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# Unit 1: Atomic Physics

B.SC III yr.

## Vector atom model -

There are some drawbacks in Sommerfield's atom model as mentioned below:

i) Sommerfeld's model explains fine structure of spectral lines hydrogen atoms but it could not predict the correct number of observed fine structure of these lines.

ii) Intensity of the spectral line could not be predicted.

iii) Distribution and arrangement of electron in atom could not be explained.

To overcome these drawbacks, a new model called vector atom model was introduced by introducing two new concepts:

a) Space Quantisation and b) Spin of electron

### a) Space Quantisation:

- According to Bohr's theory, the electron moves in a circular ~~ob~~ orbit. Since radius of orbit remains fixed hence the electron has only one degree of freedom.
- In case of Sommerfeld's elliptical orbits, the electron possesses two degrees of freedom.
- The quantum numbers, one corresponding to radius vector n and other corresponding to angle $n_\phi$ are sufficient to describe the electron orbit.
- In general, the motion of an electron in an atom is three dimensional and therefore possesses three degrees of freedom.
- Hence an additional quantum number, is required to describes the actual states of affairs.
- According to classical mechanics, when an electron moves in three dimensional orbit, it may have all orientations with respect to a fixed axis. In vector atom model which is based on quantum theory the orbits are assumed to be quantised in magnitude and direction both.

- Thus the third condition quantises the orientation of elliptical orbit in three dimension and does not alter the original Sommerfield orbits in regards to their size and shape.
- The introduction of such a spatial quantisation makes the orbit vector quantised.

For purpose of space quantisation, we need a certain preferred-direction with respect to which the orbits may receive their orientations. Such a direction can be received by applying small external magnetic field. According to rule of space quantisation, the electron orbit can only set itself in certain descrete positions with respect to field direction. This is called space quantisation.

b) Spin of electron:

- According to electron spin hypothesis, electron revolves around nucleus not only in orbit but also about its own axis. Corresponding to this, electron has two types of motions called orbital motion and spin motion.
- ∴ Therefore, the total angular momentum of electron will be due to orbital motion and spin motion of electron.
- According to quantum theory, the spin motion, like orbital motion should also be quantise.

Hence a new no. known as spin quantum no. is introduced.

According to concept of space quantisation, orbital and spin motions are vector quantities, hence the atom model is called as Vector atom model

## Quantum numbers associated with Vector atom model-

1) Principal quantum number (n):

This quantum no. belongs to the principal orbit.

to which electron belongs.

$$n = 1, 2, 3 \ldots\ldots \infty$$

Various shells of electron corresponding to different n values are denoted by K, L, M, N ....

The maximum no. of electrons present in a shell with principal quantum no. n, is $2n^2$.

## 2) Orbital Quantum Number (l):

It defines the shape of orbital occupied by the electron and the orbital angular momentum of electron. Therefore, it is also referred to as angular quantum no.

Generally, $l = 0, 1, 2 \ldots\ldots n-1$.

The orbits corresponding to $l = 0, 1, 2 \cdots$ etc. are defined as s, p, d, f etc. resp. Each l value refers to energy sub-shell. When $n=1$, $l=0$ & this is s-orbital.

For $n=2$, $l=0$ & $l=1$ & there are two orbitals i.e. s & p. The orbital angular momentum for $e^-$ is denoted as,

$$P_l = lh/2\pi$$

In wave mechanics, $\boxed{l = \sqrt{l(l+1)}}$

$$\therefore P_l = \sqrt{l(l+1)}\ h/2\pi \quad (h = \text{plank's constant})$$

Note that the orbital quantum no. (l) is related to azimuthal quantum no. $n_\phi$ of Sommerfeld theory by eq$^n$ $l = (n_\phi - 1)$

## 3) Spin Quantum Number (s):

This quantum number accounts for spin of electrons about their own axis. Its magnitude is always half. If electron spins clockwise, then $s = +1/2$ and if electron spins anticlockwise then $s = -1/2$. Here, the angular momentum is denoted by $P_s$ & given by,

$$\boxed{P_s = \frac{sh}{2\pi}}$$

In wave mechanics, $\boxed{s = \sqrt{s(s+1)}}$

$$\therefore \boxed{P_s = \sqrt{s(s+1)} \cdot \frac{h}{2\pi}}$$

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

This quantum number represents the resultant angular momentum of the electron due to both orbital and spin motions.

