ATOMIC , MOLECULAR &NUCLEAR PHYSICS

UNIT I : ATOMIC PHYSICS

ATOM MODELS:

- **Faradays Model:** First modern conception of atom
- **Discovery**– Electrolysis of atom.
- Fixed quantity of positive and negative charge of equal magnitude.

- **J.J.Thomson Model:**
- Idea of intrinsic nature of atom
- **Discovery**—Electron ,e/m of electron, electrical nature of matter.
- Entry of electron in atom
- Atom electrically neutral
- Uniform distribution of positive charge over atomic dimension
- Account for first observed spectra of element
- Electros were arranged inside positive sphere

ATOM MODELS:

- **Rutherford Atom Model:** The nuclear atom model
- Resulted from scattering of α particles by thin sheet
- Concept of nucleus
- Fails to explain the stability of atom
- **Bohr Atom Model:**
- Nature of orbit of electrons revolves round nucleus
- Explanation of origin of spectral lines
- **Sommerfeld Atom Model:** Relastivistic atom model
- Fine structure of spectral line
- Elliptical orbits

THE VECTOR ATOM MODEL:

- Extension of Ruterford-Bohr-Sommerfeld model.
- Bohr model explains series of spectra of H atom not fine structure.
- Sommerfeld model explains fine structure but not about relative intensities and complex spectra of alkali metals
- Old theories inadequate new discoveries Zeeman and Stark effect.
- To explain distribution of orbital electrons
- Complex spectra of atom and relations with atomic structure
- The vector atom model basically deals with the total
 angular momentum of an atom which is results of the combination of orbital & spin angular momentum.

The vector atom model:

Important features of vector atom model

(A) Spatial/Space quantization :

(B) Spinning electron hypothesis :

(A) Spatial/Space quantization :

Bohrs theory--   Orbits are quantized.

Quantum theory—Direction or orientation of orbits in space also quantized

To specify orientation of electrons orbit in space need fixed reference axis

Direction of axis is direction of external magnetic field

Different permitted orientations electron orbit determined by projection of quantized orbit on field direction i.e.quantized

SPINNING ELECTRON:

- Introduced by Uhlenbeck and Goudsmith in 1926
- Fine structure and anomalus Zeeman effect
- Hypothesis- electron spins about an axis of its own
- Also revolve around nucleus –analogues to planets
- Quantum mechanics-spin of electron quantized
- Idea of spatial quantization –Orbital and spin motions are quantized.
- The orbital & spin motion both are quantized in magnitude & direction because they are considered as quantized vector.
- Hence the atom model based on this quantized vectors is called as vector atom model.

QUANTUM NUMBER ASSOCIATED WITH VECTOR ATOM MODEL :

(1)Principal quantum no. (n) :

The serial no. of the shell's starting from the inner most is designated as its principal quantum no.

It can take only integral values excluding zero i.e.

n = 1,2,3,4 _ _ _ _ _

(2)Orbital quantum no. (l) :

This may take value any integral value 0,1,2,3,4, _ _ _ (n-1).

If n=4 l can have four values 0,1,2,3,4

(a) An electron for which l=0 , then it is *s*- electron .

(b) An electron for which l=1 , then it is *p*- electron .

(c) An electron for which l=2 , then it is *d* electron .

(d) An electron for which l=3 , then it is *f* electron .

➤ The orbital angular momentum

$$p_{l} = l\hbar$$

The orbital angular momentum is

$$p_{l} = [l(l+1)]^{1/2}\hbar$$

(3) Spin quantum no. :

This has only one value take ½ the spin angular momentum

$$p_{s} = s\hbar$$

$$p_{s} = s \cdot h/2\pi$$

$$p_{s} = [s(s+1)]^{1/2}\hbar$$

(4) Total angular momentum quantum no. :

Represents total angular momentum of the electron which sum of the orbital angular momentum & spin angular momentum .

