

Angular problems in many-electron atoms

Terminology:

- ① State \rightarrow condition of the motion of all electrons
- ② Energy level \rightarrow collection of states having the same energy in the absence of

External magnetic or electric field.
It is characterized by J .

- ③ Sublevel \rightarrow An external field splits an energy level into several sublevels, each characterized by one or more magnetic quantum no.

- ④ Term \Rightarrow A collection of levels characterized by the total angular momentum and multiplicity
($2S+1$) \Rightarrow Spectroscopic term

- ⑤ Configuration: - The specification of the quantum no. n and l for the orbitals of all electrons of an atom is called the electronic configuration of the atom.
eg: the electron configuration of $6C$ atom
 $\rightarrow 1s^2, 2s^2, 2p^2$

Atoms with several optically active electrons

In the previous chapter we have determined the electronic configuration (n & l values of individual electrons) of the atoms by application of the Pauli principle. But this does not tell us the term types associated with the ground state and the excited state configuration of the atom. The term type is obtained by adding together the angular momentum vectors \vec{l} and \vec{s} of the individual electrons. For this purpose we have to first investigate the interaction (coupling) between the angular momentum vectors of the electrons

Let us consider a multielectron atom (ions) having a nuclear charge $+Ze$, surrounded by N electrons ($N \leq Z$). The electrons constitute a core of completely filled ~~subshells~~ subshells surrounding the nucleus and few of them remain in a partially filled subshell and are optically active

Hamiltonian for each atom consists of the following terms

① The K.E. of the electrons

$$\sum_{i=1}^N \frac{p_i^2}{2m} \quad \text{--- ①}$$

② The electrostatic interaction energy
 among the electrons & the nuclei

$$= \sum_{i=1}^N \frac{ze^2}{r_{ij}} \quad \text{--- ②}$$

③ The mutual electrostatic energy of the electrons

$$\sum_{i=1}^N \sum_{j=2}^N \frac{e^2}{r_{ij}} \quad \text{--- ③}$$

r_{ij} → distance between i & j electrons

④ The spin-spin correlation energy

⑤ The spin-orbit magnetic interaction energy of the electrons

Besides the above, there are a number of smaller interaction terms including the relativistic corrections.

In the Hartree approximation central field approximation, each electron is treated as if it were moving independently in a spherically symmetrical potential that describes the average of its Coulombic interactions with the nucleus of other electrons i.e. $H \rightarrow$ includes only those terms 1 to $1H$

In general, we can divide the atoms into two main classes in this respect

- (A) For most atoms, mainly the lighter ones, terms III & IV are the largest of the remaining terms; the term (V) ^{term} is unacceptably smaller; while the rest terms are negligible \approx L-S coupling
- (B) For some atoms, the heavier one, term (V) spin-orbit interaction predominates over other atoms, such atoms are governed by J-T coupling

③ l-s coupling

P-8

interaction energies

$$W_{li lj} = a_{ij} \vec{l}_i \cdot \vec{l}_j \quad (1)$$

between the orbital magnetic moments & between their spin moments of electrons e_i & e_j and

$$W_{s_i s_j} = b_{ij} s_i s_j \quad (2) \quad \text{between their spin moments}$$

are large compared to the interaction energy

$$W_{l_i s_i} = c_{ii} l_i s_i \quad (3)$$

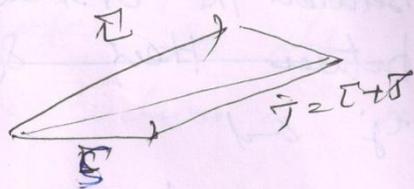
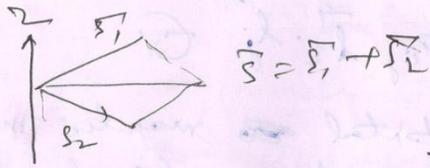
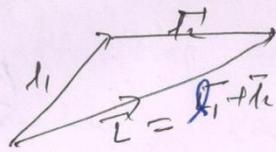
(between the orbital magnetic moment $\mu_{li} = \mu_B l_i$ and spin moment $M_s = g_s \mu_B s_i$ of the same electron, then the orbital angular momentum l_i of the different electrons couple to a total orbital moment

$L = \sum l_i$ with $|L| = \sqrt{L(L+1)} \hbar$ (3)

$$S = \sum s_i \quad \text{with } |S| = \sqrt{S(S+1)} \hbar \quad (4)$$

The total angular momentum of the electron shell is $J = L + S$ with $|J| = \sqrt{J(J+1)} \hbar$ (5)

This coupling case is named l-s coupling or (shown in the P8).



