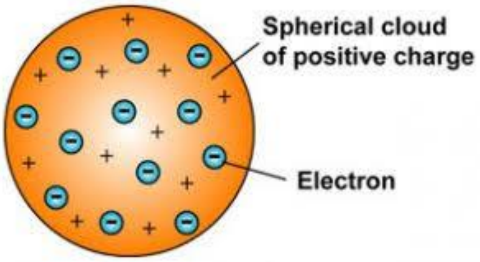
- **All matter consists of tiny particles called atoms**
- **Atoms are indestructible and unchangeable**
- **Elements are characterized by the weight of their atoms**
- **When elements react, it is their atoms that have combined to form new compounds**

Postulates of Dalton's Atomic Theory:

- **All matter is composed of extremely small particles called Atoms.**
- **All atoms of a given element are identical, having the same mass, size and chemical properties.**
- **All atoms of different elements are different.**
- **Atoms cannot be created, divided into smaller particles or destroyed.**
- **Law of definite proportions: Different atoms combine in simple whole number ratios to form compounds.**

J.J Thomson: 1856

J.J Thomson was a physicist who is credited for discovering the electron. He used his research on cathode ray tube technology in this discovery.



Using what he had discovered, Thomson predicted what an atom should look like. These are the key points to Thomson's Atomic Model:

1. Because of its design this model is known as the plum pudding model

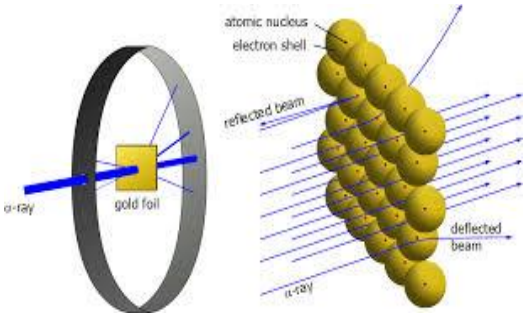
2. Each atom is a sphere filled with positively charged 'fluid'. This resembles the sticky jam part of a pudding.

3. Corpuscles (later called electrons), are the negatively charged particles suspended in this 'fluid'. This resembles the plums in the pudding.

4. He did not predict the movement of these electrons

Ernest Rutherford: 1871

Ernest Rutherford was not convinced about the model of the atom proposed by Thomson. He thus set up his now famous Gold Foil Experiment.



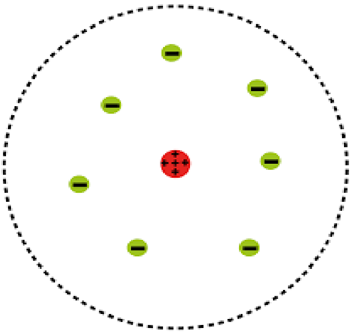
1. He fired alpha particles (positively charged) at a gold foil.

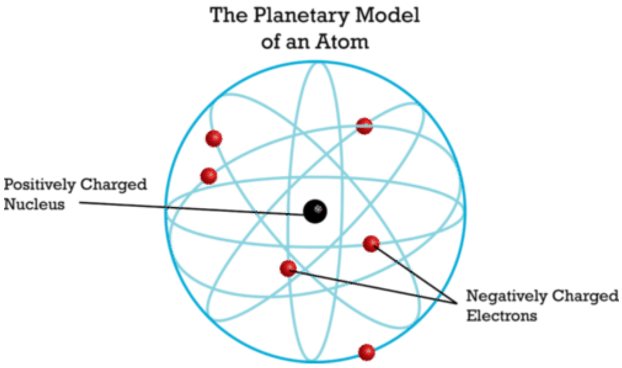
2. He measured the deflection as the particles came out the other side.

3. Most of the particles did not deflect at all. Every now and then a particle would deflect all the way back.

4. He said that there must be a positive centre of the foil. He called this centre the nucleus

Rutherford's Atomic Model





1. **The nucleus of the atom is a dense mass of positively charged particles.**
2. **The electrons orbit the nucleus**
3. **A problem raised was: Why are the negatively charged particles not attracted by the positively charged nucleus**
4. **Rutherford stated that the atom was like a mini solar system and that the electrons orbited the nucleus in a wide orbit. That is why it is known as the planetary model.**

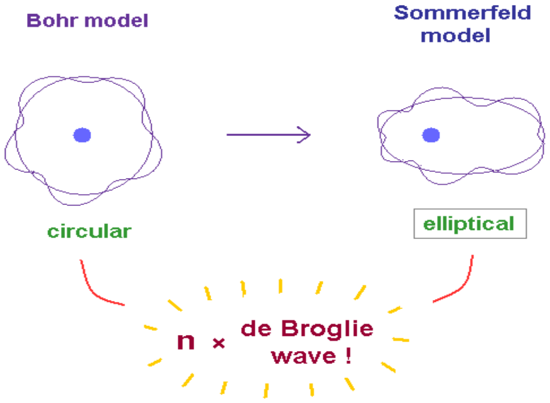
Niels Bohr: 1910

Niels Bohr agreed with the planetary model of the atom, but also knew that it had a few flaws. Using his knowledge of energy and quantum physics he was able to perfect Rutherford's model. He was able to answer why the electrons did not collapse into the nucleus.

Bohr's Atomic Model

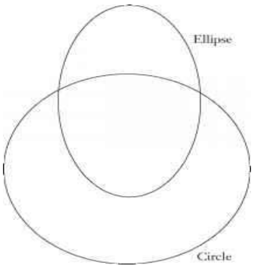
1. **Electrons orbit the nucleus in orbits that have a set size and energy.**
2. **The lower the energy of the electron, the lower the orbit.**
3. **This means that as electrons fill up the orbitals, they will fill the lower energy level first.**
4. **If that energy level is fill (or at capacity), a new energy level will begin.**
5. **Radiation is when an electron moves from one level to another.**

Sommerfeld's extension model

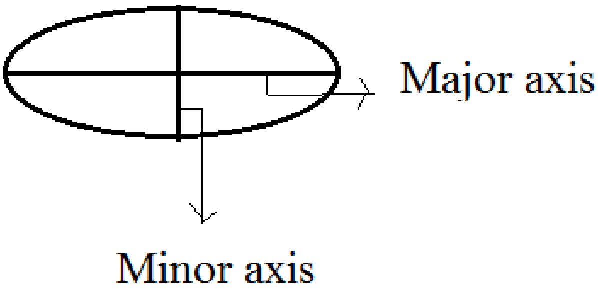


Postulates of Sommerfeld model

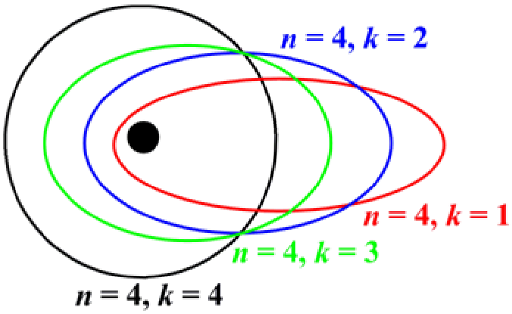
1. **The orbits may be both circular or elliptical**



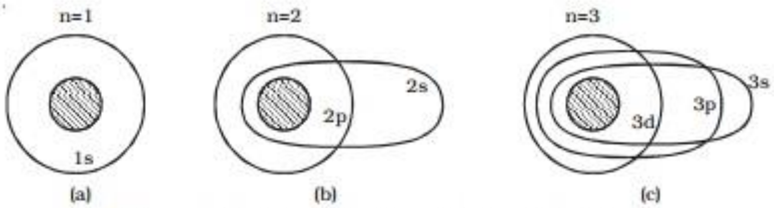
2. **When path is elliptical, then there are two axis – major and minor axis., When length of major and minor axis become equal then orbit is circular.**



3. **The angular momentum of electron moving in an elliptical orbit is kh/2π.**



4. **Sommerfeld suggested that orbits are made up of sub energy levels . These are s,p,d,f. These sub shells possess slightly different energies.**



(a) (b) (c)

Fig Various sub-shells for the electrons

5. **When an electron jumps from one orbit to another orbit, the difference of energy (ΔE) depends upon sub energy levels.**

6. **It explains the splitting of individual spectral lines of hydrogen & thus fine spectrum. It could not predict the exact number of lines which are actually present in the fine spectrum.**

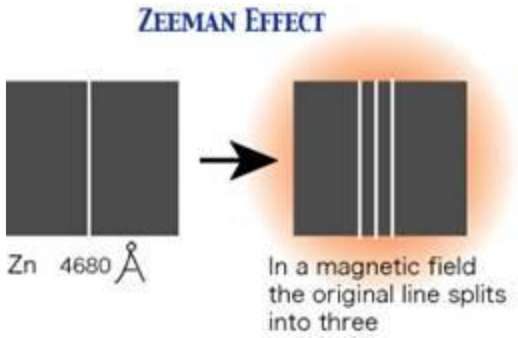
Defects of Sommerfeld atomic model-

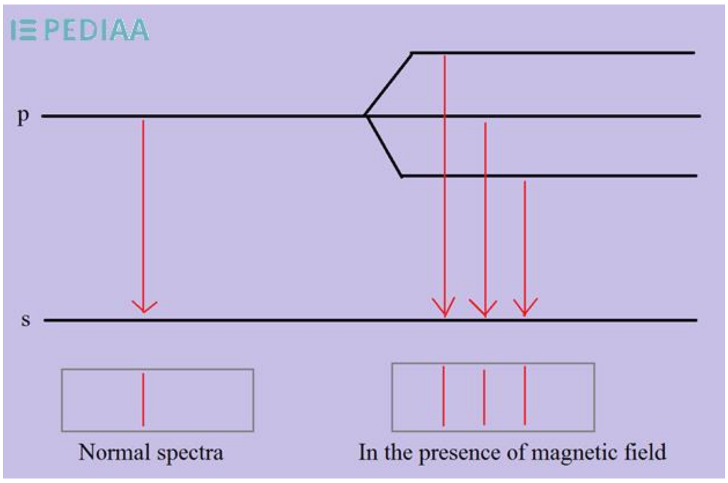
- This model does not explain the behavior of system having more than one electron.

- This model does not explain the Zeeman and Stark effect.

Zeeman effect:

Zeeman effect, in physics and astronomy, the splitting of a spectral line into two or more components of slightly different frequency when the light source is placed in a magnetic field. It was first observed in 1896 by the Dutch physicist Pieter Zeeman as a broadening of the yellow D-lines of sodium in a flame held between strong magnetic poles. Later the broadening was found to be a distinct splitting of spectral lines into as many as 15 components.





Zeeman effect Vs Stark effect:

Zeeman effect	**Stark effect**
Zeeman effect describes the splitting of the spectral lines of an atom in the presence of a strong magnetic field.	**Stark effect is the splitting of the spectral lines observed when the radiating atoms, ions, or molecules are subjected to a strong electric field.**
Can be observed in an applied magnetic field	**Can be observed in an applied electric field**
Result of the interaction between the magnetic moment of the atom and the external magnetic field	**Arises due to the interaction between the electric moment of the atom and the external electric field**

1.2 Spectral Series of Hydrogen Atom

It has been shown that the energy of the outer orbit is greater than the energy of the inner ones. When the hydrogen atom is subjected to external energy, the electron jumps from lower energy state to higher energy state i.e., the hydrogen atom is excited. The excited state is not stable hence the electron returns to its ground state in abt 10^{-8} secs. The excess of energy is now radiated in the form radiations of different wavelengths. The different wavelengths constitute spectral series which are characteristic of atom emitting them.

The wavelengths of the different members of the series can be found from the following relation

$$\frac{1}{\lambda} = R_H\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

$$R_H = 1.090678 \times 10^7 m^{-1}$$

(a) Lyman series: The series consists of all wavelengths which are emitted when an electron jumps from the outer orbit to the first orbit i.e., the electronic jumps to K give rise to Lyman series.
Here n1 = 1 and n2 = 2,3,4, ………
The wavelengths of different members of Lyman series are:
(i) First member:
In this case n1 = 1, n2 =2, hence

$$\frac{1}{\lambda} = R\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{3R}{4}$$

$$\lambda = \frac{4}{3R} \quad \text{or } \lambda = \frac{4}{3 X 10.97 X 10^6} = 1216 \text{ X } 10^{-10} \text{ m} = 1216 \text{ A}^{o}$$

This series of wavelength lies in ultraviolet region.

(b) Balmer series: This series consists of all wavelengths which are emitted when an electron jumps from an outer orbit to the second orbit i.e., the electronic jumps to L orbit give to Balmer series.

n1 = 2 and n2 = 3,4, 5,………

The wavelengths of different members of Balmer series are:

(ii) First member:

In this case n1 = 2, n2 =3, hence

$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5R}{36}$$

$$\lambda = \frac{36}{5R} \quad \text{or } \lambda = \frac{36}{5\ X\ 10.97\ X\ 10^6} = 6563\ \text{X}\ 10^{-10}\ \text{m} = 6563\ \text{A}^o$$

This series of wavelength lies in visible and near ultraviolet region.

(c) Paschen series: This series consists of all wavelengths which are emitted when an electron jumps from an outer orbit to the third orbit i.e., the electronic jumps to M orbit give rise to Paschen series.

n1 = 3 and n2 = 4, 5, 6,………

The wavelengths of different members of Paschen series are:

(iii) First member:

In this case n1 = 2, n2 =3, hence

$$\frac{1}{\lambda} = R\left[\frac{1}{3^2} - \frac{1}{n_2^2}\right] \text{ where n2 = 4, 5, 6, …….}$$

For first member, the wavelength is 18750 A^o. This series lies in infra-red region.

(d) Brackett series: This series consists of all wavelengths which are emitted when an electron jumps from an outer orbit to the fourth orbit i.e. the electronic jumps to N orbit give rise to Brackett series.

n1 = 4 and n2 = 5, 6, 7,………

The wavelengths of different members of this series can be obtained from the formula:

$$\frac{1}{\lambda} = R\left[\frac{1}{4^2} - \frac{1}{n_2^2}\right] \text{ where } n_2 = 5, 6, 7, \text{ ………}$$

This series lies in the infra-red region of the spectrum.

(e) **Pfund series: This series consists of all wavelengths which are emitted when an electron jumps from an outer orbit to the fifth orbit i.e. the electronic jumps to O orbit give rise to Pfund series.**

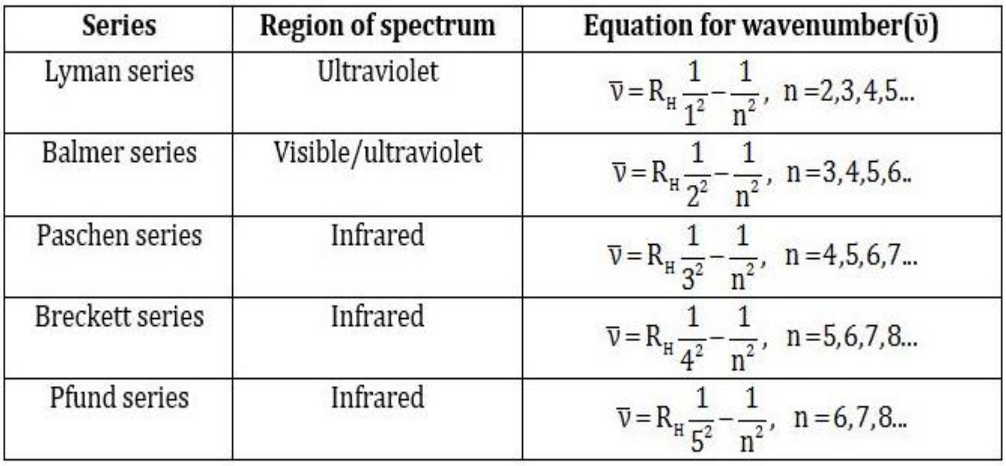
n1 = 5 and n2 = 6, 7, 8,………

The wavelengths of different members of this series can be obtained from the formula:

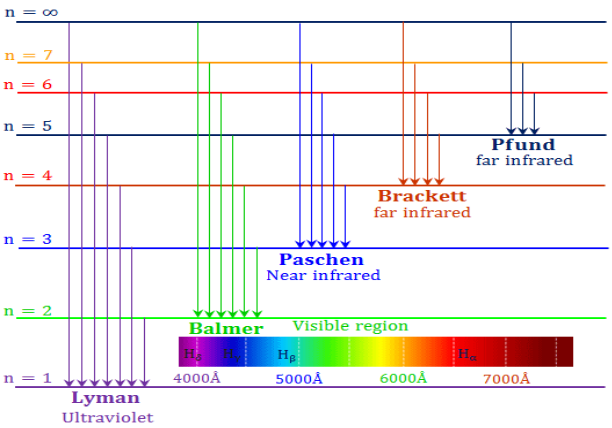
$$\frac{1}{\lambda} = R\left[\frac{1}{5^2} - \frac{1}{n_2^2}\right] \quad \text{where } n_2 = 6, 7, 8, \ldots\ldots$$

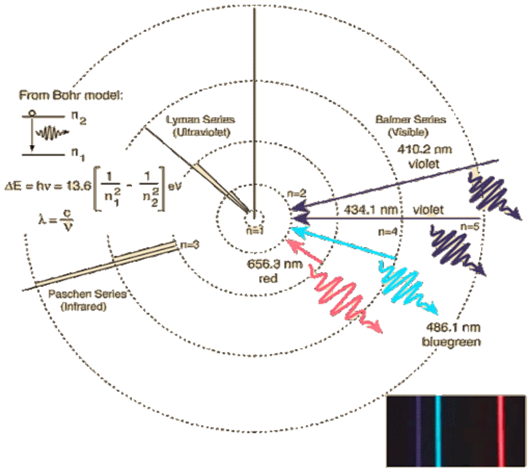
This series lies in the infra-red region of the spectrum.

The results are tabulated below:



Series	Region of spectrum	Equation for wavenumber($\bar{\nu}$)
Lyman series	Ultraviolet	$\bar{\nu}=R_H \frac{1}{1^2}-\frac{1}{n^2}$, n =2,3,4,5...
Balmer series	Visible/ultraviolet	$\bar{\nu}=R_H \frac{1}{2^2}-\frac{1}{n^2}$, n =3,4,5,6..
Paschen series	Infrared	$\bar{\nu}=R_H \frac{1}{3^2}-\frac{1}{n^2}$, n =4,5,6,7...
Breckett series	Infrared	$\bar{\nu}=R_H \frac{1}{4^2}-\frac{1}{n^2}$, n =5,6,7,8...
Pfund series	Infrared	$\bar{\nu}=R_H \frac{1}{5^2}-\frac{1}{n^2}$, n =6,7,8...



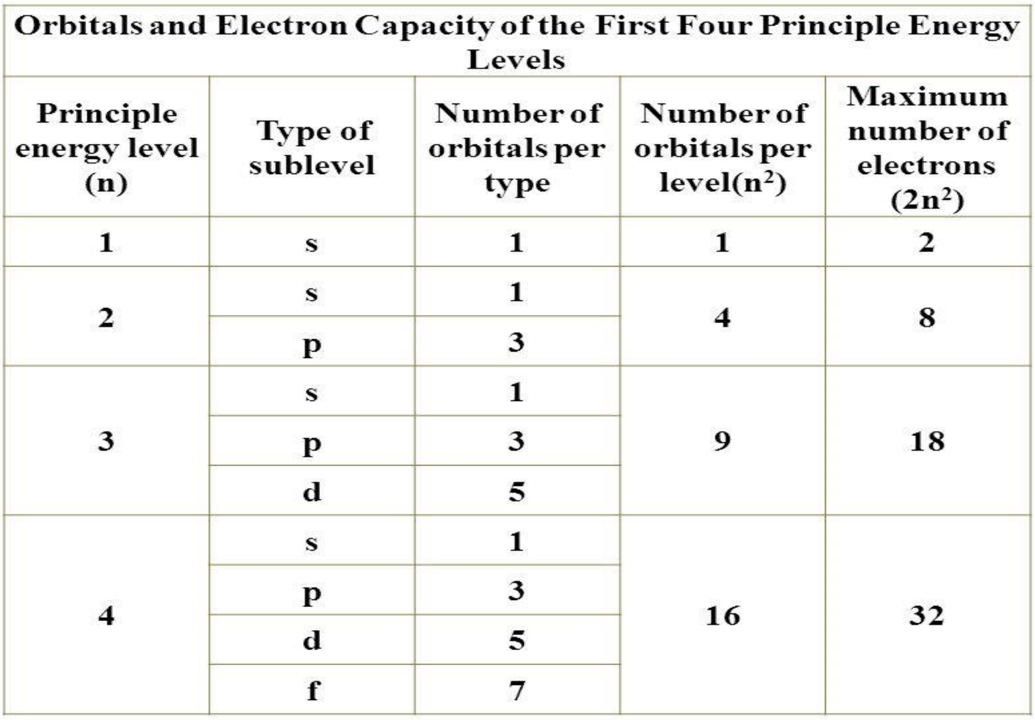


Energy level diagram **Orbit diagram**

1.3 Electronic Configuration and Quantum Numbers:

- **The electron configuration of an atom is the representation of the arrangement of electrons distributed among the orbital shells and subshells.**
- **The electron configuration is used to describe the orbitals of an atom in its ground state, but it can also be used to represent an atom that has ionized into a cation or anion by compensating with the loss of or gain of electrons in their subsequent orbitals.**
- **Many of the physical and chemical properties of elements can be correlated to their unique electron configurations.**
- **The valence electrons, electrons in the outermost shell, are the determining factor for the unique chemistry of the element.**

Electron configurations are the summary of where the electrons are around a nucleus. Each neutral atom has a number of electrons equal to its number of protons and place those electrons into an arrangement around the nucleus that indicates their energy and the shape of the orbital in which they are located. Here is a summary of the types of orbitals and how many electrons each can contain:



Orbitals and Electron Capacity of the First Four Principle Energy Levels

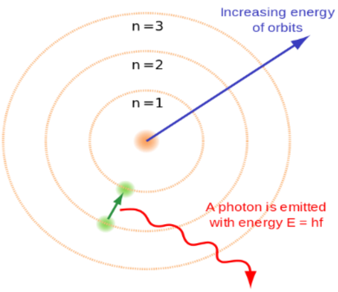
Principle energy level (n)	Type of sublevel	Number of orbitals per type	Number of orbitals per level(n^2)	Maximum number of electrons ($2n^2$)
1	s	1	1	2
2	s	1	4	8
	p	3		
3	s	1	9	18
	p	3		
	d	5		
4	s	1	16	32
	p	3		
	d	5		
	f	7		

Need 2 electrons to fill an s orbital, 6 electrons to fill a p orbital, 10 electrons to fill a d orbital and 14 electrons to fill the f orbital.

Quantum Number:

An atom consists of a large number of orbitals which are distinguished from each other on the basis of their shape, size and orientation in space. The orbital characteristics are used to define the state of an electron completely and are expressed in terms of three numbers as stated, Principal quantum number, Azimuthal quantum number and Magnetic quantum number and Spin Quantum number.

Quantum number are those numbers that designate and distinguish various atomic orbitals and electrons present in an atom. A set of four numbers through which we can get the complete information about all the electrons in an atom, be it energy, location, space, type of orbital occupied, and even the orientation of that orbital is called Quantum Numbers.



Principal Quantum Number

The Principal Quantum Number represents the principal energy level or shell in which an electron revolves around the nucleus. It is denoted by the letter n and can have any integral value except the 0 i.e. n = 1, 2, 3, 4 … ….etc. The energies of the various principal shells will follow the sequence as :

K < L < M < N < O…..

1 < 2 < 3 < 4 < 5…….

Azimuthal Quantum Number

Azimuthal quantum number, also known as orbital quantum number determines the subshell to which an electron belongs. As a matter of result, the number of electronic jump increases and the number of lines at the same time.

- For a given value of n, it can have any integral value ranging from 0 to n – 1.
- For the 1st Shell, say K, n =1, you can have only one value i.e. l = 0
- For the 2nd Shell, say L, n = 2, you can have two values i.e. l = 0 and 1
- For the 3rd Shell, say M, n = 3, you can have three values i.e. l = 0, 1 and 2

For the 4th shells, say N, n = 4, you can have 4 values i.e. l = 0, 1, 2 and 3.

Magnetic Quantum Number

Magnetic Quantum Number denoted by the symbol m is what represents the orientation of atomic orbital in space. The value of the Magnetic Quantum Number, m, depends on the value of l. Magnetic Quantum Number can have a total number of (2l + 1).

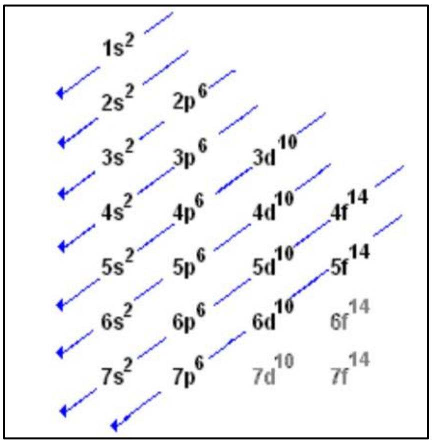
Sublevel	l	m_l
s	0	0
p	1	-1, 0, +1
d	2	-2, -1, 0, +1, +2
f	3	-3, -2, -1, 0, +1, +2, +3

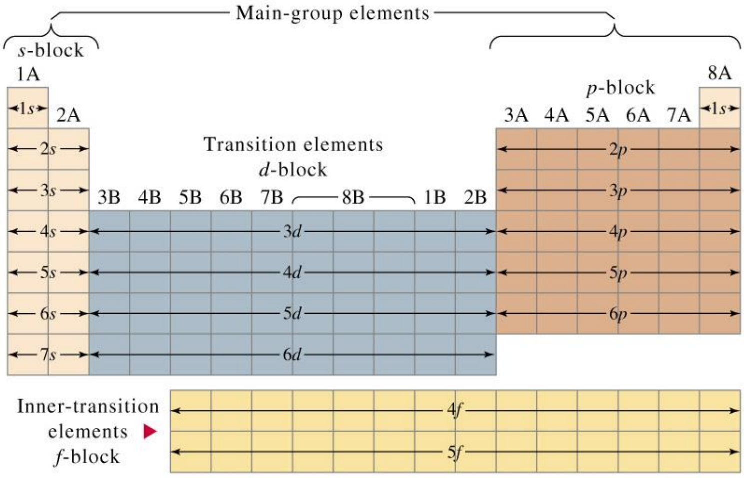
Spin Quantum Number

Spin Quantum Number represents the direction of the spin of the electrons. This can either be in the direction of clockwise or even anti-clockwise. Spin Quantum Number is denoted by the symbol s. It can have about only two values i.e. +1/2 or -1/2

Order of Fill

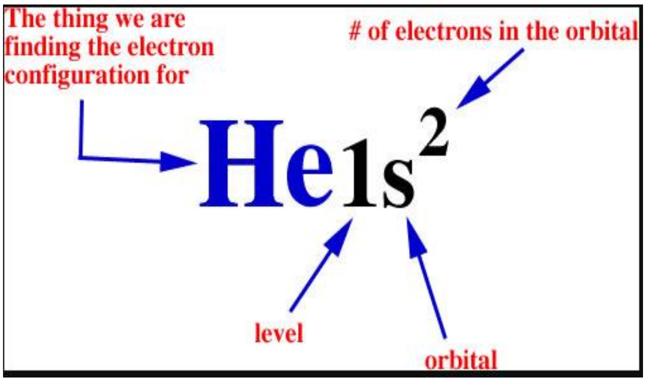
The order in which electrons are placed into the orbitals is based on the order of their energy. This is referred to as the Aufbau principle. The lowest energy orbitals fill first. Just like the quantum numbers themselves this order was determined by calculation and is summarized by the following chart:





How to Write an Electron Configuration

The symbols used for writing the electron configuration start with the shell number (n) followed by the type of orbital and finally the superscript indicates how many electrons are in the orbital.



For example:

Looking at the periodic table, you can see that Oxygen has 8 electrons. Based on the order of fill above, these 8 electrons would fill in the following order 1s, 2s and then 2p. So Oxygen's electron configuration would be O $1s^2 2s^2 2p^4$.

Periodic Properties

The important thing about electronic configurations is their relationship to the periodic table. Basically the periodic table was constructed so that elements with similar electron configurations would be aligned into the same groups (columns).

$1s^1$																	$1s^2$
$2s^1$	$2s^2$											$2p^1$	$2p^2$	$2p^3$	$2p^4$	$2p^5$	$2p^6$
$3s^1$	$3s^2$											$3p^1$	$3p^2$	$3p^3$	$3p^4$	$3p^5$	$3p^6$
$4s^1$	$4s^2$	$3d^1$	$3d^2$	$3d^3$	$3d^5$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^{10}$	$3d^{10}$	$4p^1$	$4p^2$	$4p^3$	$4p^4$	$4p^5$	$4p^6$
$5s^1$	$5s^2$	$4d^1$	$4d^2$	$4d^4$	$4d^5$	$4d^5$	$4d^7$	$4d^8$	$4d^{10}$	$4d^{10}$	$4d^{10}$	$5p^1$	$5p^2$	$5p^3$	$5p^4$	$5p^5$	$5p^6$
$6s^1$	$6s^2$		$5d^2$	$5d^3$	$5d^4$	$5d^5$	$5d^6$	$5d^7$	$5d^9$	$5d^{10}$	$5d^{10}$	$6p^1$	$6p^2$	$6p^3$	$6p^4$	$6p^5$	$6p^6$
$7s^1$	$7s^2$		$6d^2$	$6d^3$	$6d^4$	$6d^5$	$6d^6$	$6d^7$	$6d^8$	$6d^{10}$	$6d^{10}$	$7p^1$	$7p^2$	$7p^3$	$7p^4$	$7p^5$	$7p^6$

$5d^1$	$4f^1$	$4f^3$	$4f^4$	$4f^5$	$4f^6$	$4f^7$	$4f^7$	$4f^9$	$4f^{10}$	$4f^{11}$	$4f^{12}$	$4f^{13}$	$4f^{14}$	$4f^{14}$
$6d^1$	$6d^2$	$5f^2$	$5f^3$	$5f^4$	$5f^6$	$5f^7$	$5f^7$	$5f^9$	$5f^{10}$	$5f^{11}$	$5f^{12}$	$5f^{13}$	$5f^{14}$	$5f^{14}$

The periodic table demonstrates how the configuration of each element was aligned.

The configuration of an element gives the element its properties and similar configurations yield similar properties.

n	l	m_l	m_s	Number of orbitals	Orbital Name	Number of electrons	Total Electrons
1 **(K shell)**	0	0	½ - ½	1	1*s*	2	2
2 **(L Shell)**	0	0	½ - ½	1	2*s*	2	8
	1	-1, 0, +1	½ - ½	3	2*p*	6	
3 **(M-shell)**	0	0	½ - ½	1	3*s*	2	18
	1	-1, 0, +1	½ - ½	3	3*p*	6	
	2	-2, -1, 0, +1, +2	½ - ½	5	3*d*	10	
4 **(L-shell)**	0	0	½ - ½	1	4*s*	2	32
	1	-1, 0, +1	½ - ½	3	4*p*	6	
	2	-2, -1, 0, +1, +2	½ - ½	5	4*d*	10	
	3	-3, -2, -1, 0, +1, +2, +3	½ - ½	7	4*f*	14	

Quantum Number Chart

1.4 Electronegativity(χ)

Definition

Tendency of an atom to attract electrons towards itself (attract bonding pair of electrons)

Factors affecting electronegativity

- **atomic number**
- **charge of nucleus**
- **size of the atom**
- **attraction of electron decreases as the distance from the nucleus increases; larger atom have lesser attraction to the atom**

Reason for increase in electronegativity

- number of protons in the nucleus increases - EN/attraction increases

- EN increases left to right in a row in the periodic table and bottom to top in column

Importance

- **determines the nature of bonds between atoms**
- **differences in EN between atoms indicate the type of bond**
- **used to derive – Ionization Energy and Electron Affinity**

Eg: NaCl – ionic bond ; Na^+ - sodium cation ; Cl^- - chlorine anion

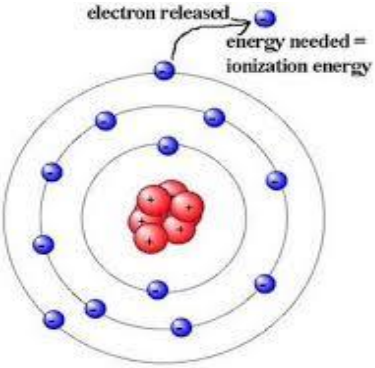
- EN of Na – 0.93 and EN of Cl – 3.16

Ionization Energy

- **amount of energy required to remove an electron from an atom.**

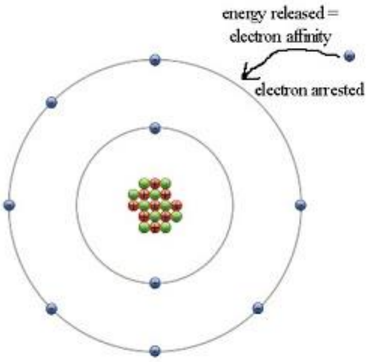
$$X(g) + \text{energy} \rightarrow X^+(g) + e^-$$

- **All ionization energies are positive values because all of these removals require input of energy.**
- **The more electronegative the element, the higher the ionization energy.**



Electron Affinity

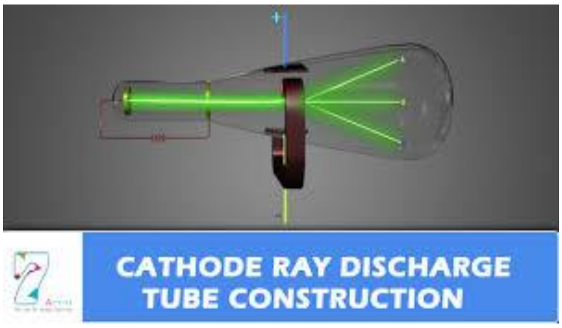
- **Electron Affinity of an element is the amount of energy gained or released with the addition of an electron.**
- **Eelectronegativity and Electron Affinity increases in the same pattern in the periodic table. Left to right and bottom to top.**
- **measure of the attraction between the incoming electron and the nucleus - the stronger the attraction, the more energy is released.**
- **The factors which affect this attraction are exactly the same as those relating to ionization energies - nuclear charge, distance and screening.**



1.5 Cathode rays

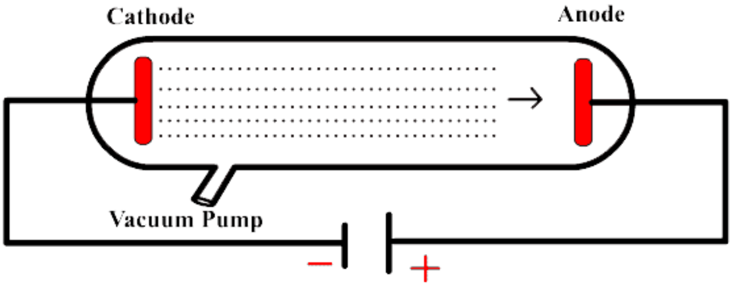
Introduction:

Cathode rays (e-beam) are streams of electrons observed in discharge 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).
They were first observed in 1869 by German physicist Julius Plücker and Johann Wilhelm Hittorf, and were named in 1876 by Eugen Goldstein, or cathode rays.
In 1897, British physicist J. J. Thomson showed that cathode rays were composed of a negatively charged particle, which was later named the electron.



Cathode Ray Tube :

- A Crookes tube - experimental electrical discharge tube (vacuum) - cathode rays, streams of electrons, were discovered.
- English physicist William Crookes -1869-1875.
- Crookes tube consists of a partially evacuated glass bulb of various shapes, with two metal electrodes, the cathode and the anode, one at either end.
- When a high voltage is applied between the electrodes, cathode rays (electrons) are projected in straight lines from the cathode.
- It was used by Crookes, Johann Hittorf, Julius Plücker, Eugen Goldstein, Heinrich Hertz, Philipp Lenard and others to discover the properties of cathode rays.
- culminating in J.J. Thomson’s 1897 identification of cathode rays as negatively charged particles named *electrons*. Crookes tubes are now used only for demonstrating cathode rays.
- Wilhelm Röntgen discovered X-rays using the Crookes tube in 1895.



Explanation

Magnetic Deflection:

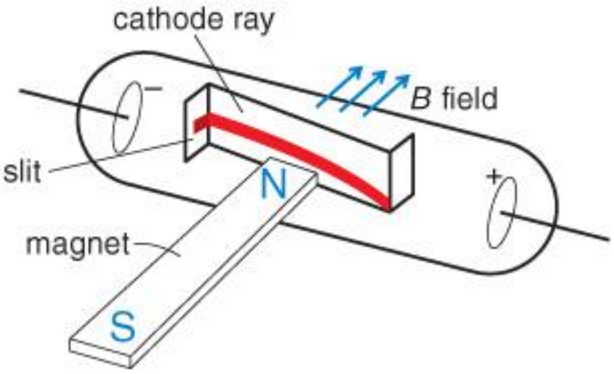
Cathode rays are subject to the Lorentz force, which governs the motion of charged particles within magnetic fields.
The force exerted on a charge *q* moving with speed v within a magnetic field B and electric field E, is calculated with the following formula:

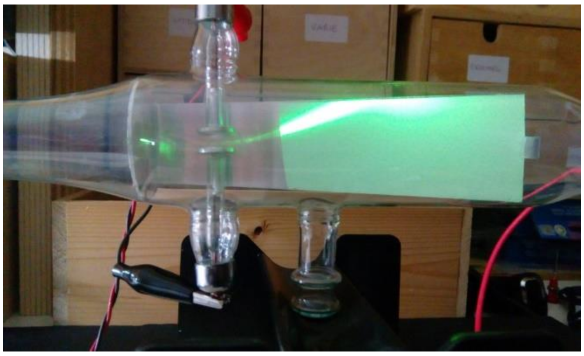
$$\vec{F} = \underset{\text{Electric force}}{q\vec{E}} + \underset{\text{Magnetic force}}{q\vec{v}\ x\ \vec{B}}$$

In our case, the electric field is null and the moving charged particles are electrons, so the formula becomes:

$F = –e(v \text{ x } B)$

Given the vector product between v and B, the force is perpendicular to both the direction of the magnetic field and the velocity direction. The picture below illustrates the effect of Lorentz interaction.

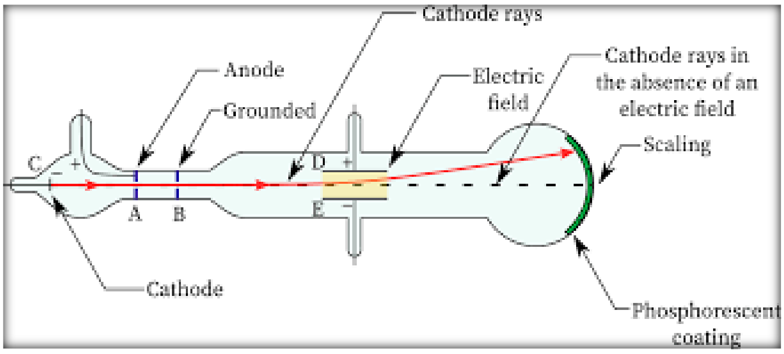




1.6 JJ – Thomson Experiment – Charge of an electron

- **Introduction**
- **Construction**
  - **Cathode Ray Tube**
- **Description**
  - **magnetic field deflection**
  - **electric field deflection**
- **Derivation**
- **Conclusion**

Introduction – 1897 JJ Thomson



Description:

Cathode Ray Tube:

Cathode and anode placed opposite ends.

The region between cathode and anode has filled by gas at low pressure.

When a high voltage is applied between them, the gas is ionized.

The negative particles that are formed after ionization of the gas are attracted towards the anode.

These negatively charged particles are nothing but electrons are called as cathode rays.

These rays are passing to the air through the slits. At the end of the tube is a large sphere, coated by some phosphorous material. Such that the beam after striking over phosphorous material create a bright spot. The scale is provided to measure the deflection of the beam. When there is no electrical or magnetic field, the beam travel in a straight line and there is no deflection. The beam passes between two parallel aluminium plates. When they are connected to a battery, the beam experiences electric field in downward direction and experience force opposite upward direction.

Derivation: Charge to mass ratio of an electron

(i) Force due to electric field:

The magnitude of the force is given by

$$F_e = e.E \qquad (1)$$

Where, Fe = Force on the charged particle

E = Magnitude of electrical field

e = Quantity of charge of an electron

(ii) Force due to magnetic field:

The magnitude of this force is given by

$$F_H = evH \qquad (2)$$

Where F_H = Force experienced by the charge

e = quantity of charge

v = velocity of the charge

H = magnitude of the magnetic field.

(iii) Firstly, both electrical and magnetic fields are applied simultaneously. They are adjusted to such a manner, these two forces cancel out each other. This is achieved when zero deflection of the beam. And this stage,

$$F_e = F_H \qquad (3)$$

$$eE = evH \qquad (4)$$

$$v = E/H \qquad (5)$$

Now the magnet is removed, the force on the electron is due to only electric field. In this situation, there is a force $F_e = eE$ acting along upward direction (Y – direction). There is no force along x – direction.

In the X-direction there is no force, the electron move with the constant velocity $v = E/H$.

Thus the distant travel is $x = vt = Et/H$ ……. (6)

In the Y- direction there is a force $F_e = eE$

Acceleration (a) = $F_e /m = eE/m$ (7)

Therefore distance $y = ½\, a\, t^2 = ½\, (eE/m)\, t^2$ (8)

Where a is the acceleration.

From eq.6 $t = xH/E$ (9)

substitute eq. (9) into eq. (8), we get

$$y = ½\, a\, t^2 = ½\, (eE/m)\, (x^2H^2/E^2)$$

$$y = (eE/2m)\, t^2$$

$$e/m = 2yE/ x^2H^2$$

in this equation, E, H, y and x are known quantities.

From the experimental results, the $e/m = 1.7588196 \times 10^{11}$ C/Kg.

1.7 Millikan's Oil Drop Experiment: – To determine charge of an electron

- **Introduction**
- **Construction**
- **Description**
- **Derivation**
- **Conclusion**

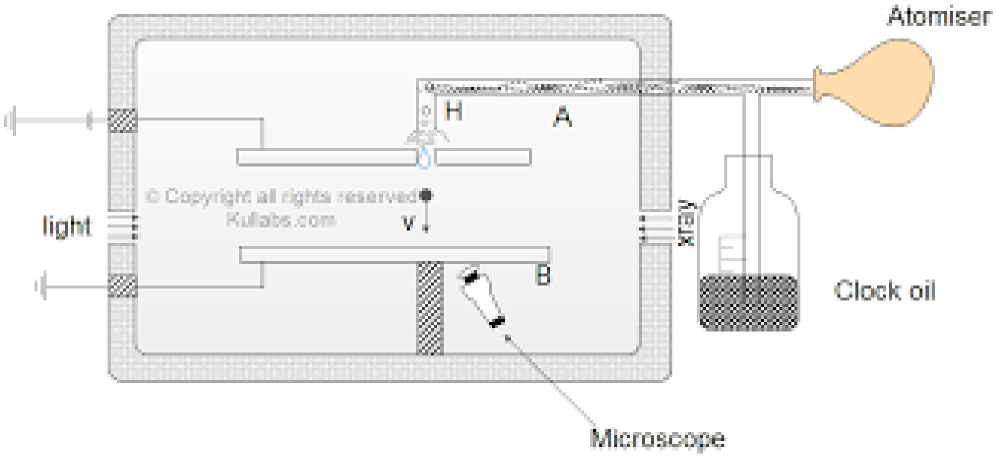
Introduction

- This method was developed by American Physicist R.K. Millikan -1917 – accurate method – measuring electronic charge

Construction

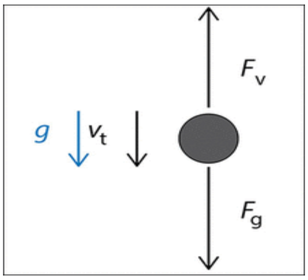
- A and B optically plane metallic discs having 20cm in dia and 1.6 cm apart
- The discs are held together by an insulating rod of glass and parallel to each other
- PD applied between A and B by storage batteries

- In upper plate A, there is a tiny hole.
- Through the tiny hole minute droplets of heavy non-volatile oil is introduced between two plates by using spray atomizer D.
- Plate A and B is connected to +ve and –ve terminal of the battery.
- X-ray source is used to produce X-rays that ionize the gases and in turn charge the oil drop.