The vector J is defined by equation

$j = l + s$

j is always positive

Spin angular momentum $s = \pm 1/2$
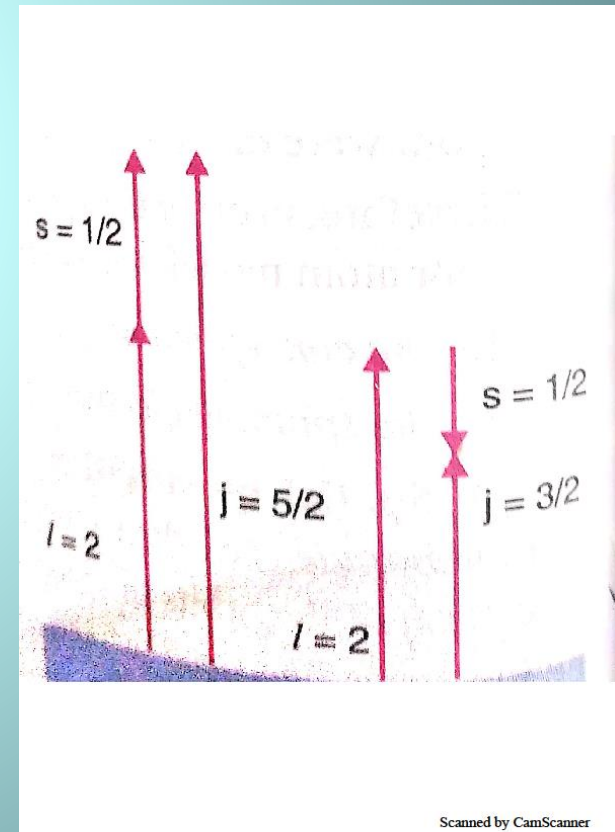
therefore $j = l \pm s$

for e.g. $l=2$ & $s=1/2$

$j = l+s$ for s is parallel   to l

and $j = l-s$ for s is antiparallel   to l

$j = 5/2$ & $3/2$

s = 1/2

s = 1/2

j = 5/2   j = 3/2

l = 2

l = 2

(5) Magnetic orbital quantum no. :

The projection of the orbital quantum no. (l) the magnetic filed direction is called as magnetic orbital quantum no.

The possible m_l values are $l, l-1, l-2, \ldots\ldots 0,-1,-2,\ldots -l$
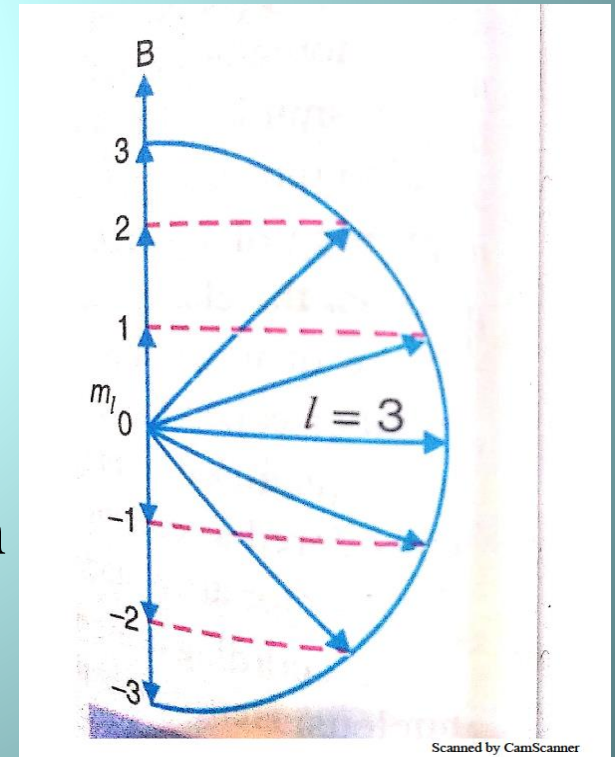
There are $(2l+1)$ possible values of m_l

for e.g.

$$l=3 \rightarrow 3,2,1,0,-1,-2,-3$$

$$m_l = (2l+1)$$

$$= (2\times3+1) = \quad 7$$
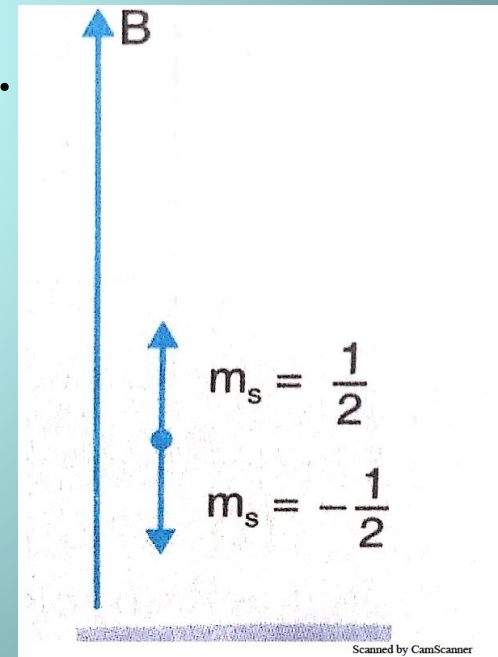
Permitted orientations of l are 7 for which

$$ml=3,2,1,0,-1,-2,-3$$

(6) Magnetic Spin quantum no. :

- This is the projection of the spin vector *s* along the direction of the mag. field .

- The spin angular momentum *s* can assume only two possible positions with respect to the magnetic field it may be parallel or anti parallel .