Pg. (1)

Total no. of fine structure components equals the smaller of the two no. $(2L+1)$ or $(2S+1)$. This gives the number of possible relative orientations between the S & L .

The energy of a fine structure component is $E_j = E(nL, S) + \frac{c \cdot L \cdot S}{2} \quad \text{--- (9)}$

Cent term gives the coupling energy of the interaction between L & S
 $c \rightarrow$ Coupling coeff (unit 10^3 cm^{-1})

$$J^2 = (L+S)^2 = L^2 + S^2 + 2L \cdot S \quad \text{--- (10)}$$

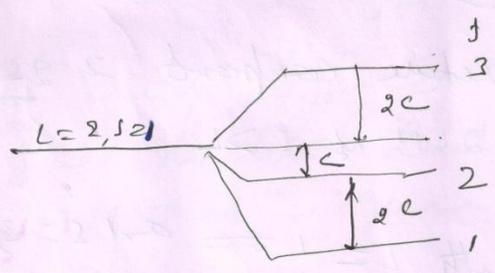
--- (10) = act. Here fine structure & coupling energy
 $c \cdot L \cdot S = \frac{c}{2} [(J+1)(J) - L(L+1) - S(S+1)]$

The labeling fine structure components is $\frac{2L+1}{2} \times \frac{2S+1}{2} = L_S$

The following nomenclature is used in accordance with labeling of levels in one-electron atom

- $l=0, s$ -level
- $l=1, p$ -level
- $l=2, d$ -level
-

The electron configurations with $L=2, S=2$ respects in three fine structure components with quantum no $J=1, 2, 3$. (Pg 24). The corresponding vector coupling are shown in fig (2.4)



Energy levels for $L=2, S=2$

$$E_j(n, L, S, J) = E(n, L, S) + \frac{c}{2} [J(J+1) - L(L+1) - S(S+1)]$$

(FW, $L=2, S=2$)

- $= E(n, L, S) + 2c \text{ for } J=3$
- $= E(n, L, S) = 1c \text{ for } J=2$
- $= E(n, L, S) - 2c \text{ for } J=1$

Fig 2(a): L-S coupling for $L=2, S=2$

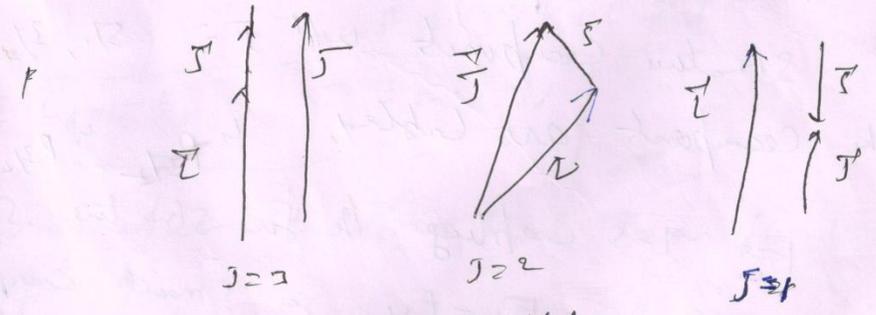


Fig 2(b): Vector addition

The energies of the fine structure components are calculated using equation (2.5)

$$E_j(n, L, S, J) = E(n, L, S) + \frac{c}{2} [(J+1/2) - 6/2] h^2$$

$$= \cancel{E(n, L, S)} + \frac{c}{2} [(J+1) - 6/2] h^2$$

$$= E(n, L, S) + 2ch^2 \quad \text{for } J=3$$

$$= E(n, L, S) - ch^2 \quad \text{for } J=2$$

$$= E(n, L, S) - 2ch^2 \quad \text{for } J=1$$

The fine structure components are not equally spaced.

* The no. of fine structure components is $2S+1$ if $L > S$ or $2L+1$ if $S > L$.

* The carbonium with $L=1$ and $S=3/2$ has three possible fine structure components with $J=5/2, 3/2$ & $1/2$.

the components are labeled $P_{5/2}, P_{3/2}, P_{1/2}$

* For L-S coupling, the fine structure splitting $\Delta E_{FS} = E_j - E_{j'}$ is small compared to the energetic separation level with respect to value of L or S .

* L-S coupling is valid mainly for light atoms with small Z values.