Usually we have, $j = l \pm s$

where positive sign is used when s is parallel to $l$ and negative sign is used when s is antiparallel to $l$.

· Generally,

$$\boxed{p_j = jh/2\pi}$$

In wave mechanics, $\boxed{j = \sqrt{j(j+1)}}$

$$\therefore \boxed{p_j = \sqrt{j(j+1)} \cdot h/2\pi}$$

## 5) Magnetic Orbital Quantum Number ($m_l$)

When an atom is placed in a strong magnetic field, then electrons with same values of n and $l$ differ in their behaviour. To account for this, one more quantum no. $m_l$ is introduced, called as magnetic orbital quantum number. This $m_l$ gets produced due to spilting of spectral lines in presence of magnetic field of strength H, (zeeman effect). According to the rule of space quantisation, the orientations of $l$ with respect to the field direction i.e. direction of H are limited and are determined by fact that projection of $l$ in field direction assumes only integral values. This projection of $l$ in field direction is called as magnetic orbital quantum no.

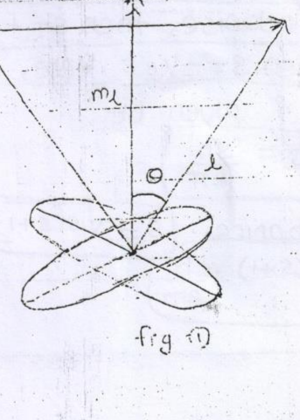


fig (1)

Consider fig, ① which shows vector l inclined at an angle θ with the field direction.

∴ Projection $m_l = l\cos\theta$

Since $m_l$ is to be integer and $\cos\theta$ can be maximum equal to units. We write permitted values of $m_l$ from $+l$ to $-l$ at unity intervals.

i.e. $m_l = +l, (l-1), (l-2), \ldots 1, 0, \ldots 1, \ldots (l-2), -(l-1), -l$

i.e. for each value of $l$, $m_l = (2l+1)$

6) Magnetic Spin Quantum Number ($m_s$)

It is a vector representing the spin angular momentum possessing in presence of magnetic field.

The numerical value of $m_s$ is the projection of spin vector 's' in the field direction.

By analogy with $m_l$, $m_s$ can have any of the $(2S+1)$ values from $-S$ to $+S$ excluding zero.

But $\boxed{S = \pm\frac{1}{2}}$ and never zero.

$$\therefore \boxed{m_S = +\frac{1}{2} \quad \text{or} \quad m_S = -\frac{1}{2}}$$

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

Its numerical value is the projection of the total angular momentum vector j in the field direction. $m_j = m_l \pm m_s$

∴ Possible values of $m_j$ are

$\boxed{-j, -(j-1), \ldots -1, 0, +1, \ldots (j-1), j}$

excluding zero for a single electron.

Thus, the motion of electron in presence of a strong magnetic field is such that each electron level gets splitted into $\boxed{(2j+1) \text{ sublevels.}}$

## Coupling schemes-

There are several ways in which the different vectors of electrons may combine to give the vectors representing the atom as a whole. The method of combination depends on interaction or 'coupling' between the component vectors, since the orbital and spin motions of electron producing magnetic fields result in mutual perturbation.

It is usual to distinguish two types of combination, known as Russell-Saunders or L-S coupling and j-j coupling.

### 1) L-S coupling -

L-S coupling is one which occurs most frequently and hence is known as the normal coupling. In this type the several spin vectors s of the electrons combine to form a resultant vector S; the several orbital vectors $l$ of electrons likewise combine to form a resultant vector L and then S and L combine to make the vector J which represents the total angular momentum of the atom. The process may be symbolicall represented as.

$$(s_1+s_2+s_3+\ldots\ldots)+(l_1+l_2+l_3+\ldots\ldots) = S+L = J$$

This sort of coupling is the most natural one when the interactions between the individual spins on one hand and the individual orbital momenta on the other are very strong.