- m_s can have only two values +1/2 or -1/2 .

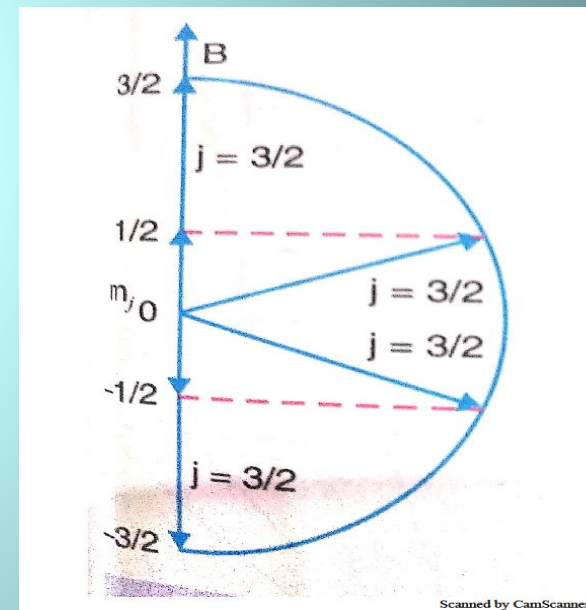# (7) Magnetic total angular momentum quantum no(m_j).:

- This is the projection of total angular momentum vector j on the direction of the magnetic field .

- For single electron j can have only odd half integral values

$$j = l \pm \tfrac{1}{2}$$

 m_j must have only odd half integral values

m_j can have only (2j+1) values

From +j to –j zero excluding

Coupling Scheme :

- In atom having two or more electron , the orbital & spin angular momentum of all its electrons can be added together in two ways .

- The method combination depend on the interaction or coupling between the orbital & spin angular momentum .

- There are two types of scheme have been developed they are

  (1) L-S coupling :

  (2) j-j coupling :

L-S coupling :

- Occurs frequently so normal coupling.
- All orbital angular momentum vectors of the various electrons combine to form a resultant L &

  independently all their spin

  angular momentum vectors

  combine to form the resultant S .

These resultants L&S then

  combine to form the total

  angular momentum J of the atom.
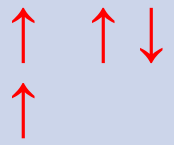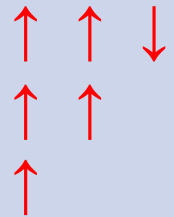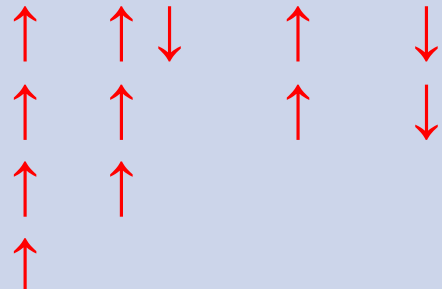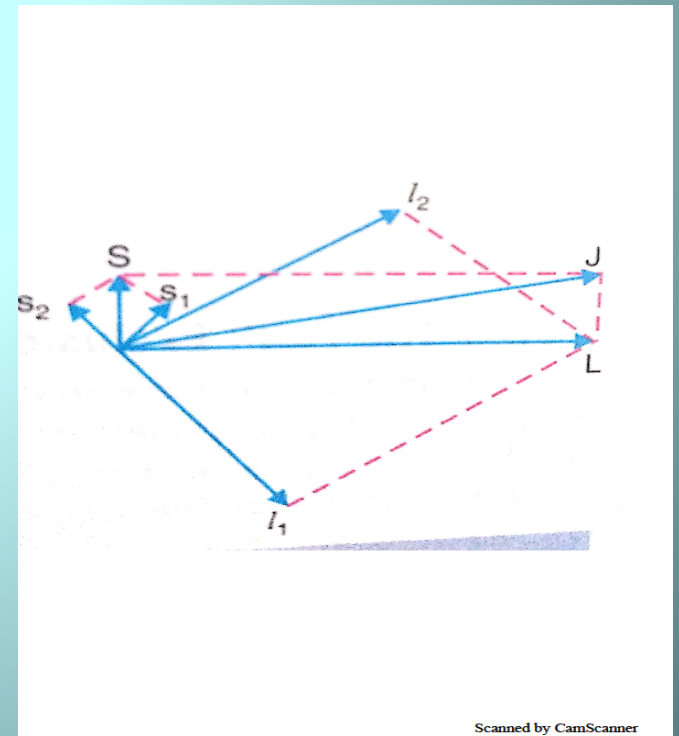
- This scheme may be summarized as follows

$$L=\sum l_i \qquad S=\sum s_i \qquad \rightarrow J=L+S,$$

L is always an integer including zero & S is an integer for an even number of electrons & odd multiple of ½ multiple of ½ for an no. of electrons .