Description and Derivation

(i) Absence of any electric field between the two plates



Gravitational Force $F_G = (4/3\pi r^3)\,(\rho - \rho_{air})\,g$ **(1)**

From Stokes Law,

Viscous Force $F_v = 6\,\pi\,\eta\,r\,v_1$ **(2)**

η = **viscosity of air**
r = **radius of oil drop**
v_1 = **velocity of the oil drop**

when oil drops fall with constant velocity – no force acting on it

$$F_G = F_v$$

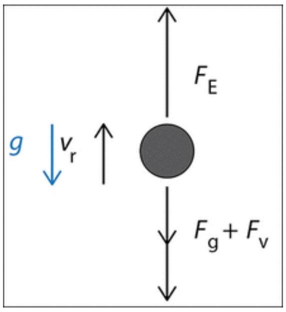
$$(4/3\pi r^3)\,(\rho - \rho_{air})\,g = 6\,\pi\,\eta\,r\,v_1 \qquad (3)$$

$$r^2 = (9\,\eta\,v_1) / 2g(\rho - \rho air) \qquad (4)$$

(ii) Presence of any electric field between the two plates

- additional upward electric force qE acts on the charged oil drop

- the terminal velocity reduced to v_2.



The equation of motion of the drop becomes

$$(4/3\pi r^3)(\rho - \rho_{air})\, g - qE = 6\pi\eta r v_2 \qquad (5)$$

where q = charge on the oil drop

From eq. (3) and (5)

$$qE = 6\pi\eta r (v_1 - v_2)$$

$$q = 6\pi\eta r (v_1 - v_2) / E \qquad (6)$$

$$r^2 = (9\eta v_1) / 2g(\rho - \rho air)$$

$$r = [(9\eta v_1) / 2g(\rho - \rho air)]^{1/2} \qquad (7)$$

Sub. Eq. (7) in (6)

$$q = (6\pi\eta / E)\, [(9\eta v_1) / 2g(\rho - \rho air)]^{1/2} (v_1 - v_2) \qquad (8)$$

$$q = 1.602 \times 10^{-19}\ C$$

Mass of Electron:

Direct measurement of mass of an electron – difficult

From JJ Thomson experiment,

Charge to mass ratio of an electron $e/m = 1.76 \times 10^{11}$ C/kg

Mass $m = e/(e/m) = 1.602 \times 10^{-19} / 1.76 \times 10^{11} = 9.1 \times 10^{-31}$ **kg**

1.8 Generation of free ions:

- 1886 – E. Goldstein – Canal rays/ positive rays

- Canal rays – emerge from holes in the cathode

- W. Wien – these rays deflected in magnetic field – concluded positively charged particle

Construction and working: Goldstein discharge tube

- anode, perforated cathode and fluorescent screen

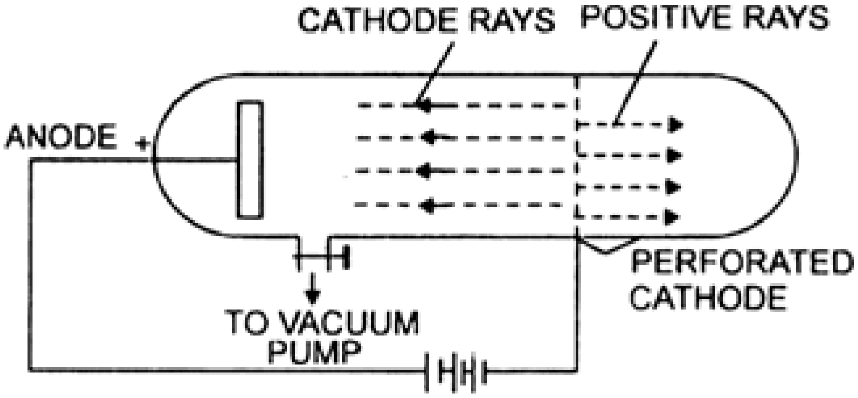
- high PD applied between electrodes – electrons are emitted from cathode and travel towards anode

- electron collide with atoms/molecules of gas – knock out electrons from them

- gas is ionized – positively charged ions are attracted by cathode.

- these ions pass through the holes in the cathode and constitute positive rays

- light is produced when these rays strike the screen



Properties of positive rays

- deflected by E and H in directions opposite to cathode rays

- travel in straight line

- produce phosphorescence and fluorescence

- affect a photographic plate

- specific charge of positive rays particle is much smaller than the cathode rays particle

1.9 Bainbridge Mass Spectrograph Determination of atomic masses

- **Introduction**
- **Principle**
- **Construction**
- **Working**
- **Derivation**
- **Applications**

Introduction

- Aston -1919 developed – first mass spectrograph.

- It is a device used for measuring mass of the positive ions and the masses of isotope.

Principle

- Uniform magnetic field acting normal to the path of ions having same velocity deflects the ions of different masses from a straight path to circular path of different radii, $R \ \alpha \ M$.

Construction

(i) Ionization Chamber:

-used to ionize the gas whose mass or isotope is to be determined and positive ions are produced.

(ii) Velocity Selector:

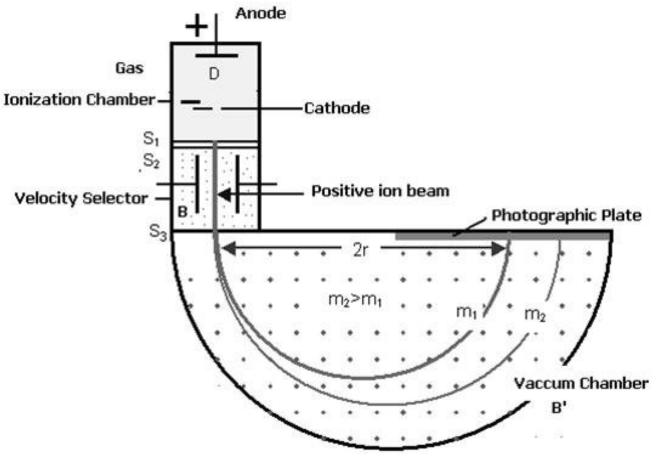
- It has two fields electric and magnetic field both are applied perpendicular to the moving ion beam.

- A potential (V) is applied between two electrodes to produce the electric field.

- A magnetic field (strength B) is applied at right angles to the electrostatic field and so the electrostatic and electromagnetic forces act in opposite directions to each other.

(iii) Vacuum / Analyzing Chamber:

- a semi-spherical cavity in which another magnetic field 'B is applied perpendicular to the moving positive ion.



Working

- The ions are formed at point D and pass through slit S1 through cathode C.
- A potential V is applied between two plates A and B, where the ions are reached.
- A magnetic field B is applied at right angles to the electrostatic field and thus the electrostatic and electromagnetic forces act in opposite directions to each other.

Derivation

(i) The force exerted by electric field is

$$F_e = qE$$

(ii) The force exerted by magnetic field is

$$F_H = Bqv$$

A charged particle having charge q and having velocity v will pass through slit S2 if the resultant force acting on this particle is zero(i.e.) it travels along a straight line.

$$qE = Bqv$$

and the velocity v of the particle is $v = E/B$

Only the particles having a certain velocity can enter the deflection chamber F. Thus, the combination of slits and reflecting plates in the instrument is called velocity selector. In the chamber which is also known as deflection chamber, the ions are under the effect of magnetic field, only thus these ions move in circular orbits. The lighter ions have larger path radius while the heavy ones have smaller path radius. If mass of an ion is m, then

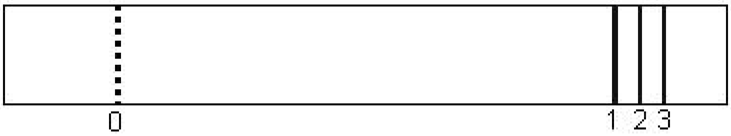
$$Bqv = mv^2 / r$$

$$r = mv / Bq$$

Mass of an ion $m = r B^2 q / E$

The radius of path of an ion is directly proportional to the mass of the ion.

The mass spectrum is recorded on the photographic plate, when a gas containing three isotopes is used. Note the wider line for the mass m_1, showing its relatively greater abundance.



Applications:

- Mass spectrometers are sensitive detectors of isotopes based on their masses.

- used in carbon dating and other radioactive dating process.

- A number of space crafts and satellites used mass spectrometer to analyze the solar wind.

- used to identify and analyze the residual gases in high vacuum systems.

UNIT – II – Quantum Concepts on Atom – SPH1311

2.1 Introduction

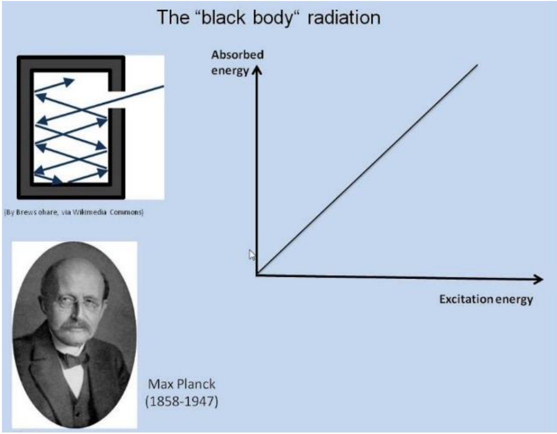
Failure of classical theory

- it is a macroscopic theory
- it fails to explain micro-concepts like stability of atoms, black body radiation, photo-electric effect, Compton effect etc.
- hydrogen spectrum – discrepancies
- New theory called as Quantum theory predicted by Max Planck in the year 1900.
- Corpuscular theory of light –minute fast moving elastic particle
- Wave theory – light travels in the form of wave in ether
- Maxwell’s electromagnetic theory – 1864 – reason for quantum theory.

2.2 Concept of Black body and Block body radiation

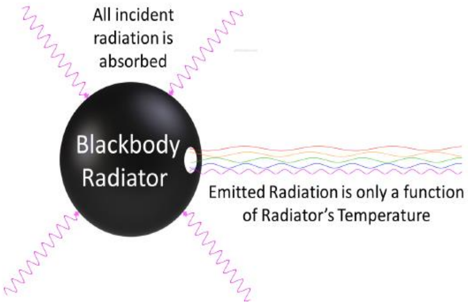
Introduction:

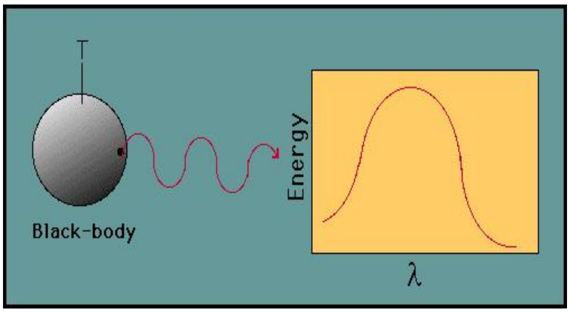
- Black body notion is important in studying thermal radiation and electromagnetic radiation energy transfer in all wavelength bands.
- Black body as an ideal radiation absorber and it is used as a standard for comparison with the radiation of real physical bodies
- its characteristics are used in describing and studying artificial electromagnetic radiation (in radio and TV- broadcasting and communication).



Perfect black body:

- is the one which absorbs and emits all the radiations (corresponding to all wavelengths) that fall on it.
- the radiation given out by a perfect black body – black body radiation.





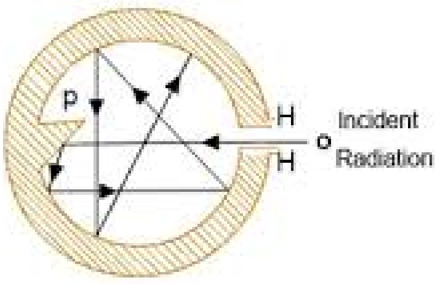
Kirchoff's Law

- Ratio of emissive power to the coefficient of absorption, of any given wavelength is the same for all bodies at a given temperature and is equal to the emissive power of the black body at that temperature.

$$e_\lambda / a_\lambda = E$$

2.2.1 Experiment

- **Hollow copper sphere coated with lamp black on its inner surface**
- **A fine hole – made for radiations to enter into the sphere**
- **When the radiations – pass through the hole – undergoes multiple reflections – completely absorbed**
- **Black body acts as – perfect absorber**
- **When it is placed in a temp bath of fixed temp – heat radiations come out through the hole – not through the wall**
- **Radiations emitted only from the inner surface of the sphere – not from the outer surface**
- **Perfect black body is a perfect absorber and perfect radiator of all wavelengths.**

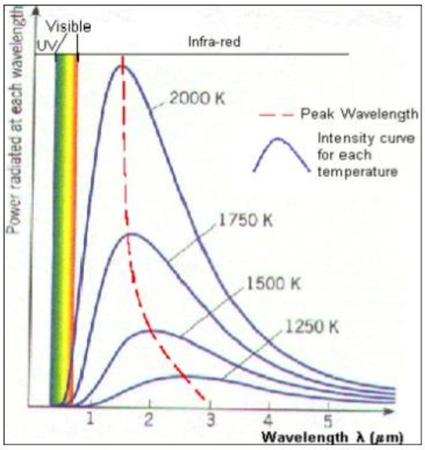


2.2.2 Energy Spectrum

- **Perfect black body is allowed to emit radiations at different temp – the distribution of energy for different wavelengths at various temp**

- **Energy distribution is not uniform for any given T**
- **Intensity of radiation (E) increases w.r.t increase in λ**
- **At particular λ it becomes maximum – after it starts decreasing**

- As the temperature increases, **the peak wavelength emitted by the black body decreases**.
- As temperature increases, the **total energy emitted increases**, because the total area under the curve increases.
- The curve gets **infinitely close to the x-axis** but never touches it.



2.2.3 Laws for explaining the energy distribution w.r.t wavelength

- **Stefan- Boltzmann's law**
- **Wien's Displacement law**
- **Rayleigh-Jean's law**
- **Planck's Radiation law**

Stefan-Boltzmann's law:

The Stefan-Boltzmann law states that total spectral radiant exitance leaving a blackbody is proportional to the fourth power of its temperature (T).

$$E = \sigma T^4$$

Wien's Displacement law:

The wavelength distribution peaks at a value that is inversely proportional to the temperature.

$$\lambda_{max} = \frac{constant}{T}$$

It states that the product of the wavelength (λ_m) corresponding to maximum energy and the absolute temp (T) is a constant

λ_m **T = constant**

It shows that, as the temperature increases, the wavelength corresponding to maximum energy decreases. Wien also showed that the max energy (Emax) is directly proportional to the fifth power of the absolute temperature

$E_{max}\ \alpha\ T^5$

E_{max} = constant T^5

It holds good only for shorter wavelengths.

Rayleigh-Jean's Law

The energy distribution is directly proportional to the absolute temperature and is inversely proportional to the fourth power of the wavelength.

$$E_\lambda = \frac{8\pi KT}{\lambda^4}$$

Conclusion:

- Both Wien's and Rayleigh-Jean's law do not agree with the experimental results.

- Therefore classical theory was not able to explain the emission of black body radiation.

- MaxPlanck used Quantum theory to explain the black body radiation.

Planck's radiation law:

- **a mathematical relationship formulated in 1900 - German physicist Max Planck to explain the spectral-energy distribution of radiation emitted by a blackbody.**

2.3 Planck's law equation

The wavelength of the emitted radiation is inversely proportional to its frequency,

$\lambda = c/v$

The value of Planck's constant is defined as 6.62607015 × 10^{-34} joule·second.

Postulates:

Planck postulated that the energy of light is proportional to the frequency, and the constant that relates them is known as Planck's constant (h).

$E\ \alpha\ \upsilon$; $E = h\,\upsilon$

His work led to Albert Einstein determining that light exists in discrete quanta of energy, or photons.

The smallest amount of energy that can be emitted or absorbed in the form of electromagnetic radiation is known as quantum.

2.3.1 Planck's Quantum theory of black body radiation – Derivation:

To derive the Planck's radiation law,

Let us consider 'N' number of Planck's oscillators and 'E' be their total energy.

Then, the average energy of an oscillator is given by

$$\overline{E} = \frac{ET}{N} \qquad (1)$$

- **(i) To derive N value**
- **(ii) To derive E value**

(i) To find N

Let there be N_0, N_1, N_2 …… N_r oscillators having energy 0, E, 2E, ……rE

Then we can write

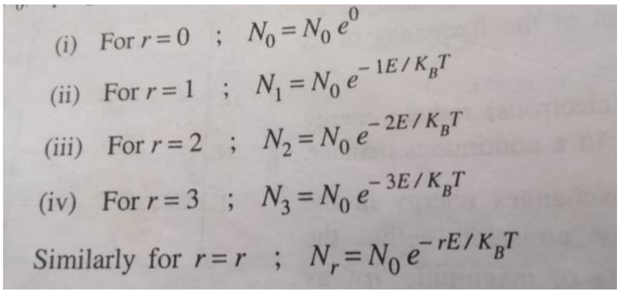
Tot. No. of oscillators $N = N_0 + N_1 + N_2 \ldots\ldots N_r$ **(2)**

Tot. energy of oscillators $ET = 0N_0 + EN_1 + 2EN_2 \ldots\ldots rEN_r$ **(3)**

According to Maxwell's distribution formula, the number of oscillators having energy rE is given by,

$$N_r = N_0\, e^{\frac{-rE}{K_B T}}$$

For various of r, i.e. r = 0, 1, 2,….r, the number of oscillators N_0, N_1, N_2 …… N_r can we got as follows:



(i) For $r=0$; $N_0 = N_0 e^{0}$

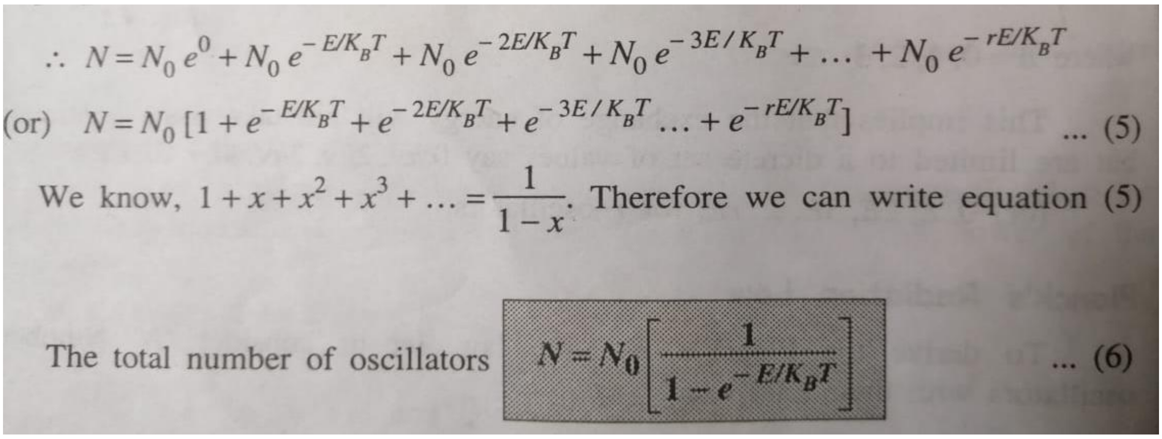
(ii) For $r=1$; $N_1 = N_0 e^{-1E/K_BT}$

(iii) For $r=2$; $N_2 = N_0 e^{-2E/K_BT}$

(iv) For $r=3$; $N_3 = N_0 e^{-3E/K_BT}$

Similarly for $r=r$; $N_r = N_0 e^{-rE/K_BT}$

The tot. no. of oscillators can be got by substituting the values of N_0, N_1, N_2 …… N_r in equation (2)



$$\therefore\ N = N_0\, e^{0} + N_0\, e^{-E/K_BT} + N_0\, e^{-2E/K_BT} + N_0\, e^{-3E/K_BT} + \ldots + N_0\, e^{-rE/K_BT}$$

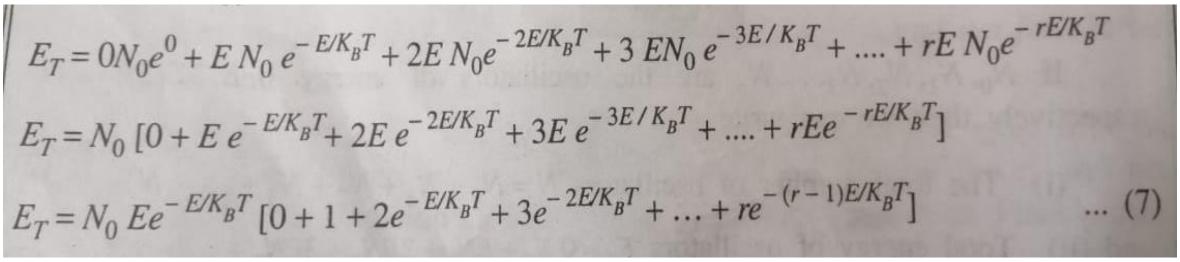
(or) $$N = N_0\,[1 + e^{-E/K_BT} + e^{-2E/K_BT} + e^{-3E/K_BT} \ldots + e^{-rE/K_BT}] \qquad \ldots (5)$$

We know, $1 + x + x^2 + x^3 + \ldots = \dfrac{1}{1-x}$. Therefore we can write equation (5)

The total number of oscillators $$\boxed{N = N_0\left[\frac{1}{1 - e^{-E/K_BT}}\right]} \qquad \ldots (6)$$

(ii) To find E_T

Similarly, by substituting the values of N_0, N_1, N_2 …… N_r in equation (3), the total energy can be written as



$$E_T = 0N_0e^{0} + E\,N_0\,e^{-E/K_BT} + 2E\,N_0e^{-2E/K_BT} + 3\,EN_0\,e^{-3E/K_BT} + \ldots. + rE\,N_0e^{-rE/K_BT}$$

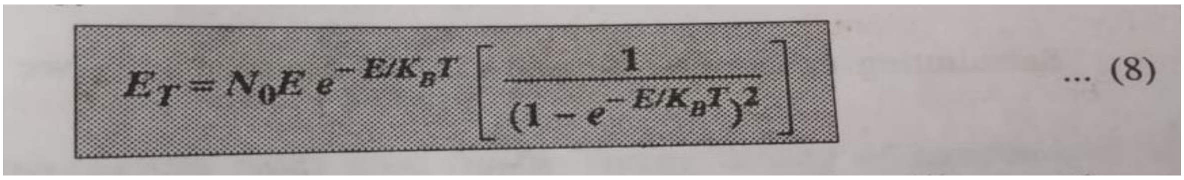
$$E_T = N_0\,[0 + E\,e^{-E/K_BT} + 2E\,e^{-2E/K_BT} + 3E\,e^{-3E/K_BT} + \ldots. + rEe^{-rE/K_BT}]$$

$$E_T = N_0\,Ee^{-E/K_BT}\,[0 + 1 + 2e^{-E/K_BT} + 3e^{-2E/K_BT} + \ldots + re^{-(r-1)E/K_BT}] \qquad \ldots (7)$$

We know $1 + 2x + 3x^2 + \ldots.+ rx^{r-1} \quad = \quad 1/(1-x)^2$

Therefor eq. (7) becomes

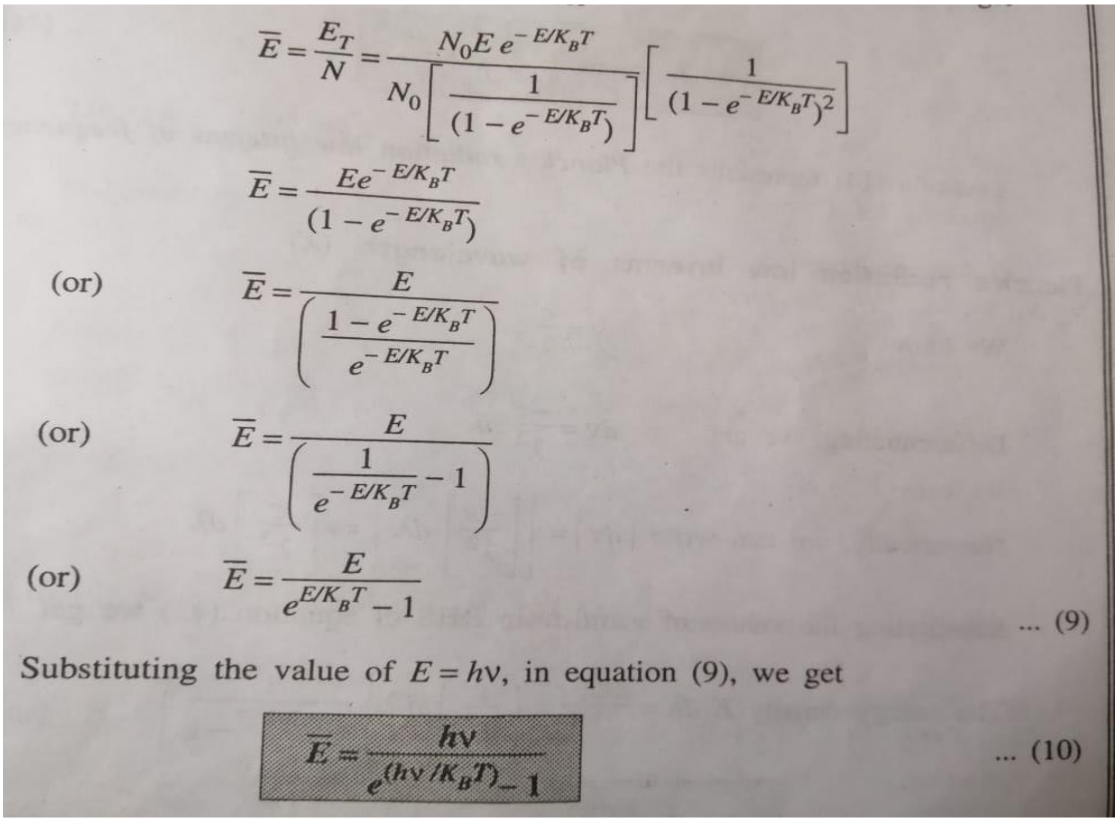
The total energy of oscillators



$$\boxed{E_T = N_0E\,e^{-E/K_BT}\left[\frac{1}{(1 - e^{-E/K_BT})^2}\right]} \qquad \ldots (8)$$

Substituting the values of eq. (6) and (8) in eq.(1) we get

The average energy of the oscillator



$$\overline{E} = \frac{E_T}{N} = \frac{N_0 E\, e^{-E/K_BT}}{N_0\left[\frac{1}{(1-e^{-E/K_BT})}\right]}\left[\frac{1}{(1-e^{-E/K_BT})^2}\right]$$

$$\overline{E} = \frac{Ee^{-E/K_BT}}{(1-e^{-E/K_BT})}$$

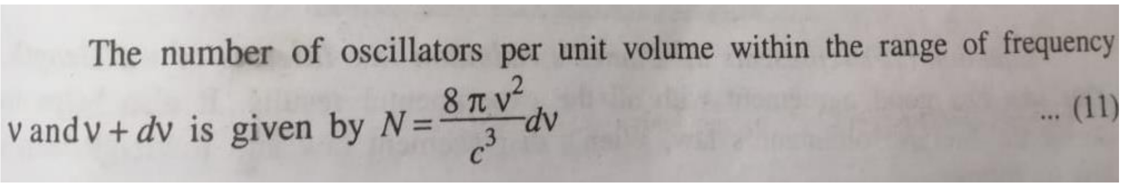
(or)
$$\overline{E} = \frac{E}{\left(\frac{1-e^{-E/K_BT}}{e^{-E/K_BT}}\right)}$$

(or)
$$\overline{E} = \frac{E}{\left(\frac{1}{e^{-E/K_BT}}-1\right)}$$

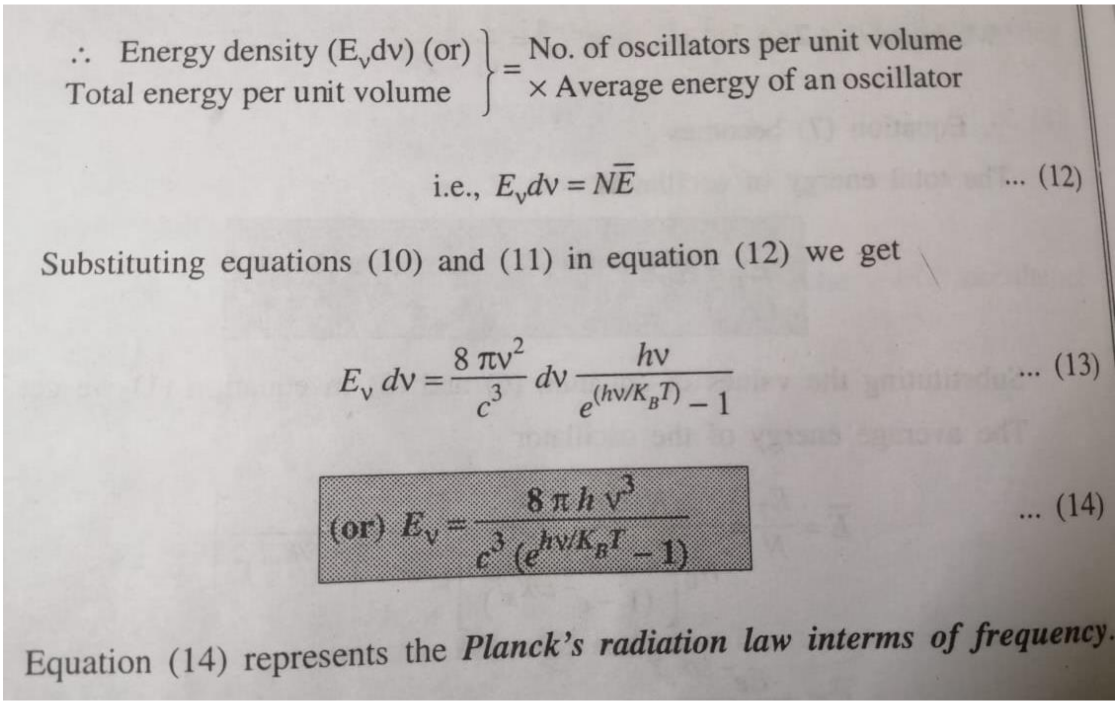
(or)
$$\overline{E} = \frac{E}{e^{E/K_BT}-1} \quad \text{... (9)}$$

Substituting the value of $E = h\nu$, in equation (9), we get

$$\boxed{\overline{E} = \frac{h\nu}{e^{(h\nu/K_BT)}-1}} \quad \text{... (10)}$$



The number of oscillators per unit volume within the range of frequency ν and $\nu + d\nu$ is given by $N = \frac{8\pi\nu^2}{c^3}d\nu$ ... (11)



$\therefore$ Energy density ($E_\nu d\nu$) (or) Total energy per unit volume $\Big\}$ = No. of oscillators per unit volume × Average energy of an oscillator

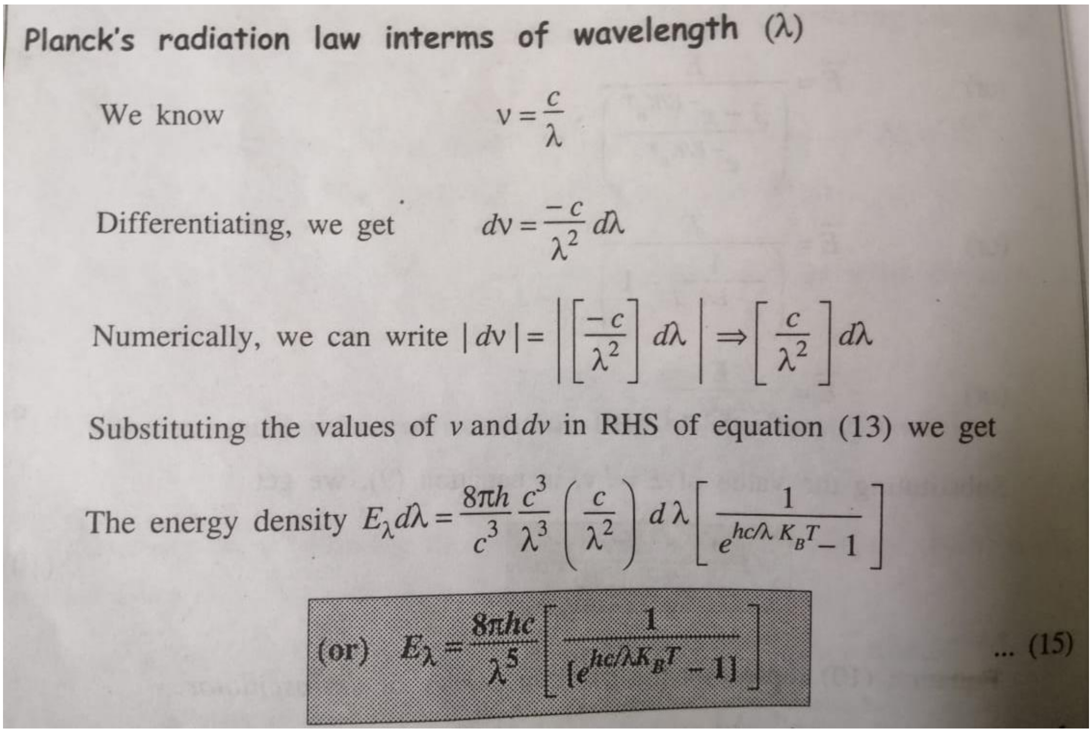
$$\text{i.e., } E_\nu d\nu = N\overline{E} \quad \text{... (12)}$$

Substituting equations (10) and (11) in equation (12) we get

$$E_\nu\, d\nu = \frac{8\pi\nu^2}{c^3}\, d\nu\, \frac{h\nu}{e^{(h\nu/K_BT)}-1} \quad \text{... (13)}$$

$$\boxed{\text{(or) } E_\nu = \frac{8\pi h\nu^3}{c^3(e^{h\nu/K_BT}-1)}} \quad \text{... (14)}$$

Equation (14) represents the ***Planck's radiation law interms of frequency***.



Planck's radiation law interms of wavelength (λ)

We know $\nu = \frac{c}{\lambda}$

Differentiating, we get $d\nu = \frac{-c}{\lambda^2} d\lambda$

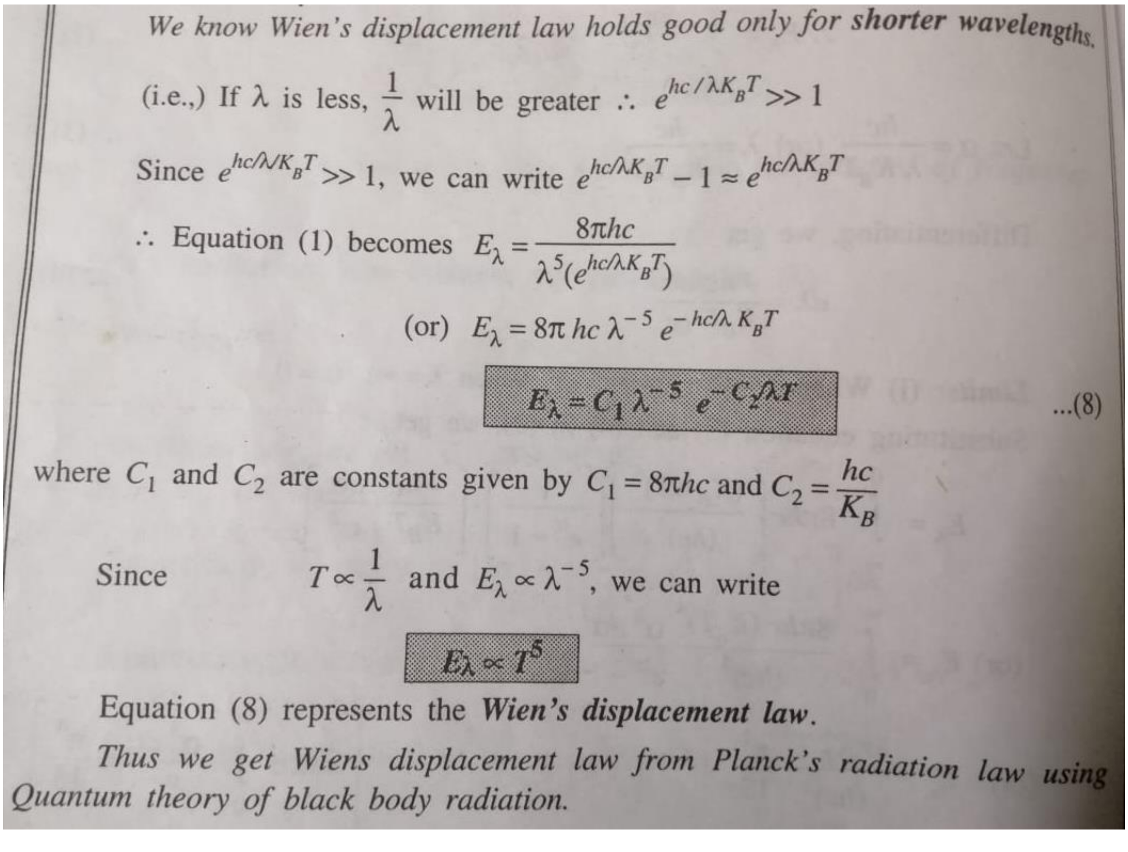
Numerically, we can write $|d\nu| = \left|\left[\frac{-c}{\lambda^2}\right] d\lambda\right| \Rightarrow \left[\frac{c}{\lambda^2}\right] d\lambda$

Substituting the values of v and dv in RHS of equation (13) we get

The energy density $E_\lambda d\lambda = \frac{8\pi h}{c^3}\frac{c^3}{\lambda^3}\left(\frac{c}{\lambda^2}\right) d\lambda \left[\frac{1}{e^{hc/\lambda K_B T}-1}\right]$

$$\boxed{\text{(or)} \quad E_\lambda = \frac{8\pi hc}{\lambda^5}\left[\frac{1}{[e^{hc/\lambda K_B T}-1]}\right]} \quad \text{... (15)}$$

(i) Wien's Displacement Law derivation from Planck's Law



We know Wien's displacement law holds good only for ***shorter wavelengths.***

(i.e.,) If λ is less, $\frac{1}{\lambda}$ will be greater $\therefore\ e^{hc/\lambda K_B T} >> 1$

Since $e^{hc/\lambda/K_B T} >> 1$, we can write $e^{hc/\lambda K_B T} - 1 \approx e^{hc/\lambda K_B T}$

$\therefore$ Equation (1) becomes $E_\lambda = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda K_B T})}$

(or) $E_\lambda = 8\pi\, hc\, \lambda^{-5}\, e^{-hc/\lambda K_B T}$

$$\boxed{E_\lambda = C_1 \lambda^{-5}\, e^{-C_2/\lambda T}} \quad \text{...(8)}$$

where C_1 and C_2 are constants given by $C_1 = 8\pi hc$ and $C_2 = \frac{hc}{K_B}$

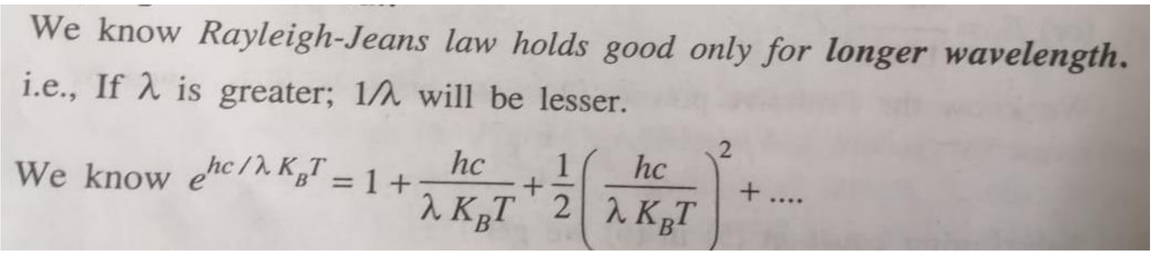
Since $T \propto \frac{1}{\lambda}$ and $E_\lambda \propto \lambda^{-5}$, we can write

$$\boxed{E\lambda \propto T^5}$$

Equation (8) represents the ***Wien's displacement law.***

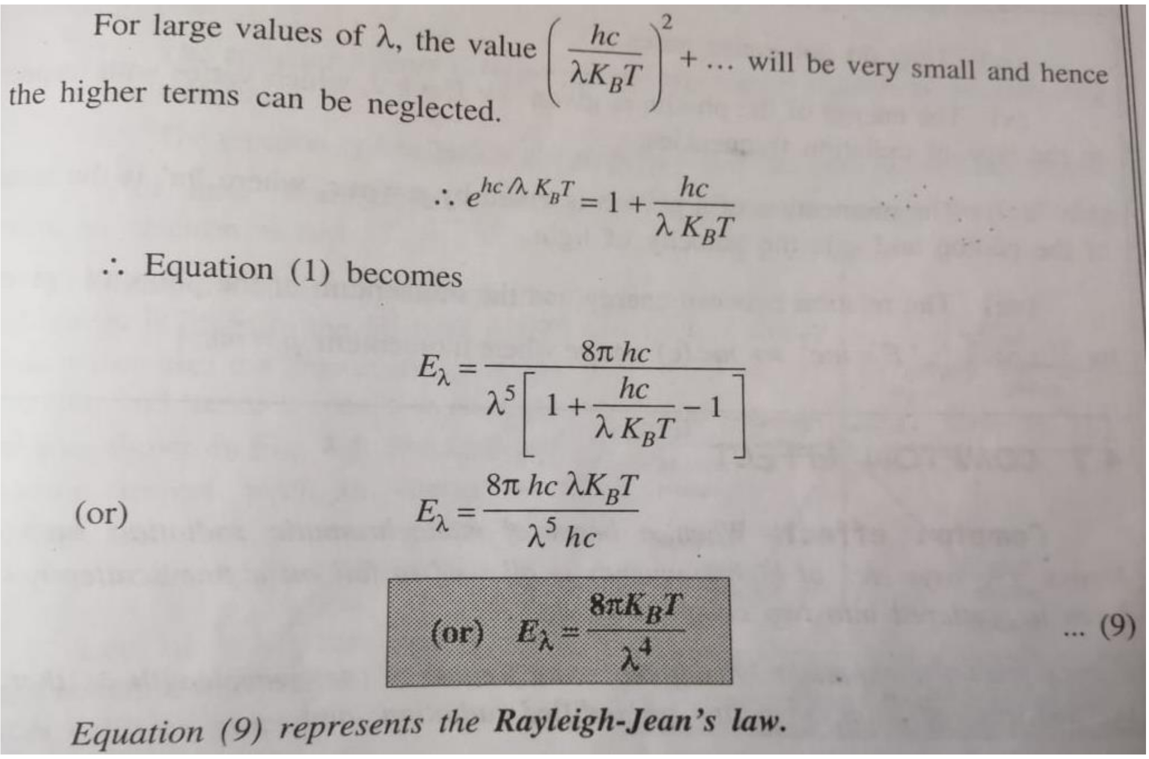
Thus we get Wiens displacement law from Planck's radiation law using Quantum theory of black body radiation.