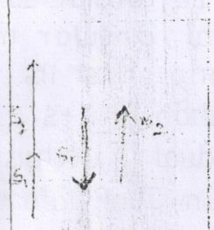
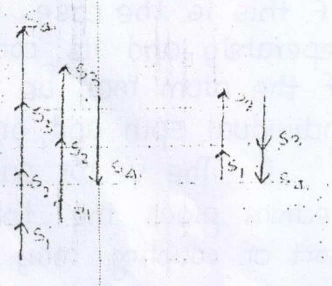
The guiding principles in this coupling are:

i) All the three vectors L, S and J are quantised.

ii) L is always an integer including zero i.e. L may be 0, 1, 2, 3 etc

iii) S is an integer or half integer depending on the number of electrons involved and on direction of spin vectors. Thus, for instance, for an atom containing a single electron, S can have only the value ½, for a two electron S may have either 1 or 0 depending on whether spin vectors are parallel or antiparallel. For a three electron system, S is-

3/2 or 1/2 and for a four electron system, S may be, 2, 1 or 0, due to the same reason, as readily seen from following table:

| Two electrons | Three electrons | Four electrons |
|---|---|---|
|  |  |  |
| $S = 1, 0$ | $\frac{3}{2}, \frac{1}{2}$ | $2, 1, 0$ |

"It follows that S is an integer for an even no. of electrons and half integer for an odd number of electrons."

iv) Hence J, the vector sum of L and S must be an integer (0, 1, 2, 3 etc.) if S is an integer i.e. for even electron systems and half integer (1/2, 3/2, 5/2 etc) i.e. for odd electron systems. It can be proved that, in general, the possible number of values, which J can assume, are,

$$\boxed{\begin{array}{l}(2S+1) \text{ if } L > S \text{ and}\\ (2L+1) \text{ if } L \leq S\end{array}}$$

The quantity $(2S+1)$ is known as multiplicity $(r)$ of L state. It is simply permitted values of J for a given values of L. $r = (2S+1)$. In particular, if $L = 0$, J can have only one value, $J = S$.

J must always be positive, never negative, since it represents the total angular momentum of atom.

2) J - J coupling

Under certain circumstances, the interaction between the spin and orbital vectors in each electron may be stronger than that between either the spin vectors or the orbital vectors of the different electrons. If this is the case, each electron may be considered seperately and its contribution to the total angular momentum of the atom may be obtained by combining first its individual spin and orbital vectors by relation $j = l + s$.

The vector sum of all the individual j vectors of electrons gives the total angular momentum J of atom. This sort of coupling may be symbolically represented as,

$$[(s_1+l_1)+(s_2+l_2)+(s_3+l_3)+\cdots\cdots] = (j_1+j_2+j_3+\cdots\cdots) = J$$

These two types of 'coupling' are limiting cases, between which a whole range of intermidiate types may occur, which makes the problem very difficult of treatment. For most known cases, however the L-S coupling is effective.

Pauli's exclusion principle-

Sometimes, termed also as equivalence principle.

Statement:

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

In other words, it is impossible for two electrons in an atom to be identical as regards all their quantum numbers i.e. one of two in such a case will be excluded from entering into the constitution of the atom. Hence the name "exclusion principle."

The principle may be stated in yet another way: two systems of quantum numbers which are deducible from each other by interchange of two electrons represent only one state. Thus understood, the principle enunciates the

" No two electron in an atom can have the same set of four quantum number."

OR

"No two electron in an atom can exist in the same quantum set"

indistinguishability of electrons which have identical quantum numbers. Hence the name 'equivalence principle.'