Hence, J must be an integer , if S is an integer & J must be an odd multiple of ½ .

In particular , if L=0, J can have only one value namely

$$J=L+S \longrightarrow J=S$$

2 electron	3 electron	4 electron
↑ ↑↓ ↑	↑ ↑ ↓ ↑ ↑ ↑	↑ ↑↓ ↑ ↓ ↑ ↑ ↑ ↓ ↑ ↑ ↑
$S = 1,0$ $S = \mid S_1 + S_2 \mid$ to $\mid S_1 - S_2 \mid$ $S = (1,0)$	$s = 3/2 , ½$ $S = \mid S_1 + S_2 \mid$ to $\mid S_1 - S_2 \mid$ $S = (1,0) (1/2)$ $S = 3/2, 1/2$	$s = 2,1,0$ $S = ½, 1/2, 1/2,1/2$ $S = (1,0) (1,0)$ $S = (2,1,0)$

j-j coupling :

- This method is employed when the interaction between the spin & orbital vectors of each electron is stronger than the interaction between either the spin vectors or the orbital vectors of the different electron.

  The orbital & spin angular momentum of each electron in the atom are added to obtain the resultant angular momentum of the electron .
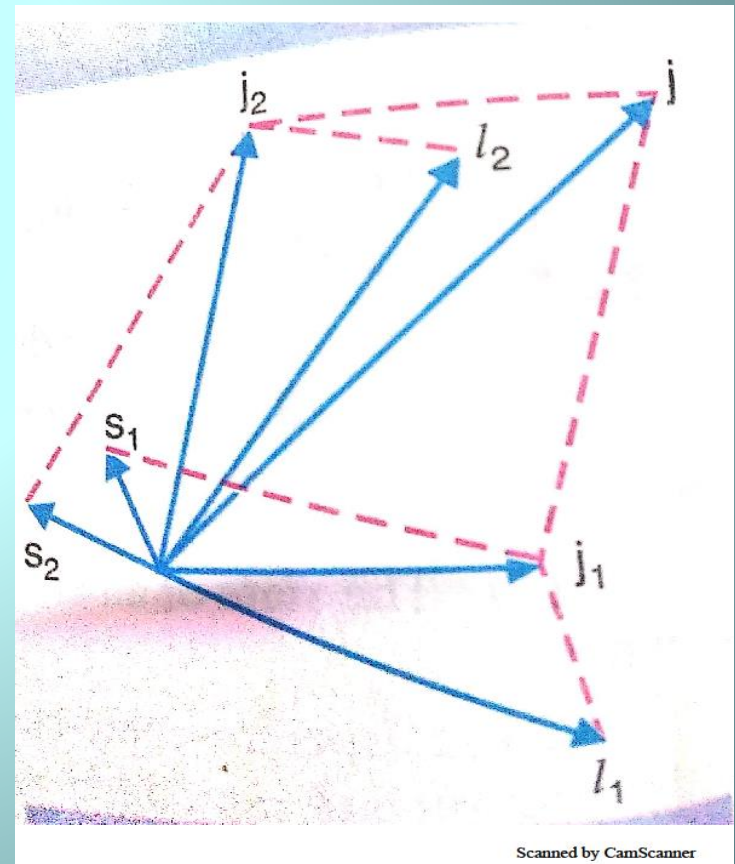
j-j coupling

- Thus ,

$j_i = l_i + s_i$ The vectors sum of all the individual j vectors gives the total angular momentum J of the atom .

Thus $J = \sum j_i$

$[(l_1+s_1)+(l_2+s_2)+(l_3+s_3)+\ldots\ldots]$

$= j_1+j_2+j_3+\ldots=J$

Pauli Exclusion Principle :

- Statement : No two electrons in atom exist in the same quantum state .

OR

"Every completely defined quantum state in an atom can be occupied by only one electron

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

- If two electrons have all their quantum numbers identical , then one of those two electrons would be excluded from entering in to the constitution of the atom . Hence the name Exclusion Principle .

Pauli's exclusion principle explains:

- Fundamental and universal

- Occurrence or nonoccurrence of spectral lines in optical and X-ray spectra

- Complete scheme of arrangement of atoms in periodic table

- .