Quantum mechanical calculations show that fine structure constant C is proportional to $C \propto Z^4/n^3$.

* C is largest for lowest atomic levels (small values of n). with $l \neq 0, s \neq 0$

The average energies of all fine structure components

$$\bar{E} = \frac{1}{K} \sum_{J=1}^K (2J+1) E_J = E(n, l, s)$$

The energy difference between the two fine structure levels corresponding to J & $J+1$ is given by

$$\begin{aligned} \dots E_{J+1} - E_J &= A [(J+1)(J+1) - J(J-1)] \\ &= A (J+1) (J+1 - J) \end{aligned}$$

$$\boxed{E_{J+1} - E_J = 2A(J+1)}$$

Determination of spectral term for L-S coupling

Atom with one optical electron
 For a hydrogen-like atom

is.

$$s = \frac{1}{2}, l = 0, \text{ multiplicity} = 2s + 1 = 2$$

$$J = (l - s) \rightarrow (l + s)$$

1-10

(10)

$$= \frac{1}{2}$$

The ground state term of a hydrogen-like atom is $1s$

$$^2S_{1/2}$$

The excited state configuration and corresponding term for a hydrogen-like atom would be

$$2s, 3s, 4s \dots \quad ^2S_{1/2}$$

$$2p, 3p, 4p \dots \quad ^2P_{1/2}, ^2P_{3/2}$$

$$3d, 4d \dots \quad ^2D_{3/2}, ^2D_{5/2}$$

(2) Atom with two or more non equivalent orbital electrons

Let us consider an atom having two orbital electrons with orbit numbers

$$l_1, l_2$$

For this, we have

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

The possible values of S & L are

$$S = |s_1 - s_2| \dots |s_1 + s_2|$$

$$= 0, 1, \quad (2S+1) = 1, 3$$

$$L = |l_1 - l_2| \dots |l_1 + l_2|$$

$$= 1, 2, 3, \quad [P, D, F, G, H, I]$$

These levels are

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(11)

$1P^1D^1F$ $3P$ $3D^3P$
How to get the effect of L & S ~~effect~~ interaction

$$J = |L-S| \dots |L+S|$$

For doublet term, we

$$\left\{ \begin{array}{l} S=0 \\ L=1 \end{array} \right. ; J=1, \dots ; 1P_1^0$$

$$\left\{ \begin{array}{l} S=0 \\ L=2 \end{array} \right. ; J=2 \quad 1D_2$$

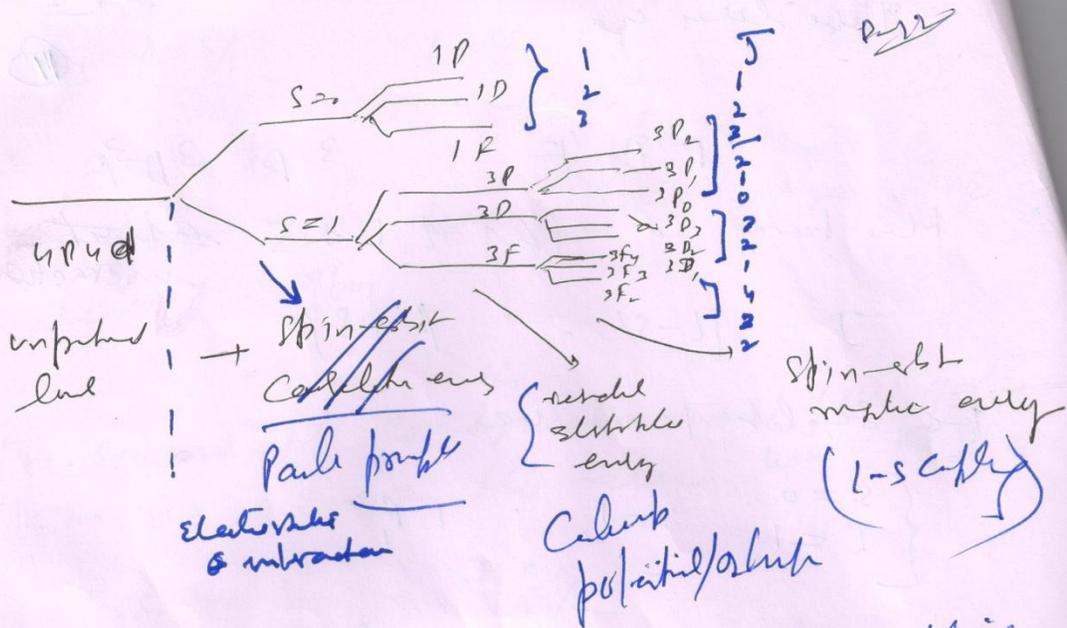
$$\left\{ \begin{array}{l} S=0 \\ L=3 \end{array} \right. ; J=3 \quad 1F_3$$