Explanation:

It is clear that the principle defines a certain minimum individuality of the electron in the atom. Among the several quantum numbers associated with the electron, four, $n, l, m_l$ and $m_s$ or $n, l, j$ and $m_j$ can be shown to be strictly required to specify completely the state of any particular electron, the former set being used in presence of a strong magnetic field which breaks the coupling between $l$ and $s$ in the electron and the latter in the rest of cases.

The principle was first introduced by Pauli to explain certain experimental facts, such as

a) the occurrence and non-occurrence of spectral lines in optical and X-ray spectra - it was found that for the missing energy states of atoms all the four quantum numbers of the electrons agreed and

b). the complete scheme of the successive formation of atoms as arranged in periodic table, discovered by Bohr, Stoner and others - such an arrangement required the association of above stated four quantum numbers with each electron.

Naturally then, the principle finds its chief use in the elucidation of electronic structure and atomic spectra. It has also been very helpful in defining the special quantum property of term multiplicity actually observed. It has been realised later that the principle is much more universal and fundamental, holding good for the totality of electrons in any molecule, may, even for the more comprehensive system of conduction elections that belong to a metal in the bulk state on the one hand and for the constituent particles of nucleus in the ultramicroscopic state on the other.

The principle, though justified by the new quantum mechanics, has not yet received a rigorous theoretical proof and for the present it must be regarded as something empirical added to and regulating the vector model of atom.

Selection Rules:

It is experimentally found that all the possible combinations of permitted energy states of an atom do not actually appear as spectral lines. Selection rules are certain principles, which give the reason for such a state of affairs.

The first selection rule devised in connection with the older atom model referred to the azimuthal quantum no. $n_\phi$ or k and it was $\Delta K = \pm 1$ as we have been seen. This was formulated on an empirical basis, but was later justified theoretically by Rubinowicz by applying the theorem of conservation of momentum to process of emission of an electromagnetic radiation by an atom. This simple rule, however, was soon found inadequate.

For the vector atom model, three selection rules have been devised, one for L, another for J and a third for S.

a) The selection rule for $\Delta L$:

Most of observed spectral lines are due to transition between states, in which a single electron jumps from one orbit to another and in such cases, the selection rule is $\Delta L = \pm 1$ i.e. only those lines are observed for which the value of L changes by $\pm 1$.

b) The selection rule for J:

Spectral lines arise only when transitions take place between states for which $\Delta J = \pm 1$ or 0, $0 \rightarrow 0$ being however, excluded.

c) The selection rule for S:

It is given by $\Delta S = 0$, which means that states with different S (hence different multiplicities) do not combine with one another. Theory and experiment, however, show that this selection rule is adhered to less and less strictly as the atomic no. increases. Hence it is only an approximate rule holding good in case of light atoms.

Note:

In the presence of a magnetic field, the orbital magnetic quantum number $m_l$ either does not change or changes by $\pm 1$ ie. $\boxed{\Delta m_l = 0 \text{ or } \pm 1}$. The spin magnetic quantum no. $m_s$ remains unchanged i.e $\boxed{\Delta m_s = 0}$ In consequence

$$\boxed{\Delta m_J = 0 \text{ or } \pm 1}$$

These selection rules were first introduced on a purely empirical basis in study of optical and x-ray spectra & zeeman effect. Later, they were obtained by a rigorously deductive method in wave mechanics and hence they now rest on a permanent theoretical basis.

These rules furnish invaluable help in allocation of observed spectral series to the proper quantum no. With their aid, energy level diagrams can be constructed both for the natural complex multiplet lines and for zeeman effect of such lines.

Transitions which contravene these rules are sometimes observed, but intensities of such 'forbidden lines' as they are called, are usually weak in comparison with the normal lines.

## The Intensity Rules -

The intensity rules have been devised to supplement the selection rules, in order to predict also the intensity of the lines that occur. These were originally postulated on an empirical basis in study of optical and x-ray spectra. Later, a full theoretical derivation was given on a wave mechanical basis.