- Explanation of electronic structure and atomic spectra

- Defining the special quantum property of closed shells

- e.g. k – shell

  n=1 , l=0 & hence $m_l = 0$, since

  s=1/2 $m_s = +1/2$ or -1/2

Hence k – shell can have two electrons

for electron – 1 with quantum numbers ,

  n=1 , l=0 , $m_l = 0$, $m_s = +1/2$

for electron – 2 with quantum number ,

  n=1 , l=0 , $m_l = 0$, $m_s = -1/2$

Max. no. of electrons in a sub shell is $2(2l+1)$ of l

- Orbital quantum no . (l) :   0   1   2   3   4

- No. of possible electron state :   2   6   10   14   18

❖ Sub-shell symbol   :   s   p   d   f   g

❖ Distribution of electrons in a shell with n=sum of electrons in constituents n subshells

$$= \sum_{l=0}^{l=l-1} (2l+1) = 2 \sum_{l=0}^{l=l-1} (2l+1)$$

❖ Shell symbol   :   K   L   M   N   O

❖ Quantum no.(n)   :   1   2   3   4   5

❖ No. of electron ($2n^2$)   :   2   8   18   32   50

Selection rules :

It is experimentally found that all possible combinations of permitted energy states of an atom do not appear as spectral line.

Selection rules are principle, which give reason for such a state of affairs.

For vector atom model three selection rules one each for L,J and S

Selection Rule for L :

Most of the observed spectral lines are due to transition between state

In which a single electron jump from one orbit to another

The selection rule is $\Delta L = \pm 1$ i.e. Only those lines are observed for which the value of L changes by ± 1

Selection Rule for J :

Spectral lines arises only when transition takes place between states for which $\Delta J = \pm 1$ Or 0, $0 \rightarrow 0$ being excluded

Selection rule for S:

- Selection rule for S is $\Delta S=0$ i.e. States with different S do not combine with one another .

- This rule is good for light atoms

- Helps in allocation of observed spectral series to proper quantum numbers.

- Energy level diagram can be constructed

Intensity Rules:

- Supplement to selection rule
- Predict intensity of lines that occurs
- Postulated on empirical basis in the study of optical and X-ray spectra.
- **Rules are:**
- a) Those transitions are strong, give rise to intense line in which L and J changes in the same sense
- The transitions are weaker, more the change in direction of L and J is different.
- b) Transition in the decreasing sense (L $\rightarrow$ L-1) is stronger
- Than increasing sense (L $\rightarrow$ L+1)
- c) The oppositely directed transitions do not occur
-

Intensity Rules:

- $\Delta L = -1$, $\Delta J = -1$ Most intense line (a)
- $\Delta L = -1$, $\Delta J = 0$ Less intense line (a)
- $\Delta L = +1$, $\Delta J = +1$ Weaker line (b)
- $\Delta L = -1$, $\Delta J = 0$ Weakest line (a and b)

- $\Delta L = -1$, $\Delta J = +1$ No line (c)
- $\Delta L = +1$, $\Delta J = -1$ No line (c)
- **Interval Rule:**
- Called Lande Rule
- **Statement:** Frequency interval between two levels with two angular momenta $(J+1)$ and J respectively proportional to $(J+1)$

(1) The selection rule for L is $\Delta L = \pm 1$ i.e. only those lines are observed for which the value of L changes by ± 1 .

e.g. L can changes from 0 to 1 ($\Delta L = 1$) from 1 to 0 ($\Delta L = -1$).

(2) In symbol , a transition is possible between S & P levels ($\Delta L = \pm 1$) , but not possible between S & D levels ($\Delta L = \pm 2$) .

(3) The selection rule for J is $\Delta J = \pm 1$ or 0 but 0→0 is excluded .

(4) The selection rule for S is given by $\Delta S = 0$.

Zeeman effect :

- Zeeman effect is magneto-Optical phenomenon

- **Zeeman effect** :a source of light producing line spectra (spectrum) is placed in a magnetic field , the spectral lines are split up into components.
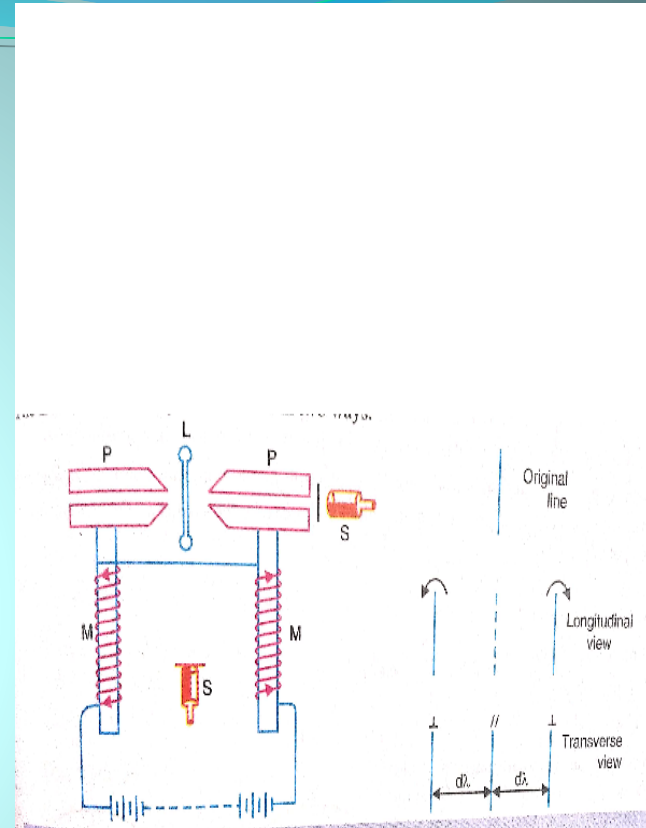
- When the splitting occurs into two or three lines , it is called normal Zeeman effect . The splitting of spectral line of magnetic field is strong.