For triplet term

$$\left\{ \begin{array}{l} S=1 \\ L=1 \end{array} \right. ; J=0, 1, 2 ; \underline{3P_0, 3P_1, 3P_2}$$

$$\left\{ \begin{array}{l} S=1 \\ L=2 \end{array} \right. ; J=1, 2, 3 ; \underline{3D_1, 3D_2, 3D_3}$$

$$\left\{ \begin{array}{l} S=1 \\ L=3 \end{array} \right. ; J=2, 3, 4 ; \underline{3F_2, 3F_3, 3F_4}$$



Energy level diagram of two equivalent orbital carbon electrons w/ L-S coupling.

For another example, consider the combination 3d 4s 5p

For this we have

$$s_1 = \frac{1}{2}, \quad s_2 = \frac{1}{2}, \quad s_3 = \frac{1}{2}$$

For combinations s_1, s_2, s_3 , we have

$$s_1 = 0, 1$$

This combination with s_3

we obtain, $S = \frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

The multiplicity $(2S+1) \Rightarrow 2, 2, 4$ which corresponds to two sets of doublets and one set of "quartet" states.

Considering orbital momenta combination P-13

We first combine 3d and 4s electrons

$$\text{For 1st } l_1 = 2, l_2 = 0$$

$$L' = 2,$$

Now we add 5p electron to L' , where

$$l_3 = 1$$

This gives $L = 1, 2, 3$ (P, D, F states)

Therefore, we have two sets of three doublets and one set of three quartets, i.e. nine terms.
= All these terms are odd because the combination

3d 4s 4p is odd ($2 + 0 + 1 = 3$).

We can write these terms as

$$2P, 2D, 2F; \quad 4P, 4D, 4F$$

Including spin-orbit interaction, we can write various levels as

$$\left\{ \begin{array}{l} S = \frac{1}{2} \\ L = 1 \end{array} \right. ; \quad J = \frac{1}{2}, \frac{3}{2} ; \quad 2P_{\frac{1}{2}, \frac{3}{2}}^{(2)}$$

$$\left\{ \begin{array}{l} S = \frac{1}{2} \\ L = 2 \end{array} \right. ; \quad J = \frac{3}{2}, \frac{5}{2} ; \quad 2D_{\frac{3}{2}, \frac{5}{2}}^{(2)}$$

$$\left\{ \begin{array}{l} S = \frac{1}{2} \\ L = 3 \end{array} \right. ; \quad J = \frac{5}{2}, \frac{7}{2} ; \quad 2F_{\frac{5}{2}, \frac{7}{2}}^{(2)}$$

$$\left\{ \begin{array}{l} S = 3/2 \\ L = 1 \end{array} \right. , J = 1/2, 3/2, 5/2, \quad 4P_{3/2}, 3/2, 1/2$$

$$\left\{ \begin{array}{l} S = 3/2 \\ L = 2 \end{array} \right. , J = 1/2, 3/2, 5/2, 7/2, 9/2, \quad 4D_{3/2}, 3/2, 5/2, 7/2$$

$$\left\{ \begin{array}{l} S = 3/2 \\ L = 3 \end{array} \right. , J = 3/2, 5/2, 7/2, 9/2, 11/2, \quad 4F_{3/2}, 5/2, 7/2, 9/2$$

Atom with two or more two equivalent electrons

(P-75)

Selection rules of L-S coupling

The selection rules for the electric dipole transition in multi-electron atoms are closely similar to the selection rules for the one-electron atom:

- ① Most of the transitions occurs in which only one electron jumps ~~to~~ at a time, and such that its l -value changes by one unit i.e.

$$\Delta l = \pm 1 \rightarrow \text{Laporte rule}$$

in case more than one electron jumps the Laporte rule requires that the sum of the individual Δl 's must change by an odd no of unit

For example, if we have a transition involving two electrons simultaneously, then Δl must be even for one electron and odd for the other.