The intensity rules are:

a) Those transitions are strong, giving rise to intense lines, in which L and J change in same sense, the

b) transitions are weaker, the more the change in direction of L and J is different.

c) A transition in the decreasing sense (L → L-1) is, ceteris paribus, stronger than a transition in increasing sense (L → L+1)

d) The case of oppositely directed transitions does not occur, in general, either in X-ray spectra or in doublet spectra; because it would lead to a final state, in which (J-L) would be two units greater than in the initial state, which is forbidden.

Hence, we may distinguish following cases:

$\Delta L = -1$ , $\Delta J = -1$ ; most intense line (a)
$\Delta L = -1$ , $\Delta J = 0$ ; less intense (a)
$\Delta L = +1$ , $\Delta J = +1$ ; weaker (b)
$\Delta L = +1$ , $\Delta J = 0$ ; weakest (a and b)
✓ $\Delta L = +1$ ; $\Delta J = +1$ ; } no line (c)
$\Delta L = +1$ , $\Delta J = -1$ ; }

Note:

It can be shown both theoretically and experimentally the the total intensity of all the lines coming to or starting from any given J term of a multiplet is proportional to (2J+1).

## The Interval Rule-

Lande discovered a rule regarding the interval in frequency between the different levels constituting a multiplet. It is called the 'Lande Interval rule' and states that the frequency interval between two levels with total angular momenta (J+1) and J resp. is proportional to (J+1).

There are, however, many deviations from this interval rule, chiefly in cases when the coupling scheme follows neither the L-S type or j-j type, but is intermidiate both these extreme cases.

a triplet when viewed in the transverse direction i.e. perpendicular to direction of the magnetic field, and a double in the longitudinal direction i.e. parallel to magnetic field.

## b) Anamolous Zeeman Effect-

If the splitting of spectral lines is into the more than three components in presence of weak magnetic field, then it is called as anamolous Zeeman effect.

With ordinary weak fields, a more complex resolution of a greater number of components known as the anamolous effect, is obtained.

However, the electron theory is able to explain only the normal effect.

## Experimental Arrangement-

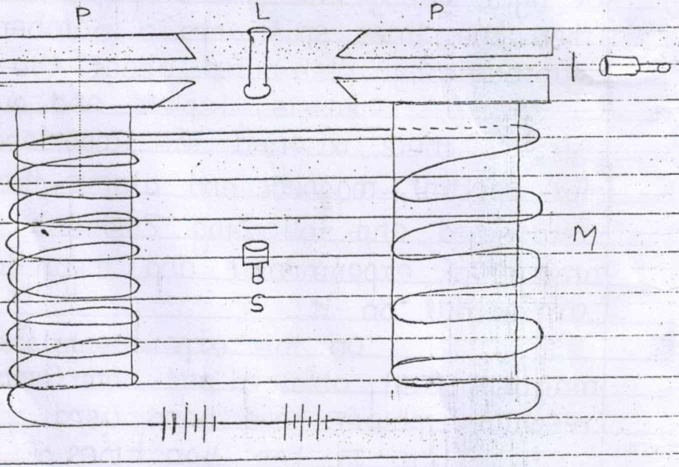


fig ② Experimental Arrangement for Zeeman Effect

An electromagnet MM capable of producing a very strong magnetic field and having conical pole-pieces PP, through which holes have been drilled length wise, is set up as shown in fig ②

The Lande' splitting factor 'g'

'g' is simply a factor which affects the ratio of magnetic moment to the mechanical angular momentum of atomic particles. It characterises therefore atomic and sub-atomic magnets, such as the orbital and spin magnets.

In order to determine this 'g' factor we shall first of all derive an expression for the magnetic moment corresponding to the orbital motion of electron.

## Zeeman Effect :

Zeeman effect is a magneto- optical phenomenon in which spectral lines are affected by an applied magnetic field and split into several components.

This was first observed by Zeeman in 1896 and hence called as Zeeman effect. He found that 'if a source of light giving line spectra is placed on a magnetic field then the lines split into a number of component lines, symmetrically distributed about the original line.