(ii) Rayleigh-Jean's Law derivation from Planck's Law



We know *Rayleigh-Jeans law holds good only for* ***longer wavelength.***
i.e., If λ is greater; $1/\lambda$ will be lesser.

We know $e^{hc/\lambda K_BT} = 1 + \frac{hc}{\lambda K_BT} + \frac{1}{2}\left(\frac{hc}{\lambda K_BT}\right)^2 + ...$



For large values of λ, the value $\left(\frac{hc}{\lambda K_BT}\right)^2 + \ldots$ will be very small and hence the higher terms can be neglected.

$$\therefore e^{hc/\lambda K_BT} = 1 + \frac{hc}{\lambda K_BT}$$

$\therefore$ Equation (1) becomes

$$E_\lambda = \frac{8\pi hc}{\lambda^5\left[1 + \frac{hc}{\lambda K_BT} - 1\right]}$$

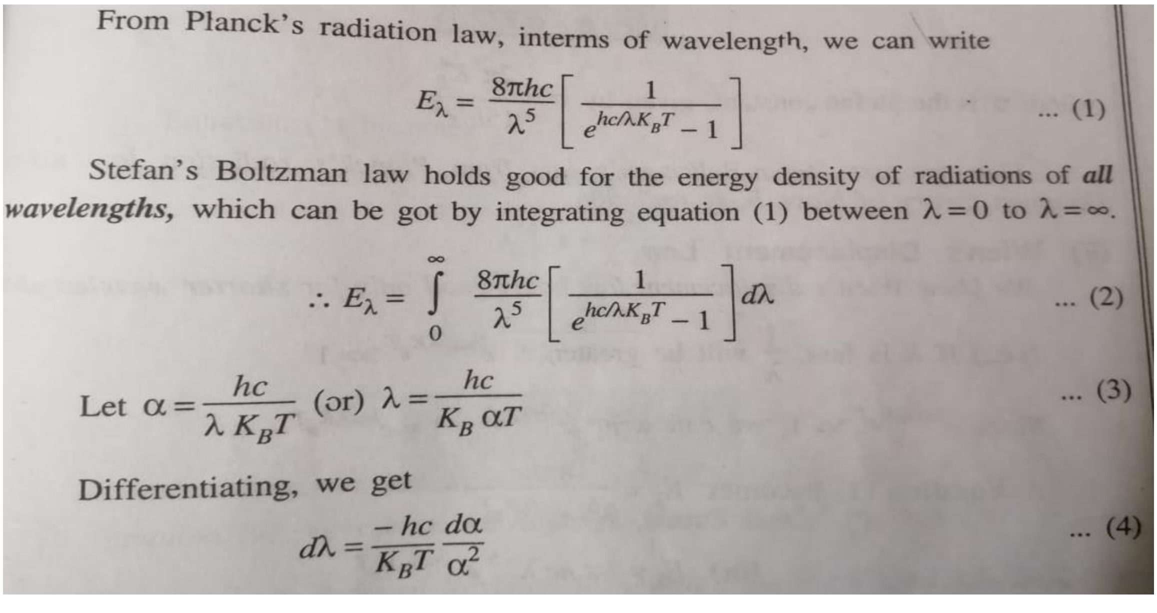
(or)

$$E_\lambda = \frac{8\pi hc\,\lambda K_BT}{\lambda^5 hc}$$

$$\boxed{\textbf{(or)}\quad E_\lambda = \frac{8\pi K_BT}{\lambda^4}} \qquad \ldots (9)$$

Equation (9) represents the ***Rayleigh-Jean's law.***

(iii) Stefan-Boltzmann's Law derivation from Planck's Law



From Planck's radiation law, interms of wavelength, we can write

$$E_\lambda = \frac{8\pi hc}{\lambda^5}\left[\frac{1}{e^{hc/\lambda K_BT} - 1}\right] \qquad \ldots (1)$$

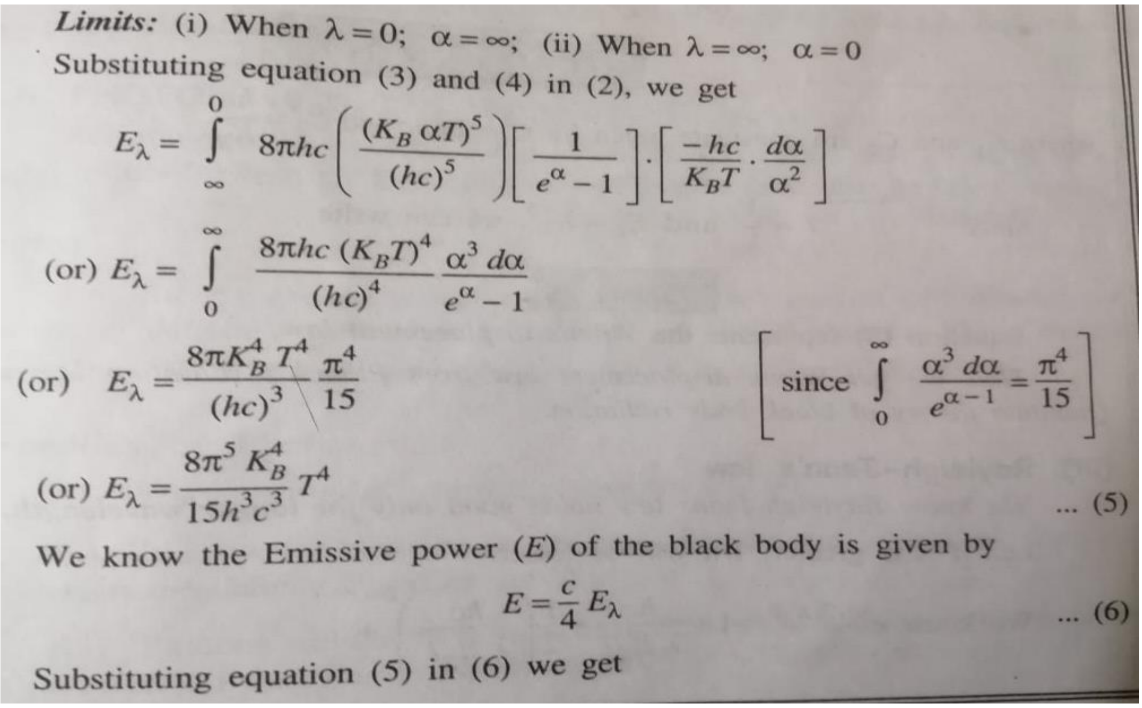
Stefan's Boltzman law holds good for the energy density of radiations of ***all wavelengths,*** which can be got by integrating equation (1) between $\lambda = 0$ to $\lambda = \infty$.

$$\therefore E_\lambda = \int_0^\infty \frac{8\pi hc}{\lambda^5}\left[\frac{1}{e^{hc/\lambda K_BT} - 1}\right] d\lambda \qquad \ldots (2)$$

Let $\alpha = \frac{hc}{\lambda K_BT}$ (or) $\lambda = \frac{hc}{K_B \alpha T}$ ... (3)

Differentiating, we get

$$d\lambda = \frac{-hc}{K_BT}\frac{d\alpha}{\alpha^2} \qquad \ldots (4)$$



Limits: (i) When $\lambda = 0$; $\alpha = \infty$; (ii) When $\lambda = \infty$; $\alpha = 0$

Substituting equation (3) and (4) in (2), we get

$$E_\lambda = \int_\infty^0 8\pi hc\left(\frac{(K_B\,\alpha T)^5}{(hc)^5}\right)\left[\frac{1}{e^\alpha - 1}\right]\cdot\left[\frac{-hc}{K_B T}\cdot\frac{d\alpha}{\alpha^2}\right]$$

$$\text{(or) } E_\lambda = \int_0^\infty \frac{8\pi hc\,(K_B T)^4}{(hc)^4}\,\frac{\alpha^3\,d\alpha}{e^\alpha - 1}$$

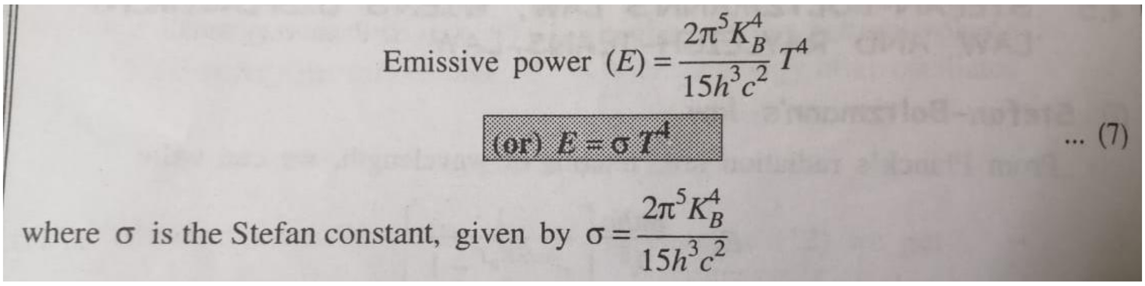
$$\text{(or)} \quad E_\lambda = \frac{8\pi K_B^4\,T^4}{(hc)^3}\,\frac{\pi^4}{15} \qquad \left[\text{since } \int_0^\infty \frac{\alpha^3\,d\alpha}{e^{\alpha-1}} = \frac{\pi^4}{15}\right]$$

$$\text{(or) } E_\lambda = \frac{8\pi^5\,K_B^4}{15h^3c^3}\,T^4 \qquad \dots (5)$$

We know the Emissive power (E) of the black body is given by

$$E = \frac{c}{4}\,E_\lambda \qquad \dots (6)$$

Substituting equation (5) in (6) we get



$$\text{Emissive power } (E) = \frac{2\pi^5 K_B^4}{15h^3c^2}\,T^4$$

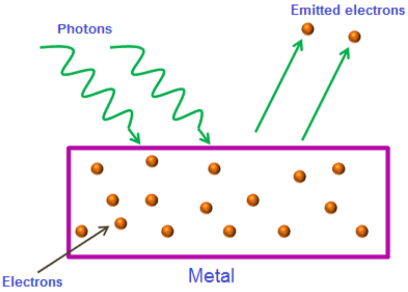
$$\boxed{\text{(or) } E = \sigma T^4} \qquad \dots (7)$$

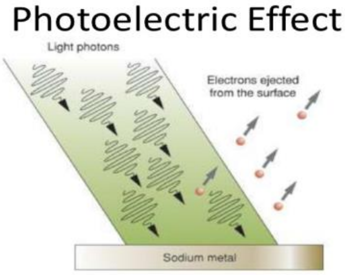
where σ is the Stefan constant, given by $\sigma = \dfrac{2\pi^5 K_B^4}{15h^3c^2}$

2.4 Photoelectric effect

Introduction

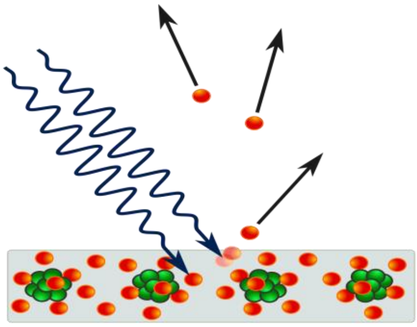
- **The process of emission of electrons from a metal plate, when illuminated by light of suitable wavelength – Photoelectric effect.**
- **Emitted electrons – photoelectrons**
- **Alkali metals – photoelectric emission occurs – under the action of visible light**
- **Zinc, Cadmium, etc..- sensitive to only UV light**





Experimental determination of photoelectric effect

- **Emission of electrons from a metal plate, when illuminated by light or other radiations (UV, X-rays) of suitable wavelength /frequency – photoelectric effect**
- **Hertz – he allowed UV light to fall on zinc plate.**
- **Experimental verification done by Hallwaches, Leonard, JJ Thomson, R.A. Millikan and others**
- **Millikan – 1868-1953 – effect with no. of alkali metals over a wide range of frequency – Nobel prize 1923.**



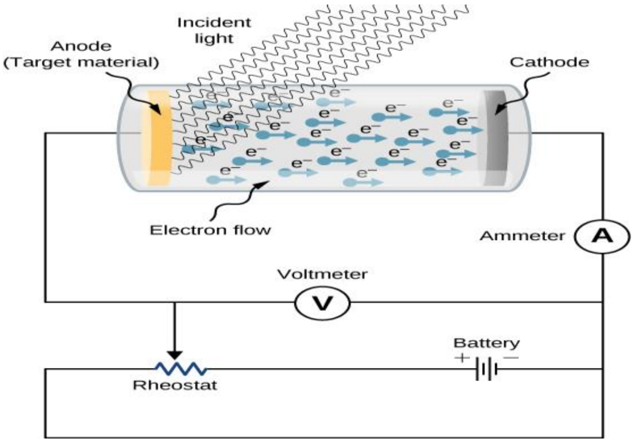
- **The apparatus consist of two photosensitive surfaces A and B enclosed – evacuated quartz bulb.**
- **Plate A connected - -ve terminal of battery ; B – connected to +ve terminal thro G or micrometer**
- **Absence of light – no flow of current – no deflection if G**
- **When monochromatic light is allowed to fall on plate A – current starts flowing in the circuit – indicated by G – current is known as photo current**
- **When light falls on metallic surface – electrons are ejected**
- **The no. of electrons emitted and their kinetic energy depends upon the following factors:**

- Potential difference between two electrodes …..between A and B

- the intensity of incident radiation

- frequency of incident radiation

- the photometal used



Laws of photoelectric emission

- **For every metal, there is a particular minimum frequency of the incident light, below there is no photoelectric emission, whatever be the intensity of the radiation. The minimum frequency, which can cause photoelectric emission is called the threshold frequency.**
- **The number of electrons emitted per second (i.e) photoelectric current is proportional to the intensity of incident light – provided the frequency is greater than the threshold frequency.**
- **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**
- **Photoelectric emission is an instantaneous process. The time lag, if any between incidence of radiation and emission of the electrons, is nevere more than 3 x 10^{-9} sec.**

Characteristics / Photoelectrons

- **Effect of potential difference**
- **Effect of intensity of incident radiation**
- **Effect of frequency of incident radiation**
- **Effect of photometal**

Characteristics of the Photoelectric Effect

(i) The effect of frequency of incident radiation: (threshold frequency)

- The collector plate B is made sufficiently positive w.r.t the emitter photosensitive plate A.

- The surface of plate A is illuminated with monochromatic light of different frequencies.

- It is observed that the photoelectric current is produced only when the frequency υ of the incident light is greater than a certain minimum value υ_0.

- This minimum value of the frequency is called – threshold frequency for the given surface.

- The wavelength corresponding to threshold frequency – threshold wavelength.

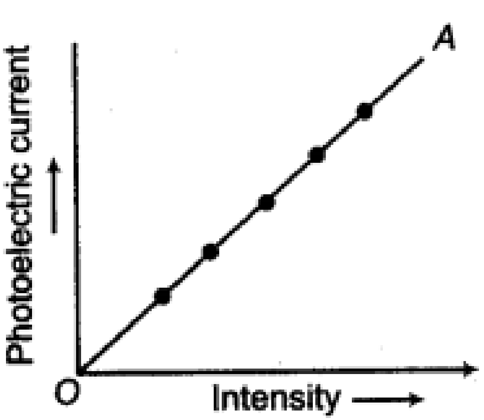
- This frequency is just able to liberate electrons without giving them additional energy

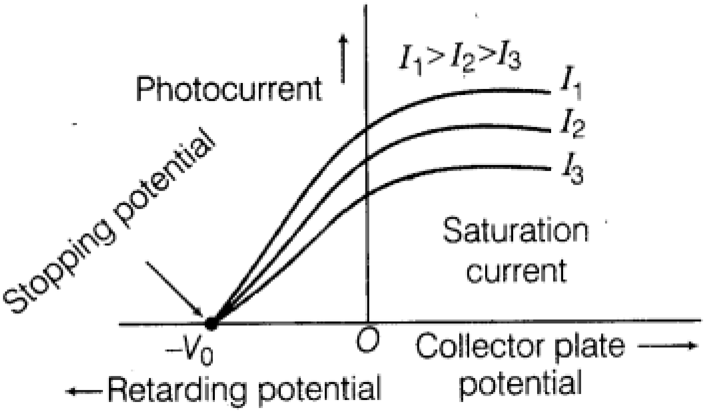
(ii) Effect of the intensity of incident light

- To study the effect of the intensity of the incident light, the collector plate B is made sufficiently positive w.r.t the emitter plate A.

- By keeping the frequency of the incident light and potential difference V constant, the photoelectric current I is measured for the various intensities of the incident light.

- The photoelectric current is proportional to the intensity of the incident light.





(iii) Effect of potential difference

- for a given photometallic surface A – Intensity and frequency of the incident radiation fixed.

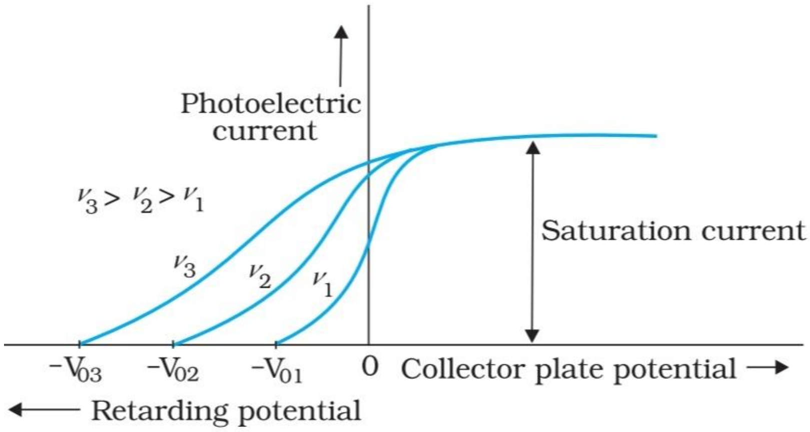
- Starting with small positive potential- reduced to zero – made negative

- I Vs PD(V) between two plates

- When +ve potential of the plate B increased – I also increased

- Saturation current – I reaches maximum (certain limiting) when positive potential is further increased

- When B is negative – I goes on decreasing until it is stopped entirely – retarding potential/stopping potential.

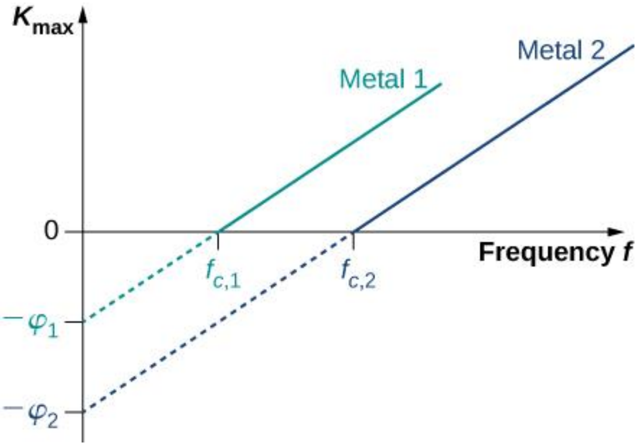


(iv) Effect of photometal:

- stopping potential V_0 and frequency for a number of photometals

- From the graph, it is clear that all the lines have the same slope slope but their interactions with the frequency axis are different.

- it can be concluded that the threshold frequency is a function of photometal (i.e) it depends on the nature of photometal.



Einstein’s photoelectric equation:

According to Einstein (photoelectric effect – 1905)

- **Light of frequency υ consists of a shower of corpuscles or photons – energy hυ**
- **Energy is completely transferred to a free electron in the metal – when a photon of light of frequency υ is incident on a 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.**

- **ϕ - is the energy spent in extracting the electron from the emitter to which it is bound – photoelectric work function**
- **$1/2mv^2$ is the K.E. of the photoelectron**
- **Then $h\upsilon = \phi + 1/2mv^2$ …..Einstein's Photoelectric equation (1)**

If υ_o is the threshold frequency which just ejects an electron from the metal without any velocity then, $\phi = h\upsilon_o$

$$h\upsilon = h\upsilon_o + \frac{1}{2}mv_{max}^2 \tag{2}$$

v_{max} is the maximum velocity acquired by the electron

$$\frac{1}{2}mv_{max}^2 = h(\upsilon - \upsilon_o) \tag{3}$$

The work function of a metal is defined as the

$$\frac{1}{2}mv_{max}^2 = h(\upsilon - \upsilon_o) \tag{4}$$

The work function of a metal is defined as the energy which is just sufficient to liberate electrons from the metal surface with zero velocity.

Eq. (3) suggests that the energy of the emitted photoelectrons is independent of the intensity of the incident radiation but increases with the frequency.

2.5 Compton Effect

- **Definition: Compton shift**
- **Theory**
- **Derivation**
- **Special Cases**

Compton Shift

- **When a photon of energy 'hυ' collides with an electron of a scatterer at rest – photon gives its energy to the electron.**
- **The scattered photon has lesser energy/lower frequency/higher wavelength compared to the wavelength of incident photon.**
- **The electron gains energy – it recoils with the velocity ' v ' – this effect is called Compton effect and the shift in wavelength is called Compton shift.**

Result of Compton scattering,

(i) Unmodified radiations

(ii) Modified radiations

(iii) Recoil electron

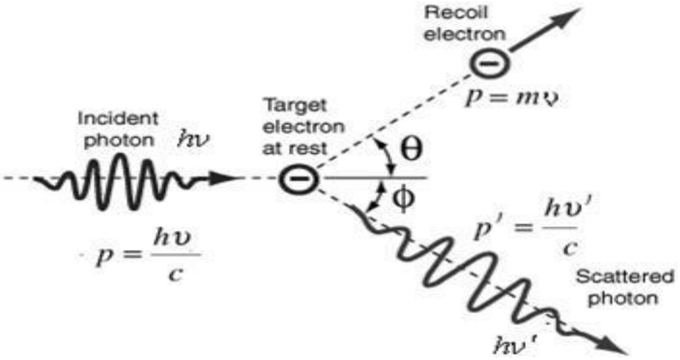
Compton effect: 1921 – A.H. Compton

- a beam of monochromatic radiation such as X-rays, γ – rays etc., of high frequency – fall on a fine scatterer, the beam is scattered into two components

(i) one component having the same frequency/wavelength as that of the incident radiation – unmodified radiation

(ii) other component having lower frequency/higher wavelength compared to incident radiation – modified radiation

(iii) Recoil electron



Theory of Compton effect

Principle & Working

- **in Compton scattering the collision between a photon and an electron is considered.**
- **by applying the laws of conservation of energy and momentum – expression for Compton wavelength is derived**
- **During the collision process – a part of energy is given to the electron – which in turn increases the K.E. of the electron – so it recoils at an angle of ϕ.**

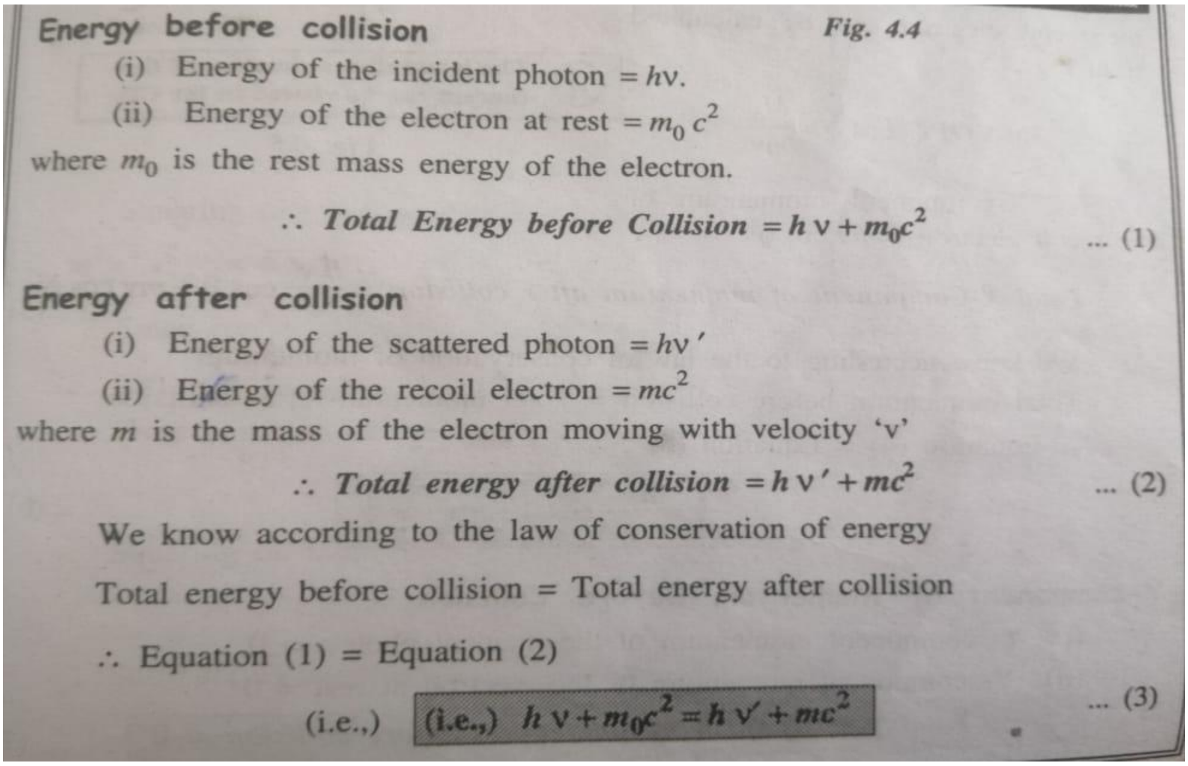
The scattered photon moves with an energy $h\upsilon'$ (less than $h\upsilon$), at an angle θ with respect to the original direction.

Derivation:

- Find energy and momentum components before and after collision process

1) **Energy before collision**
2) **Energy after collision**
3) **X-component of momentum before collision**

4) **X-component of momentum after collision**
5) **Y-component of momentum before collision**
6) **Y-component of momentum after collision**
7) **Change in wavelength / Compton Shift**
8) **Special cases**



Energy before collision *Fig. 4.4*

(i) Energy of the incident photon $= h\nu$.

(ii) Energy of the electron at rest $= m_0 c^2$

where m_0 is the rest mass energy of the electron.

$\therefore$ ***Total Energy before Collision*** $= h\nu + m_0c^2$ ... (1)

Energy after collision

(i) Energy of the scattered photon $= h\nu'$

(ii) Energy of the recoil electron $= mc^2$

where m is the mass of the electron moving with velocity 'v'

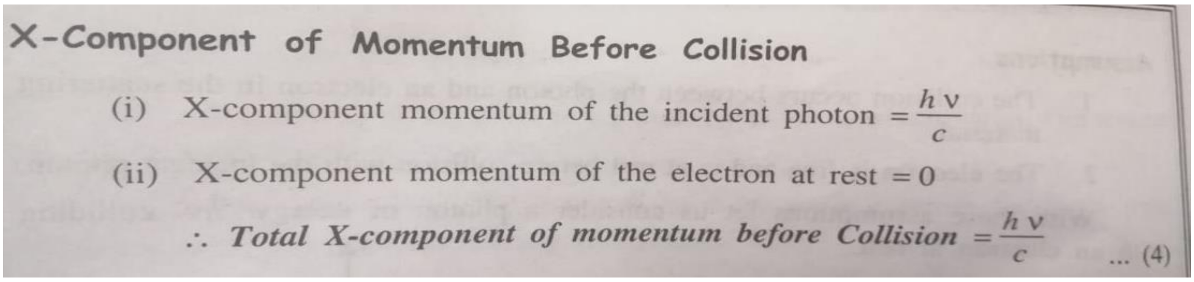
$\therefore$ ***Total energy after collision*** $= h\nu' + mc^2$ ... (2)

We know according to the law of conservation of energy

Total energy before collision = Total energy after collision

$\therefore$ Equation (1) = Equation (2)

(i.e.,) $\boxed{\text{(i.e.,) } h\nu + m_0c^2 = h\nu' + mc^2}$ ... (3)

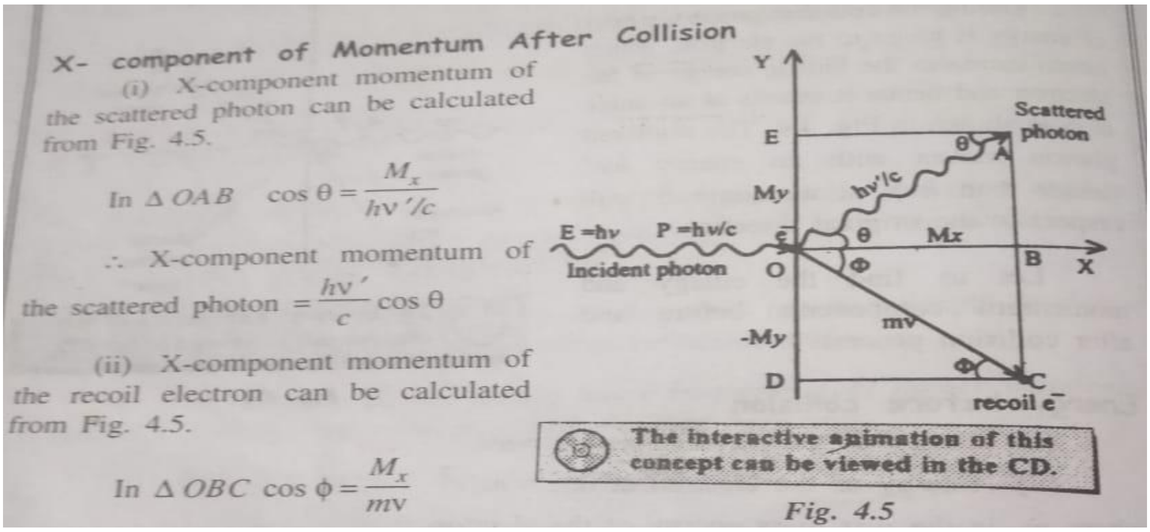


X-Component of Momentum Before Collision

(i) X-component momentum of the incident photon $= \frac{h\nu}{c}$

(ii) X-component momentum of the electron at rest $= 0$

$\therefore$ ***Total X-component of momentum before Collision*** $= \frac{h\nu}{c}$ ... (4)



X- component of Momentum After Collision

(i) X-component momentum of the scattered photon can be calculated from Fig. 4.5.

In $\Delta OAB \quad \cos\theta = \dfrac{M_x}{h\nu'/c}$

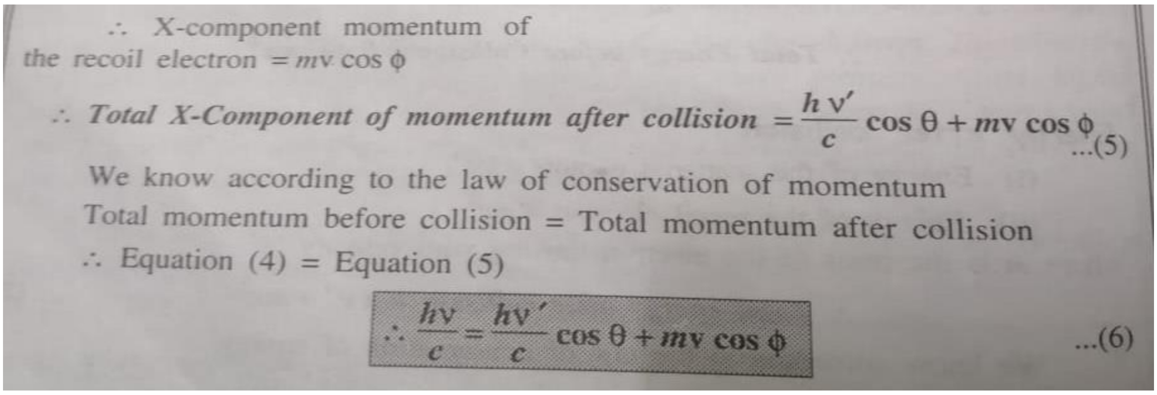
$\therefore$ X-component momentum of the scattered photon $= \dfrac{h\nu'}{c}\cos\theta$

(ii) X-component momentum of the recoil electron can be calculated from Fig. 4.5.

In $\Delta OBC \; \cos\phi = \dfrac{M_x}{mv}$

The interactive animation of this concept can be viewed in the CD.

Fig. 4.5



$\therefore$ X-component momentum of the recoil electron $= mv\cos\phi$

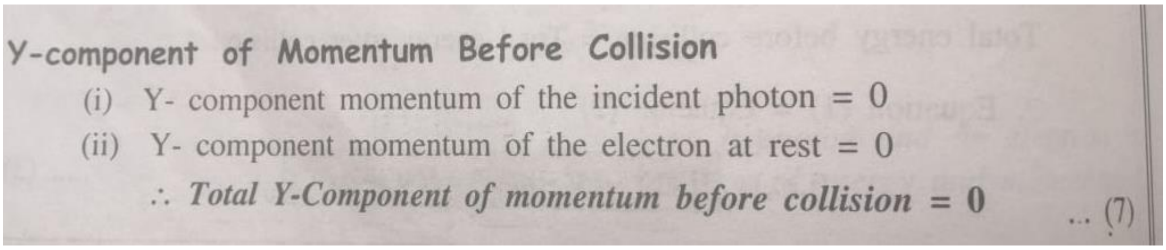
$\therefore$ *Total X-Component of momentum after collision* $= \dfrac{h\nu'}{c}\cos\theta + mv\cos\phi$ ...(5)

We know according to the law of conservation of momentum

Total momentum before collision = Total momentum after collision

$\therefore$ Equation (4) = Equation (5)

$$\boxed{\therefore \frac{h\nu}{c} = \frac{h\nu'}{c}\cos\theta + mv\cos\phi} \quad ...(6)$$

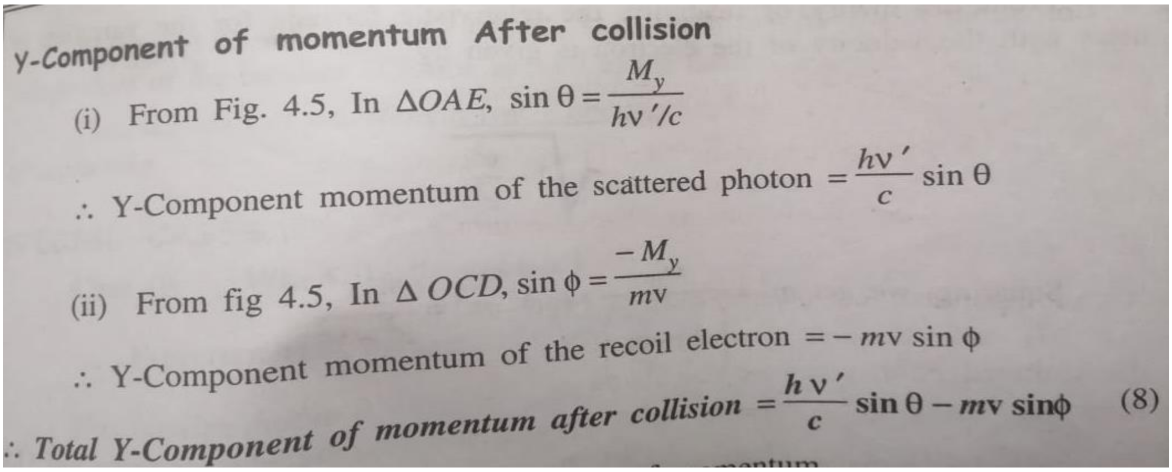


Y-component of Momentum Before Collision

(i) Y- component momentum of the incident photon = 0

(ii) Y- component momentum of the electron at rest = 0

$\therefore$ *Total Y-Component of momentum before collision* = 0 ... (7)



Y-Component of momentum After collision

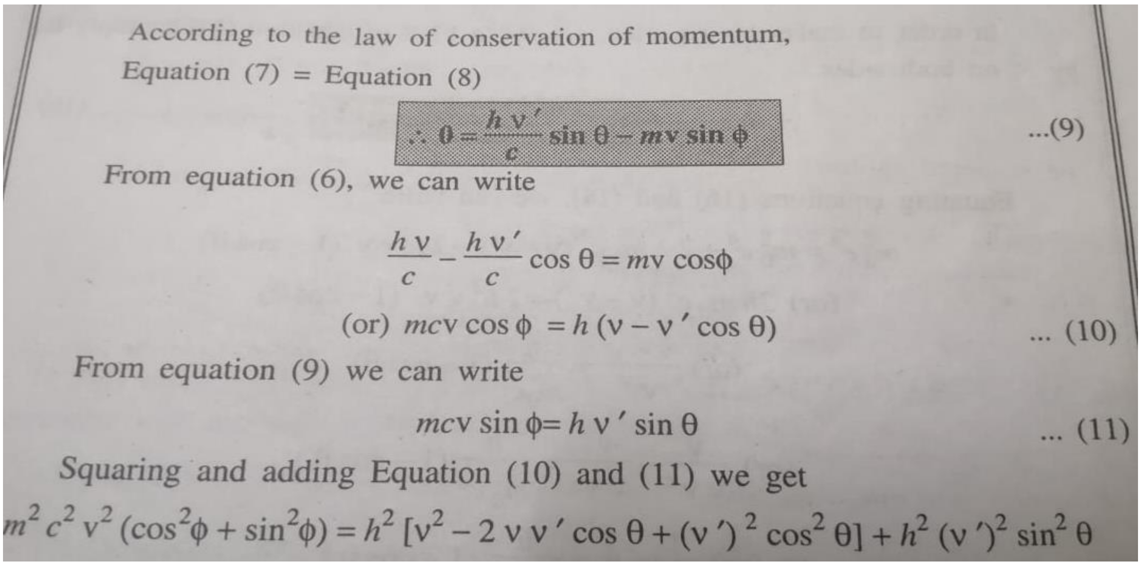
(i) From Fig. 4.5, In ΔOAE, $\sin\theta = \dfrac{M_y}{h\nu'/c}$

$\therefore$ Y-Component momentum of the scattered photon $= \dfrac{h\nu'}{c}\sin\theta$

(ii) From fig 4.5, In ΔOCD, $\sin\phi = \dfrac{-M_y}{mv}$

$\therefore$ Y-Component momentum of the recoil electron $= -mv\sin\phi$

$\therefore$ *Total Y-Component of momentum after collision* $= \dfrac{h\nu'}{c}\sin\theta - mv\sin\phi$ (8)



According to the law of conservation of momentum,

Equation (7) = Equation (8)

$$\boxed{\therefore 0 = \frac{h\,\nu'}{c}\sin\theta - mv\sin\phi} \qquad ...(9)$$

From equation (6), we can write

$$\frac{h\,\nu}{c} - \frac{h\,\nu'}{c}\cos\theta = mv\cos\phi$$

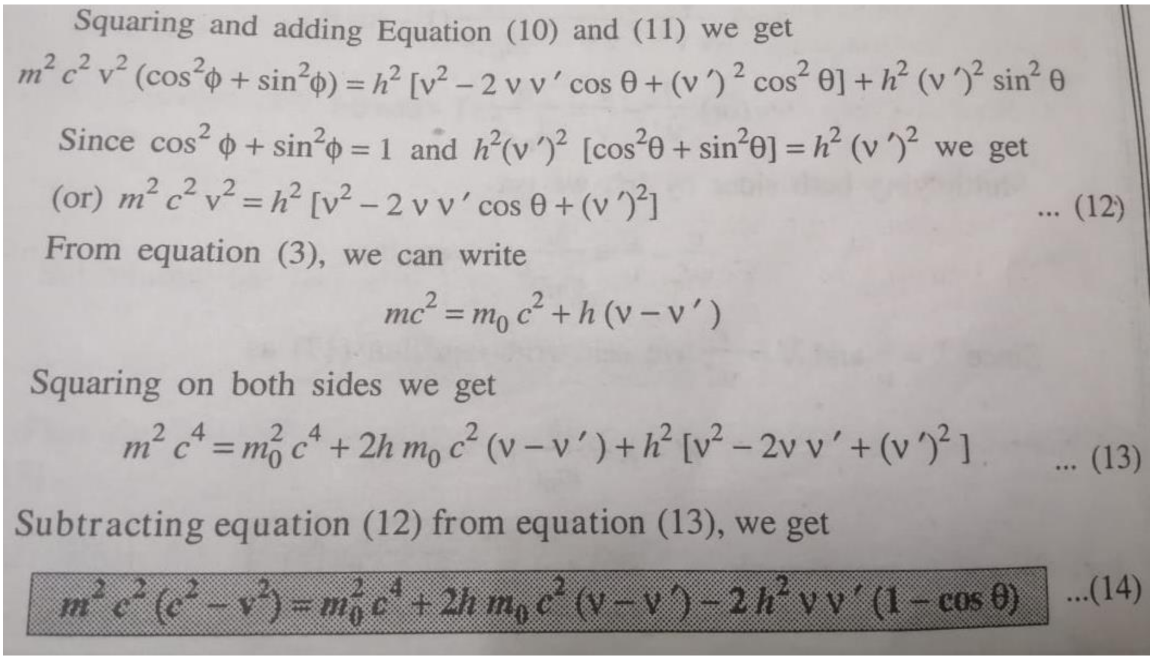
$$\text{(or) } mcv\cos\phi = h\,(\nu - \nu'\cos\theta) \qquad ...\ (10)$$

From equation (9) we can write

$$mcv\sin\phi = h\,\nu'\sin\theta \qquad ...\ (11)$$

Squaring and adding Equation (10) and (11) we get

$$m^2 c^2 v^2 (\cos^2\phi + \sin^2\phi) = h^2 [\nu^2 - 2\,\nu\,\nu'\cos\theta + (\nu')^2\cos^2\theta] + h^2 (\nu')^2 \sin^2\theta$$



Squaring and adding Equation (10) and (11) we get

$$m^2 c^2 v^2 (\cos^2\phi + \sin^2\phi) = h^2 [\nu^2 - 2\,\nu\,\nu'\cos\theta + (\nu')^2\cos^2\theta] + h^2 (\nu')^2 \sin^2\theta$$

Since $\cos^2\phi + \sin^2\phi = 1$ and $h^2(\nu')^2\ [\cos^2\theta + \sin^2\theta] = h^2\,(\nu')^2$ we get

$$\text{(or) } m^2 c^2 v^2 = h^2 [\nu^2 - 2\,\nu\,\nu'\cos\theta + (\nu')^2] \qquad ...\ (12)$$

From equation (3), we can write

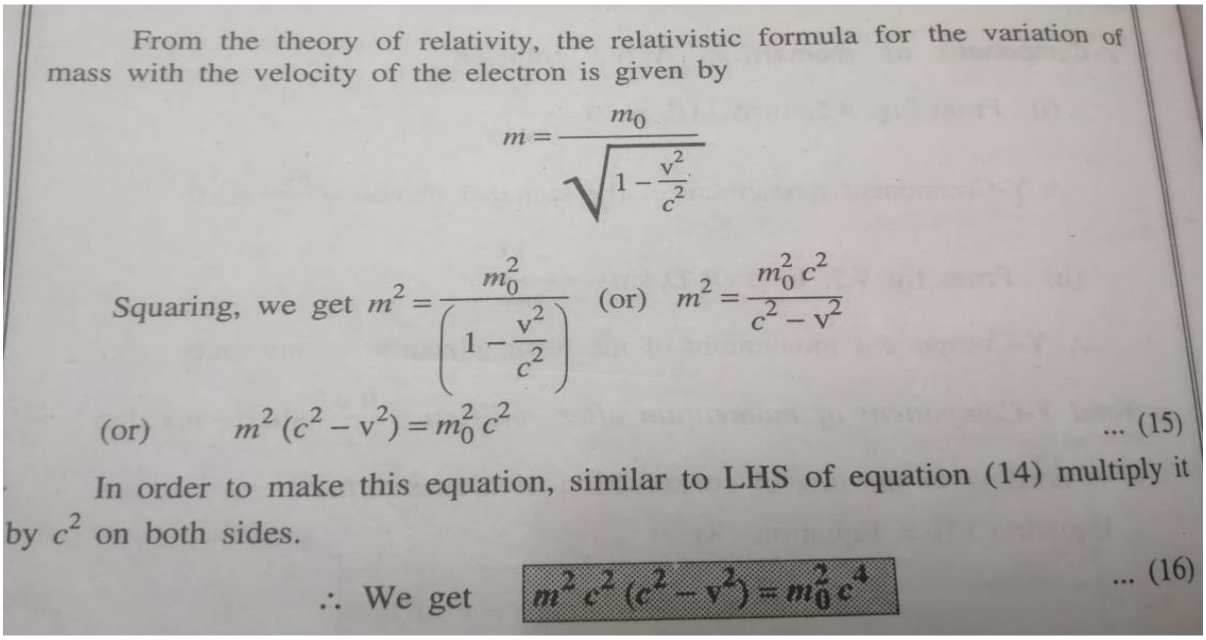
$$mc^2 = m_0 c^2 + h\,(\nu - \nu')$$

Squaring on both sides we get

$$m^2 c^4 = m_0^2 c^4 + 2h\, m_0 c^2 (\nu - \nu') + h^2 [\nu^2 - 2\nu\,\nu' + (\nu')^2] \qquad ...\ (13)$$

Subtracting equation (12) from equation (13), we get

$$\boxed{m^2 c^2 (c^2 - v^2) = m_0^2 c^4 + 2h\, m_0 c^2 (\nu - \nu') - 2\,h^2\,\nu\,\nu'(1 - \cos\theta)} \qquad ...(14)$$



From the theory of relativity, the relativistic formula for the variation of mass with the velocity of the electron is given by

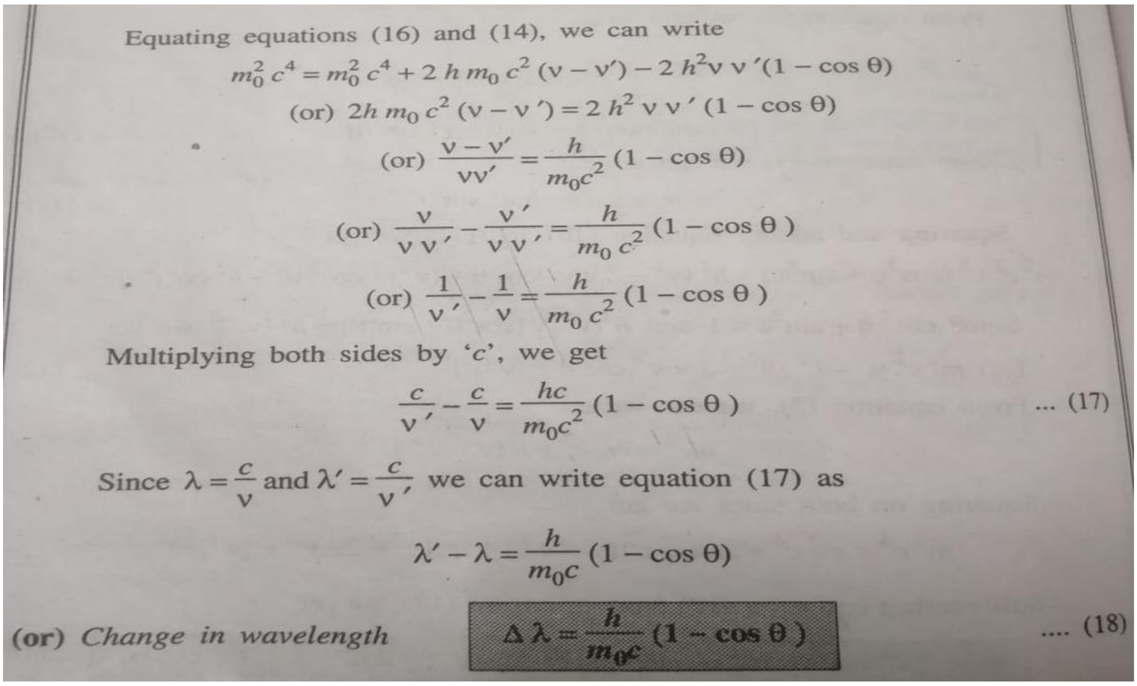
$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$$

Squaring, we get $m^2 = \dfrac{m_0^2}{\left(1 - \dfrac{v^2}{c^2}\right)}$ (or) $m^2 = \dfrac{m_0^2 c^2}{c^2 - v^2}$

(or) $m^2 (c^2 - v^2) = m_0^2 c^2$ ... (15)

In order to make this equation, similar to LHS of equation (14) multiply it by c^2 on both sides.