- The splitting of spectral line into more than three components in ordinary weak magnetic field is called Anomalous Zeeman effect.

Experimental arrangement :

- MM is an electromagnet capable of producing a very strong magnetic field .

- Its conical pole pieces PP have longitudinal holes drilled through them .

- A source of light (L) emitting line spectrum (e.g. sodium vapors lamp) is placed between the pole pieces.

- The spectral lines are observed with the help of a spectrograph (S) of high resolving power .

- the Zeeman effect may be observed in two ways :

(A) the positions of the spectral line is noted without applying the magnetic field .

- The mag. Field is now switched on & the spectral line is viewed longitudinally through the hole drilled in the pole pieces & hence parallel to the direction of the field .

- It is found that the spectral line in split into two components one slightly shorter in wavelength than original line.

- The original line is not present .

- Both the lines are found to be circularly polarized in opposite directions . This is called normal longitudinal Zeeman effect.

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

- Consider an electron moving in a circular orbit or radius r with linear velocity v & angular velocity ω

- The centripetal force acting on the electron towards the centre is

$$F = mv^2 / r = m \omega^2 r^2 / r = m r \omega^2$$

If the electron in motion clockwise then the force Bev is outward & if the electron motion anti-clockwise then the force is inward.

$$m r \omega^2 - Bev = m(\omega + d\omega)^2 r$$

$$m r \omega^2 - Bev = m(\omega^2 + 2\omega d\omega + d\omega^2)$$

as dω is very small , $d\omega^2$ is neglected .

$$m\,r\,\omega^2 - Bev = m(\omega^2 + 2\omega d\omega)\,r$$

$$m\,r\,\omega^2 - Bev = m\,r\,\omega^2 + 2m\omega d\omega r$$

$$-Bev = 2m\omega d\omega r \qquad\qquad (v = r\omega)$$

$$-Be\,r\omega = 2mr\omega d\omega$$

$$-Be = 2md\omega$$

$$d\omega = -Be / 2m \quad \ldots\ldots\ldots(1)$$

for clockwise moving electron

$$d\omega = Be / 2m \quad \ldots\ldots\ldots(2)$$

$$d\omega = \pm Be / 2m \quad \ldots\ldots\ldots(3)$$

If υ is frequency of revolution of electron then ,

$$\omega = 2\,\pi\,\upsilon$$

$$d\omega = 2\,\pi\,d\upsilon$$

$$d\upsilon = d\omega/2\pi \qquad\qquad [\, d\omega = \pm Be / 2m \,]$$

$$d\upsilon = \pm Be / 2m\,2\pi$$

$$d\upsilon = \pm Be / 4\pi m$$

- This gives the change in frequency the spectral lines.
- If υ & λ are the frequency & wavelength of the original line then .

$$υ = c / λ$$

$$dυ = - c / λ^2 \ dλ$$

$$dλ = -λ^2 / c \ dυ$$

$$dλ = -λ^2 / c \ (\pm Be/4πm)$$

$$dλ = \pm Be \ λ^2 / 4πmc$$

$$dλ – \text{is the Zeeman Shift}$$

STARK EFFECT :

- The Stark effect is the electrical analogue of the Zeeman effect .

- The Stark effect is the splitting of spectral lines due to the action of an external electric field on the radiating substance .

The Stark line splitting is vey minute & can be observed only with instruments having a high resolving power .