Doublets, triplets and even more complex systems were observed. The importance of the phenomenon for spectral, magnetic and atomic theories was at once recognised and following Zeeman's discovery, an enormous amount of experimental and theoretical researches has been carried out on it.

On the experimental side, the most powerful magnetic field obtained and interferometers of very high resolving power have been used.

It has two types of Zeeman effect:

a) Normal Zeeman Effect:

With very strong magnetic fields, a spectral line splits up into a comparatively simple triplet called normal effect. This is obtained with strong magnetic field. It consists

A source L emitting spectral lines, say a sodium vapour lamp is placed between the pole-pieces. The spectral lines are observed with high resolving power instrument such as a Lammer Grebreke Plate in conjuction with a constant deviation spbectrometer (S).

Working -

The moment of the current feeding the electromagnet is switched on, the two lines appear and the original line i.e. two components that appear whenever the field is on. viewing the spectral lines longitudinally through the hole drilled on in the pole pieces and hence parallel to direction of field and on establishing the magnetic field the line is found to split up into two (doublets), one having slightly shorter wavelength and other slightly greater wavelength than that of the original line which is no longer seen.

The change in wavelength $d\lambda$, known as the Zeeman slit is the same in both cases as shown in fig (2)

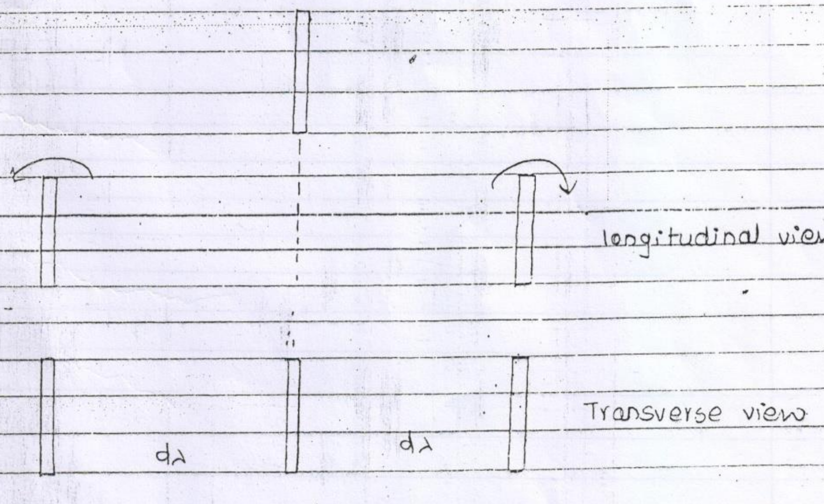


fig ② Normal Zeeman effect

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Analysing the nature of polarisation of two lines, they are found to be circularly polarised in opposite direction as shown by the arrows above the line as shown in fig ⑧.

When viewed transversely i.e perpendicular to the direction of the magnetic field the lines becomes a triplet, the central one having the same wavelength as that of original line.

The moment, the current feeding the electromagn is switch off, the two lines disappear and the original line alone is seen.

## * STARK EFFECT :-

INTRODUCTION :- The stark effect is the electrical analogue of the zeeman effect. soon after the discovery of the zeeman effect in 1896, a similar resolution of spectral lines in an applied electric field was looked for. But it was only in 1913 that stark succeeded for the first time in demostrating such a phenomenon in the spectrum of the hydrogen atom. The chief practical difficulty difficulty, which was also the cause of failure of earlier invesgators, was the absence of a proper technique. The aim was to subject hydrogen atoms emitting spectral lines to a powerful electric field.

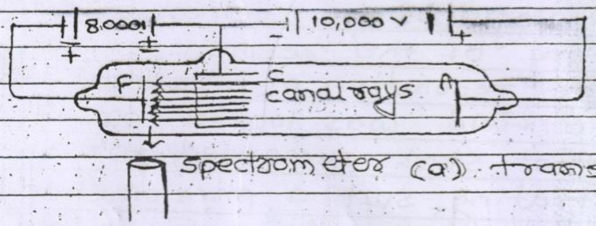
This was not, however, possible with the ordinary Geissler ~~the~~ tube containing hydrogen since the gas in such a tube is comparatively a good conductor and hence incapable of maintaining a strong electric field.