∴ We get $\boxed{m^2 c^2 (c^2 - v^2) = m_0^2 c^4}$ ... (16)



Equating equations (16) and (14), we can write

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

$$\text{(or)}\ 2h\,m_0\,c^2 (\nu - \nu') = 2\,h^2\,\nu\,\nu'\,(1 - \cos\theta)$$

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

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

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

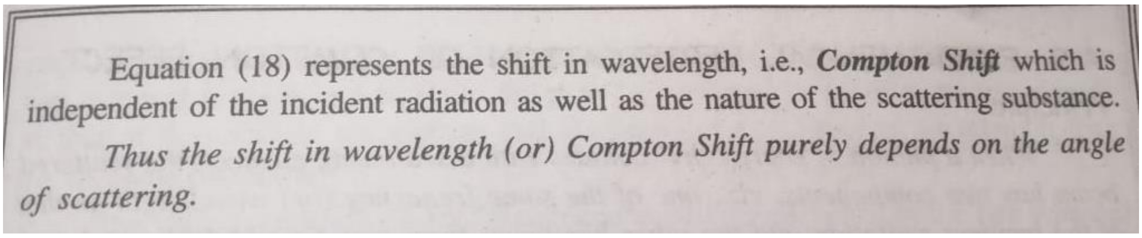
Multiplying both sides by 'c', we get

$$\frac{c}{\nu'} - \frac{c}{\nu} = \frac{hc}{m_0 c^2}(1 - \cos\theta) \quad \text{... (17)}$$

Since $\lambda = \dfrac{c}{\nu}$ and $\lambda' = \dfrac{c}{\nu'}$ we can write equation (17) as

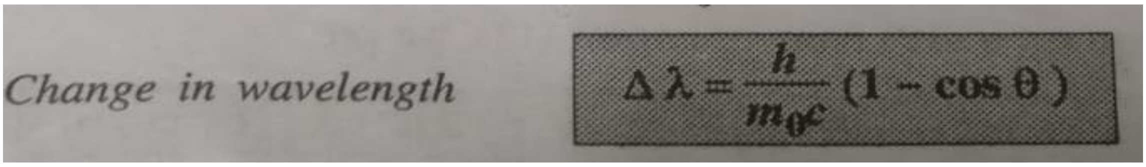
$$\lambda' - \lambda = \frac{h}{m_0 c}(1 - \cos\theta)$$

(or) *Change in wavelength* $\boxed{\Delta\lambda = \dfrac{h}{m_0 c}(1 - \cos\theta)}$ .... (18)



Equation (18) represents the shift in wavelength, i.e., ***Compton Shift*** which is independent of the incident radiation as well as the nature of the scattering substance.

Thus the shift in wavelength (or) Compton Shift purely depends on the angle of scattering.



Change in wavelength $\boxed{\Delta\lambda = \dfrac{h}{m_0 c}(1 - \cos\theta)}$

Special Cases:

Case (i) when $\theta = 0$; $\cos\theta = 1$

Eq. (18) becomes $\Delta\lambda = 0$

This implies that at $\theta = 0$ the scattering is absent and the outcoming radiation has the same wavelength or frequency as that of the incident radiation. Thus we get the output as a single peak.

Case (ii) when $\theta = 90^o$; $\cos\theta = 0$

Eq. (18) becomes $\Delta\lambda = \frac{h}{m_{0c}}$

Substituting the values of h, m_o and c we get

$$\Delta\lambda = 0.02424\ A^o$$

This wavelength is called Compton Wavelength, which has a good agreement with the experimental results.

Case (iii) when $\theta = 180^o$; $\cos\theta = -1$

Eq. (18) becomes $\Delta\lambda = \frac{h}{m_{0c}} [1-(-1)]$

$$\Delta\lambda = \frac{2h}{m_{0c}}$$

Substituting the values of h, m_o and c we get

$$\Delta\lambda = 0.04848\ A^o$$

Thus for = 180^o the shift in wavelength is found to be maximum. Therefore, when the angle of scattering (θ) varies from 0 to 180^o , the wavelength shifts from λ to $\lambda + \frac{2h}{m_{0c}}$.

2.5.1 Experimental verification of Compton Effect

Principle

When photon of energy hv collides with a scattering element, the scattered beam has two component one component having same frequency and the other has lower frequency. Hence, the shift in wavelength is called as Compton shift and the effect is known as Compton effect.

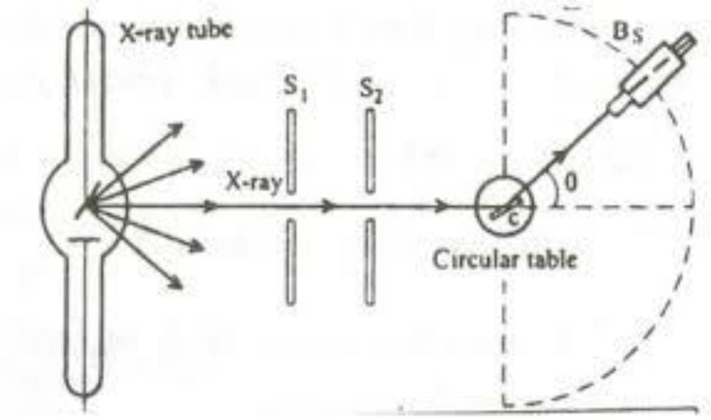
Construction & Working

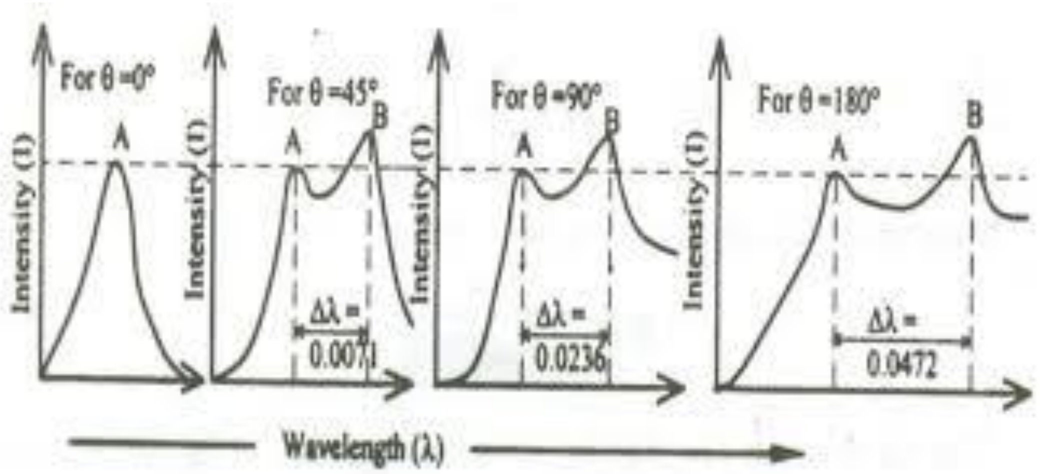
- X-ray tube is used to producing X-rays

- small block of carbon C acting as a scattering element mounted on a circular table

- Bragg's spectrometer (B) freely swing in an arc to catch the scattered photons

- Slits S1 and S2 – to focus the X-rays onto the scattering element





- **(i)** **Scattering angle $\theta = 0^o$ scattered radiation peak same as that of the incident radiation peak 'A'.**
- **(ii)** **Scattering angle increased – got two scattered peaks A and B**
  - **A is found to be of same wavelength as that of incident wavelength**
  - **B is of greater wavelength than the incident radiation**

2.6 Photon and its properties

Definition: Photon

The discrete energy values in the form of small packets or bundles or quantas of definite frequency or wavelength are called photons.

These photons propagates like a particle with speed of light (3×10^8 m/s)

Properties:

(i) **Photons are similar to that of electrons**

(ii) **For electrons the definite quantities are ‘e’ and ‘m’. Similarly for photons the definite quantities are ‘h’ and ‘c’**

(iii) **Photons will not have any charge. They are neutral and hence they are not affected by magnetic (or) electric field.**

(iv) **They do not ionise gas.**

(v) **Energy of the photon is given by $E = h\upsilon$, which varies w.r.t the type of radiation frequencies.**

(vi) **The momentum of photon is given by $p = m/\lambda$**

(vii) **The relation between energy and the momentum of the photon is given by**

$$E = m c^2$$

$$m = E/ c^2$$

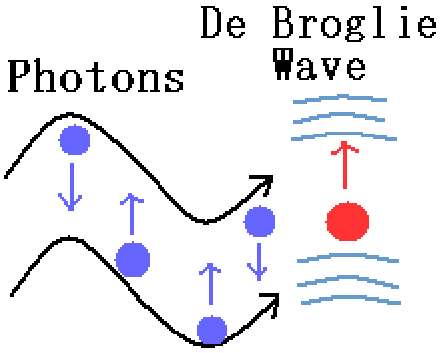
$$m = h\upsilon / c^2 = h / c\lambda$$

the momentum of the photon is given by,

$$p = mc = (h\upsilon / c^2) \times c = h\upsilon / c = h / \lambda$$

2.6.1 Dual Nature of Radiation (light) and Matter (particles) – Matter waves

- **De-Broglie concept of dual nature**
- **De-Broglie wavelength**
- **Other forms of de-Broglie wavelength**
  - **(i) de-Broglie wavelength in terms of energy**
  - **(ii) de-Broglie wavelength in terms of voltage**
  - **(iii) de-Broglie wavelength in terms of temperature**



Matter Waves: de-Broglie concept

In 1924, Lewis de-Broglie proposed that matter has dual characteristic just like radiation. His concept about the dual nature of matter was based on the following observations:

- **The whole universe is composed of matter and electromagnetic radiations. Since both are forms of energy so can be transformed into each other.**
- **As the radiation has dual nature, matter should also possess dual character.**

(i) de-Broglie wavelength

From the theory of light – photon as a particle - the total energy of the photon is

$$E = m c^2 \qquad (1)$$

where m = mass of the particle

c = velocity of light

Photon as a wave, the total energy is given by

$$E = h \upsilon \qquad (2)$$

where h = Planck's constant

υ = frequency of radiation

From eqs (1) and (2) , $E = m c^2 = h \upsilon \qquad (3)$

momentum = mass x velocity

$$p = mc$$

Eq.(3) becomes $h \upsilon = m c^2 = pc$

$$p = h \upsilon / c \qquad \text{since } c/\upsilon = \lambda$$

$$p = h / \lambda$$

The wavelength of a photon $\lambda = h/p$ (4)

De-Broglie suggested eq.(4) can be applied both – for photons and material particles.

If m is the mass of the particle and v is the velocity of the particle,

Momentum $p = mv$

De-Broglie wavelength $\lambda = h/mv$ (5)

Other forms of de-Broglie wavelength

(i) de-Broglie wavelength in terms of energy

Kinetic Energy $E = \frac{1}{2} mv^2$

Multiplying by 'm' on both sides $E\,m = \frac{1}{2} m^2v^2$

$$m^2v^2 = 2\,E\,m$$

$$mv = \sqrt{2Em}$$

De-Broglie wavelength $\lambda = h / \sqrt{2Em}$ (6)

(ii) de-Broglie wavelength in terms of voltage

If a charged particle of charge 'e' is accelerated through a potential difference 'V'

the K.E of the particle $= \frac{1}{2} mv^2$ (7)

also the energy $= eV$ (8)

Equating eqs. (7) and (8) we get

$$\frac{1}{2} mv^2 = eV$$

Multiplying by 'm' on both side we get

$$m^2v^2 = 2\,m\,e\,V$$

$mv = \sqrt{2meV}$ (9)

Substituting eq. (9) in (5), we get

De-Broglie wavelength $\lambda = h / \sqrt{2meV}$ (10)

(ii) de-Broglie wavelength in terms of temperature

When a particle like neutron is in thermal equilibrium at temp T, then they possess Maxwell distribution of velocities.

Their K. E $E_k = \frac{1}{2} m\, v_{rms}^2$ (11)

Energy = 3/2 K_B T **(12)**

Equating eqs. (11) and (12)

$$\tfrac{1}{2}\, m\, v_{rms}^2 = 3/2\ K_B\ T$$

$$m^2v^2 = 3\ m\ K_B\ T$$

$$mv = \sqrt{3mK_B\ T}$$

De-Broglie wavelength $\lambda = h / mv = h / \sqrt{3mK_B\ T}$ **(13)**

2.7 Heisenberg uncertainty principle

Uncertainty principle, also called Heisenberg uncertainty principle or indeterminacy principle – 1927 - German physicist Werner Heisenberg

the position and the velocity of an object cannot both be measured exactly, at the same time, even in theory.

The very concepts of exact position and exact velocity together, in fact, have no meaning in nature.

Position and momentum cannot be measured accurately simultaneously

$$\Delta x\ \Delta p \geq \frac{h}{4\pi}$$

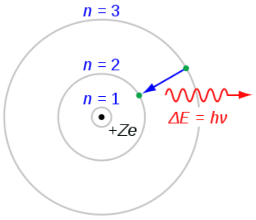
Δx **= Uncertainty of Position**

Δp **= Uncertainty of Momentum**

2.8 Bohr Atom Model

Introduction:

- **Bohr assumed basically Rutherford nuclear-model**
- **It overcomes the defect of the Rutherford model**



Basic Postulates:

(i) **An electron cannot revolve round the nucleus in all possible orbits**

(ii) The electron can revolve round the nucleus only in those allowed or permissible orbits – angular momentum of the electron is an integral multiple of $\hbar$ ($\hbar$ is the Planck's constant)

(iii) $\hbar = h/2\pi$

(iv) These orbits are called stationary orbits and an electron revolving in these orbits does not radiate energy – non-radiating paths of electrons.

Explanation:

For an electron of mass m, moving with a speed v in an orbit of radius r,

$L = mvr = mr^2\omega = n\hbar$. (n is Principal Quantum number; it takes integral values, excluding zero; n = 1, 2, 3……)

An atom radiates energy only when an electron jumps from a stationary orbit of higher energy to one of lower energy.

The difference of energies is radiated and must be quantum of energy $h\upsilon$.

If the electron jumps form an initial orbit of energy E_i to a final orbit of energy E_f ($E_i > E_f$), a photon of frequency

$\upsilon = E_i - E_f / h$ …..is emitted $(E_2 - E_1) = h\upsilon$

The Bohr formula:

Based on these postulates, Bohr derived the formulae for

(i) The radii of the stationary orbits

(ii) Velocity of revolving electron

(iii) The total energy of the electron in the orbit

(iv) Orbital frequency of electron

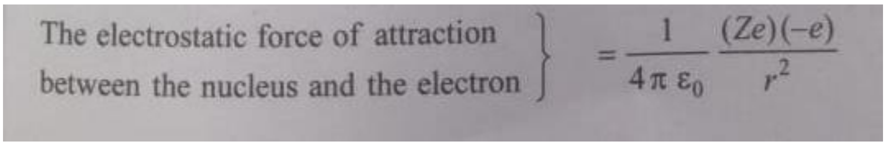
Consider an atom whose nucleus has a positive charge Ze and mass M.

For hydrogen, Z=1.

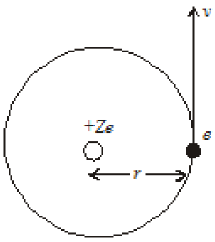
Let an electron of charge (-e) and mass m move round the nucleus in an orbit of radius r.

Since M >>m, the nucleus is stationary (mass of the nucleus is negligible)

The electrostatic force of attraction,



$$\left.\begin{array}{l}\text{The electrostatic force of attraction}\\ \text{between the nucleus and the electron}\end{array}\right\} = \frac{1}{4\pi\varepsilon_0}\frac{(Ze)(-e)}{r^2}$$



The centrifugal force on the electron = mv^2 /r

The system will be stable if $mv^2 /r = (1/ 4\pi \varepsilon_0) (Ze^2 /r^2)$ ….(1)

According to Bohr's first postulate, $mvr = n \hbar = nh / 2 \pi$ ….(2)

$$v = nh / 2 \pi mr$$

The frequency $h \upsilon$ of the emitted radiation is related by the eq. $E_2 – E_1 = h \upsilon$ …(3)

Drawbacks of Bohr Atom Model

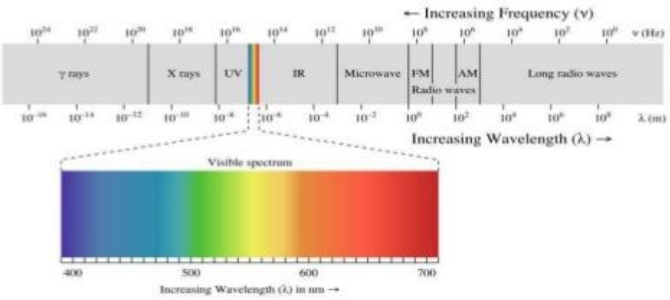
- **In Bohr theory, we have two rival theories – classical and quantum. The equilibrium is governed by the classical laws, while the emission of radiation is explained by quantum rules.**
- **Bohr's theory could not explain the fine structure of the spectral lines**
- **The theory does not give any information about the relative intensities of different lines.**
- **With the help of Bohr theory, it is difficult to treat dynamical problems of atoms containing more than one valence electron**

Bohr's theory could not explain Zeeman Effect and Stark effect in which the spectral lines could be split up under the influence of magnetic and electric fields.

2.9 Atomic Spectra

When atoms are excited by photon they emit light of certain wavelengths which correspond to different colors. The emitted light can be observed as a series of colored lines with dark spaced in between, this series of colored line or atomic spectra.

Diagram of Atomic Spectra



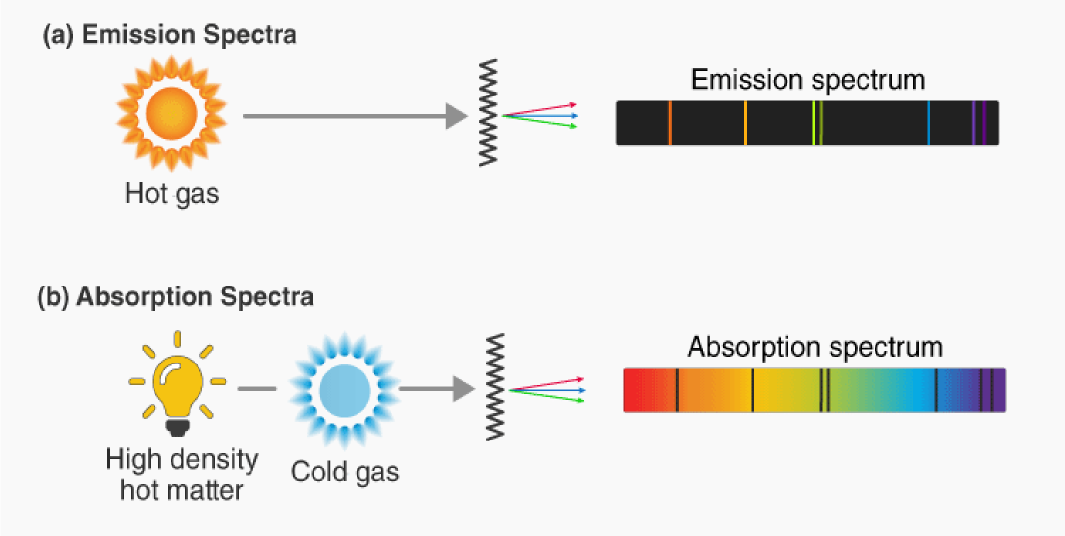
What is Atomic Spectra?

The spectrum of the electromagnetic radiation emitted or absorbed by an electron during transitions between different energy level within an atom.

When an electron gets excited from one energy level to another, it either emits or absorbs light of a specific wavelength. The collection of all these specific wavelengths of the atom in a given set of conditions like pressure, temperature, etc is the atomic spectra of atoms.

There are three types of atomic spectra:

- **emission spectra**
- **absorption spectra**
- **continuous spectra.**



What is Emission Spectrum?

When energy is absorbed by electrons of an atom, electrons move from lower energy levels to higher energy levels. These excited electrons have to radiate energy to return to ground states from the excited state, which is unstable. The emission spectrum is formed by the frequencies of these emitted light.

The lines come from photons of a specific energy, emitted by electrons making transitions between specific energy levels of the atom. When an electron in an atom falls from a higher energy level to a lower energy level, it emits a photon to carry off the extra energy. This photon's energy is equal to the energy difference between the two energy levels.

What is Absorption Spectrum?

An absorption spectrum is constituted by the frequencies of light transmitted with dark bands when energy is absorbed by the electrons in the ground state to reach higher energy states.

Atoms do not only emit photons; they also absorb photons. If a photon hits an atom and the energy of the photon is the same as the gap between two electron energy levels in the atom, then the electron in the lower energy level can absorb the photon and jump up to the higher energy level. If the photon energy does not correspond to the difference between two energy levels then the photon will not be absorbed (it can still be scattered).

Using this effect, if we have a source of photons of various energies we can obtain the absorption spectra for different materials.

To get an absorption spectrum, just shine white light on a sample of the material. White light is made up of all the different wavelengths of visible light put together.

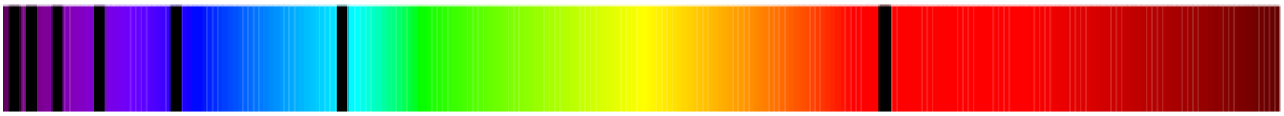
In the absorption spectrum there will be gaps. The gaps correspond to energies (wavelengths) for which there is a corresponding difference in energy levels for the particular element.

The absorbed photons show up as black lines because the photons of these wavelengths have been absorbed and do not show up.

Because of this, the absorption spectrum is the exact *inverse* of the emission spectrum.

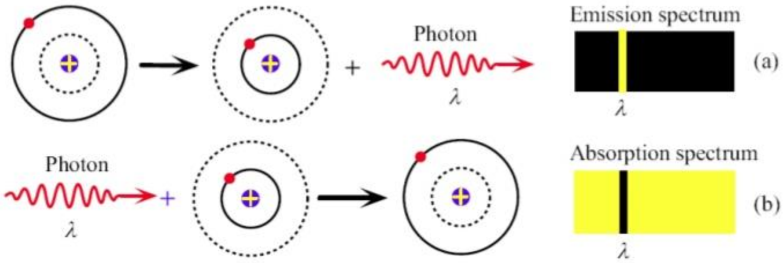
It is the exact opposite of the emission spectrum.

Both emission and absorption techniques can be used to get the same information about the energy levels of an atom.



The dark lines correspond to the frequencies of light that have been absorbed by the gas. As the photons of light are absorbed by electrons, the electrons move into higher energy levels. This is the opposite process of emission.

The dark lines, absorption lines, correspond to the frequencies of the emission spectrum of the same element. The amount of energy absorbed by the electron to move into a higher level is the same as the amount of energy released when returning to the original energy level.



The physical origin of spectra.

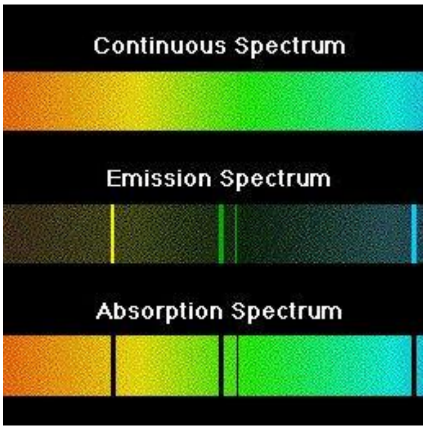
(a) Emission
(b) Absorption

What is Continuous Spectrum?

Rainbow have probably seen a continuous spectrum as it is agreed that the sun's light contain this kind of spectrum although you will learn that this is not so all the time.

When white light is passed through a prism, it produces a rainbow of colors because of the different wavelengths that refract (bend) at different angles when they go through the prism.

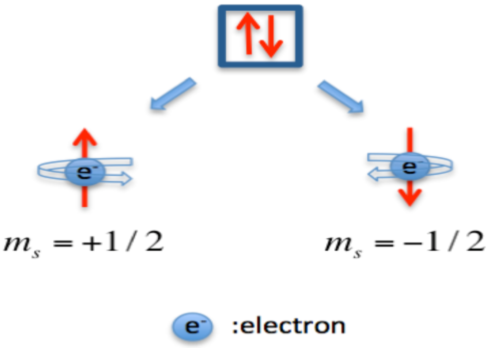
If the rainbow that is produced has all the colors from red to violet, and has no gaps between them, then it is referred to as a continuous spectrum.

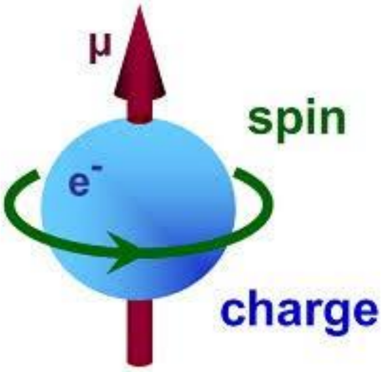


UNIT – III – Atom with One Electron-Hydrogen atom – SPH1311

3.1 Electron spin

- Spin is an intrinsic property of particles.
- This property was deduced from the Stern-Gerlach experiment.
- From other observations it can be concluded that spin is a property of elementary particles, such as protons, neutrons and electrons.
- Spin is a vector quantity.
- The characteristic values of the component of the spin in any prescribed direction are given by ħ/2 and - ħ/2.
- The spin is measured in unit of ħ and the characteristic values are ½ and -½.
- This type of behaviour can be described by a quantum number s = ½.





S.A. Goutsmit and G.E. Uhlenbeck, in 1925 - an electron has an inherent angular momentum that is a magnetic moment that is recognized as spin.

In atomic physics, the inherent angular momentum of a particular particle is parametrized by spin quantum number S.

The spin quantum number is the fourth number. The rest three are a principal quantum number, azimuthal quantum number, and magnetic quantum number.

The spin quantum number explains the unique quantum state of an electron.

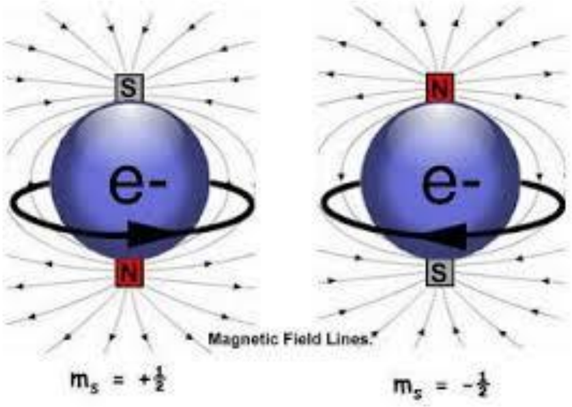
The Spins play a noteworthy role in quantum mechanics in computing the characteristics of elementary units like electrons.

The direction of spin of the particle regulates several things like the spin quantum number, angular momentum, the degree of freedom, etc.

The electron can spin in two directions:

The spin up and spin down direction are corresponding to the spinning in the +z or –z direction.

These spins (spin up and spin down) are the particles which have spin s equal to 1/2, i.e for electrons.

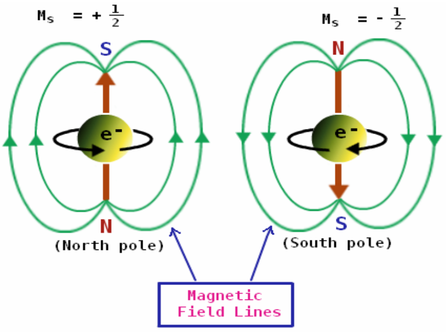


3.2 Electron Spin Theory

The electron spin theory describes the electron as a quantum particle instead of the simple sphere as in the classical theory.

The theory says that the electron spin direction and its influence on certain properties like the magnetic properties of the atom.

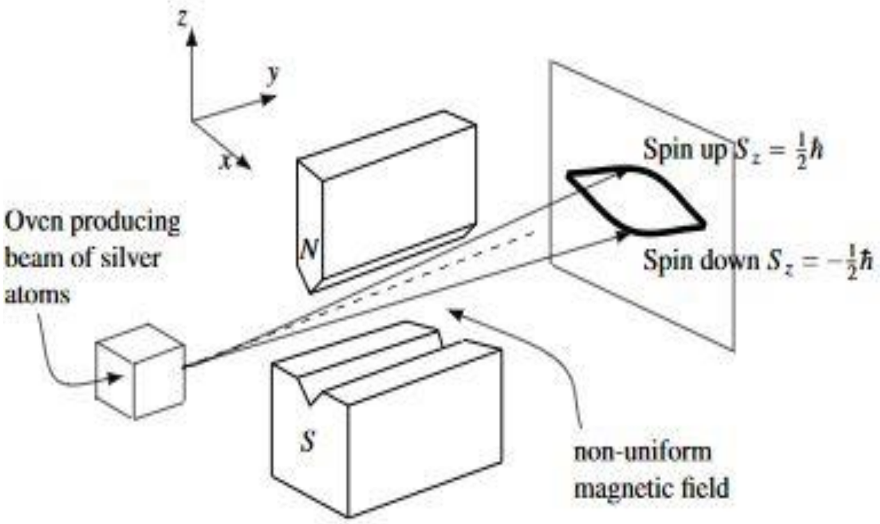
In the quantum theory, the electron is thought of like the minute magnetic bar, and its spin points the north pole of the minute bar. If two proximate electrons have a similar spin direction, the magnetic field formed by them strengthens each other and therefore a strong magnetic field is gained. If the proximate electrons have an opposite spin direction, the magnetic field formed by them cancels each other and no magnetic field is existent.



3.3 Stern-Gerlach experiment:

Stern-Gerlach experiment, demonstration of the restricted spatial orientation of atomic and subatomic particles with magnetic polarity, performed in the early 1920s by the German physicists Otto Stern and Walther Gerlach.

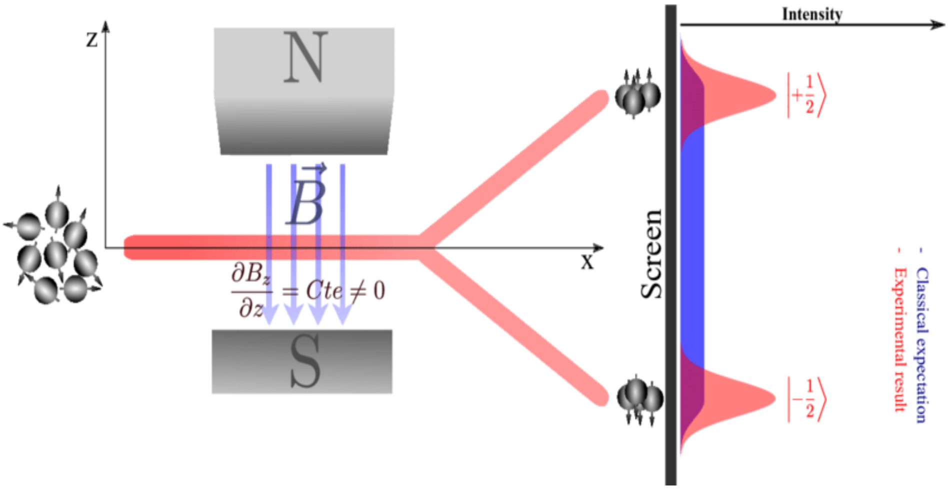
In the experiment, a beam of neutral silver atoms was directed through a set of aligned slits, then through a nonuniform (nonhomogeneous) magnetic field, and onto a cold glass plate.



An electrically neutral silver atom is actually an atomic magnet: the spin of an unpaired electron causes the atom to have a north and south pole like a tiny compass needle.

In a uniform magnetic field, the atomic magnet, or magnetic dipole, only precesses as the atom moves in the external magnetic field.

In a nonuniform magnetic field, the forces on the two poles are not equal, and the silver atom itself is deflected by a slight resultant force, the magnitude and direction of which vary in relation to the orientation of the dipole in the nonuniform field.



A beam of neutral silver atoms directed through the apparatus in the absence of the nonuniform magnetic field produces a thin line, in the shape of the slit, on the plate.

When the nonuniform magnetic field is applied, the thin line splits lengthwise into two distinct traces, corresponding to just two opposite orientations in space of the silver atoms.

If the silver atoms were oriented randomly in space, the trace on the plate would have broadened into a wide area, corresponding to numerous different deflections of the silver atoms.

This restricted orientation, called space quantization, is manifested by other atoms and subatomic particles that have nonzero spin (angular momentum), with its associated magnetic polarity, whenever they are subjected to an appropriate nonuniform magnetic field.

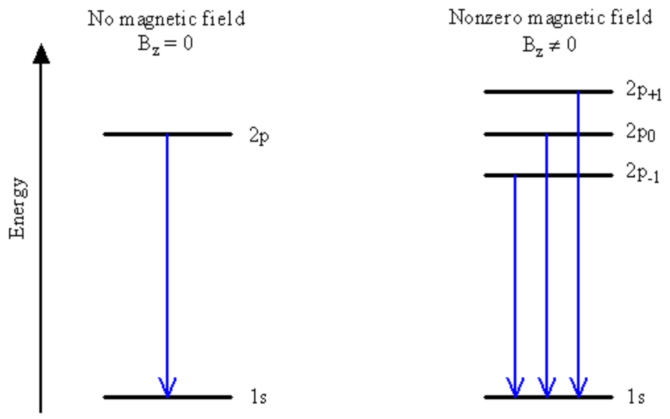
3.4 Normal and anomalous Zeeman Effect

- **Zeeman effect**
- **Normal Zeeman effect**
    - **Experimental arrangement for the normal Zeeman effect**
    - **normal longitudinal Zeeman effect**
    - **normal transverse Zeeman effect**
- **Anamolous Zeeman effect**

What is Zeeman effect?

- **Zeeman effect is a magnet-optical phenomenon**
- **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 – normal Zeeman effect – explained quantitatively by classical theory.**

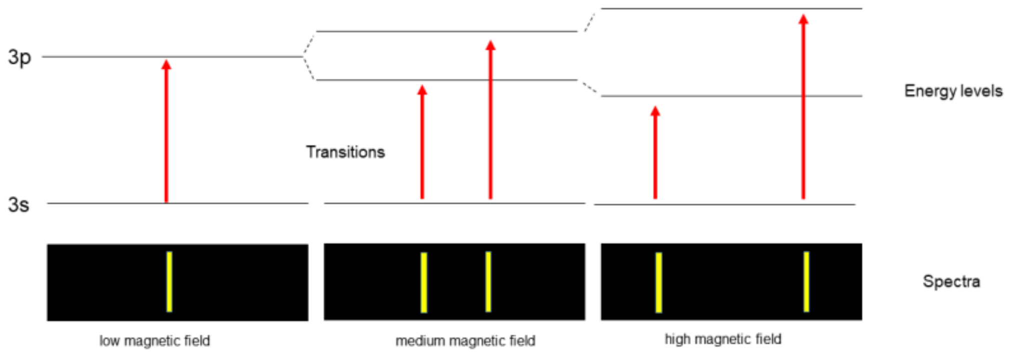
The splitting of a spectral line into more than three components in ordinary weak magnetic field – anomalous Zeeman effect – cannot by explained by classical theory.



The Zeeman effect is the splitting of energy levels of atoms and molecules upon the presence of a magnetic field.

The effect describes the splitting of spectral lines by a magnetic field into multiple closely spaced lines, with the spacing of the lines being dependent on the strength of the magnetic field.

Due to this, the spacing can be used to measure the magnetic field of distant bodies such as the Sun and other stars, the Earth and also plasmas.

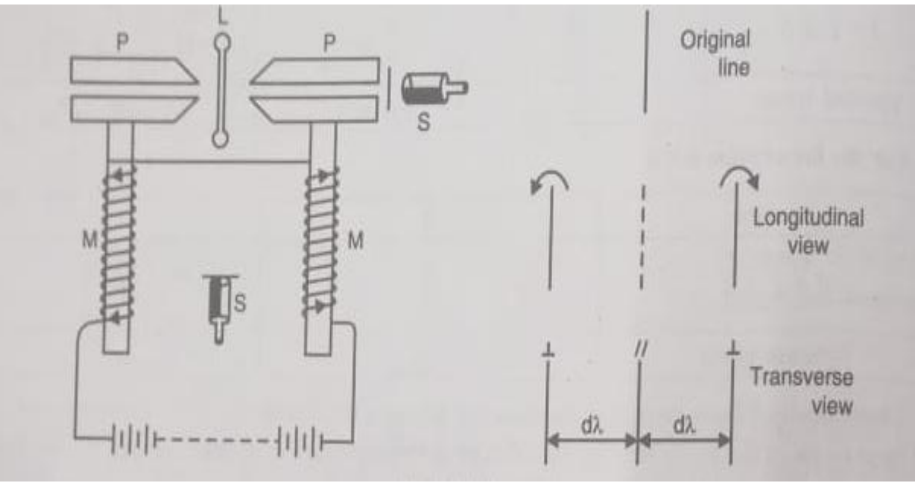


Zeeman effect

3.4.1 Experimental arrangement for the normal Zeeman effect

Description and explanation:

- **MM – electromagnet – very strong magnetic field**
- **PP – conical pole-pieces – longitudinal holes drilled through them**
- **L – light source (sodium vapour lamp) – emitting line spectrum – placed between pole-pieces**
- **S – spectrograph (high resolving power) – observe spectral lines**



Observation of Zeeman effect: two ways to observe Zeeman effect

<u>Longitudinal view</u> (normal longitudinal Zeeman effect)

- **H switched on**

- **Spectral line is viewed through the hole drilled in the pole-pieces longitudinally - parallel to the direction of the field**
- **Spectral line is split into two components:**

  - one slightly shorter in λ

  - other slightly longer in λ

  - original is not present
- **Two components – symmetrically situated w.r.t position of the line**
- **Analyzing two lines with a Nicol prism – both lines – circularly polarized in opposite directions**

Transverse view (normal transverse Zeeman effect)

- **H switched on**
- **Spectral line is viewed through the hole drilled in the pole-pieces transversely - perpendicular to the direction of the field**
- **Spectral line is split into three components:**

  - one slightly shorter in λ

  - other slightly longer in λ

  - central line has same λ
- **Outer lines – symmetrically situated on either side of the central line**
- **Two outer lines – plane polarized having vibrations in a directions perpendicular to the field**

Selection Rules

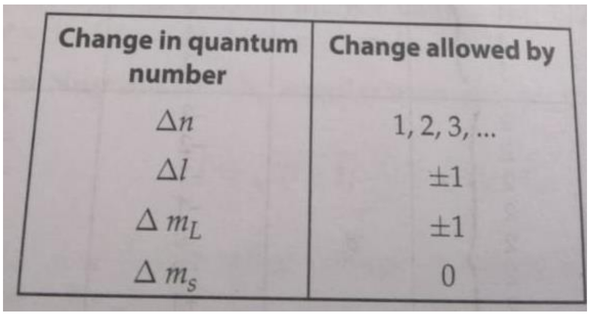
The energy level diagrams showing electron transitions from one level to the other are used to describe the structure and configuration of electrons in atoms - Grotrian diagram or Term diagram.