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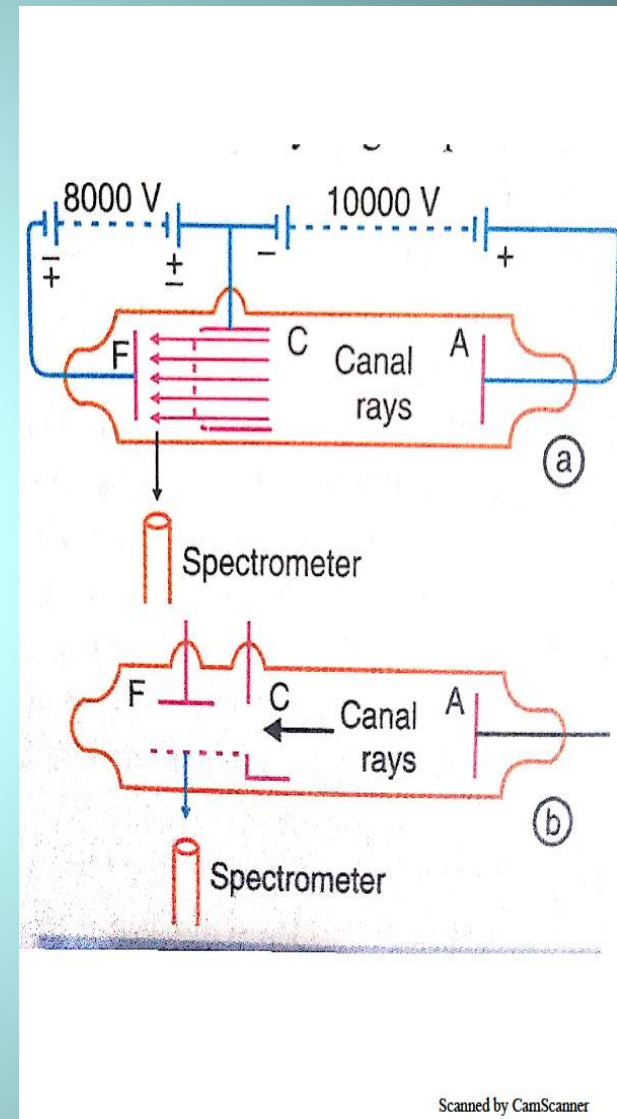
(a) Experimental study :

- Hydrogen atoms emitting spectral lines are subjected to a powerful electric field.

- The canal rays are produced in an ordinary glass discharge tube provided with a perforated cathode C .

- When the pressure in the tube is not very low, discharge takes place between the cathode C & Anode A maintained at a suitable P.D.

- An auxiliary electrode F is placed parallel & close to C at a distance of a few millimeters.

- A very strong electric field of several thousand volts per meter is , maintained between F & C . The effect produced can be studied both transversely in fig. (a) & longitudinally in fig . (b)

Results :

- The result obtained with lines of Balmer series of H atom as follows

- Every line is split up in to a number of sharp components .

- All hydrogen lines from symmetrical patterns .

- The patterns depends on the quantum number   n of the term involved .

- The number of the lines & total width of the patterns increases with n .

- Observation perpendicular to the direction of the electric field transverse view shows that the components are polarized .

- Up to fields of about 10^7 v/m , the resolutions increases in proportion to the field strength (E) . In this region , we have linear or first order Stark effect . When E exceeds 10^7 v/m there are shifts in the line patterns which are proportional to E^2 & it is called second order Stark effect .
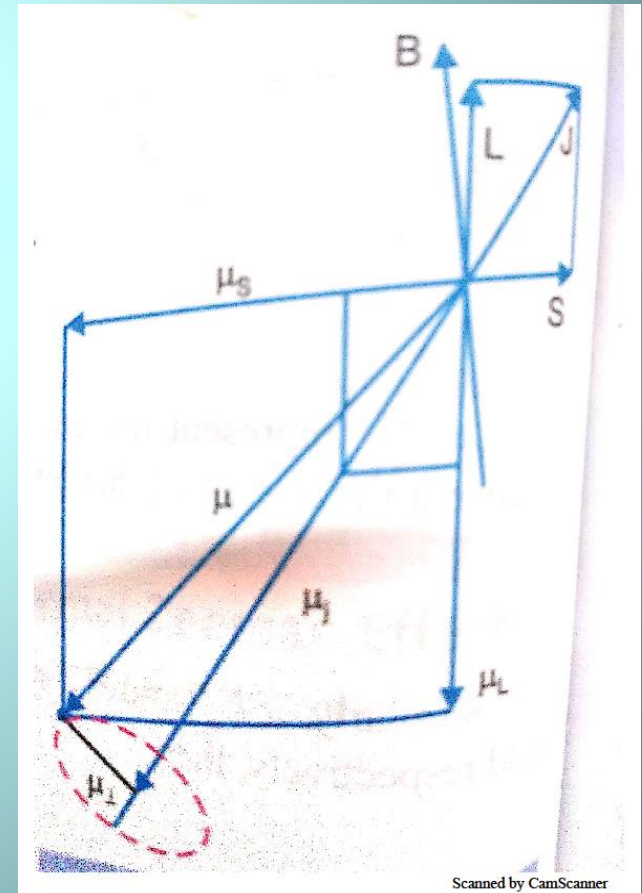
ANOMALOUS ZEEMAN EFFECT:

- Effect can be explained using idea of spin of electron.
- The total angular momentum vector j=l+s   i)
- Magnetic moment due to orbital motion of electron

$$\mu_1 = l\,\frac{eh}{4\pi m}$$

- μ_l is opposite to l because of
  negative charge
- Magnetic moment due to spin of electron

$$\mu_s = 2s\,\frac{eh}{4\pi m} \qquad iii)$$

- μs is directed opposite to S

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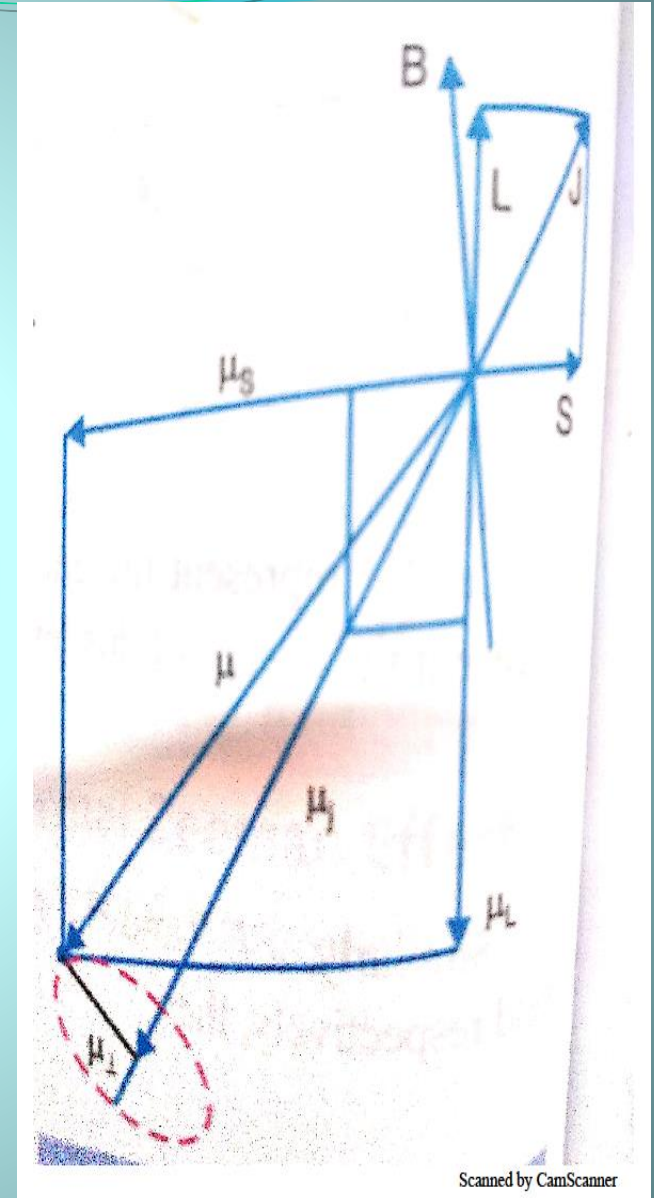
- Resultant magnetic moment μ

not along j

To find resultant μ_l and μ_s resolved into
two components one along j and
Perpendicular to it.

Perpendicular components are cancelled

The effective mag.moment of electron is

$= \mu_j =$ components of μ_l *along j*

+components of μ_s *along j*

$$= \frac{eh}{4\pi m} l \cos(l,j) + \frac{eh}{4\pi m} 2s \cos(s,j)$$

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$$= \frac{eh}{4\pi m} \left[l \cos(l,s) + 2s \cos(s,j) \right]$$

- but according to cosine law

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

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

$$\mu_j = \frac{eh}{4\pi m} \left[\frac{l^2 + j^2 - s^2}{2j} + \frac{s^2 + j^2 - l^2}{j} \right]$$

$$= \frac{eh}{4\pi m} \left[\frac{3j^2 + s^2 - l^2}{2j} \right]$$

$$= \frac{ehj}{4\pi m} \left[\frac{1 + j^2 + s^2 - l^2}{2j^2} \right]$$

- Writing

$$j^2 = j(j+1) \quad \text{and so on}$$

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

But bracket term is *g* i. e.Lande factor

$$\mu_j = \frac{ehj}{4\pi m} g$$

If atom is in weak magnetic field, total angular momentum vector j precesses about direction of magnetic field as axis The additional energy ΔE due to atomic magnet is

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

- But J cos (j,B) is projection of vector j on direction of mag.field=m_j

$$\Delta E = \frac{ehB\,gm_j}{4\pi m}$$

$\frac{ehB}{4\pi m}$ called Lorentz unit

Fig. 6.39