### Experimental study :-

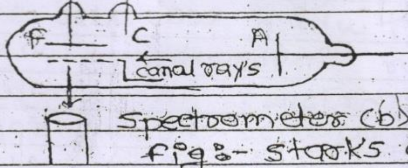
Stark in Germany and Lo surdo in Italy were able to overcome the difficulty stated above, by the use of special devices & obtained interesting results.

### Stark's method :-

It consists in applying a strong electric field to the luminiscent layer just behind the perforated cathode in a canal ray tube and analysing the resulting effect with a high resolution spectroscope



(a) transverse view



(b) longitudinal view

fig:- starks apparatus

The arrangement used by stark is shown in fig.

The canal rays are produced in an ordinary glass discharge tube provided with a perforated cathode C when the pressu in the tube is not very low, discharge takes place betn the anode A and cathode C, when the pressure in the tube is not very lo discharge takes place between the anode A an cathode C maintained at a suitable P.D., and the canal rays. stream through the perforations in the cathode and form behin the cathode. narrow cylindrical bundles of luminous rays.

A third electrode F is placed paralle and close to C at a distance of a few milli-meters and a very strong electric field of several thousand volts per cm. is maintaine betn F and C. The shortness of the spac betn F and C is a very important factor since it not only favours the productio of the resulting great potential drop, bu also prevents the spontaneous discharge betn F and C. The P.D. betn F and C is great enough to influence effectively the ions in that region and distort perceptibly their electronic orbits. The effect produced can be studied both transversely and longitudinally, i.e., at right angles and parallel to the direction of the field. For the transverse view, the light from the canal rays enters the spectroscope as in (a); for the longitudinal view the arrangement is as show in (b).

Stark observed that the lines in the spectrum emitted by the canal rays of hydrogen were split up under the action of the applied field, into numerous sharp components, some what after the manner of the zeeman effect. the components being polarised, some parallel to the field (π components). others perpendicular to it (σ components).

* Results :-

The results obtained by the two methods are chiefly in connection with the lines of the Balmer series of the hydrogen spectrum, although the effect in the spectra of other elements, such as He, Li, etc., has been investigated to a certain extent. The results obtained with the Balmer lines may be summarised as follows :-

i) Every line is split up into a number of ~~salary~~ sharp components their number increasing with the series number of the parent line. Thus the no. of components of Hβ line is greater than that of the Hα line, similarly the components of Hγ greater than those ~~of~~ Hβ.

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ii) The components are polarised in the followin manner : In the transverse view they are linearly polarised, some parallel to the directi of the field (π components) and others perpendicular (σ components). In the longitudinal view the π components are absent, while the σ components are unpolarised. The intense π components, in general, lie outsi while the intense σ components lie inside.

III) The components lie symmetrically on both sides of the original line. The distances of the components from the central line are integral multiples of the distance of the least displaced component from the centre If this smallest line interval or 'resolution' is measured in the scale of wave number it is found to be the same for all the lines of the Balmer series.

iv) Up to fields of about 100,000 volts per cm. the resolution increase proportionate to the field strength. In this region, therefore, we have what is known as the 'linear' Star effect. In the case of more intense fields more complicated effects, the so-called "quadratic" stark effect and even of higher order are observed, in addition to the linear effect. Raush von Traubenberg has succeeded in observing and analysing these higher order effects by using electric fields of strength over a million volts per cm.

v) The electric field increases from bottom upwards, from about 100,000 to 1.14 million volts per cm., & at the very top suddenly becomes zero. The magnitude of the splitting of the lines confirms the above-mentioned variation with the intensity of the field. In general the increase in resolution with the field shows the effects of higher order together with the linear effect. The photo has a particular significance in the fact that it exhibits the fading out of the different lines for different field strengths, the higher numbers of the series disappearing at lower intensities.