But the electron transitions among various energy levels are not always allowed.

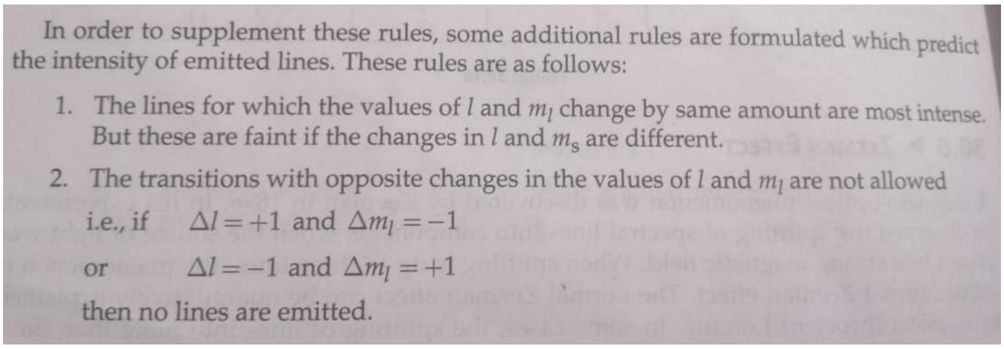
These are governed by a set of rules which are known as selection rules.

There are rules that govern the change in the values of four quantum numbers n, l, j and s.

For radiative transitions to take place, the selection rules are shown in table.



Change in quantum number	Change allowed by
Δn	1, 2, 3, ...
Δl	± 1
Δm_L	± 1
Δm_s	0



In order to supplement these rules, some additional rules are formulated which predict the intensity of emitted lines. These rules are as follows:

1. The lines for which the values of l and m_l change by same amount are most intense. But these are faint if the changes in l and m_s are different.
2. The transitions with opposite changes in the values of l and m_l are not allowed

i.e., if $\Delta l = +1$ and $\Delta m_l = -1$

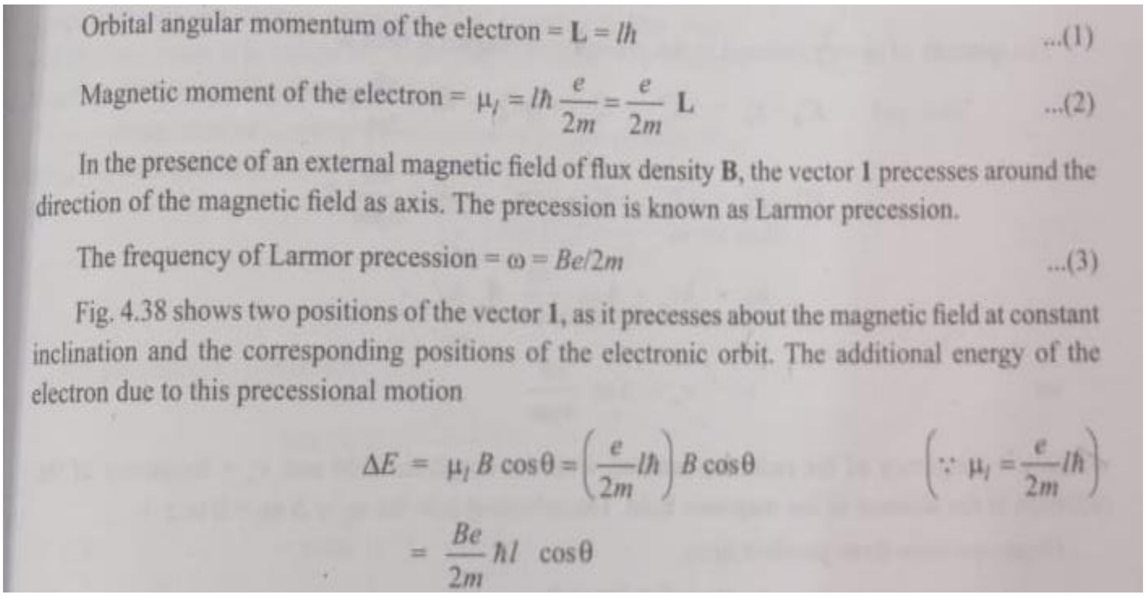
or $\Delta l = -1$ and $\Delta m_l = +1$

then no lines are emitted.

3.4.2 Quantum mechanical explanation of the normal zeeman effect

Debye explained the normal Zeeman effect without taking into account the concept of electron spin.

We neglect the spin motion of the electron,



Orbital angular momentum of the electron = $\mathbf{L} = l\hbar$ ...(1)

Magnetic moment of the electron = $\mu_l = l\hbar \dfrac{e}{2m} = \dfrac{e}{2m}\mathbf{L}$ ...(2)

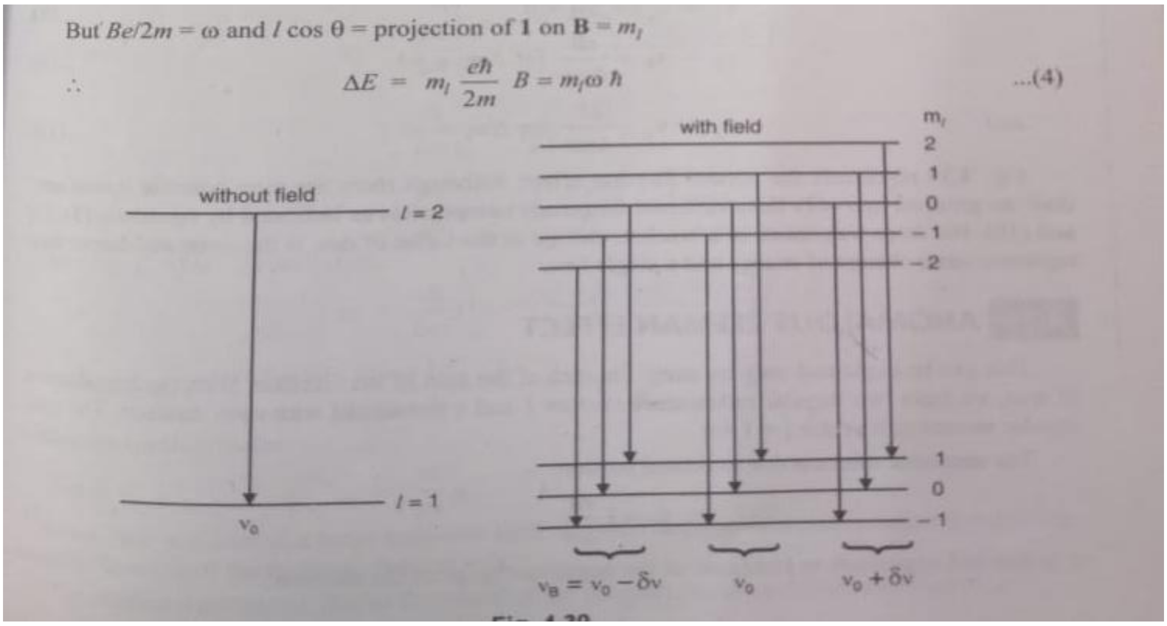
In the presence of an external magnetic field of flux density **B**, the vector **l** precesses around the direction of the magnetic field as axis. The precession is known as Larmor precession.

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

Fig. 4.38 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

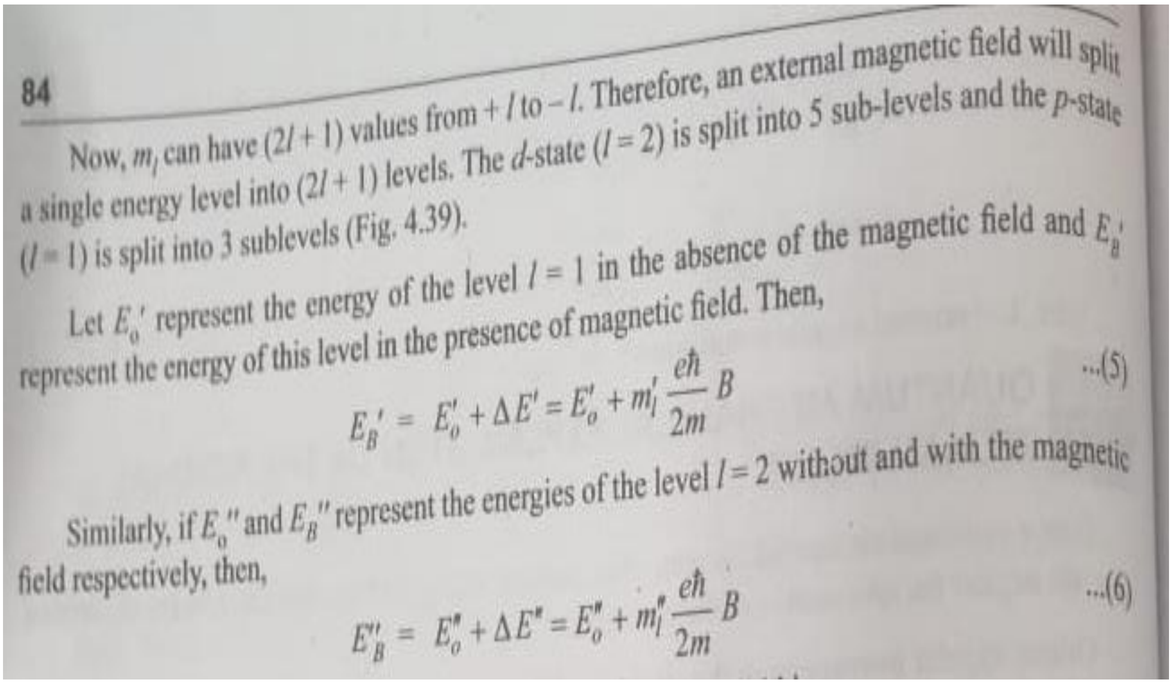
$$\Delta E = \mu_l B\cos\theta = \left(\frac{e}{2m} l\hbar\right) B\cos\theta \qquad \left(\because \mu_l = \frac{e}{2m} l\hbar\right)$$

$$= \frac{Be}{2m}\hbar l \ \cos\theta$$



But $Be/2m = \omega$ and $l \cos\theta$ = projection of $\mathbf{l}$ on $\mathbf{B} = m_l$

$$\therefore \qquad \Delta E = m_l \frac{e\hbar}{2m} B = m_l \omega \hbar \qquad \text{...(4)}$$



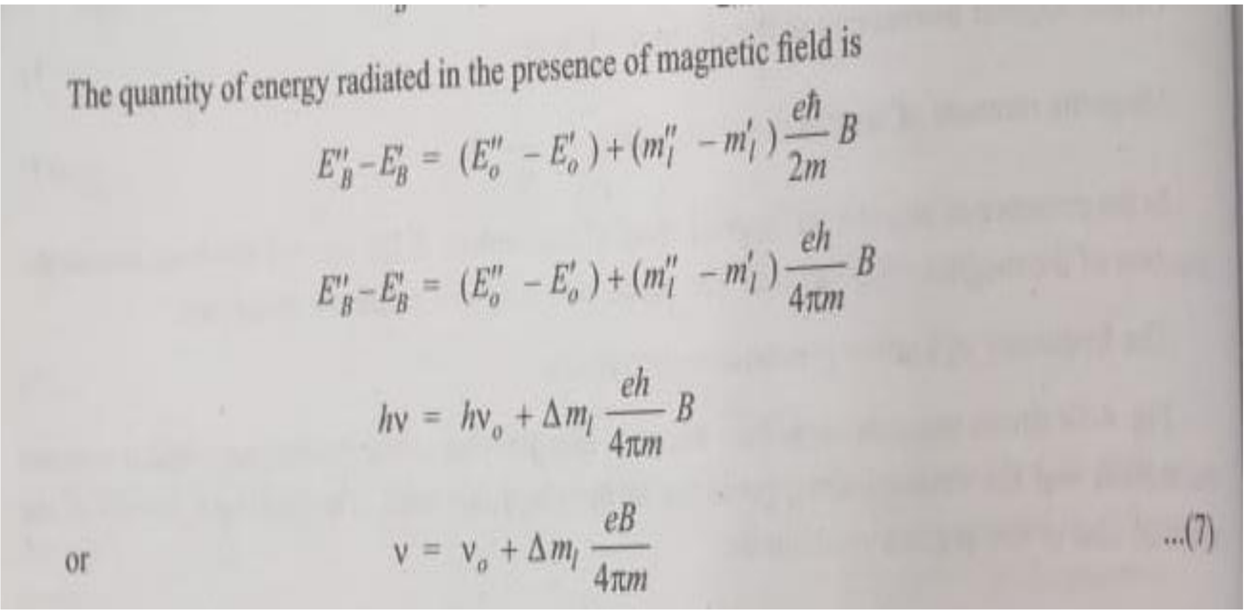
Now, m_l can have $(2l + 1)$ values from $+l$ to $-l$. Therefore, an external magnetic field will split a single energy level into $(2l + 1)$ levels. The *d*-state ($l = 2$) is split into 5 sub-levels and the *p*-state ($l = 1$) is split into 3 sublevels (Fig. 4.39).

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

$$E_B' = E_0' + \Delta E' = E_0' + m_l' \frac{e\hbar}{2m} B \qquad \text{...(5)}$$

Similarly, if E_0'' and E_B'' represent the energies of the level $l = 2$ without and with the magnetic field respectively, then,

$$E_B'' = E_0'' + \Delta E'' = E_0'' + m_l'' \frac{e\hbar}{2m} B \qquad \text{...(6)}$$



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

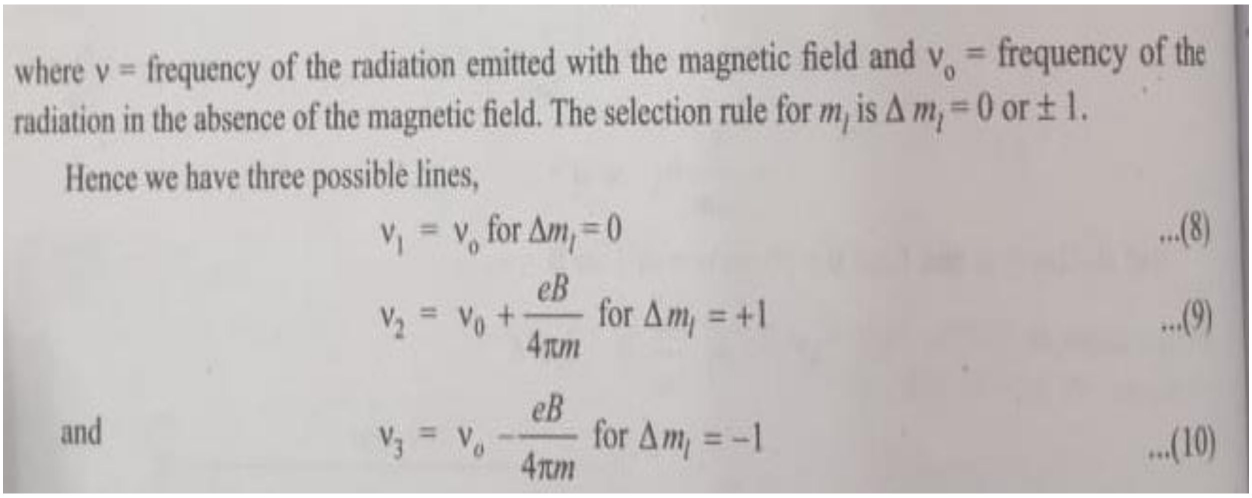
$$E''_B - E'_B = (E''_o - E'_o) + (m''_l - m'_l)\frac{e\hbar}{2m}B$$

$$E''_B - E'_B = (E''_o - E'_o) + (m''_l - m'_l)\frac{eh}{4\pi m}B$$

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

or

$$\nu = \nu_o + \Delta m_l \frac{eB}{4\pi m} \qquad ...(7)$$



where ν = frequency of the radiation emitted with the magnetic field and ν_o = 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,

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

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

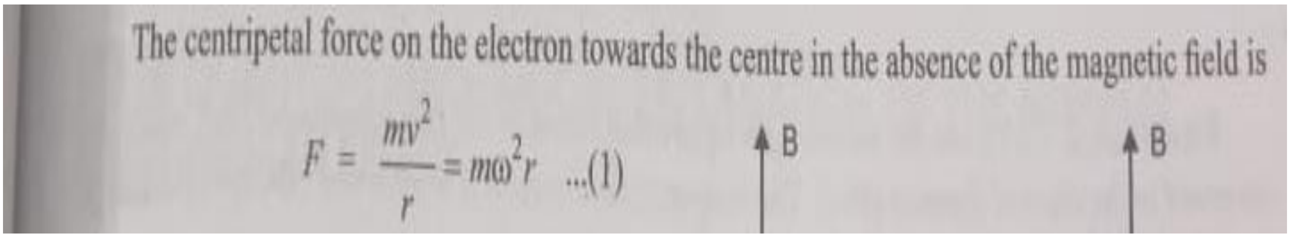
and

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

3.4.3 Expression for the Zeeman effect : (Lorentz classical theory of normal Zeeman effect)

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 is

$$F = \frac{mv^2}{r} = m\omega^2 r \quad ...(1)$$

Now let consider,

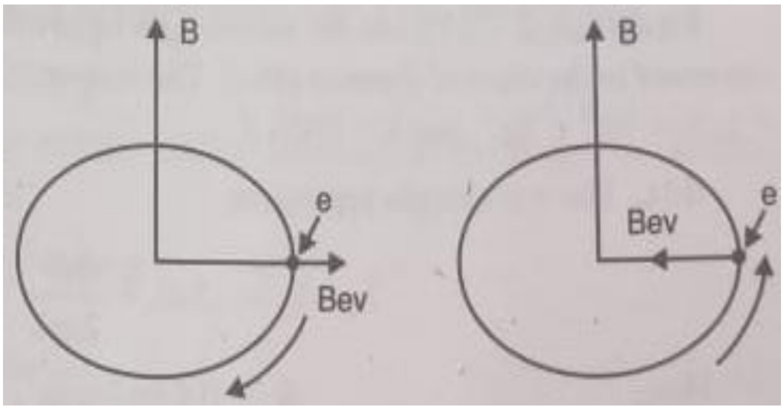
B – magnetic field of flux density is applied in a direction perpendicular to the plane of the orbits of the two circular components.

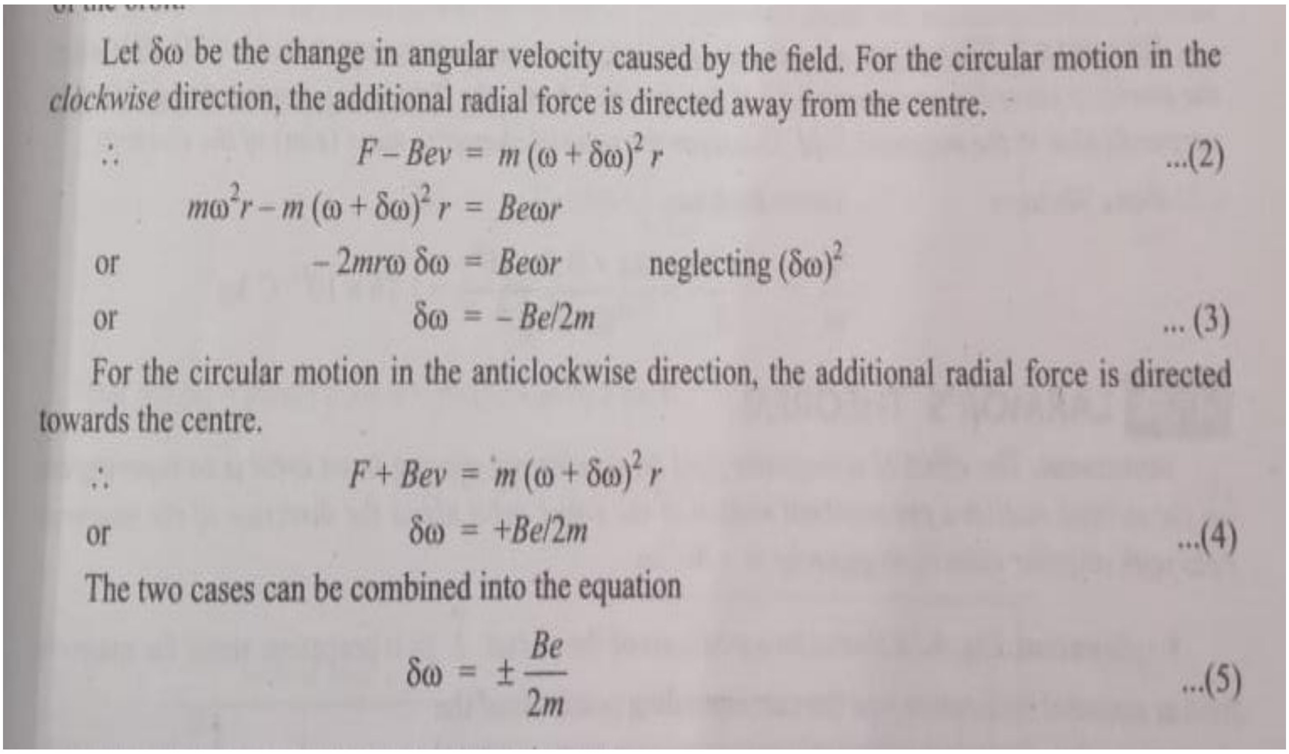
Then an additional radial force of magnitude Bev acts on the electron.

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 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.

$$\therefore \quad F - Bev = m(\omega + \delta\omega)^2 r \qquad ...(2)$$

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

$$\text{or} \quad -2mr\omega\,\delta\omega = Be\omega r \qquad \text{neglecting } (\delta\omega)^2$$

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

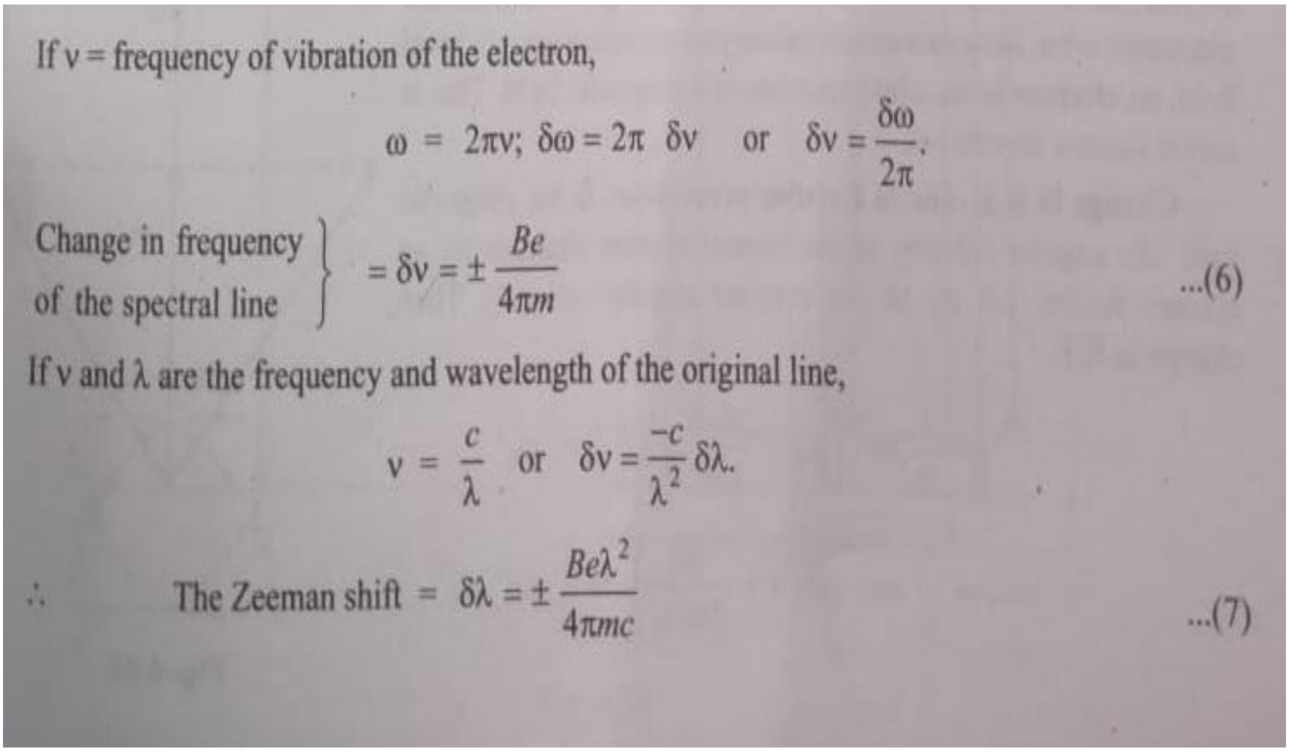
For the circular motion in the anticlockwise direction, the additional radial force is directed towards the centre.

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

$$\text{or} \quad \delta\omega = +Be/2m \qquad ...(4)$$

The two cases can be combined into the equation

$$\delta\omega = \pm \frac{Be}{2m} \qquad ...(5)$$



If ν = frequency of vibration of the electron,

$$\omega = 2\pi\nu;\ \delta\omega = 2\pi\ \delta\nu \quad \text{or} \quad \delta\nu = \frac{\delta\omega}{2\pi}.$$

$$\left.\begin{array}{l}\text{Change in frequency}\\ \text{of the spectral line}\end{array}\right\} = \delta\nu = \pm\frac{Be}{4\pi m} \qquad \text{...(6)}$$

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

$$\nu = \frac{c}{\lambda} \quad \text{or} \quad \delta\nu = \frac{-c}{\lambda^2}\delta\lambda.$$

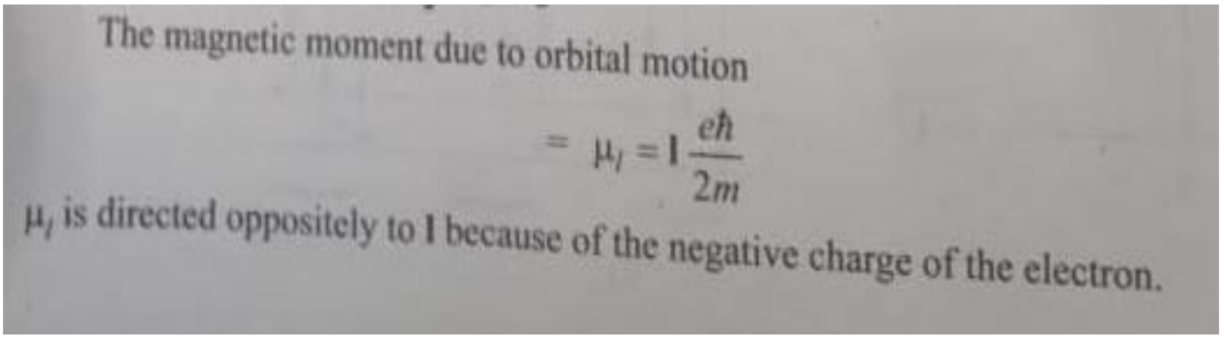
$$\therefore \qquad \text{The Zeeman shift} = \delta\lambda = \pm\frac{Be\lambda^2}{4\pi mc} \qquad \text{...(7)}$$

3.4.5 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 1 and s associated with each electron.

The total angular momentum vector j = 1 + s ….. (1)

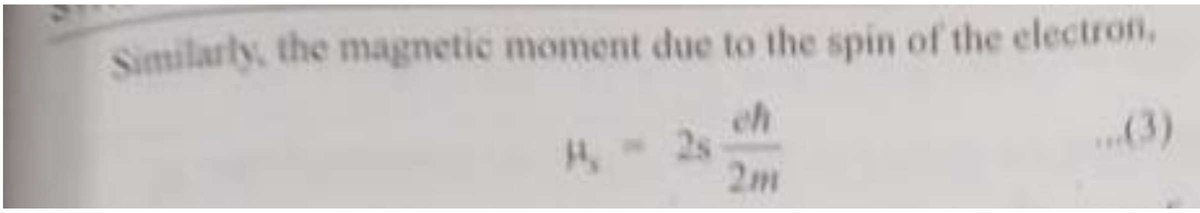


The magnetic moment due to orbital motion

$$= \mu_l = l\,\frac{e\hbar}{2m}$$

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

Similarly, the magnetic moment due to the spin of the electron



Similarly, the magnetic moment due to the spin of the electron,

$$\mu_s = 2s\frac{e\hbar}{2m} \qquad \ldots(3)$$

μ_S is directed oppositely to s because of the negative charge of the electron

Total magnetic moment (or) angular momentum = orbital magnetic moment + spin magnetic moment + nuclear magnetic moment .

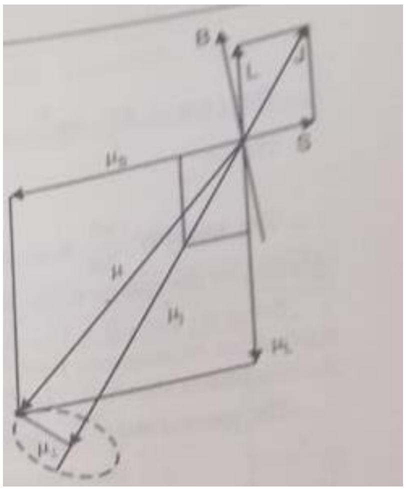
Total magnetic moment = orbital magnetic moment + spin magnetic moment

The relationships between the magnetic moments and the angular momenta are shown in figure.

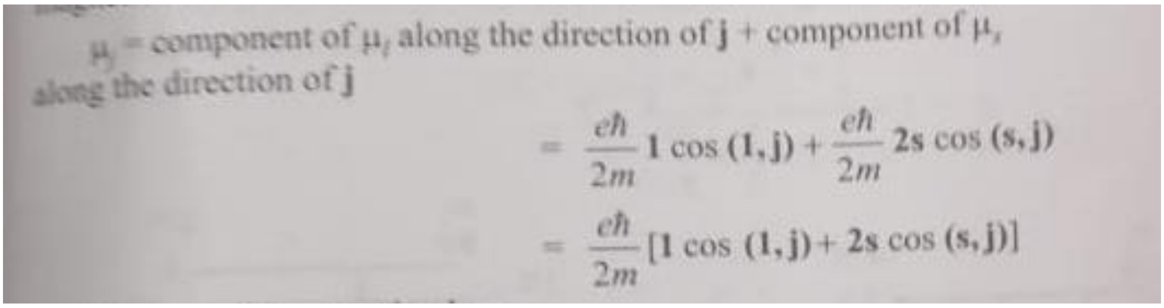
The resultant magnetic moment μ is not along j.

Since 1 and s precess about j, μ_l and μ_S must also precess about j.

To find 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.



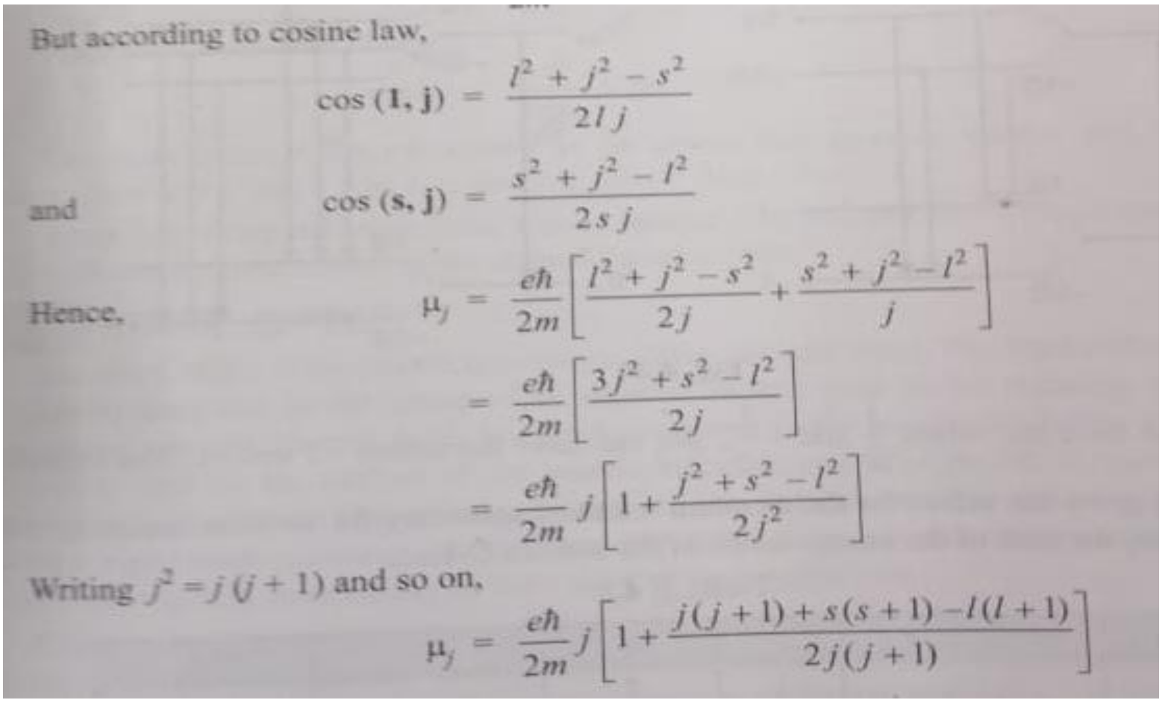
The effective magnetic moment of the electron will be



μ_j = component of μ_l along the direction of **j** + component of μ_s along the direction of **j**

$$= \frac{e\hbar}{2m}\,1\cos(1,j) + \frac{e\hbar}{2m}\,2s\cos(s,j)$$

$$= \frac{e\hbar}{2m}\,[1\cos(1,j) + 2s\cos(s,j)]$$



But according to cosine law,

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

and

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

Hence,

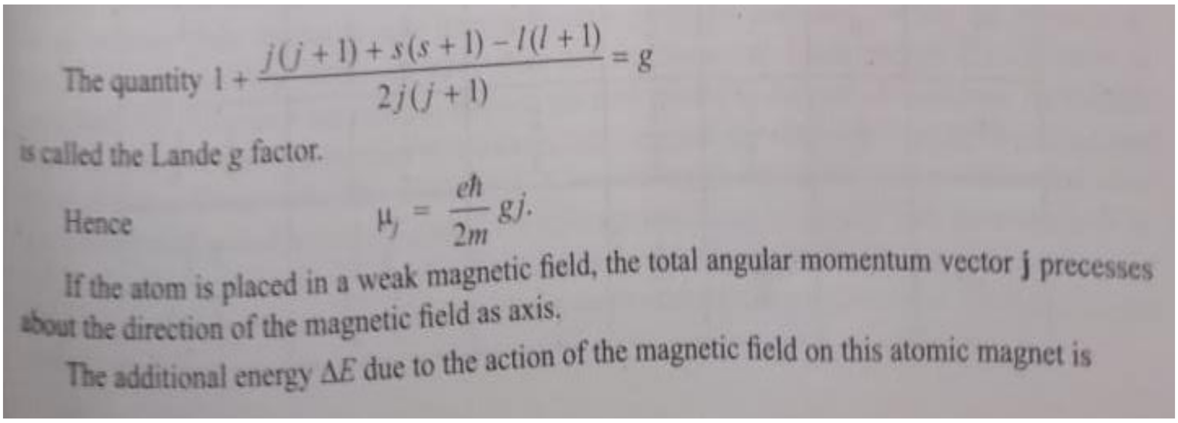
$$\mu_j = \frac{e\hbar}{2m}\left[\frac{l^2 + j^2 - s^2}{2j} + \frac{s^2 + j^2 - l^2}{j}\right]$$

$$= \frac{e\hbar}{2m}\left[\frac{3j^2 + s^2 - l^2}{2j}\right]$$

$$= \frac{e\hbar}{2m}\, j\left[1 + \frac{j^2 + s^2 - l^2}{2j^2}\right]$$

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

$$\mu_j = \frac{e\hbar}{2m}\, j\left[1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}\right]$$



The quantity $1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} = g$

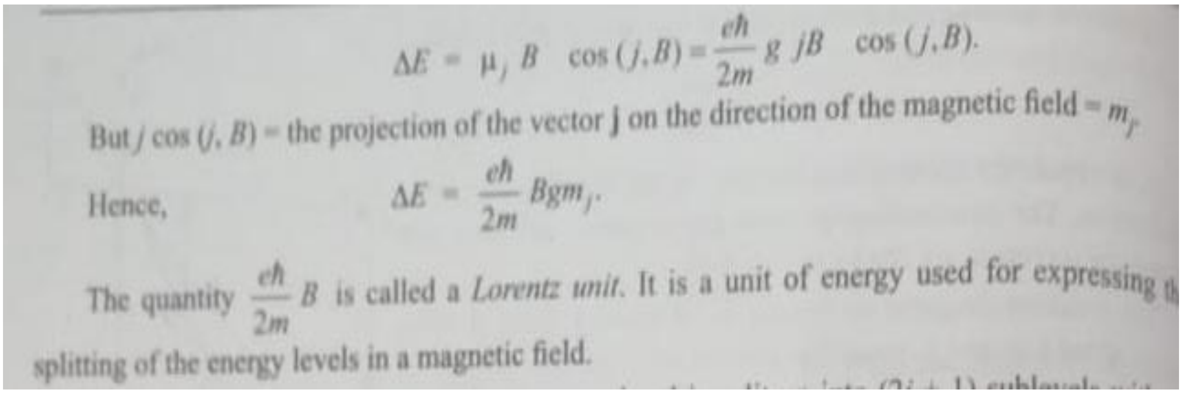
is called the Lande g factor.

Hence

$$\mu_j = \frac{e\hbar}{2m} gj.$$

If the atom is placed in a weak magnetic field, the total angular momentum vector **j** precesses about 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



$$\Delta E = \mu_j B \quad \cos(j, B) = \frac{e\hbar}{2m} g\, jB \quad \cos(j, B).$$

But $j\cos(j, B)$ = the projection of the vector **j** on the direction of the magnetic field = m_j

Hence,

$$\Delta E = \frac{e\hbar}{2m} Bgm_j.$$

The quantity $\frac{e\hbar}{2m}B$ is called a *Lorentz unit*. It is a unit of energy used for expressing the splitting of the energy levels in a magnetic field.

3.5 Optical Spectra

- **The outer (valence) electron of an atom determine the chemical and optical properties of their atoms.**

- **The electrons in the closed inner orbits do not take part in the emission of spectral lines.**

Spectral Line

Atoms are divided into two main categories,

- one electron system

alkali metals (eg. lithium, sodium and potassium)- single valence electron - Hydrogen-like spectra - one – electron spectra

- many-electron system

more than one valence electron or optical electron

they become effective in fixing the spectral properties

eg. Alkaline earth metals – two-electron system have spectra which are similar among themselves.

Spectral notation

The states of the atom,

the values of its L vector are 0,1,2,3,4,5 are represented by the capital letters S,P,D,F,G,H

the value of the total angular momentum of the atom J is written as a subscript at the lower right of the letter representing the particular L value of the atomic state.

the multiplicity of the total spin (S) is written as a superscript at the upper left of letter.

If S is the total spin, the multiplicity is equal to 2S+1.

Term Symbol : $^{2S+1}L_J$

Example:

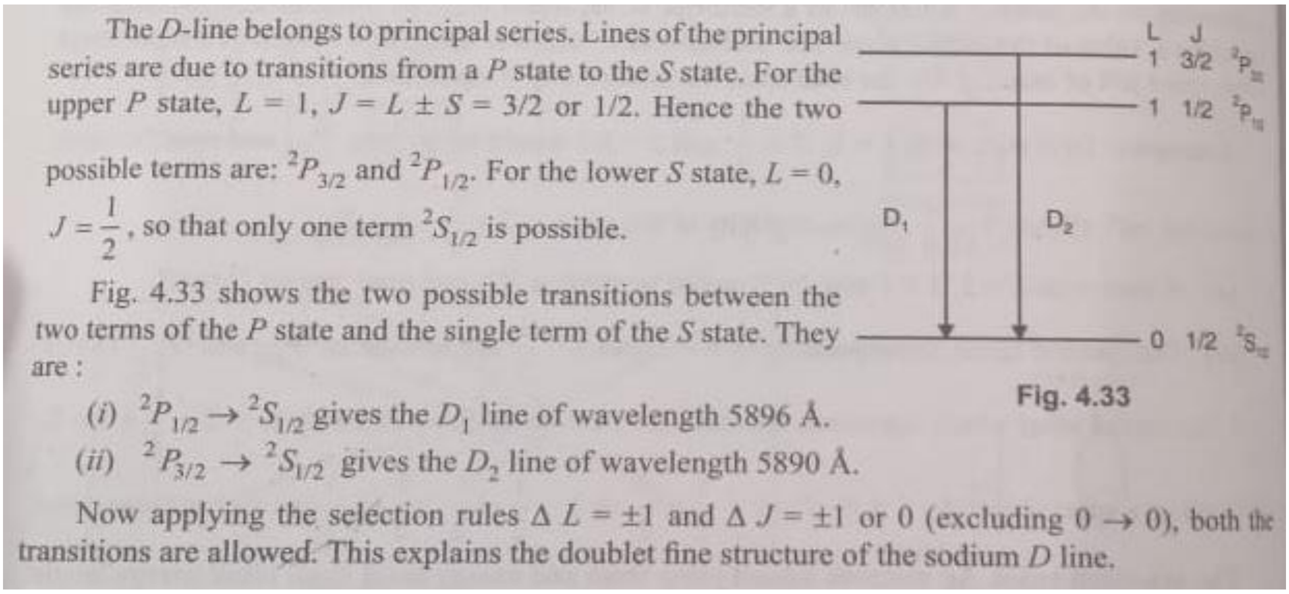
(i) **A state with L =1, S =1/2 and J = 3/2 written as $^2P_{3/2}$ (doublet P three halves)**

(ii) **A state with L =2, S =1 and J = 2 $^3D_2$ (triplet D two)**

(iii) **L = 1 and S = ½ written as $^2P_{1/2}$ and $^2P_{3/2}$ ($J = L \pm S$)**

3.6 Fine structure of the sodium D-line

- **Ten out of the eleven electrons of the normal sodium atom are interlocked in closed shells. They contribute nothing to the angular momentum of the atom.**
- **We have to consider only the states of eleventh optical electron in discussing the spectrum of neutral sodium.**



The *D*-line belongs to principal series. Lines of the principal series are due to transitions from a *P* state to the *S* state. For the upper *P* state, $L = 1$, $J = L \pm S = 3/2$ or $1/2$. Hence the two possible terms are: ${}^2P_{3/2}$ and ${}^2P_{1/2}$. For the lower *S* state, $L = 0$, $J = \frac{1}{2}$, so that only one term ${}^2S_{1/2}$ is possible.

Fig. 4.33 shows the two possible transitions between the two terms of the *P* state and the single term of the *S* state. They are :

(*i*) ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$ gives the D_1 line of wavelength 5896 Å.

(*ii*) ${}^2P_{3/2} \rightarrow {}^2S_{1/2}$ gives the D_2 line of wavelength 5890 Å.