The $H_\epsilon$ line ceases to exist at a lower field that the $H_\delta$ line, and the latter sooner than $H_\gamma$. It is seen also that the long-wave components of the stark effect of any given line disappear at a lower field strength than the corresponding short-wave components.

The Lo Surdo photograph of the Balmer lines taken by Rausch von Traubenberg and his collaborators, reproduced here, is very instructive.

## ⊛ Example of L-S coupling

consider a case of one electron in a p orbit and the other in a d orbit.

$\therefore l_1 = 1$ & $l_2 = 2$

$L = l_1 + l_2, \ldots l_2 - l_1$

$= (1+2), \ldots (2-1) = 3, \ldots, 1$

$\therefore \boxed{L = 1, 2, 3}$

$\therefore s_1 = \frac{1}{2}, s_2 = \frac{1}{2} \therefore S = s_1 + s_2, \ldots, s_1 - s_2$

$S = (\frac{1}{2} + \frac{1}{2}) . (\frac{1}{2} - \frac{1}{2}) = 1, 0$

$\therefore \boxed{S = 0, 1}$

(a) Taking $S = 0$ and $L = 1, 2$ & $3$, we will get 3 singet terms –

(i) $J = L \pm S = (1+0), (1-0) = 1$

$\therefore {}^1P_1$

(ii) $J \Rightarrow S = 0, L = 2 = 2 \therefore {}^1D_2$

(iii) $J \Rightarrow S = 0, L = 3 = 3$ ${}^1F_3$

(b) Taking $S = 1$ & $L = 1$

(i) $J = (1+1), \ldots (1-1) = 2, 0 \therefore 0, 1, 2$

$\therefore {}^3P_{0,1,2}$

(ii) $J \Rightarrow S = 1$ & $l = 2$

$\therefore J = (2+1), \ldots (2-1) = 3, 2, 1$

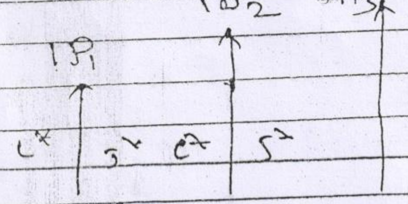
$\therefore {}^3D_{1,2,3}$

(iii) $J \Rightarrow S = 1$ & $L = 3$

$J = (3+1), \ldots (3-1) = 4, 3, 2$

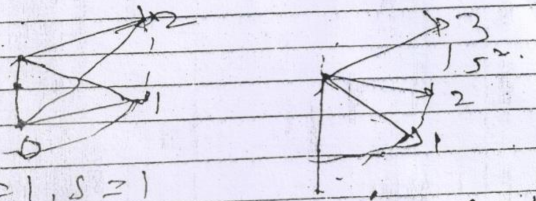
$\therefore {}^3P_{2,3,4}$ –

The vector diagrams for above cases are shown below



$L = 1, S = 0$ $\quad L = 2, S = 0$ $\quad L = 3, S \approx$

$J = 1$ $\quad J = 2$ $\quad J = 3$



$L = 1, S = 1$

$J = 0, 1, 2.$

$L = 2, S = 1$

$J = 1, 2, 3$

⊗ **pd**

$s_1 = \frac{1}{2}, l_1, \quad s_2 = \frac{1}{2} \ \& \ l_2 = 2$

for p electron $\Rightarrow j_1 = \frac{1}{2}$ or $\frac{3}{2}$

d electron $j_2 = \frac{3}{2}$ or $\frac{5}{2}$

$j_1 = \frac{1}{2} \ \& \ j_2 = \frac{3}{2} \Rightarrow J = 1, 2,$

$j_1 = \frac{3}{2} \quad j_2 = \frac{3}{2} \Rightarrow J = 0, 1, 2, 3$

$j_1 = \frac{1}{2} \quad j_2 = \frac{5}{2} \quad J = 2, 3$

$j_1 = \frac{3}{2} \quad j_2 = \frac{5}{2} \quad J = 1, 2, 3, 4$