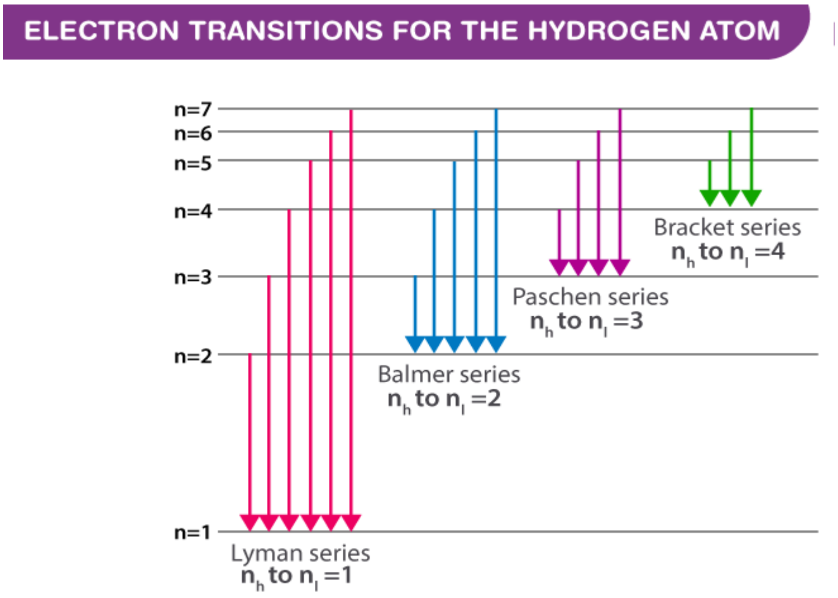
Now applying the selection rules $\Delta L = \pm 1$ and $\Delta J = \pm 1$ or 0 (excluding $0 \rightarrow 0$), both the transitions are allowed. This explains the doublet fine structure of the sodium *D* line.

Fig. 4.33

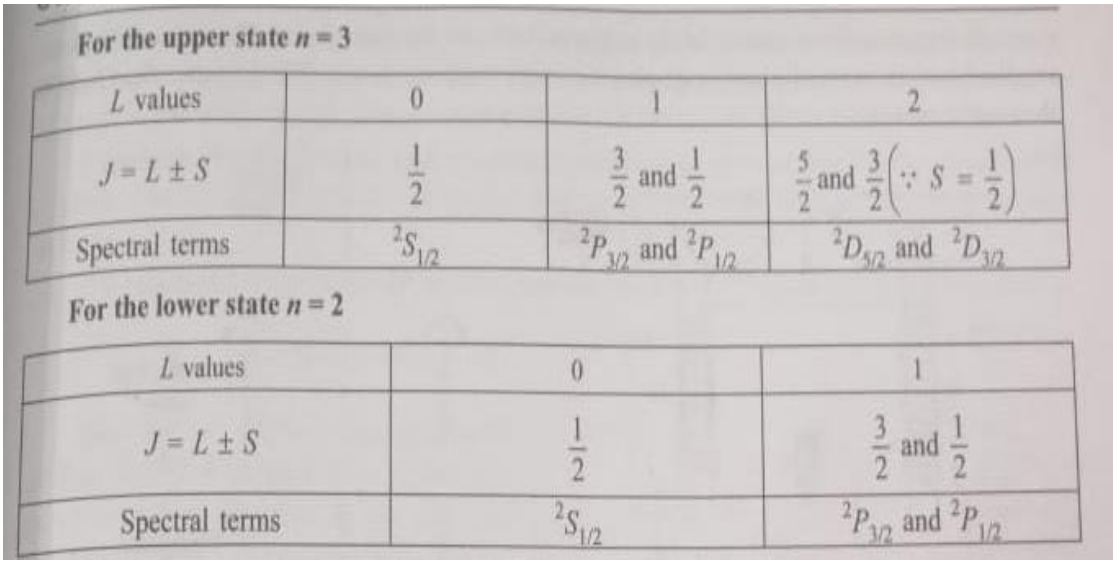
3.7 Fine structure of Hα Line

Fine structure, in spectroscopy, the splitting of the main spectral lines of an atom into two or more components, each representing a slightly different wavelength. Fine structure is produced when an atom emits light in making the transition from one energy state to another.

According to Bohr's theory, Hα line, the first of Balmer series, arises due to transition from the third quantum state (n = 3) to the second quantum state (n = 2).



Theoretically fifteen transitions are possible between the five terms of the upper state (n = 3) and three terms of the lower state (n = 2).



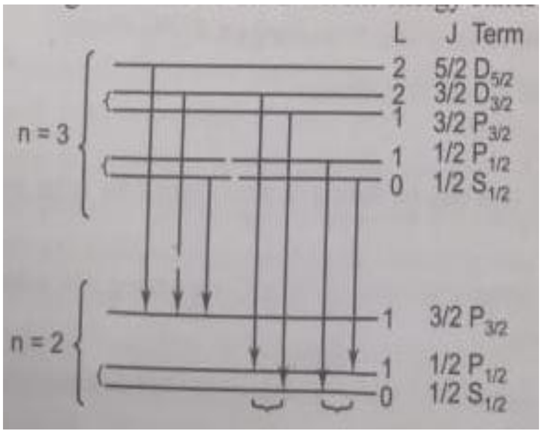
For the upper state $n = 3$

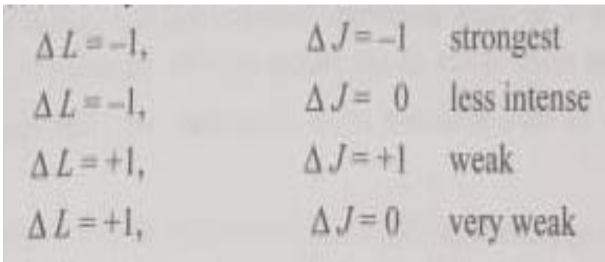
L values	0	1	2
$J = L \pm S$	$\frac{1}{2}$	$\frac{3}{2}$ and $\frac{1}{2}$	$\frac{5}{2}$ and $\frac{3}{2}\left(\because S = \frac{1}{2}\right)$
Spectral terms	${}^2S_{1/2}$	${}^2P_{3/2}$ and ${}^2P_{1/2}$	${}^2D_{5/2}$ and ${}^2D_{3/2}$

For the lower state $n = 2$

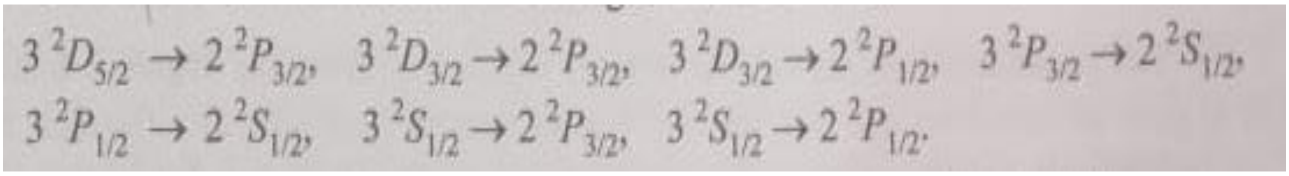
L values	0	1
$J = L \pm S$	$\frac{1}{2}$	$\frac{3}{2}$ and $\frac{1}{2}$
Spectral terms	${}^2S_{1/2}$	${}^2P_{3/2}$ and ${}^2P_{1/2}$

But by applying the selection rules namely, $\Delta L = \pm 1$ and $\Delta J = 0$ or ± 1, these transitions reduce to the following seven transitions:

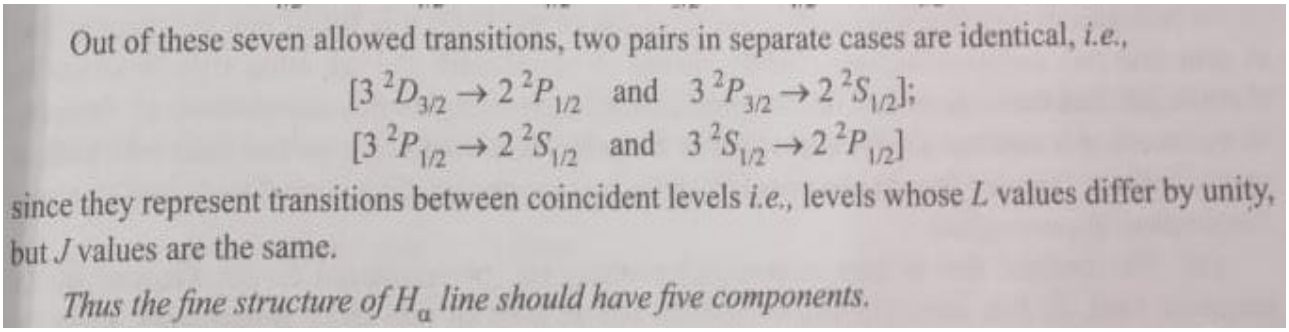




$\Delta L = -1,$	$\Delta J = -1$	strongest
$\Delta L = -1,$	$\Delta J = 0$	less intense
$\Delta L = +1,$	$\Delta J = +1$	weak
$\Delta L = +1,$	$\Delta J = 0$	very weak



$$3\,{}^2D_{5/2} \rightarrow 2\,{}^2P_{3/2},\quad 3\,{}^2D_{3/2} \rightarrow 2\,{}^2P_{3/2},\quad 3\,{}^2D_{3/2} \rightarrow 2\,{}^2P_{1/2},\quad 3\,{}^2P_{3/2} \rightarrow 2\,{}^2S_{1/2},$$
$$3\,{}^2P_{1/2} \rightarrow 2\,{}^2S_{1/2},\quad 3\,{}^2S_{1/2} \rightarrow 2\,{}^2P_{3/2},\quad 3\,{}^2S_{1/2} \rightarrow 2\,{}^2P_{1/2}.$$



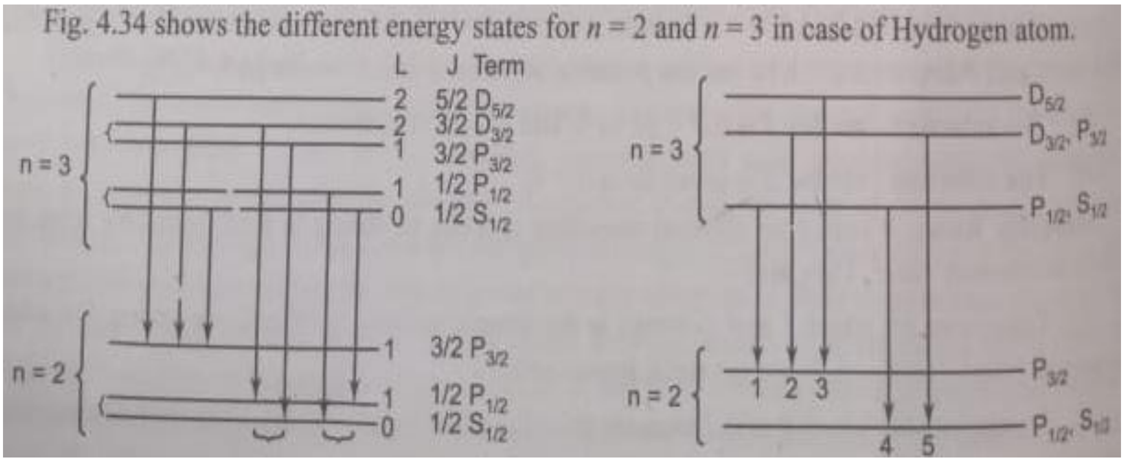
Out of these seven allowed transitions, two pairs in separate cases are identical, *i.e.*,

$$[3\,{}^2D_{3/2} \rightarrow 2\,{}^2P_{1/2} \quad \text{and} \quad 3\,{}^2P_{3/2} \rightarrow 2\,{}^2S_{1/2}];$$
$$[3\,{}^2P_{1/2} \rightarrow 2\,{}^2S_{1/2} \quad \text{and} \quad 3\,{}^2S_{1/2} \rightarrow 2\,{}^2P_{1/2}]$$

since they represent transitions between coincident levels *i.e.*, levels whose L values differ by unity, but J values are the same.

Thus the fine structure of H_α line should have five components.

Fig. 4.34 shows the different energy states for $n = 2$ and $n = 3$ in case of Hydrogen atom.



(i) (ii)

Energy level diagram: The various energy levels are drawn in as the horizontal levels as shown in above Fig.

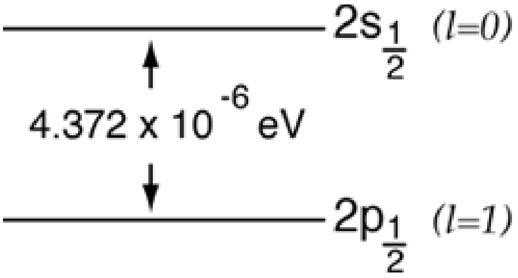
The coincident levels are drawn close to each other. There are two such levels in upper state and one in the lower state.

All the seven allowed transitions are also shown in Fig. (i).

Leaving the transitions between coincident levels, the five transitions are separately shown in Fig. (ii).

3.7 Lamb Shift

In 1951, Willis Lamb discovered that this was not so - that the 2p(1/2) state is slightly lower than the 2s(1/2) state resulting in a slight shift of the corresponding spectral line (the Lamb shift).

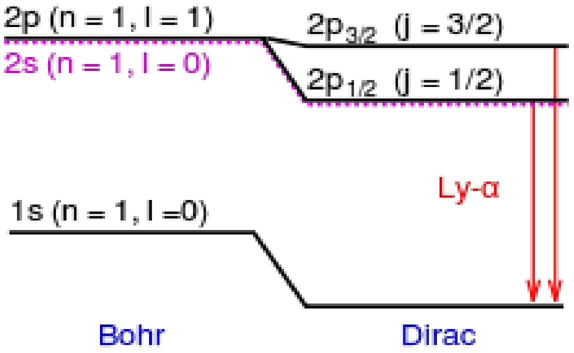


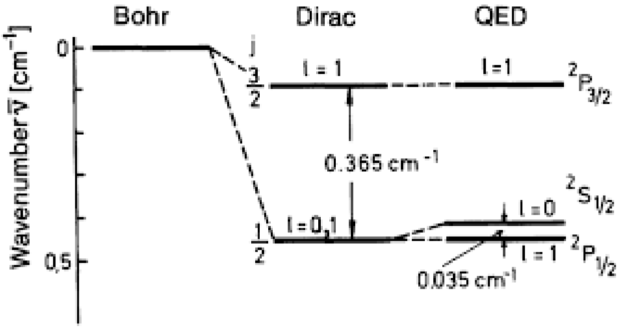
Definition: Lamb shift is a difference in energy between two energy levels $2S_{1/2}$ and $2P_{1/2}$ of the hydrogen atom which was not predicted by the Dirac equation, according to which these states should have the same energy.

The techniques of the microwave region came in very handy at the hands of W E Lamb and his colleague R C Retherford, in making fine structure measurements of the atomic spectra.

The 'Lamb Shift' was the frequency of a microwave field that induced transitions from one excited state of a hydrogen atom to another.

In particular, they found that the $2S_{1/2}$ levels of hydrogen were slightly above the $2P_{1/2}$ level, by about 1050 MHz.

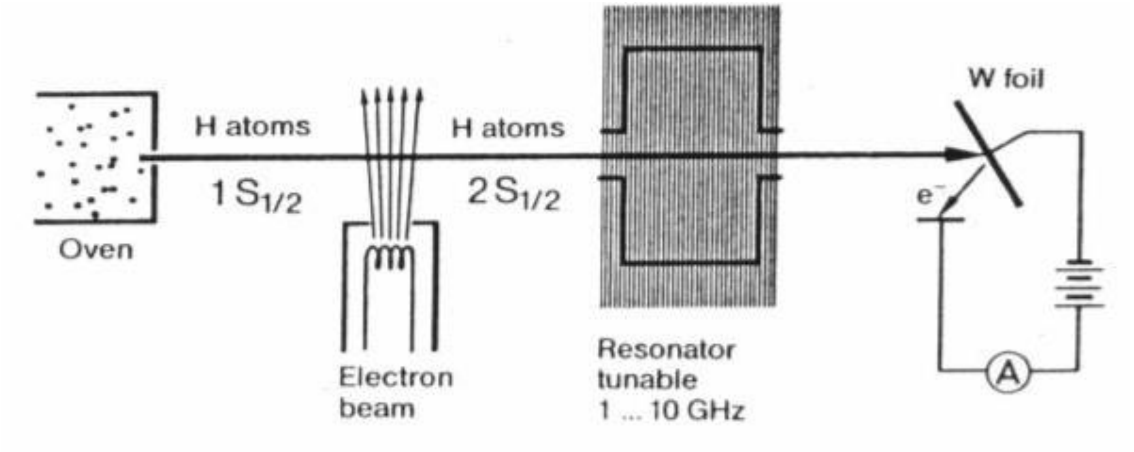




Dirac's one-particle relativistic theory predicts that the $2S_{1/2}$ and $2P_{1/2}$ states of the hydrogen atom have the same energy, Lamb and Retherford showed that the $2S_{1/2}$ level is actually higher and found a difference in energy corresponding to a frequency of about 1000 MHz.

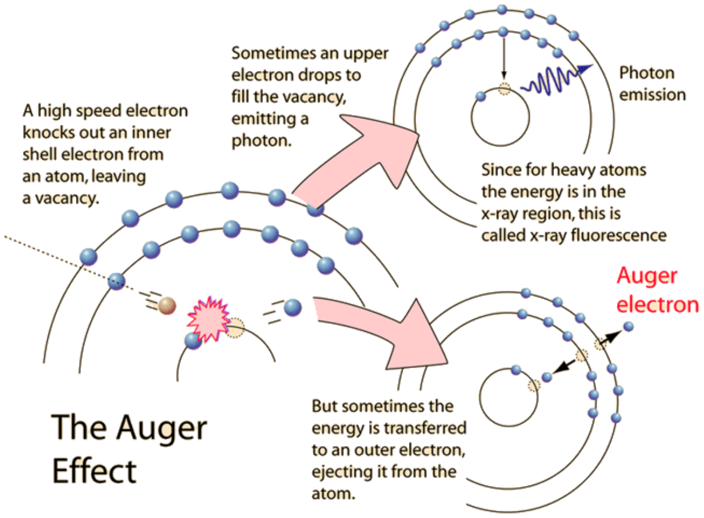
Lamb Shift

- **In 1947 W. E. Lamb and R. C. Retherford performed a brilliant experiment in which they directly measured the energy difference between the $2S_{1/2}$ and $2P_{1/2}$ states [5].**
- **In their experiment (Fig. 3), they prepared a beam of hydrogen atoms in the $1S_{1/2}$ ground state.**
- **The beam is bombarded with electrons with the result that some of the atoms are excited to the $2S_{1/2}$ state.**



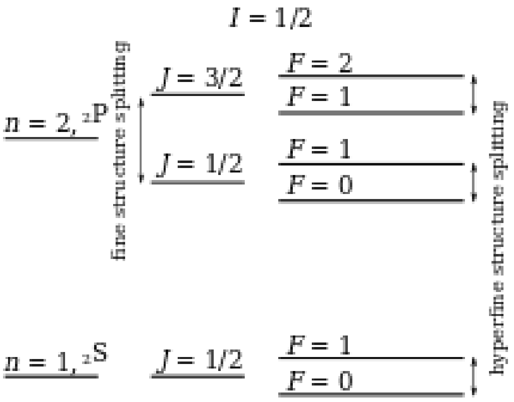
- **Optical transitions from this state that go directly to the $1S_{1/2}$ ground state are prohibited by selection rules resulting in a very long (~ 0.1 second) lifetime for the $2S_{1/2}$ state.**

- **The atoms then pass through a region where they are exposed to electromagnetic radiation with energy equal to the energy difference between the $2S_{1/2}$ and $2P_{1/2}$ states.**
- **The radiation has the effect of inducing transitions between these states, and once an atom is in the $2P_{1/2}$ state it decays to the ground state with a lifetime of 10^{-9} seconds.**
- **After passing through the region with electromagnetic radiation, the atoms strike a tungsten foil.**
- **Upon striking the foil, atoms still in the $2S_{1/2}$ state decay to the ground state and in so doing liberate electrons from the foil in a process called Auger emission.**
- **By measuring the emission current from the foil with the electromagnetic radiation turned on (fewer electrons liberated) and with the radiation turned off (more electrons liberated), Lamb and Retherford were able to determine the energy difference between the $2S_{1/2}$ and $2P_{1/2}$ states. Their initial measurements indicated this difference to be about 1000 MHz.**



3.8 Hyperfine Structure

In atomic physics, hyperfine structure is defined by small shifts and splittings in the energy levels of atoms, molecules, and ions, due to interaction between the state of the nucleus and the state of the electron clouds.



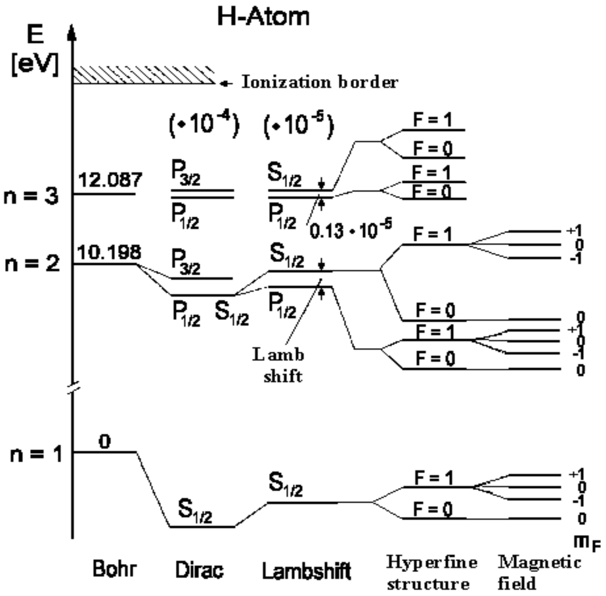
Introduction:

Hyperfine structure (HFS), in spectroscopy, the splitting of a spectral line into a number of components. The splitting is caused by nuclear effects and cannot be observed in an ordinary spectroscope without the aid of an optical device called an interferometer.

In fine structure (*q.v.*), line splitting is the result of energy changes produced by electron spin–orbit coupling (*i.e.*, interaction of forces from orbital and spin motion of electrons).

Hyperfine structure, line splitting is attributed to the fact that in addition to electron spin in an atom, the atomic nucleus itself spins about its own axis.

Energy states of the atom will be split into levels corresponding to slightly different energies. Each of these energy levels may be assigned a quantum number, and they are then called quantized levels. Thus, when the atoms of an element radiate energy, transitions are made between these quantized energy levels, giving rise to hyperfine structure.



3.9 Magnetic dipole-dipole interaction

- the hyperfine structure that originates due to the interaction between the total angular momentum of electron and the nuclear angular momentum.

- the effect of static magnetic field on this hyperfine structure

- this concept on the basis of the magnetic field strength.

Definition: Magnetic dipole-dipole interaction, also called dipolar coupling, refers to the direct interaction between two magnetic dipoles.

The nuclear magnetic moment is,

$$\vec{\mu}_N = g_I \, \mu_B \, \vec{I}$$

$$= g_I^N \, \mu_B^N \, \vec{I}$$

A *g*-factor (also called *g* value or dimensionless magnetic moment) is a dimensionless quantity that characterizes the magnetic moment and angular momentum of an atom, a particle or the nucleus.

There is a further splitting below the spin-orbit related spectral detail, aptly called *hyperfine interaction*.

It is due to the interaction between the *nuclear spin*, $\vec{I}$ →, and the combined total angular momentum, $\vec{J}$ →, and effectively adds another angular momentum to the vector model.

Nuclear spins are the combined spins of all the protons and neutrons in the nucleus and vary between isotopes of the same element.

Since nuclei are much heavier than electrons, their spin is much smaller in magnitude than that of an electron, and the nuclear spin quantum number can be zero, integer or half-integer.

The magnetic moment associated with the nuclear spin, μ_I, aligns in the magnetic field, $\vec{B}$el, induced by the moving electrons.

As a result, the nuclear spin plays the same role in the hyperfine interaction as the magnetic field does in the Zeeman effect:

The perturbation Hamiltonian is again proportional to the scalar product of the two vectors:

Naturally, an atom with a nuclear spin of zero does not show any hyperfine structure splitting, and the hyperfine interaction is strongest for s-electrons due to their non-zero probability density inside the nucleus - this is known as the *Fermi contact interaction*.

The total magnetic moment due to the electron is,

$$\vec{\mu}_{electron} = \vec{\mu}_{orbital} + \vec{\mu}_{spin}$$

$$= \vec{\mu}_l + \vec{\mu}_s$$

$$= -\mu_B[\vec{L} + g_s\vec{S}]$$

And the interaction energy with the applied magnetic field

$$E_{mag} = -\vec{\mu}_{total} . \vec{B}_z$$

We know that the Hamiltonian for the atom in the L-S coupling scheme including the interaction with nuclear magnetic moment is written as

$$H = \underbrace{H_{CF}} + \underbrace{H_{ee}} + \underbrace{H_{so}} + H_{hf}$$

The Hamiltonian of a system specifies its total energy—*i.e.*, the sum of its kinetic energy (that of motion) and its potential energy (that of position)—in terms of the Lagrangian function derived in earlier studies of dynamics and of the position and momentum of each of the particles

The total electronic quantum number J and I are not the good quantum number.

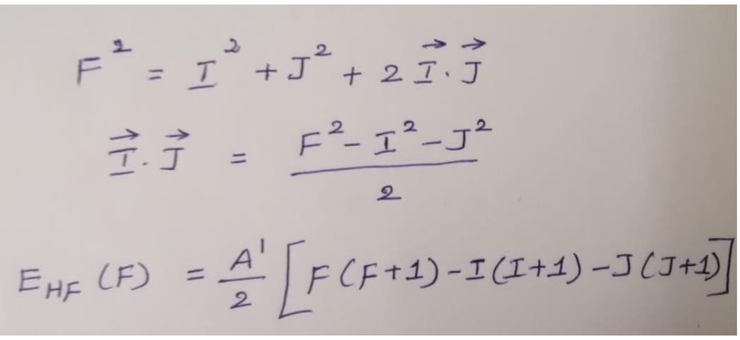
Here the hyperfine interaction is coupling the total angular momentum of the electron J and the nuclear angular momentum I. So the new angular momentum F which will be the good quantum number for the total Hamiltonian.

So we have,

$$\vec{F} = \vec{J} + \vec{I}$$

The hyperfine interaction energy

$$E_{HF} = A'_{HF}\, \vec{I} \cdot \vec{J}$$



$$F^2 = I^2 + J^2 + 2\,\vec{I} \cdot \vec{J}$$

$$\vec{I} \cdot \vec{J} = \frac{F^2 - I^2 - J^2}{2}$$

$$E_{HF}(F) = \frac{A'}{2}\left[F(F+1) - I(I+1) - J(J+1)\right]$$

When we apply the magnetic field, this will interact with the total magnetic moment of the atom.

There will be three situations of the interaction those depends on the magnitude of the magnetic field strength compared to the hyperfine interaction.

1. **The weak field case**
2. **The intermediate field and**
3. **The strong field case.**

Since the coupling strength between the nuclear spin and the total angular momentum of the electron is very small, the magnitude of the applied magnetic field should be very small.

On the other hand, the field considered to be strong compared to hyperfine interaction will be small compared to spin-orbit interaction.

3.10 Zeeman effect: hyperfine structure

The total atomic magnetic moment is the sum of the electronic and nuclear moments:

$$\vec{\mu}_{atom} = -g_J \mu_B \vec{J} + g_I \mu_N \vec{I} \simeq -g_J \mu_B \vec{J}$$

But we an neglect the nuclear contribution for most cases since

$$\mu_N << \mu_B$$

Then, the interaction Hamiltonian is,

$$H = g_J \mu_B \vec{J} \cdot \vec{B}$$

While this interaction does not depend on the nuclear spin, the expectation values depends the hyperfine structure.

We consider the weak-field and strong-field cases:

(i) Zeeman effect of a weak field :
In the weak-field regime, the interaction with the external field is weaker than A I.J So it can be treated as a perturbation to the hyperfine structure. In this regime, F and MF are good quantum numbers, but not M_I and M_J.

Taking the projection of the magnetic moments along F gives,

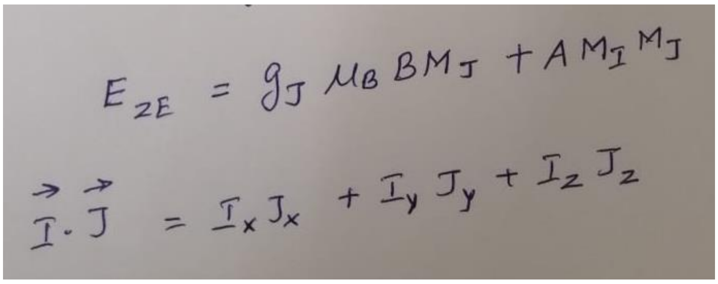
$$H = g_J \mu_B \vec{F} \cdot \vec{B} = g_F \mu_B B F_z$$

where

$$g_F = \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} g_J$$

$$E = g_F \mu_B B M_F$$

(ii) Zeeman effect of a strong field :
In the strong field regime, the interaction with the external field is greater than hyperfine interaction, F is not a good quantum number. The effect of the hyperfine interaction can be calculated as a perturbation on the eigenstates,



$$E_{ZE} = g_J \mu_B B M_J + A M_I M_J$$

$$\vec{I} \cdot \vec{J} = I_x J_x + I_y J_y + I_z J_z$$

x and y components average to zero in the precession about the field along z-direction.

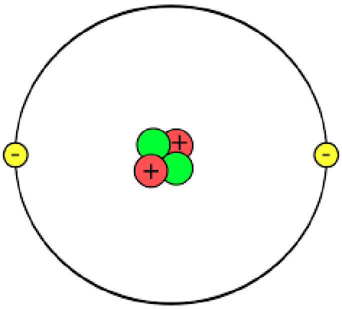
UNIT – IV – Atom with more than One Electron – SPH1311

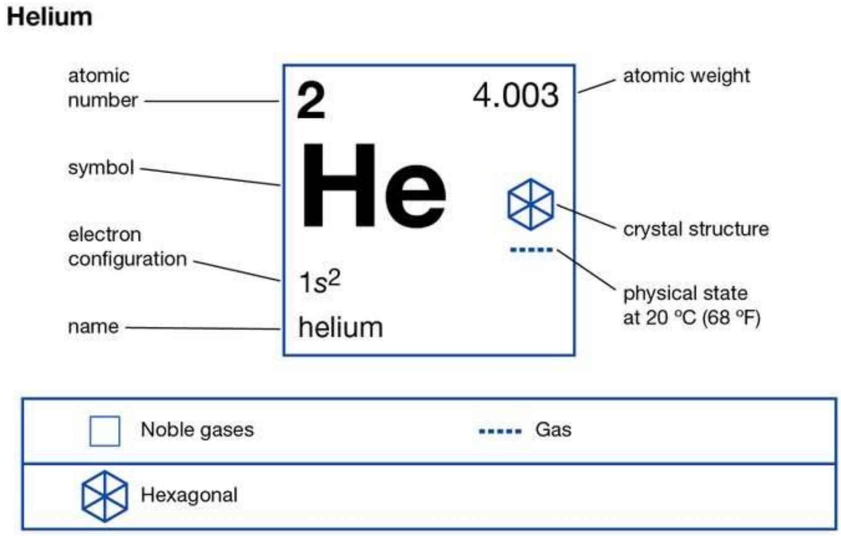
4.1 Helium atom

Introduction:

- **The Helium (He) atom has electronic configuration of $1s^2$.**
- **These two electrons in the configuration are responsible for the valency of two and hence in deciding the general characteristics of the optical spectrum.**
- **The ground state Helium has two 1s electrons.**

Both the electrons have $l = 0$ and as n, l and m_l are same; therefore, according to the Pauli Exclusion Principle their spins are antiparallel.





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4.2 Energy levels and Transitions of Helium

(i) The Ground state:

As an example of L-S coupling consider the energy levels of Helium, which is a two electron system.

The ground state configuration of helium is $1s^2$. Both the electrons are in the 1s state and therefore according to L-S coupling scheme,

s – state $\quad l = 0$

$L = l_1 + l_2 = 0 + 0 = 0$ ($L = (l_1 + l_2)\ (l_1 + l_2 - l1)$……

$S = ½ + ½ = 1$

$½ - ½ = 0$

Since for both the electrons $m_l = 0$, their m_s values have to be different.

For one electron $m_s = ½$ and for the other electron $m_2 = -1/2$.

Hence, though s = 1 and 0 are possible, the allowed value is s = 0.

Therefore, for the ground state,

L = 0, S = 0 and J =0 (J = L + S)

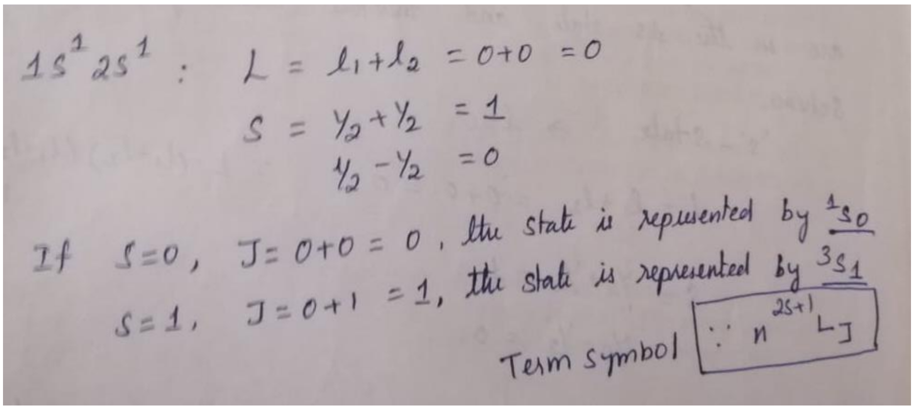
The ground state is then denoted as $^1S_0$.

(ii) The excited states:

To excite both the electrons of helium, energy more than the ionization energy is required.

Hence, all the excited states of helium are one electron states.

We expect $1s^1\ 2s^1$ to be the lowest energy level, the next level to be $1s^1\ 2p^1$, and so on.



$1s^1 2s^1$: $L = l_1 + l_2 = 0+0 = 0$

$S = ½ + ½ = 1$

$½ - ½ = 0$

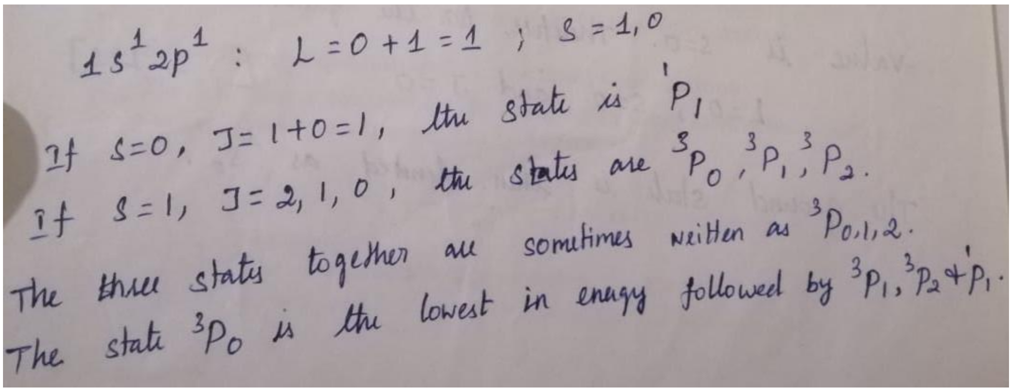
If $S=0$, $J = 0+0 = 0$, the state is represented by $^1S_0$

$S=1$, $J = 0+1 = 1$, the state is represented by $^3S_1$

Term symbol $\because n^{2S+1}L_J$

Out of these two states, Hund's rules have to be applied to find the lower one.

The $^3S_1$ is lower in energy than the state $^1s_0$.



$1s^1 2p^1$: $L = 0+1 = 1$; $S = 1, 0$

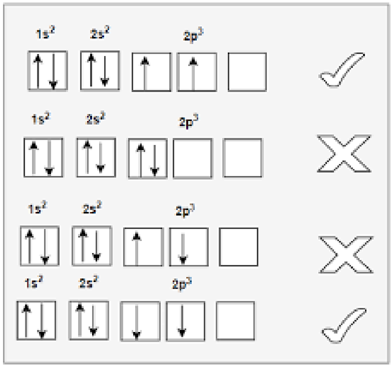
If $S=0$, $J = 1+0 = 1$, the state is $^1P_1$

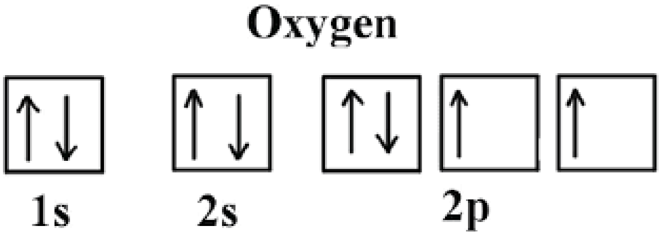
If $S=1$, $J = 2, 1, 0$, the states are $^3P_0$, $^3P_1$, $^3P_2$.

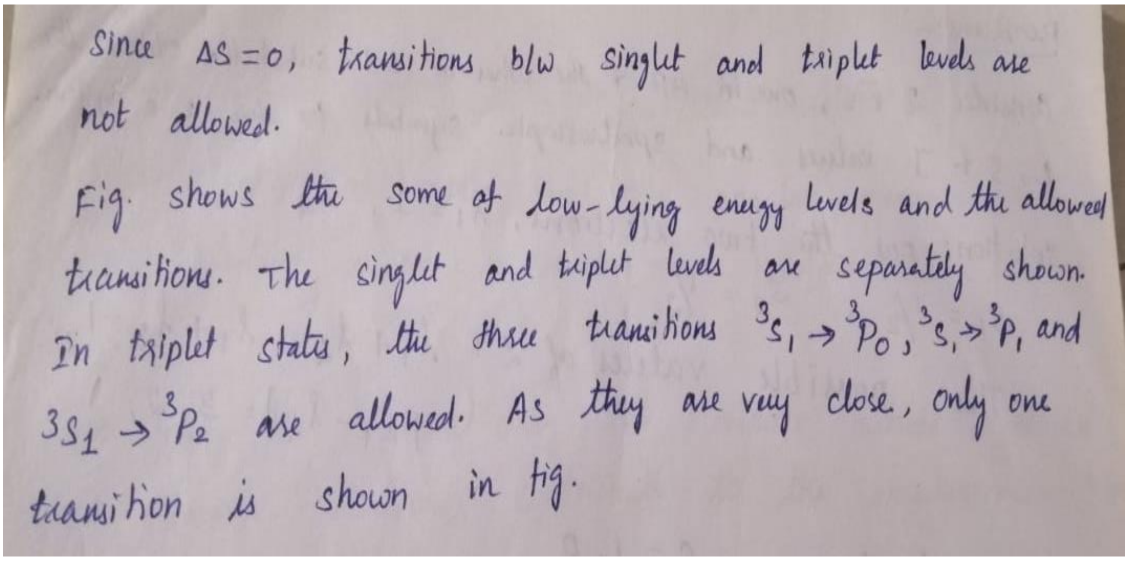
The three states together are sometimes written as $^3P_{0,1,2}$.

The state $^3P_0$ is the lowest in energy followed by $^3P_1$, $^3P_2$ & $^1P_1$.

Hund's rule: every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

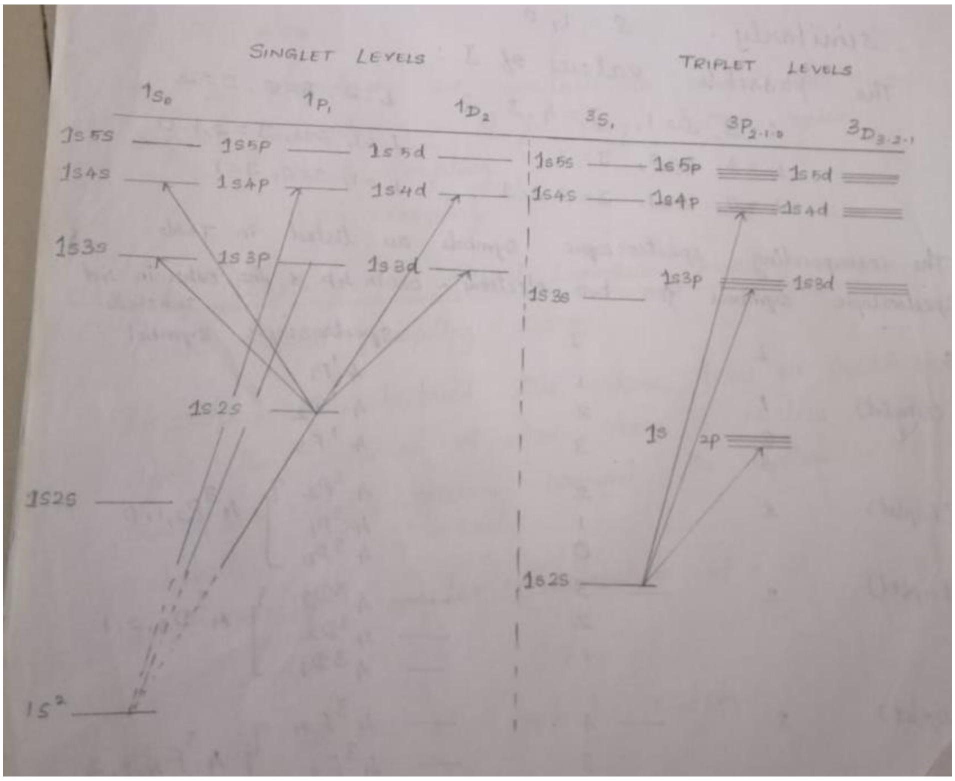






Since $\Delta S = 0$, transitions b/w singlet and triplet levels are not allowed.

Fig. shows the some of low-lying energy levels and the allowed transitions. The singlet and triplet levels are separately shown. In triplet states, the three transitions $^3S_1 \rightarrow {}^3P_0$, $^3S_1 \rightarrow {}^3P_1$ and $3S_1 \rightarrow {}^3P_2$ are allowed. As they are very close, only one transition is shown in fig.



The Helium Atom

The second element in the periodic table provides the first example of a quantum-mechanical problem which *cannot* be solved exactly.

Approximation methods applied to helium can give accurate solutions in perfect agreement with experimental results.

In this sense, it can be concluded that quantum mechanics is correct for atoms more complicated than hydrogen.

By contrast, the Bohr theory failed miserably in attempts to apply it beyond the hydrogen atom.

The helium atom has two electrons bound to a nucleus with charge Z = 2. The successive removal of the two electrons can be diagrammed as

$$\mathrm{He} \xrightarrow{I_1} \mathrm{He}^+ + e^- \xrightarrow{I_2} \mathrm{He}^{++} + 2e^-$$

The *first ionization energy* I_1, the minimum energy required to remove the first electron from helium, is experimentally 24.59 eV.

The second ionization energy, I_2, is 54.42 eV. The last result can be calculated exactly since He^+ is a hydrogen-like ion.

$$I_2 = -E_{1s}(\mathrm{He}^+) = \frac{Z^2}{2n^2} = 2 \text{ hartrees} = 54.42 \text{ eV}$$

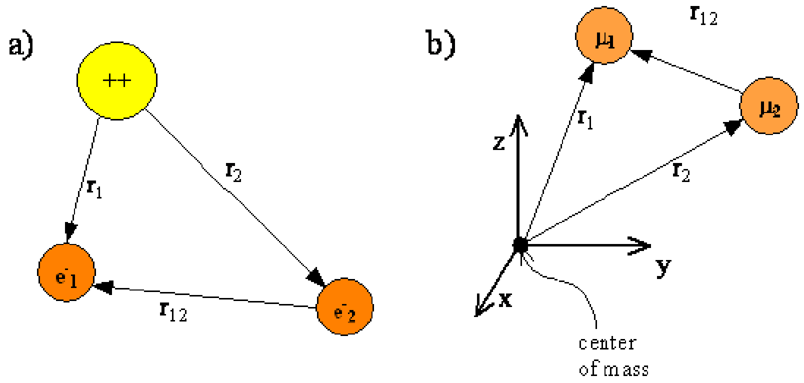
Therefore the ground-state energy of helium atom is given by $E0=-(I_1+I_2)=-79.02$ eV$=-2.90372$ hartrees.

4.2.1 Schrodinger equation and Variational calculations

A particle can behave as a wave only under motion. So, it should be accelerated by a potential field.
Therefore, the total energy (E) of the particle is equal to the sum of its potential energy (V) and kinetic energy.

$\mathbf{E = V + \frac{1}{2} mv^2}$
$\mathbf{E = V + \frac{1}{2} m^2v^2 /m}$
$\mathbf{E = V + p^2/2m}$
$\mathbf{E\Psi = V\Psi + p^2/2m\ \Psi}$

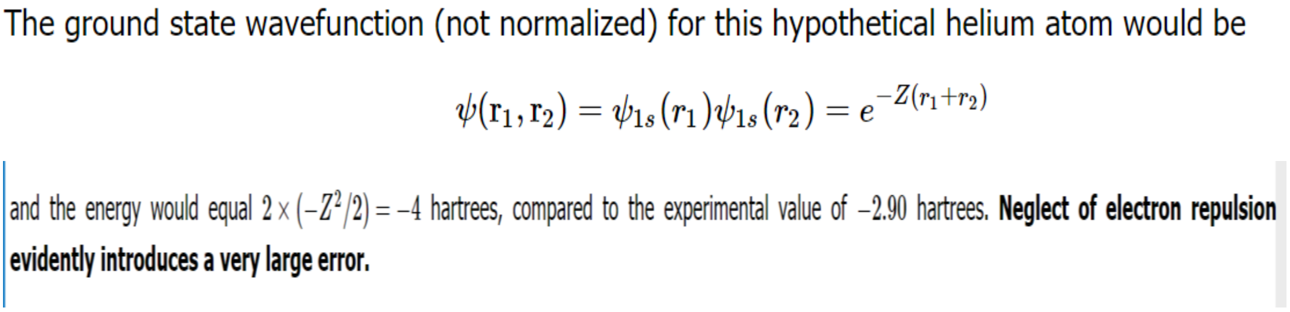
$\mathbf{E\Psi = H\Psi}$



The Schrodinger equation for He atom, using atomic units and assuming infinite nuclear mass,

$$\left\{ -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}} \right\}\psi(\mathrm{r}_1, \mathrm{r}_2) = E\psi(\mathrm{r}_1, \mathrm{r}_2)$$

The five terms in the Hamiltonian represent,
- the kinetic energies of electrons 1 and 2
- the nuclear attractions of electrons 1 and 2
- the repulsive interaction between the two electrons - it is the last contribution which prevents an exact solution of the Schrodinger equation and which accounts for much of the complication in the theory.
In seeking an approximation to the ground state, we might first work out the solution in the absence of the
In the Schrodinger eq. thus simplified, we can separate the variables r1 and r2 to reduce the equation to two independent hydrogen-like problems.



The ground state wavefunction (not normalized) for this hypothetical helium atom would be

$$\psi(\mathrm{r}_1,\mathrm{r}_2)=\psi_{1s}(r_1)\psi_{1s}(r_2)=e^{-Z(r_1+r_2)}$$

> and the energy would equal $2\times(-Z^2/2)=-4$ hartrees, compared to the experimental value of -2.90 hartrees. **Neglect of electron repulsion evidently introduces a very large error.**

A significantly improved result can be obtained with the functional form (eq.2), but with Z replaced by a adjustable parameter α, thus:

$$\tilde{\psi}(r_1,r_2)=e^{-\alpha(r_1+r_2)}$$

Using this function in the variational principle, we have

$$\tilde{E}=\frac{\int\psi(r_1,r_2)\hat{H}\psi(r_1,r_2)d\tau_1\tau_2}{\int\psi(r_1,r_2)\psi(r_1,r_2)d\tau_1 d\tau_2}$$

In quantum mechanics, the variational method is one way of finding approximations to the lowest energy eigenstate or ground state, and some excited states. This allows calculating approximate wavefunctions such as molecular orbitals. The basis for this method is the variational principle.

Where is the full Hamiltonian as in eq. (1), including the 1/r12 - term. The expected values of the five parts of the Hamiltonian work out to

$$\left\langle-\frac{1}{2}\nabla_1^2\right\rangle=\left\langle-\frac{1}{2}\nabla_2^2\right\rangle=\frac{\alpha^2}{2}$$

$$\left\langle-\frac{Z}{r_1}\right\rangle=\left\langle-\frac{Z}{r_2}\right\rangle=-Z\alpha,\left\langle\frac{1}{r_{12}}\right\rangle=\frac{5}{8}\alpha$$

The sum of the integrals in the above eq. gives the variational energy,

$$\tilde{E}(\alpha)=\alpha^2-2Z\alpha+\frac{5}{8}\alpha$$

This will be always be an upper bound for the true ground-state energy. We can optimize our result by finding the value of α which minimizes the energy (above eq). We find

$$\frac{d\tilde{E}}{d\alpha} = 2\alpha - 2Z + \frac{5}{8} = 0$$

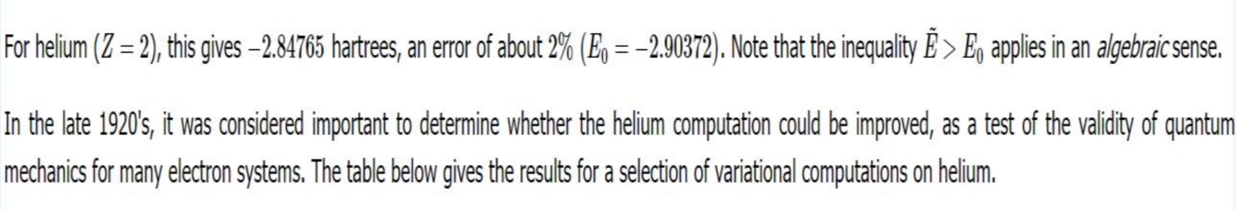
giving the optimal value

$$\alpha = Z - \frac{5}{16}$$

This can be given a physical interpretation, noting that the parameter α in the wavefunction represents an effective nuclear charge.

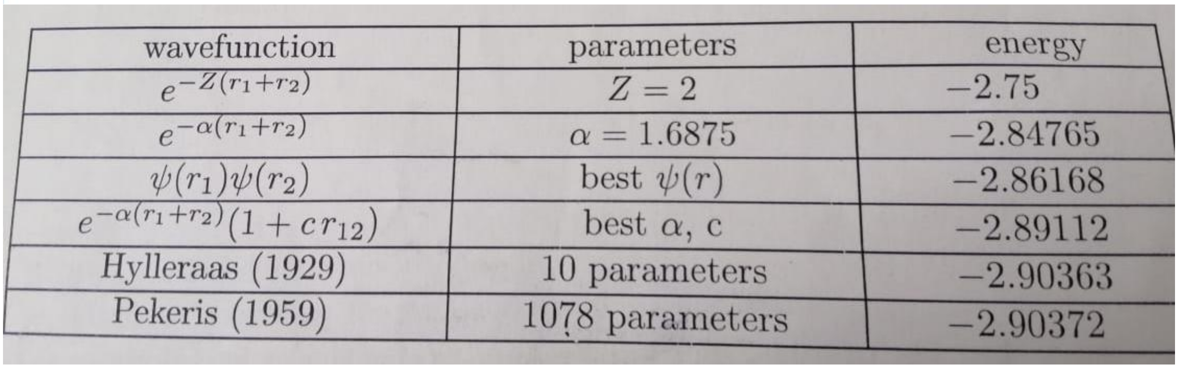
Each electron partially shield the other electron from the positively-charged nucleus by an amount equivalent to 5/8 of an electron charge. Substituting eq. 8 into 6, we obtain the optimized approximation to the energy.

$$\tilde{E} = -\left(Z - \frac{5}{16}\right)^2$$



For helium ($Z = 2$), this gives −2.84765 hartrees, an error of about 2% ($E_0 = -2.90372$). Note that the inequality $\tilde{E} > E_0$ applies in an *algebraic* sense.

In the late 1920's, it was considered important to determine whether the helium computation could be improved, as a test of the validity of quantum mechanics for many electron systems. The table below gives the results for a selection of variational computations on helium.



wavefunction	parameters	energy
$e^{-Z(r_1+r_2)}$	$Z = 2$	-2.75
$e^{-\alpha(r_1+r_2)}$	$\alpha = 1.6875$	-2.84765
$\psi(r_1)\psi(r_2)$	best $\psi(r)$	-2.86168
$e^{-\alpha(r_1+r_2)}(1 + cr_{12})$	best α, c	-2.89112
Hylleraas (1929)	10 parameters	-2.90363
Pekeris (1959)	1078 parameters	-2.90372

4.2.2 Spinorbitals and the Exclusion Principle

The simpler wavefunctions for He atom, can be interpreted as representing two electrons in hydrogenlike 1s orbitals – designated as a 1s^2 configuration.

$$\tilde{\psi}(r_1, r_2) = e^{-\alpha(r_1+r_2)}$$

According to Pauli's exclusion principle - the states that no two electrons in an atom can have the same set of four quantum numbers, the two 1s electrons must have different spins, one spin-up or α, the other spin-down or β.
A product of an orbital with a spin function is called a spinorbital. For example, electron 1 might occupy a spinorbital which we designate

$$\phi(1) = \psi_{1s}(1)\alpha(1) \qquad \text{or} \qquad \psi_{1s}(1)\beta(1)$$

Spinorbitals can be designated by a single subscript, for example ϕ_a or ϕ_b, where the subscript stands for a set of four quantum numbers.
In a two electron system the occupied spinorbitals ϕ_a or ϕ_b must be different, meaning that at least one of their four quantum numbers must be unequal.
A two-electron spinorbital function of the form,

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\Big(\phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2)\Big)$$

automatically fulfills the Pauli principle since it vanishes if a = b.

Moreover, this function associates each electron with each orbital, which is consistent with the indistinguishability of identical particles in quantum mechanics.
The factor normalizes the two-particle wavefunction, assuming the ϕ_a or ϕ_b are normalized.
The function (3) is antisymmetric with respect to interchange of electron labels, meaning that

$$\Psi(2,1) = -\Psi(1,2)$$

This antisymmetry property is an elegant way of expressing the Pauli principle.
For future reference, that the function (3) can be expressed as a 2 x 2 determinant:

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \phi_a(1) & \phi_b(1) \\ \phi_a(2) & \phi_b(2) \end{vmatrix}$$

For the $1s^2$ configuration of helium, the two orbital functions are the same and eq.(3) can be written

$$\Psi(1,2) = \psi_{1s}(1)\psi_{1s}(2) \times \frac{1}{\sqrt{2}}\Big(\alpha(1)\beta(2) - \beta(1)\alpha(2)\Big)$$

For two-electron systems, the wave function can be factored into an orbital function times a spin function.
The two-electron spin function,

$$\sigma_{0,0}(1,2) = \frac{1}{\sqrt{2}}\Big(\alpha(1)\beta(2) - \beta(1)\alpha(2)\Big)$$

The two subscripts are the quantum numbers S and M_s for the total electron spin.

Eq.(7) represents the two electron spins in opposing directions (antiparallel) with a total spin angular momentum of zero. It is called the singlet spin state since there is only a single orientation for a total spin quantum number of zero.
It is also possible to have both spins in the same state, provided the orbitals are different.
There are three possible states for two parallel spins:

$$\sigma_{1,1}(1,2) = \alpha(1)\alpha(2)$$

$$\sigma_{1,0}(1,2) = \frac{1}{\sqrt{2}}\Big(\alpha(1)\beta(2) + \beta(1)\alpha(2)\Big)$$

$$\sigma_{1,-1}(1,2) = \beta(1)\beta(2)$$

These make up the triplet spin states, which have the three possible orientations of a total angular momentum of 1.

4.3 Spectrum of He-Atom:

He atom contains two valence electrons. Therefore, it emits, same type of spectra as are given by alkaline earths.
These two electrons in the configuration are responsible for the valency of two and hence in deciding the general characteristics of the optical spectrum.
The emission spectrum of helium shows a number of series in the visible region of the spectrum, as well as in the near and far ultraviolet regions.

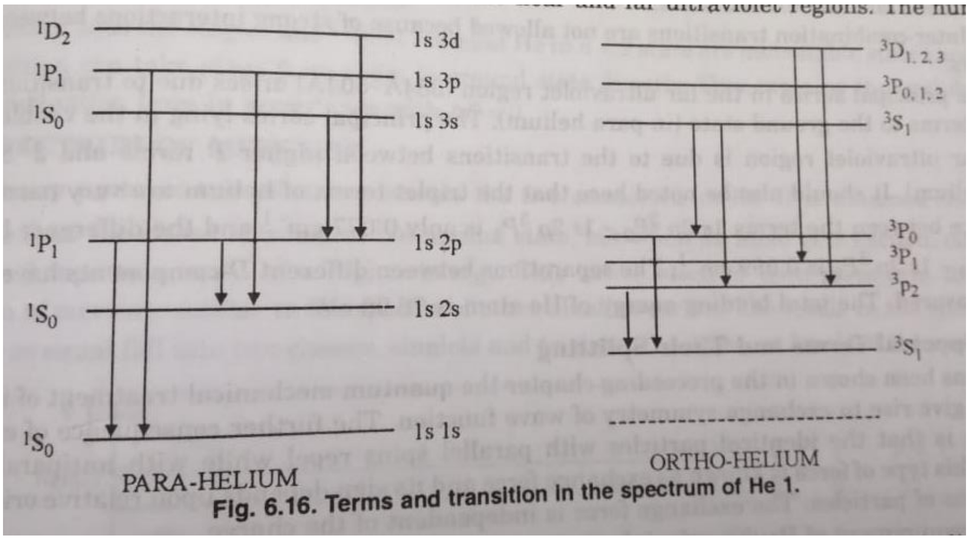
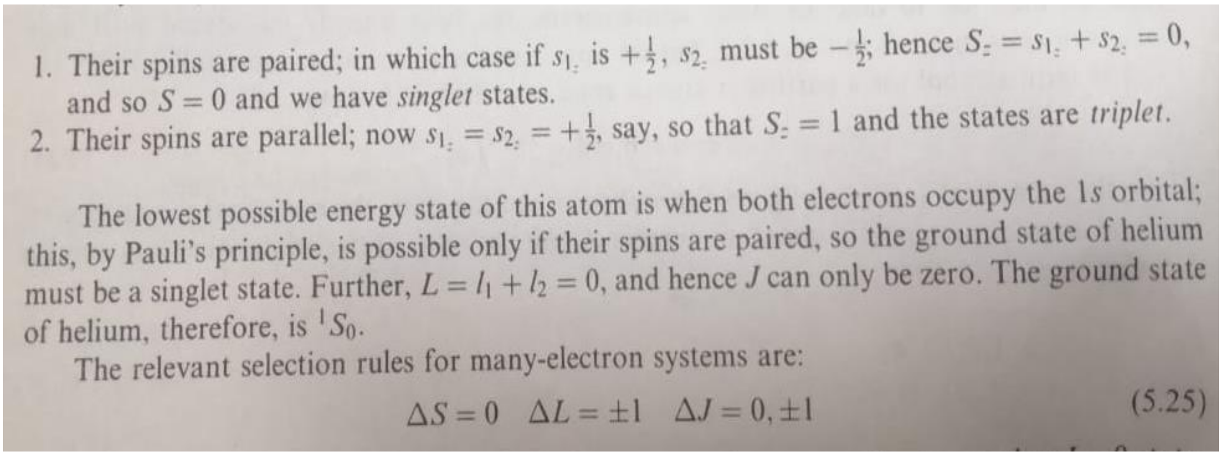


Fig. 6.16. Terms and transition in the spectrum of He 1.



1. Their spins are paired; in which case if s_{1z} is $+\frac{1}{2}$, s_{2z} must be $-\frac{1}{2}$; hence $S_z = s_{1z} + s_{2z} = 0$, and so $S = 0$ and we have *singlet* states.
2. Their spins are parallel; now $s_{1z} = s_{2z} = +\frac{1}{2}$, say, so that $S_z = 1$ and the states are *triplet*.

The lowest possible energy state of this atom is when both electrons occupy the $1s$ orbital; this, by Pauli's principle, is possible only if their spins are paired, so the ground state of helium must be a singlet state. Further, $L = l_1 + l_2 = 0$, and hence J can only be zero. The ground state of helium, therefore, is $^1S_0$.

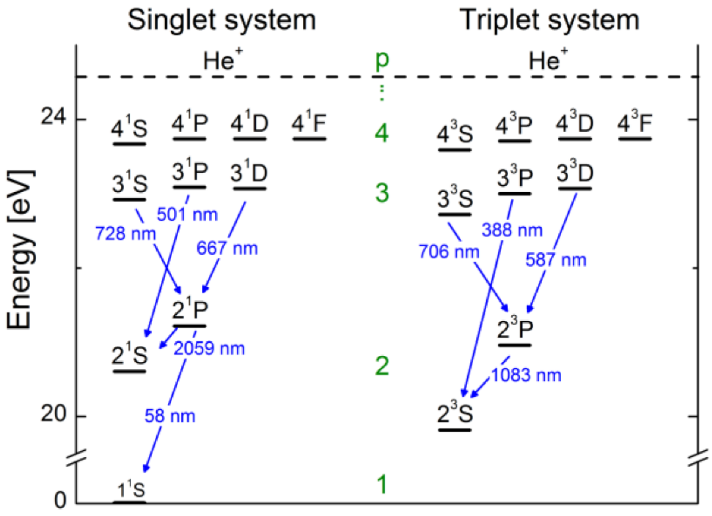
The relevant selection rules for many-electron systems are:

$$\Delta S = 0 \quad \Delta L = \pm 1 \quad \Delta J = 0, \pm 1 \tag{5.25}$$

The spectrogram for helium shows two systems:

- **one singlet system – containing all the four chief series (s,p,d and f)**
- **one triplet system – contains all the four chief series.**

The two principal series of helium lie in the visible and near ultraviolet region of the spectrum.



Due to the strictness of rule ΔS = 0 in the light elements, the atom does not show any inter-combination lines, i.e. no transition is allowed between the states represented by different multiplicities (singlet and triplet in this case).

The strictness of the rule divides the entire spectrum of helium into two parts:

(i) **The singlet system belongs to para-helium (spin antiparallel) because for singlets – S = 0.**

(ii) **The triplet system belongs to ortho-helium (spins parallel) because S = 1.**

The terms of the triplet system lie deeper than the corresponding terms for singlet state, if the same limit is assumed for all the term series.

The singlet system differs from the triplet system in having, besides others, an additional deep lying level corresponding to n=1. This is the ground state ($1\,^1S_0$) of helium atom.

The same thing can also be stated by saying that ortho helium does not exist in the state defined by the principal quantum number n = 1 ($1\,^3S_1$) due to operation of Pauli's principle.

The lowest state of ortho-helium is $2\,^3S_1$ and lies 19.72 volts above the ground state of the atom.

The state of the ortho-helium $3\,^3S_1$ does not combine with the ground state of the atom and represents meta-stable state.

The $2\,^1S_0$ state is also metastable state, because the selection rule $\Delta l = \pm 1$ restricts any transition to $1\,^1S_0$.

However the meta-stability $2\,^3S_1$ state is more strong than that of the $2\,^1S_0$ state, since it contradicts $\Delta S = 0$ and $\Delta l = \pm 1$ rule.

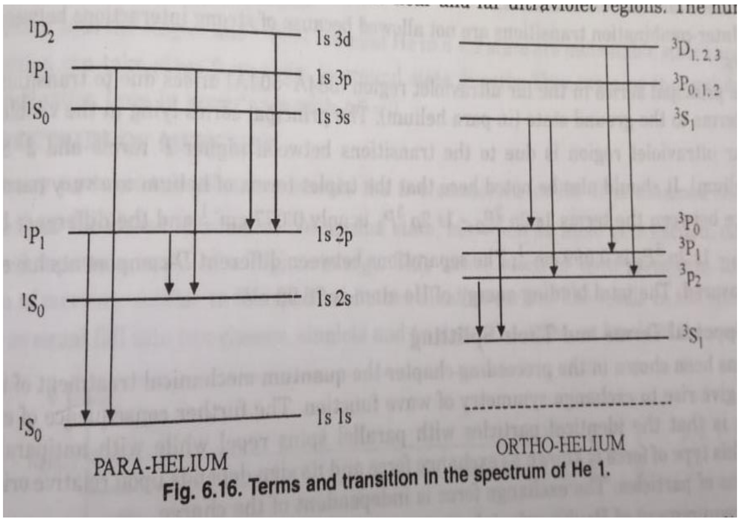


Fig. 6.16. Terms and transition in the spectrum of He 1.

Summary:

1. **Ground state is singlet ($1\,^1S_0$) and there is not corresponding energy state in triplet system.**
2. **Other than ground state, there is a state in triplet state corresponds to every singlet state.**
3. **Each triplet state is lower lying than the corresponding singlet state.**
4. **The difference between ground state and lowest lying ground state is larger in comparison to the other state and excited state.**

Inter-combination transitions are not allowed because of strong interactions between 1 and s vectors.

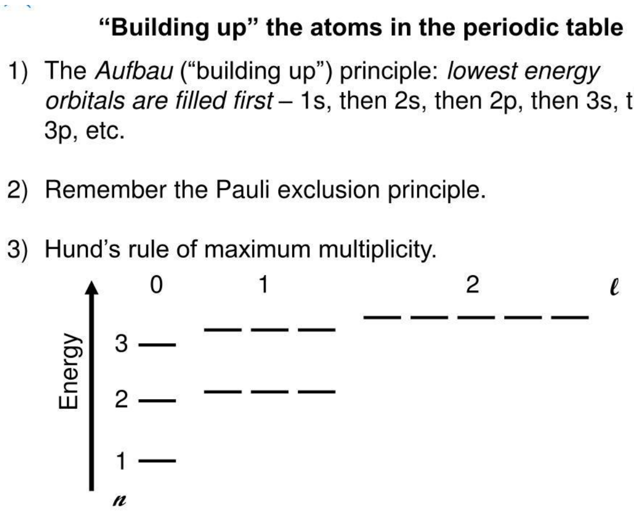
4.4 The Building-Up Principle

The Schrodinger equation shows that electrons in atoms occupy orbitals of the same type and shape as the s, p, d, ….. orbitals, but that the energies of these electrons differ from atom to atom.

There are three basic rules, known as the building-up rules, which determine how electrons in large atoms occupy orbitals.

1. **Pauli's principle: no two electrons in an atom may have the same set of values for n, l, m_l and m_s.**
2. **Electrons tend to occupy the orbital with lowest energy available.**

Hund's principle: electrons tent to occupy degenerate orbitals singly with their spins parallel.



"Building up" the atoms in the periodic table

1) The *Aufbau* ("building up") principle: *lowest energy orbitals are filled first* – 1s, then 2s, then 2p, then 3s, then 3p, etc.

2) Remember the Pauli exclusion principle.

3) Hund's rule of maximum multiplicity.

Rule 1 effectively limits to two the number of electrons in each orbital.

An example may make this clear:

We may characterize both an orbital and an electron occupying it by specifying the n, l and m quantum numbers.

Thus a 1s orbital or 1s electron has n = 1, l = 0 and ml = 0; the electron (but not the orbital) is further characterized by a statement of its spin direction, i.e. by specifying s = + ½ or s = - ½ .

Two electrons can together occupy the 1s orbital provided, according to rule 1, that one has the set of values n = 1, l = 0, ml = 0, s = +1/2 and the other n = 1, l = 0, ml = 0, s = -1/2.

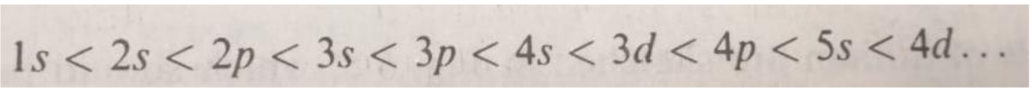
Two electrons occupying the same orbital only if their spins are paired.

A third electron cannot exist in the same orbital without repeating a set of values for n, l, ml and ms already taken up.

It would have to be placed into some other orbital and the choice is determined by rule 2: it would go into the next higher vacant or half-vacant orbital.

In general, orbital energies in many-electron atoms increase with increasing n, but they also increase with increasing l, whereas we noted for hydrogen that all s, p, d ….orbitals with the same n were degenerate.

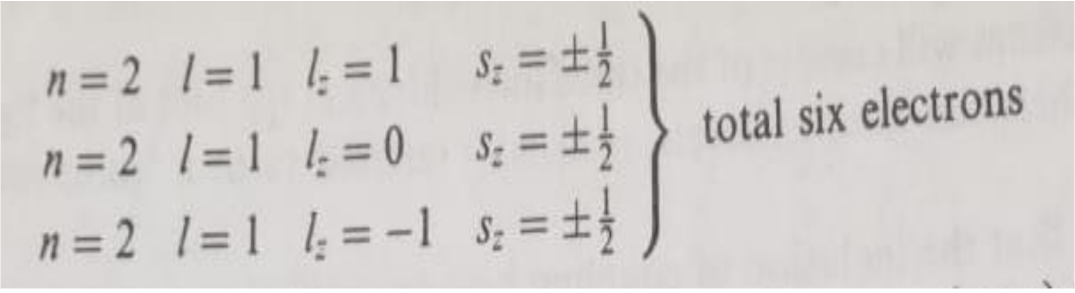
In fact the order of the energy levels for most atoms is as follows:



$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d\ldots$$

Thus when the 1s orbital is full (i.e. contains two electrons) the next available orbital is the 2s and after this the 2p.

Now we remember that there are three 2p orbitals, one along each coordinate axis, and each of these can contain two electrons. We may write the n, l, ml and ms values as:



$$\left.\begin{array}{llll} n=2 & l=1 & l_z=1 & s_z=\pm\frac{1}{2} \\ n=2 & l=1 & l_z=0 & s_z=\pm\frac{1}{2} \\ n=2 & l=1 & l_z=-1 & s_z=\pm\frac{1}{2} \end{array}\right\} \text{total six electrons}$$

All three p orbitals remain degenerate for a given n.

It is rule 3 which tells us how electrons occupy these generate orbitals.

Hund's rule states that when, for example, the $2p_x$ orbital contains an electron, the next electron will go into a different 2p say $2p_y$ orbital and a third into $2p_z$. This may due to consequence of repulsion between electrons.

A fourth electron has no choice but to pair its spin with an electron already in one 2p orbital, while a fifth and sixth will complete the filling of the three 2p's.

On this basis we can build up the electronic configurations of the 10 smallest atoms, from hydrogen to neon. This is shown in table where each box represents an orbital occupied by one or two electrons with spin directions shown by the arrows. A convenient notation for the electronic configuration is also shown in the table.

When a set of orbitals of given n and l is filled it is referred to as a closed shell. Thus the 1s2 set of helium, the 2s2 set of beryllium, and the 2p6 set of neon are all closed shells.

The convenience of this is that closed shells make no contribution to the orbital or spin angular momentum of the whole atom and hence they may be ignored when discussing atomic spectra. This represents a considerable simplification.

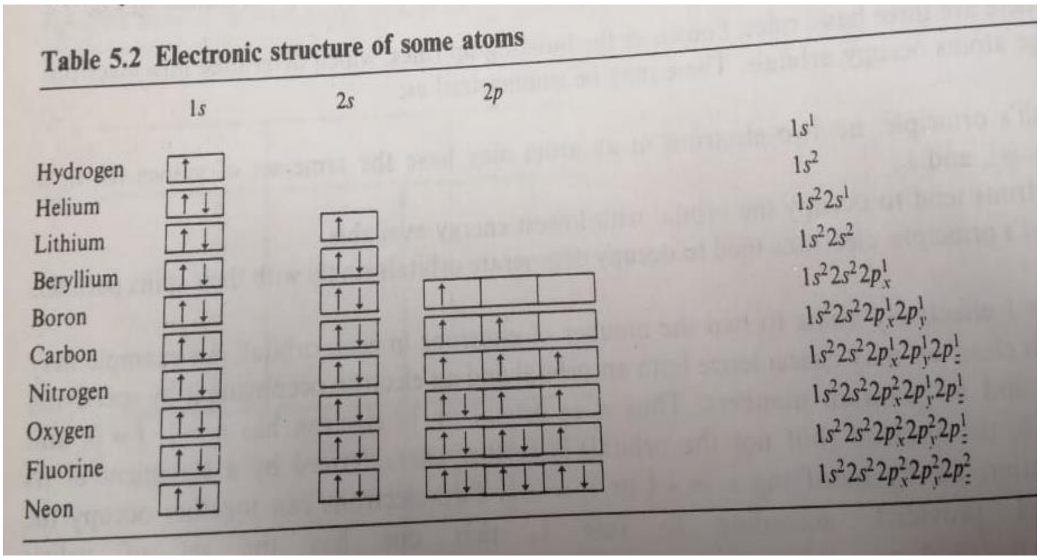


Table 5.2 Electronic structure of some atoms

	1s	2s	2p			
Hydrogen	↑					$1s^1$
Helium	↑↓					$1s^2$
Lithium	↑↓	↑				$1s^2 2s^1$
Beryllium	↑↓	↑↓				$1s^2 2s^2$
Boron	↑↓	↑↓	↑			$1s^2 2s^2 2p_x^1$
Carbon	↑↓	↑↓	↑	↑		$1s^2 2s^2 2p_x^1 2p_y^1$
Nitrogen	↑↓	↑↓	↑	↑	↑	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$
Oxygen	↑↓	↑↓	↑↓	↑	↑	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
Fluorine	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$
Neon	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$

4.5 L-S Coupling and J – J Coupling Designation of states

Total angular momentum in many electron atoms

Introduction:

- **The addition of orbital and spin angular momenta for a many electron system is much more involved than that of a one electron system.**
- **For many electron systems only the electrons outside a closed shell (valence electrons) contribute to the angular momentum of the atom.**
- **When more than one electron contributes orbital and spin angular momenta to the total angular momentum J of an atom is still the vector sum of these individual momenta.**

Generally two types of coupling known as Russel-Saunders or L-S coupling and J-J coupling.

The two procedures are available to compute the total angular momentum J of a many electron system,

(i) L – S coupling

(ii) j – j coupling

In physics, two systems are coupled if they are interacting with each other.

There are two types of coupling: L-S coupling & J-J coupling.

(i) **L-S coupling (or) Russel Saunders Coupling Scheme:**

(spin-orbital coupling scheme)

- **This is also called as normal coupling as this occurs most frequently.**
- **When more than one electron contributes orbital and spin angular momenta to the total angular momentum J of an atom, J is still the vector sum of these individual momenta.**

- In order to understand this scheme, first we should know about the structure of atom. There is nucleus at the centre and electrons revolve around the nucleus in various subshells.

  L - orbital angular momentum of electron

  S - spin angular momentum of electron

This is in case of one electron system.

Whereas , in case of many electron system, each electron have

orbital angular momentum and spin angular momentum, represented as

$L_1, L_2, L_3, \ldots\ldots;$ $S_1, S_2, S_3, \ldots\ldots$

The momenta L and S then interact via the spin-orbit effect to form the total angular momentum J. This scheme is called as LS coupling.

In the L-S coupling scheme, the orbital angular momenta $L_1, L_2, L_3, \ldots\ldots$ of the electrons combine vectorially to form a total orbital angular momentum L and similar is the case for S. Thus,

$L = L_1 + L_2 + L_3 + \ldots\ldots$

$S = S_1 + S_2 + S_3 + \ldots\ldots$

In order to understand the energy state of the atom, we would consider the resultant angular momentum (J).

The momenta L and S combine to form the total(Resultant) angular momentum J as

$J = L + S$ [coupling of orbital and spin angular momentum]

It is convention to use capital letters L, S and J for the angular momentum quantum numbers of a many electron system. These are simply integers and half integers.

When two orbital angular momenta having quantum numbers l_1 and l_2 combine, the allowed values L are

$$L = (l_1 + l_2), (l_1 + l_2 - 1), \ldots\ldots, |l_1 - l_2|$$

Similarly the allowed values are calculated for S and J. For a given value of L, the allowed values of J are

$$J = (L + S), (L + S - 1), \ldots\ldots, |L - S|$$

The L-S coupling predominates in atoms where the coupling between the individual L_i and S_i vectors is weak. Then the individual L_i vector would couple and give the L vector while the S_i vectors couple and give the s vector. This coupling scheme is applicable to lighter elements.

For L > S, there are 2S+1 values of J.

For L < S, the number of possible values of J are 2L + 1.

The value of 2S+1 is called the multiplicity of the state.

For a two electron system ($s_1 = s_2 = 1/s$), the total spin angular momentum quantum number S = 0 (spin antiparallel) or S = 1 (spin parallel).

When S = 0, we have 2S+1 = 1 and such states are referred to as singlet states.

When S = 1, we have 2S+1 = 3, these are referred as triplet state.

Often the singlet and triplet levels are grouped separately.

To describe states conveniently, one requires a notation. The symbol $n\ L_j$ used for a single electron is changed as follows.

State symbol or Term symbol = $n\ {}^{2S+1}L_j$

Where,

The superscript 2S+1 represents the multiplicity of the state,

Subscript J is the total angular momentum quantum number, and

L stand for S, P, D,…. Representing the orbital angular momentum quantum number. This way of representing states is know as the term symbol of the state.

If S = ½ , L = 1, J = 3/2, 1/2 .

The corresponding states will be ${}^2P_{3/2}$ and ${}^2P_{1/2}$, read as doublet P three halves and doublet P half.

Multiplicities associated with different number of electrons in the outer shell are given by the rule which states that the terms of atoms or ions with even numbers of valence electrons have odd multiplicities and vice versa.

The selection rules for the L –S coupling case are

$\Delta L = \pm 1$; $\Delta S = 0$; $\Delta J = 0, \pm 1$ **(J =0 is forbidden)**

The selection rule $\Delta S = 0$ does not allow transitions between singlet and triplet states.

(ii) j – j coupling:

This coupling predominates in atoms where the interaction between each L_i and S_i is considerable. In this scheme, each L_i combines with the corresponding S_i to give a J_i, the total angular momentum of the i_{th} electron. The J_i's then couple and give the total angular momentum (J) of the atom.

Thus for each active electron $J_1 = L_1 + S_1$; $J_2 = L_2 + S_2$; $J_3 = L_3 + S_3$; …..

$J = J_1 + J_2 + J_3 + \ldots\ldots. = \sum J_i$.

This coupling scheme is known as J – J coupling which is distinctly different from L – S coupling scheme, is applicable to heavy elements.

Rules for determining ground state term:

1.The ground state term is one with maximum spin multiplicity or maximum number of unpaired electrons

E.g. ^2P , ^1P, ^3P GND state term.

2. If there are more than one term with same multiplicity, ground term will be one with largest L value.

E.g. 2P, 2D GND state term.

3. For half filled or less than half filled shell, ground state term is one with lowest J value.

E.g. ^6C $^3P_2$, $^3P_1$, $^3P_0$ GND state term.

4. For more than half filled state, ground state term is one with highest J value.

E.g. ^8O $^3P_2$, $^3P_1$, $^3P_0$ GND state term

UNIT – V – Emission and Absorption of Electromagnetic Radiation – SPH1311

5.1 Transitions Probabilities

- Transition between atomic energy states is statistical process.
- For a very large number of atoms, it is possible to calculate the rate of transition between two states based on laws of probability.
- Albert Einstein was first to calculate the probability of such transition in 1917
- Thus the transition probabilities are
  1. Spontaneous transition
  2. Induced transition
     a) Induced absorption
     b) Induced emission

5.1.1 Distribution of atoms in energy levels

POPULATION OF ENERGY LEVEL: The number of atoms per unit volume that can occupy the given energy level.

Consider an assembly of atoms at absolute temperature T which are characterized by two energy levels. Let the population at energy level E1 and E_2 be N_1 and N_2.

At Thermal equilibrium, by using Boltzmann law

$$N_1 = e^{-E_1/kT}$$
$$N_2 = e^{-E_2/kT}$$

The relative population N_2/N_1

$$\frac{N_2}{N_1} = e^{-(E_2-E_1)/kT}$$

5.2 Einstein’s coefficients - Transition probabilities for absorption and induced emission

Einstein’s theory

Einstein’s theory of absorption and emission of light by an atom is based on Planck’s theory of radiation. Also under thermal equilibrium, the population of energy levels obeys the Maxwell Boltzmann distribution law, *Under thermal equilibrium*

The rate of Absorption = The rate of Emission

$$B_{12}\rho_\nu N_1 = A_{21}\ N_2 + B_{21}\rho_\nu N_2$$

$$B_{12}\rho_\nu N_1 - \ B_{21}\rho_\nu N_2 = A_{21}\ N_2$$

$$\rho_\nu (B_{12}N_1 - \ B_{21}N_2) = A_{21}\ N_2$$

$$\rho_\nu = \frac{A_{21}\ N_2}{(B_{12}N_1 - \ B_{21}N_2)}$$

Where

A, B – constants

r - Electron density

N_1 - electrons in ground state

N_2 – electrons in excited state

$$\rho_\nu = \frac{A_{21}}{\left(B_{12}\frac{N_1}{N_2} - B_{21} \right)} \qquad - - \rightarrow (7)$$

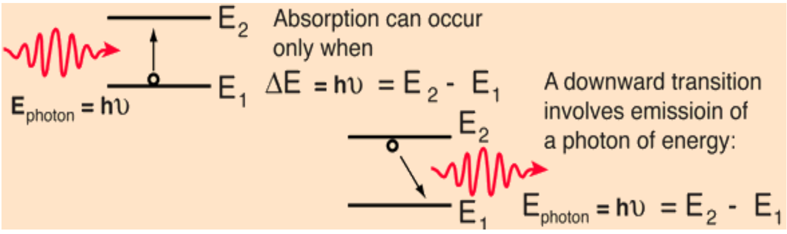
We know from the Boltzmann distribution law

$$N_1 = N_0\, e^{-E_1/K_B T}$$

$$N_2 = N_0\, e^{-E_2/K_B T}$$

Where K_B is the Boltzmann Constant, T is the absolute temperature and N_0 is the number of atoms at absolute zero. At equilibrium, we can write the ratio of population levels as follows

$$\frac{N_1}{N_2} = e^{\frac{h\nu}{K_B T}} \qquad - - \rightarrow (8)$$



Substituting equation (8) in equation (9)

$$\rho_\nu = \frac{A_{21}}{\left(B_{12}\left(e^{\frac{h\nu}{K_B T}}\right) - B_{21}\right)}$$

$$\rho_\nu = \frac{A_{21}}{B_{21}} \frac{1}{\left(\frac{B_{12}}{B_{21}}\left(e^{\frac{h\nu}{K_B T}}\right) - 1\right)} \quad - - \rightarrow (10)$$

This equation has a very good agreement with Planck's energy distribution radiation law.

$$\rho_\nu = \frac{8\pi h\nu^3}{C^3} \frac{1}{e^{\frac{h\nu}{K_B T}} - 1} \quad - - \rightarrow (11)$$

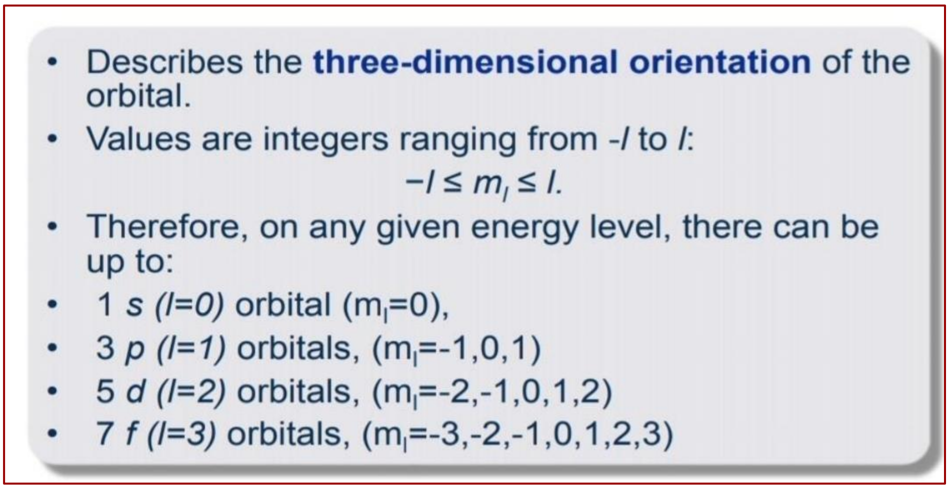
Therefore comparing equations (6) and (7), we can write

$$B_{12} = B_{21} = \mathrm{B} \quad \text{and} \quad \frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{C^3} \quad - - \rightarrow (12)$$

The constants ***A*** and ***B*** are called as Einstein Coefficients, which accounts for spontaneous and stimulated emission probabilities.

5.3 Magnetic Quantum Number

- **The magnetic quantum number (symbol ml) is one of four quantum numbers in atomic physics**
- **The magnetic quantum number distinguishes the orbitals available within a subshell, and is used to calculate the azimuthal component of the orientation of orbital in space.**
- **Electrons in a particular subshell (such as s, p, d, or f) are defined by values of ℓ (0, 1, 2, or 3).**
- **The value of ml can range from -ℓ to +ℓ, including zero. Thus the s, p, d, and f subshells contain 1, 3, 5, and 7 orbitals each, with values of m within the ranges 0, ±1, ±2, ±3 respectively. Each of these orbitals can accommodate up to two electrons (with opposite spins), forming the basis of the periodic table.**

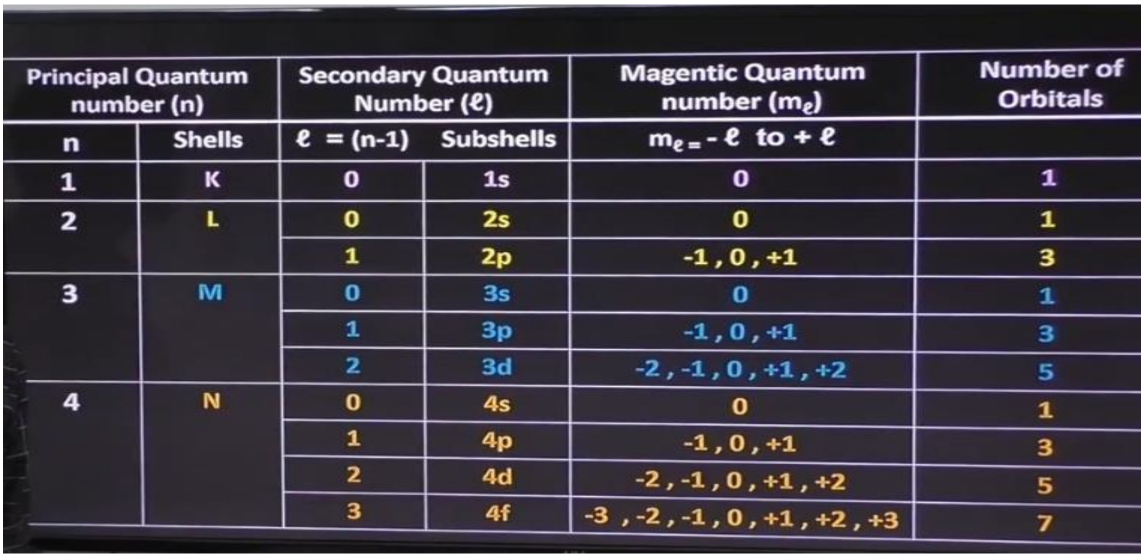


- Describes the **three-dimensional orientation** of the orbital.
- Values are integers ranging from *-l* to *l*:

$$-l \le m_l \le l.$$

- Therefore, on any given energy level, there can be up to:
- 1 *s (l=0)* orbital ($m_l=0$),
- 3 *p (l=1)* orbitals, ($m_l=-1,0,1$)
- 5 *d (l=2)* orbitals, ($m_l=-2,-1,0,1,2$)
- 7 *f (l=3)* orbitals, ($m_l=-3,-2,-1,0,1,2,3$)

- **Orbitals with the same value of n from a shell.**
- **Different orbital types within a shell are subshells (s,p,d,f)**



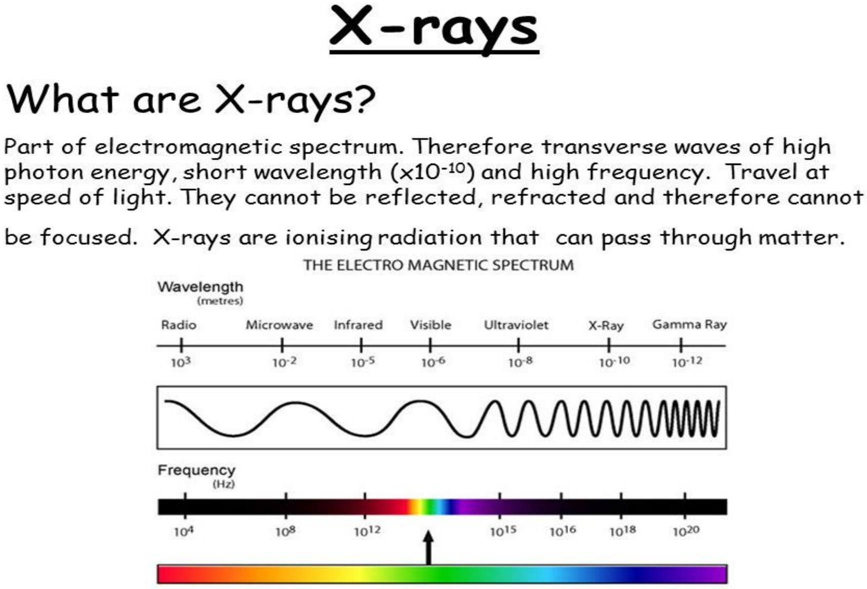
Principal Quantum number (n)		Secondary Quantum Number (ℓ)		Magentic Quantum number (m_ℓ)	Number of Orbitals
n	Shells	ℓ = (n-1)	Subshells	$m_\ell = -\ell$ to $+\ell$	
1	K	0	1s	0	1
2	L	0	2s	0	1
		1	2p	-1 , 0 , +1	3
3	M	0	3s	0	1
		1	3p	-1 , 0 , +1	3
		2	3d	-2 , -1 , 0 , +1 , +2	5
4	N	0	4s	0	1
		1	4p	-1 , 0 , +1	3
		2	4d	-2 , -1 , 0 , +1 , +2	5
		3	4f	-3 , -2 , -1 , 0 , +1 , +2 , +3	7

Spin quantum number

- **Represents information about spin of the quantum particle**
- **Denoted by S**
- **Possible values =+ ½**
- **Magnitude = $[s(s+1)\ h]^{\frac{1}{2}}$**

In terms orbital angular momentum L=$[l(l+1)\ h]^{\frac{1}{2}}$

5.4 X-rays



X-rays

What are X-rays?

Part of electromagnetic spectrum. Therefore transverse waves of high photon energy, short wavelength (x10^{-10}) and high frequency. Travel at speed of light. They cannot be reflected, refracted and therefore cannot be focused. X-rays are ionising radiation that can pass through matter.

Properties of X-rays

1. **X-rays travel in straight lines**
2. **X-rays are electrically neutral**
3. **X-rays are polyenergetic and heterogeneous**
4. **X-rays travel at the speed of light**
5. **X-rays are highly penetrating, invisible rays**
6. **X-rays cannot be deflected by electric field or magnetic field**
7. **X-rays cannot be focused by lens**
8. **Photographic film is blackened by X-rays**

5.4.1 X-ray Spectra

An X-ray spectrum is a plot of intensity of X-rays versus wavelength, energy or frequency.

The observed intensity variation with respect to energy of X-rays from an X-ray tube is found to be of mainly two types of spectra:

1. **Continuous X-ray spectrum**
2. **Characteristic X-ray spectrum**

Continuous X-rays are created when free moving electrons electromagnetically interact with nuclei, whereas

Characteristic X-rays are formed during the electron transition processes that occur when an inner shell electron is released from an atom.

i) Continuous X-ray spectra

It consists of radiations of all possible wavelengths, from a certain lower limit to higher values continuously, as in the case of visible light.

The continuous X-ray spectrum refers the range of photon energies produced in an X-ray tube due to the properties of Bremsstrahlung radiation.

Origin - Continuous X-ray spectra

X-rays are produced, when high velocity electrons strike the target material of high atomic number. It has also been mentioned in the production of X-rays, that most of the energy of the electrons goes into the heating of the target material.

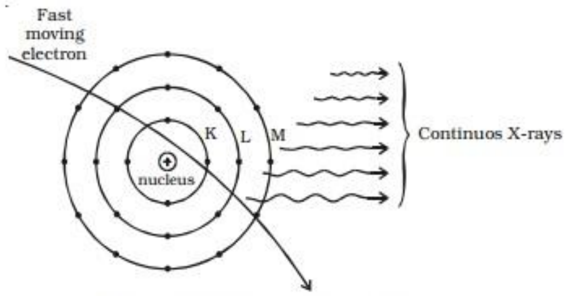
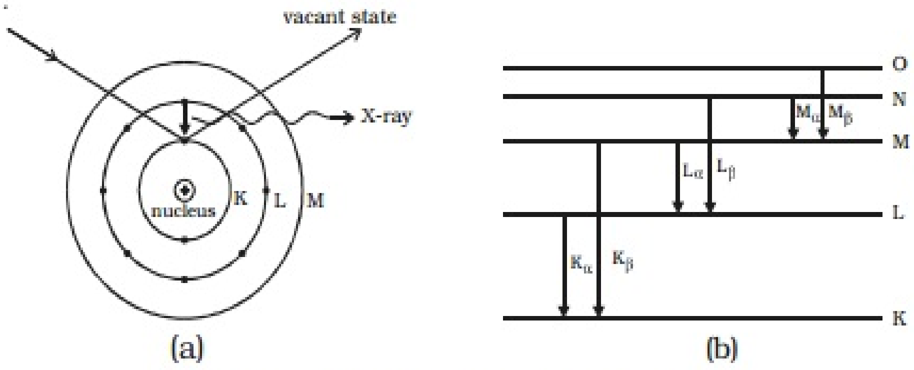


Fig Origin of continuous X – rays



(a) (b)

Fig Characteristic X–ray spectra

A few fast moving electrons penetrate deep into the interior of the atoms of the target material and are attracted towards the nuclei by the attractive forces of their nuclei. Due to these forces, the electrons get deflected from their original path.

As a result of this, the electrons are decelerated, and hence energy of the electron decreases continuously. This loss of energy during retardation is given off in the form of X-rays of continuously varying wavelength.

The X -rays consist of continuous range of frequencies up to a maximum frequency ν_{max} or minimum wave length λ_{min}. This is called as continuous X -rays. The minimum wave length depends on the anode voltage.

If *V* is the potential difference between the anode and the cathode

$eV = h\nu_{max} = hc / \lambda_{min}$

The minimum wavelength of the given radiation is,

$\lambda_{min} = hc /eV$

where h is Planck's constant, c is the velocity of light and e, the charge of the electron. Substituting the known values in the above equation.

$\lambda_{min} = 12400/V\ A^0$

For the given operating voltage, the minimum wave length is same for all metals.

It is worthwhile to mention that sometimes X-rays are classified according to their penetrating power.

The most penetrating radiation is termed hard radiation whereas the radiation with relatively less penetrating power is called medium radiation.

The radiation with very low penetrating power is termed soft radiation.

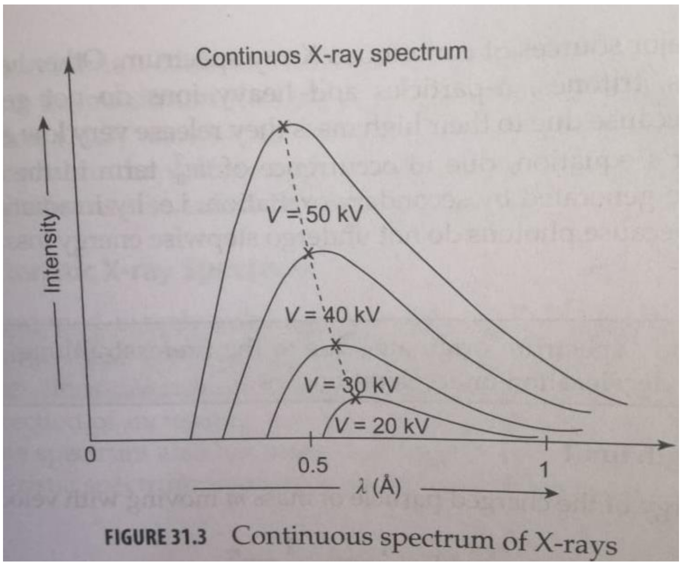


FIGURE 31.3 Continuous spectrum of X-rays

One can understand the nature of the spectral distribution of the continuous X-rays on the basis of the theory of bremsstrahlung based on electromagnetic theory.

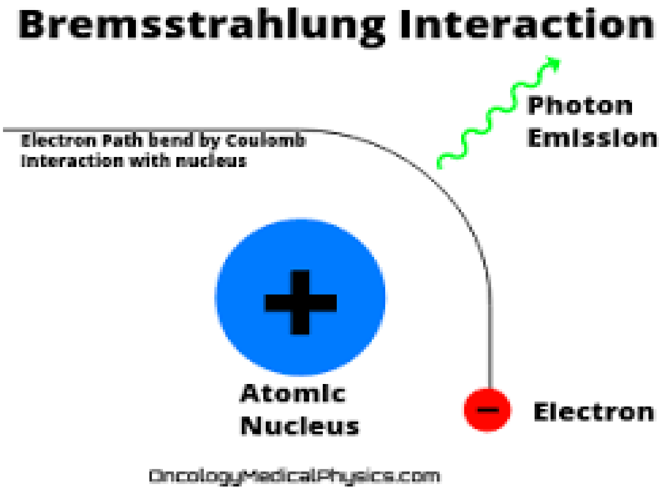
Due to deceleration of the electron beam in the direction of its motion within the target inside the X-ray tube, we have to take the spectral energy distribution of the bremsstrahlung X-ray for electrons of different energies and assign different weights to these curves.

These are based on the adsorption of X-rays within the X-ray tube, in air and in window of the ionization chamber, other variation of reflecting power of the crystal grating for different wavelengths and different ionizing powers of the beams of different wavelengths.

One finds that the spectral energy distribution of the bremsstrahlung radiation is independent of the frequency and can be expressed as

$I_\lambda = I_\nu (\nu_2/c_2)\ \alpha\ 1/\lambda_2$

Eq. explains the observed spectral distribution of the continuous X-rays.

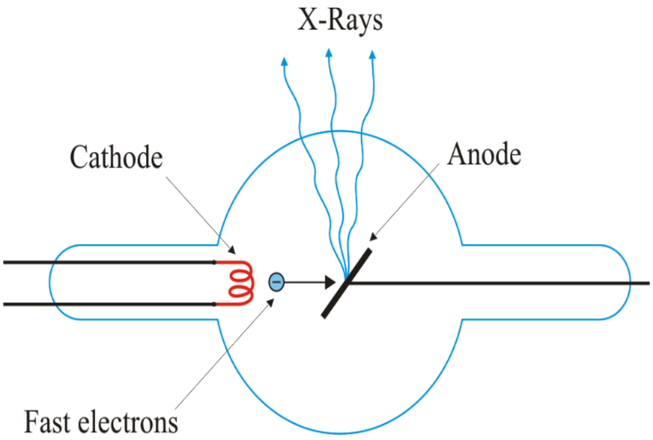


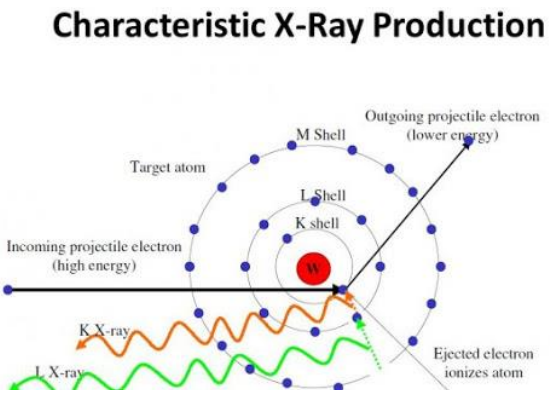
Characteristic X-ray

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.

(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.





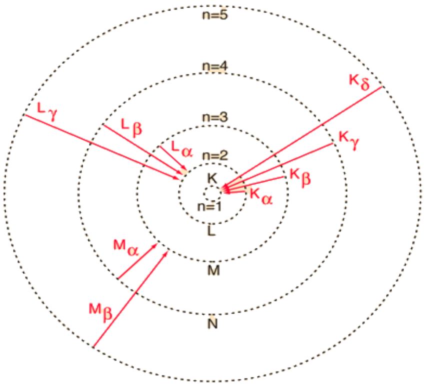
The peaks obtained in the X-ray spectrum give us the line spectrum which is characteristic of the element used in the target.

- The group of lines of shortest wavelength is called the K-series.

- Two lines of this series are detected - these lines are termed as K_α and K_β lines in the order of decreasing wavelengths.

- The next group is called the L-series of longer wavelengths (L_α, L_β , L_γ, 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.

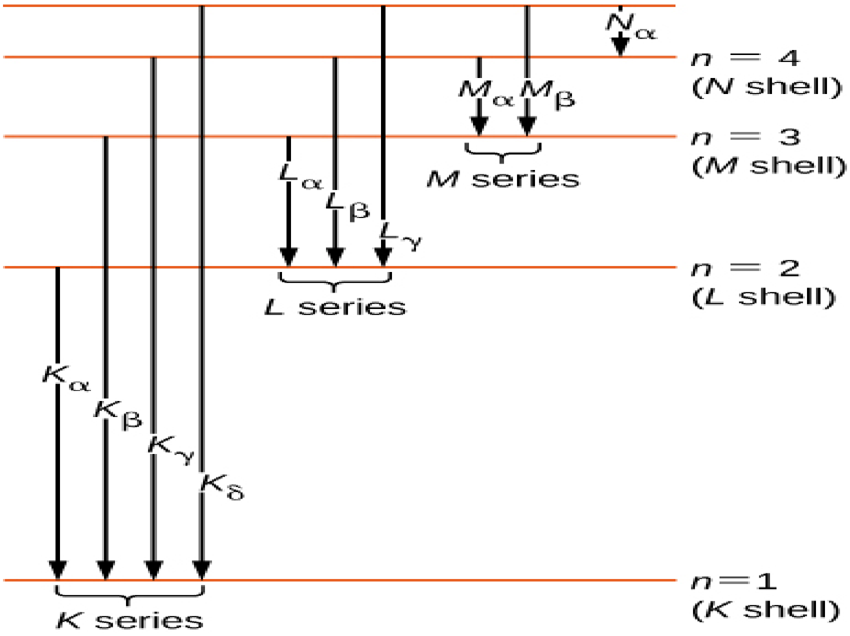
Suppose an atom in the target of an X-ray tube is bombarded by a high-speed electron and a K-electron is removed.

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.

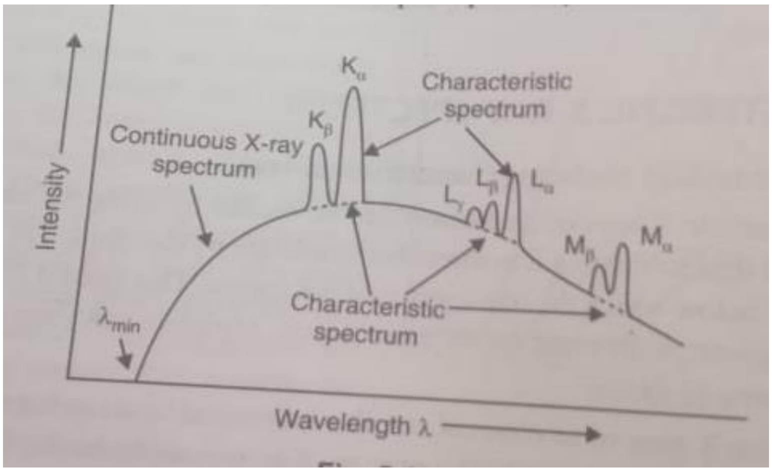
These possible transitions can result in the K_α and K_β Lines and the limiting line.

Similarly, the longer wavelength L-series originates (L_α, L_β , L_γ , etc.) when an L electron is knocked out of the atom, M-series when an M electron is knocked out and so on (fig).



It is clear that continuous spectra and line spectra both emitted by the same target are of different origin. The continuous spectrum is the result of the inverse photoelectric effect, with electron K.E. being transformed into photon energy hν. The line spectrum has its origin in electronic transition within atoms that have been disturbed by the incident electrons.

Fig. shows a characteristic spectrum superimposed upon continuous spectrum.

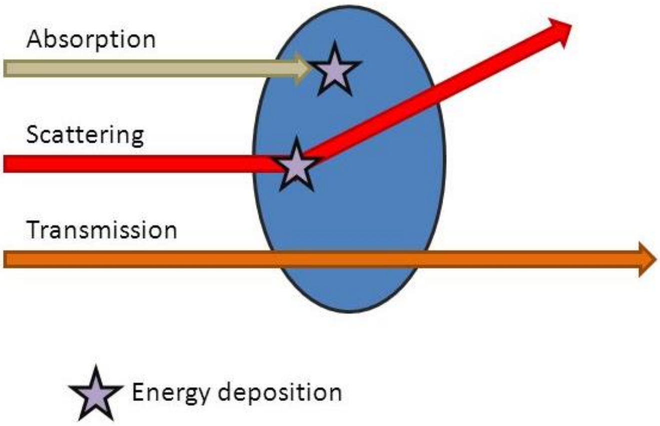


Auger Effect

It a type of transition in which there is no emission of electromagnetic radiation, but emission of two electrons from the same atom is called Auger transition or Auger effect.. Also known as radiation less transition.

5.5 Interaction of X-rays with matter

X-rays traveling through matter can be transmitted, absorbed or scattered.



Absorption of X-rays

When a parallel beam of X-rays is incident over a slab of matter, a portion of it is being absorbed by the slab and the remaining part is transmitted.

The absorbed portion of X-rays depends upon its intensity and thickness of the slab.

Let a beam of X-rays of wavelength λ and intensity I be incident over the slab of the material of uniform thickness dx.

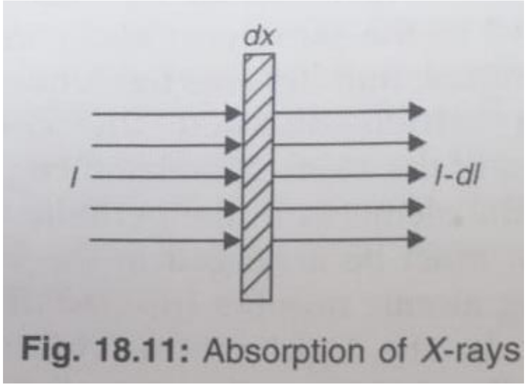


Fig. 18.11: Absorption of X-rays

If corresponding diminution in intensity is dI, we have

$$dI \ \alpha \ - I \ dx$$

or $$dI = - \mu \ I \ dx$$

Where the constant of proportionality μ is called the linear coefficient of absorption of the material and is equal to the fractional decrease in the intensity of the X-rays per unit thickness of the absorber.

Arranging eq. 1 and integrating it, one obtains

$$\int \frac{dI}{I} = -\int \mu dx$$

or $\log_e I = -\mu x + C$

Where C is integration constant, which can be determined from initial conditions. Thus, at x = 0, the intensity $I = I_0$. Substituting, we have

$\log_e I_0 = C$

If after traversing a distance x in the slab, the corresponding intensity is I,

$\log_e I = -\mu x + \log_e I_0$ or $\log_e \left(\frac{I}{I_0}\right) = -\mu x$

$I = I_0 \exp(-\mu x)$ …… 2

Using eq. 2 and knowing initial intensity and intensity after traversing a distance x in the material, μ can be determined.

μ has the dimension of m^{-1}.

The plot of log I against x is a straight line of slope – μ.

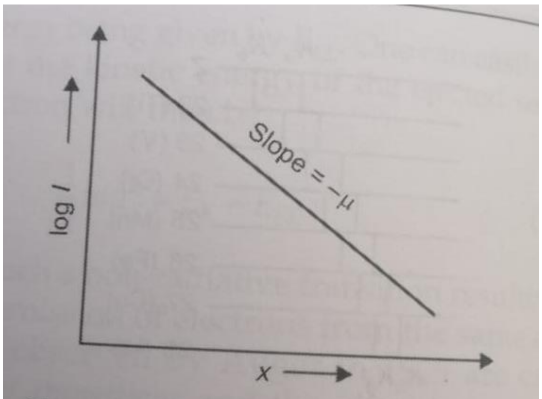


Fig. 18.12: The plot of log I versus x

The intensity of X-rays depends upon the energy transmitted through unit area placed perpendicular to the direction of propagation, whereas its absorption depend upon the number of atoms of the absorbing material.

Hence, linear coefficient of absorption also depends upon the density of the material.

If the density of material is ρ, the quantity μ/ρ is called the mass absorption coefficient (μ_m) of the material.

μ_m of the material depends on the nature of the material (element) and represents the amount of energy absorbed by unit mass of it, when the beam of X-rays is transmitted through unit area.

The absorption by specific atom is called the atomic absorption coefficient (μ_A) and is given by

$$\mu_A = \frac{\mu/\rho}{N/M} = \frac{\mu M}{\rho N}$$

Where M and N are atomic weight of the material and Avogadro number respectively.

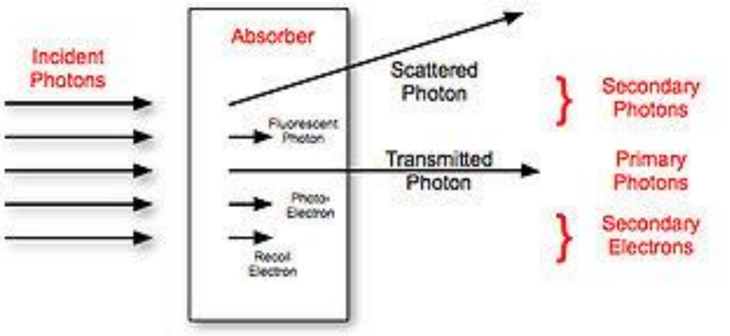
5.6 Scattering of X-rays

When a beam of X-rays is allowed to fall on a plate of some chosen element, then along with the absorption of these rays, which transformed into heat, etc. a portion is transmitted through the plate.

The rays going out from the plate consist of a part of primary X-rays and part of secondary radiations.

The secondary radiations contains four important types of radiations:

- **Scattered X-rays**
- **Characteristic X-rays**
- **Scattered β-rays**
- **Characteristic β-rays**



(i) Scattered X-rays

These are similar to incident X-rays which have only changed their direction of propagation by passing through the absorbing material.

Like primary rays, these are heterogeneous and independent of the nature of the absorbing material.

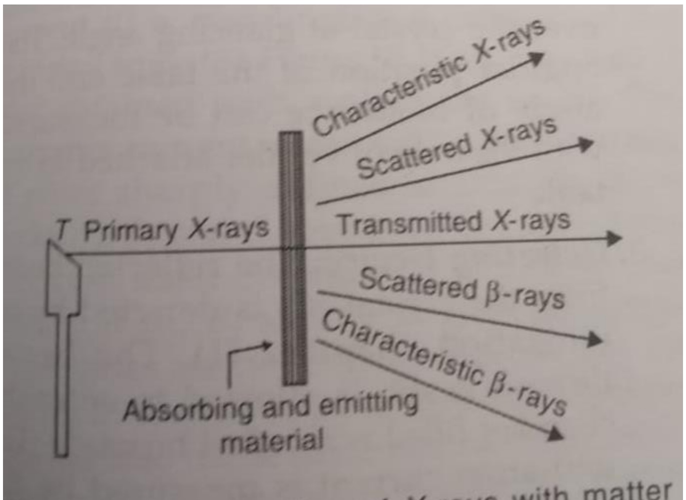


Fig. 18.13: Interaction of X-rays with matter

(ii) <u>Characteristic X-rays</u>

These are typical of the nature of the absorber material.

These are homogeneous and do not depend on the quality of the primary rays.

(iii) <u>Scattered β-rays</u>

These are the fast moving electrons (β-particles) produced by photoelectric process.

Like scattered X-rays, these are independent of the nature of the absorber material but depend on the quality of the primary or incident rays.

(iv) <u>Characteristic β-rays</u>

These are similar to scattered β-rays with the exception of being characteristic of the absorber material.

5.7 Measurement of X-ray wavelength

Henry Moseley discovered that the wavelength (energy) of an X-ray depends on the nuclear charge of an atom.

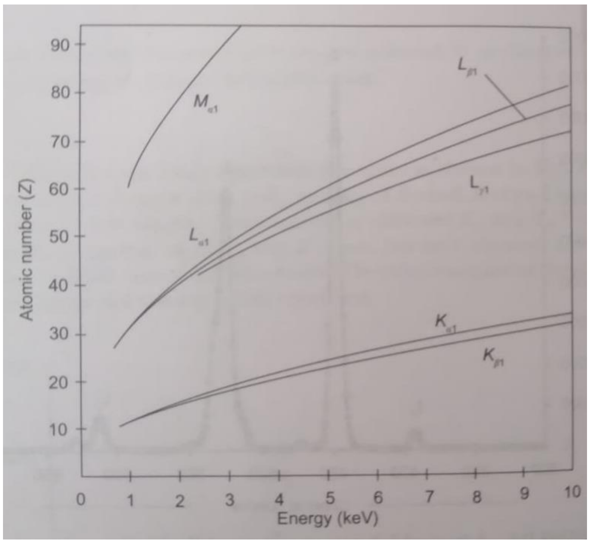
In 1913, he photographed the X-ray spectrum of ten elements that occupied consecutive places in the periodic table.

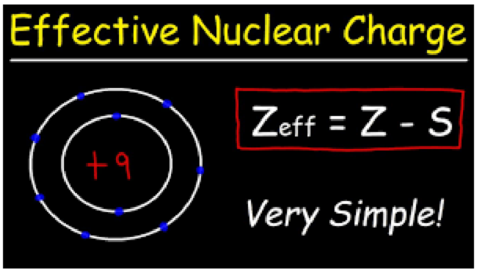
He concluded that there was a fundamental quantity which increases by regular steps as we pass from one element to the next.

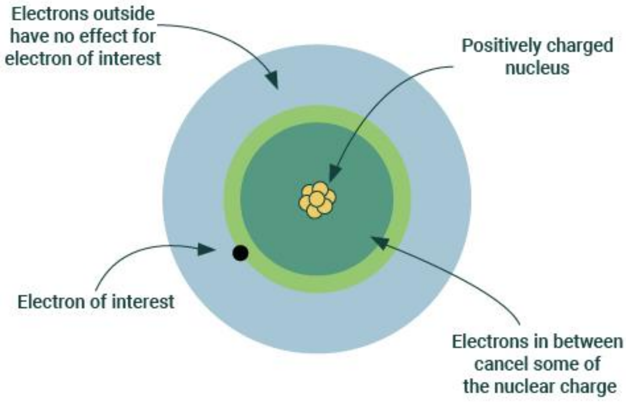
In 1920, Rutherford identified this quantity as the atomic number (Z).

The $K_{\alpha 1}$ lines shifted to higher energy with increased atomic number because the inner-shell electrons are more tightly bound by the higher number of protons in the nuclei (Fig.1).

The energy of transition is proportional to the number of shells changed; $K_{\alpha 1}$ radiation is less energetic than $K_{\beta 1}$.



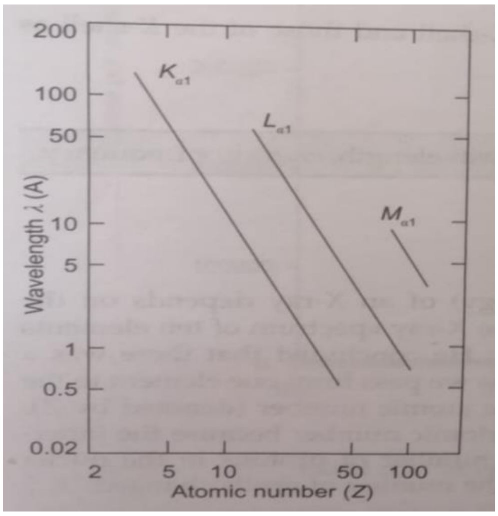




Moseley's law describes the relationship between atomic number and wavelength of a spectral line as

$$\lambda = \frac{K}{(Z-\sigma)^2}$$

Where K and σ are constants for a given spectral line. The plot of λ versus atomic number Z is shown in fig.2



The constant is equal to 1 for the K-lines and 7.4 for more shielded L-lines. For energy, this expression is approximately equivalent to

$$E\ (\mathrm{keV}) = K\ (Z-1)^2$$

Where Z = atomic number

$K = 1.042 \times 10^{-2}$ for the K-shell

$K = 3.446 \times 10^{-4}$ for the M-shell

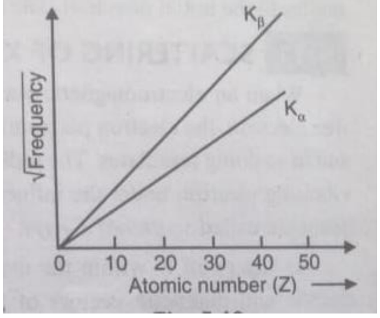
Moseley's determination of this relationship provided a simple test of the order of the elements according to Z. It showed where elements were missing from the periodic table and led to the discovery of some of these elements.

For example, hafnium (Hf), which chemically is almost identical to zirconium (Zr), was identified by D.Coster and G. von Hevesy in 1923 from its X-ray spectrum.

5.7.1 Moseley's Law (in terms of frequency)

Moseley plotted the square root of the frequencies $\sqrt{\nu}$ of a given line (say K) against the atomic numbers (Z) of the elements emitting that line.

Moseley obtained a straight line as shown in fig. 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.



Moseley's law:

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

$$\nu = Z^2 Rc\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Here, R is Rydberg's constant and c the velocity of light.

K line originates from the transition of electron from second to first orbit.

n1 =1 and n2 = 2.

Frequency of K line = $\nu = Z^2 Rc\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{3}{4} cRZ^2$

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 weight. For example, argon $_{18}Ar^{40}$ comes before potassium ($_{19}K^{39}$), cobalt ($_{27}Co^{58.9}$) comes before nickel ($_{28}Ni^{58.7}$), 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.

5.8 Photoionization

• What is photoionization?

Removal of a bound electron by a photon

Loosely refers to any situation where external photons are the dominant source of ionization (and heating)

Photoionization

• What happens when an external photon source illuminates the gas?

- **The photons ionize the atoms in the gas.**
- **The photoelectrons created in this way collide with ambient electrons (mostly) and heat the gas**
- **The gas cools by radiation**
- **The gas temperature adjusts so that the heating and cooling balance**

In a photoionized gas the temperature is not a free parameter

and

The ionization balance is determined by the shape and strength of the radiation field

Coronal ionization

Assume all processes are in a steady state, so that for each ion species the rate of creation= rate of destruction.

Also assume that electron velocity distribution is Maxwellian, kT_{ion} ~$kT_{electron}$, so that electron collisions are much more frequent than ion collisions.

Ion destruction is due to electron impact ionization by thermal .

Ion creation is due to recombination (radiative and dielectronic).

Processes

- **Photoionization (+heating)**
- **Recombination (+cooling)**

Ionization and Thermal Balance

For each ion:

Ionization = recombination

~photon flux ~electron density

For the gas as a whole

Heating = cooling

~photon flux ~electron density

=> All results depend on the ratio photon flux/gas density or "ionization parameter"

5.9 Recombination

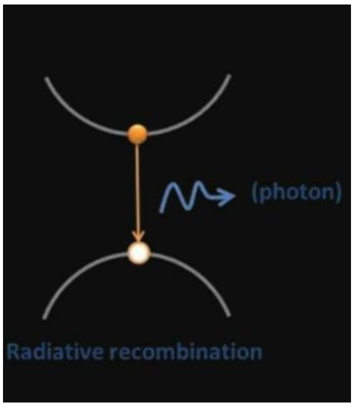
Radiative recombination refers to direct band-to-band transitions of an electron from the conduction band the valence band while emitting a photon . It is the inverse process of photon absorption.

Radiative (Band-to-Band) Recombination Radiative recombination is the recombination mechanism that dominates in direct bandgap semiconductors.

The light produced from a light emitting diode (LED) is the most obvious example of radiative recombination in a semiconductor device.

The key characteristics of radiative recombination are:

In radiative recombination, an electron from the conduction band directly combines with a hole in the valence band and releases a photon; and the emitted photon has an energy similar to the band gap and is therefore only weakly absorbed such that it can exit the piece of semiconductor



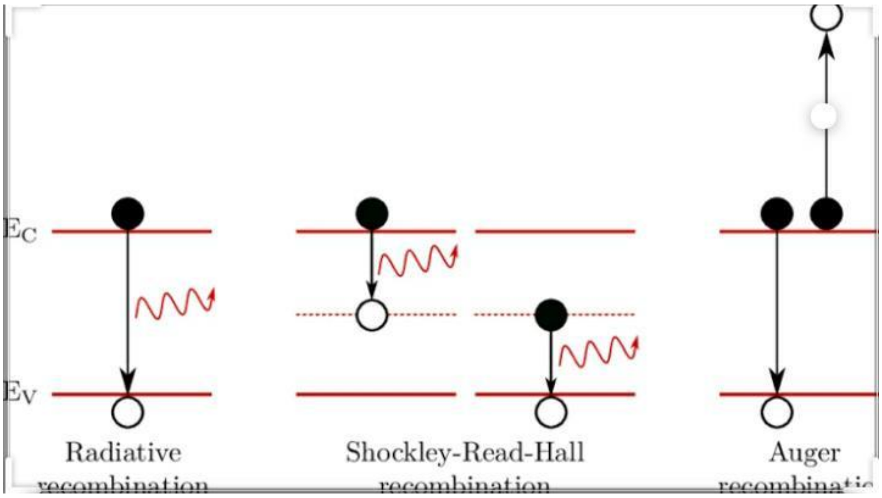
Types of Recombination

when the electron stabilizes back down into the valence band, it also effectively removes a hole. This process is called recombination.

There are three basic types of recombination in the bulk of a single-crystal semiconductor.

These are:

1. **Radiative recombination**
2. **Auger recombination1 and**
3. **Shockley-Read-Hall recombination.2,3**



Electrons lose energy and stabilize back to the valence band, recombining with a hole.

There are three types of recombination;

Radiative, Shockley-Read-Hall, and Auger.

Auger and Shockley-Read-Hall recombination dominate in silicon-based solar cells.

Among other factors, recombination is associated with the lifetime of the material, and thus of the solar cell.

5.10 X-ray fluorescence

XRF (X-ray fluorescence) is a non-destructive analytical technique used to determine the elemental composition of materials.

XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays ("a fingerprint") that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition.

Introduction:

- **Fluoroscopy is a type of medical imaging that shows a continuous x-ray image on a monitor, much like an x-ray movie.**
- **During the fluoroscopy procedure, in x-ray beam is passed throughout the body. The image is transmitted to the monitor so that the movement of the body part or on an instrument through the body can be seen in detail**

Fundamental Principles of X-Ray Fluorescence (XRF)

The XRF method depends on fundamental principles that are common to several other instrumental methods involving interactions between electron beams and x-rays with samples,

including: X-ray spectroscopy (e.g., SEM - EDS), X-ray diffraction (XRD), and wavelength dispersive spectroscopy.

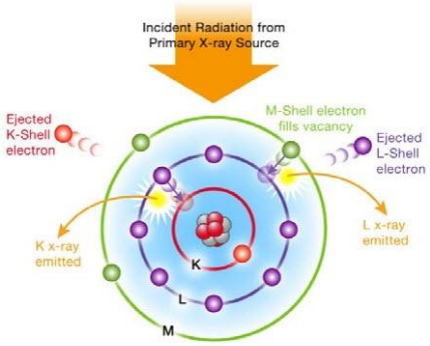
- The analysis of major and trace elements in geological materials by x-ray fluorescence is made possible by the behavior of atoms when they interact with radiation.
- When materials are excited with high-energy, short wavelength radiation (e.g., X-rays), they can become ionized. If the energy of the radiation is sufficient to dislodge a tightly-held inner electron, the atom becomes unstable and an outer electron replaces the missing inner electron.
- When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. The emitted radiation is of lower energy than the primary incident X-rays and is termed fluorescent radiation.

Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the sample.

The X-ray fluorescence process

1. A solid or a liquid sample is irradiated with high energy X-rays from a controlled X-ray tube.
2. When an atom in the sample is struck with an X-ray of sufficient energy (greater than the atom's K or L shell binding energy), an electron from one of the atom's inner orbital shells is dislodged.
3. The atom regains stability, filling the vacancy left in the inner orbital shell with an electron from one of the atom's higher energy orbital shells.

The electron drops to the lower energy state by releasing a fluorescent X-ray. The energy of this X-ray is equal to the specific difference in energy between two quantum states of the electron. The measurement of this energy is the basis of XRF analysis



Strengths and Limitations of X-Ray Fluorescence (XRF)?

Strengths

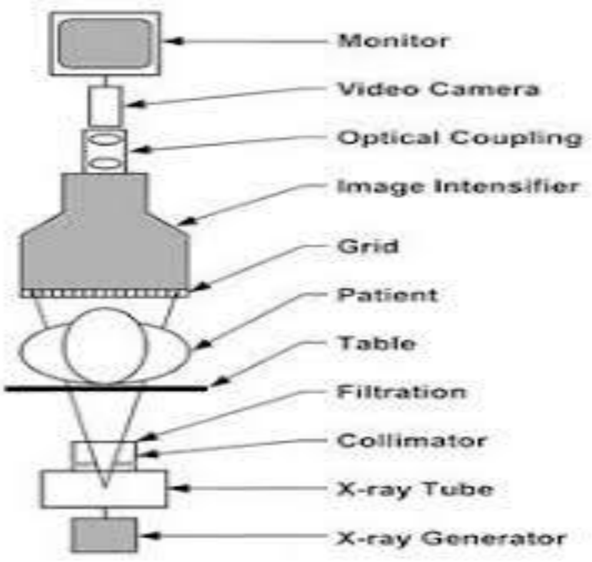
- **X-Ray fluorescence is particularly well-suited for investigations that involve:bulk chemical analyses of major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) in rock and sediment**
- **bulk chemical analyses of trace elements (>1 ppm; Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr, Zn) in rock and sediment**

Limitations

- **In theory the XRF has the ability to detect X-ray emission from virtually all elements, depending on the wavelength and intensity of incident x-rays. However...In practice, most commercially available instruments are very limited in their ability to precisely and accurately measure the abundances of elements with Z<11 in most natural earth materials.**
- **XRF analyses cannot distinguish variations among isotopes of an element, so these analyses are routinely done with other instruments (see TIMS and SIMS).**

XRF analyses cannot distinguish ions of the same element in different valence states, so these analyses of rocks and minerals are done with techniques such as wet chemical analysis or Mossbauer spectroscopy.

Fluoroscopic system using an x-ray image intensifier and camera:



X-ray Source:

- **The high voltage generator and x-ray tube is used in most fluoroscopy system as that of used in radiology.**
- **In case of cardiovascular imaging, extra heat capacity is needed to allow angiographic “run”, sequences of higher dose- radiographic images acquires in rapid succession to visualize opacified vessels. In that case, there is a high demand on ray tube, here special x-ray system is used.**

- **focal spot sizes:**

  small- 0.3mm with high spatial resolution and low radiation. output.

  large- 1.0mm or 1.2mm, when higher power is needed.
- **The radiation output can be either continuous or pulsed, with pulsed is commonly used.**
- **Automatic exposure rate control maintains the radiation dose per frame**

Beam filtration

It is common for fluoroscopic imaging systems to be equipped with beam hardening filters between the X-ray tube exit port and the collimator.

Added aluminum and/or copper filtration can reduce skin dose at the patient's entrance surface, for high contrast imaging, barium or iodine k-edge is used.

This is user selectable, to switch between low dose and higher dose modes during a fluoroscopic procedure.

Collimation

Shutters that limiting extent of the X-ray present in all X-ray equipment.

the collimation may be circular or rectangular in shape, matching the shape of the image receptor.

When the operator selects a field of view, the collimator automatically move under motor control to be just a bit larger than the visible field.

When the source-to-image distance (SID) changes, the collimator blades adjust to maintain the field of view.

Patient table and pad:

Patient tables provides strength to support patients and for a particular weight limit.

It is important that the table not absorb much radiation to avoid shadows, loss of signal and loss of contrast in the image.

Carbon fiber technology offers a good combination of high strength and minimal radiation absorption, making it an ideal table material

Anti-scatter grid:

Anti-scatter grids are standard components in fluoroscopic systems, since a large percentage of fluoroscopic examinations are performed in high-scatter conditions, such as in the abdominal region. So as to avoid more scattering, anti-scatter grids are used.

Image intensifier:

The X-ray image intensifier (Figure 2) is an electronic device that converts the X-ray beam intensity pattern into a visible image suitable for capture by a video camera and displayed on a video display monitor

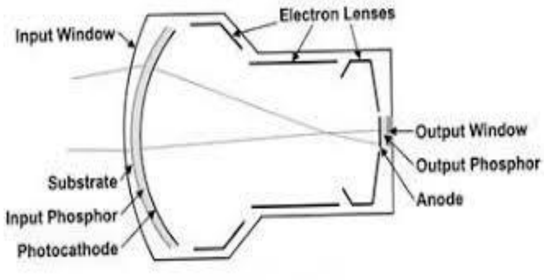
The key components of an XRII are

an input phosphor layer,

a photocathode,

electron optics

an output phosphor



- **The cesium iodide (CsI) input phosphor coverts the X-ray image into a visible light image**
- **The photocathode is placed in close proximity to the input phosphor, and it releases electrons in direct proportion to the visible light from the input phosphor that is incident on its surface**
- **The electrons are steered, accelerated and multiplies the electron impinging upon the surface of output phosphor.**
- **a video camera is optically coupled to this phosphor screen, video signal is then displayed directly and rendered for display.**
- **The use of video technology added an important convenience factor of observing the image simultaneously and offers the ability to record sequences.**
- **Image intensifiers are available in a variety of input diameters, ranging from about 10–15 cm up to 40 cm**

The video cameras used are vidicon or plumbicon analog devices.

Flat panel detector:

- **The introduction of flat panel detector allows for the replacement of the image intensifier in fluoroscopic design**
- **It offers increased sensitivity to x-ray, so that, they have the potential to reduce patient radiation dose.**
- **Resolution and contrast ratio are improved.**
- **They are more expensive to purchase and repair when compared to intensifiers**

It is mainly used in vascular and cardiac imaging.

Contrast agents:

- **A number of substance have been used as radiocontrast agents, including silver and bismuth, cesium, thorium, tin, zirconium, tantalum, tungsten and lanthanide compound.**
- **The use of thoria as a agent was rapidly stopped as it cause liver cancer**

Fluoroscopy procedures:

- **Insertion of an IV into patient's hand or arm.**
- **Patient moved onto x-ray table.**
- **Additional line may be inserted for catheter procedures.**
- **X-Ray scanner used to create fluoroscopic images of the body.**
- **Dye may be injected into the IV at this point.**
- **Type of care will be decided on after the procedure has finished**