Since, we have $\Delta l = \pm 1$, for one electron

$\Delta l_1 = \pm 1$, } for two electrons system

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② For the atom as a whole,
the quantum nos L, S & J must
change as follows

$$\Delta l = 0, \pm 1, \left(\begin{array}{l} \text{In one electron} \\ \text{then } \Delta l = 0, \text{ is} \\ \text{not allowed} \end{array} \right)$$

$$\Delta S = 0$$

$$\Delta J = 0, \pm 1, \text{ but } J = 0 \leftarrow / \rightarrow J = 0$$

J-J Coupling

If the interaction energy

$$W_{L_i S_i} = c_i L_i S_i \quad \text{--- ①}$$

between the magnetic moment of an
electron due to the orbital angular momentum
and its spin moment becomes larger
than the magnitude of interaction

$$W_{L_i S_i} = a_{ij} L_i S_j \text{ or } W_{S_i S_j} = b_{ij} S_i S_j \quad \text{②}$$

between the different electrons, the
order of coupling changes. How
 L_i and S_i initially couple to form the
resultant angular momentum

$$J_i = L_i + S_i \quad \text{--- ③}$$

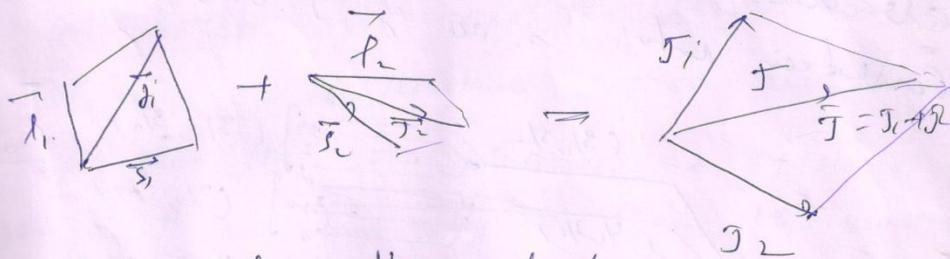
of the electron e_i or the
vectors J_j of the different electrons

Couple to the total angular momentum ^{P-1A}

J of the atomic state

$$J \rightarrow \sum \vec{j}_i$$

This is called spin-orbit coupling, which is mainly observed for heavy atoms with large Z value is called the J - L coupling. The vector coupling diagram is shown in the below figure



Let us learn for the electronic contribution up and down under J - L coupling

For p-electron $l = 1, s = \frac{1}{2}, j_1 = \frac{1}{2}, \frac{3}{2}$

For d-electron $l = 2, s = \frac{1}{2}, j_2 = \frac{3}{2}, \frac{5}{2}$

For (j_1, j_2) combination the possible value of J is

$$\left(\frac{1}{2}, \frac{3}{2}\right) \left(\frac{1}{2}, \frac{5}{2}\right), \left(\frac{3}{2}, \frac{3}{2}\right) \left(\frac{3}{2}, \frac{5}{2}\right)$$

Thus the spin-orbit effect splits the unperturbed level into four levels at which $\left(\frac{1}{2}, \frac{3}{2}\right)$ level is lowest & $\left(\frac{3}{2}, \frac{5}{2}\right)$ highest

the four (j_1, j_2) combination gives $J = 1, 2$

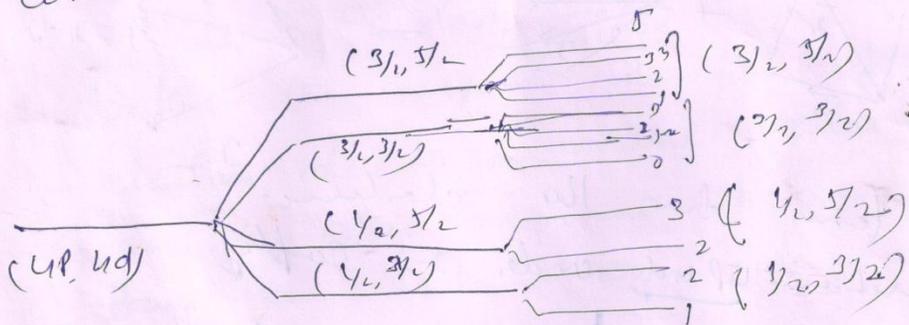
$$\left(\frac{1}{2}, \frac{3}{2}\right) \text{ gives } J = 1, 2$$

$$\left(\frac{1}{2}, \frac{5}{2}\right) \text{ gives } J = 2, 3$$

$$\left(\frac{3}{2}, \frac{3}{2}\right) \text{ gives } J = 0, 1, 3$$

$$\left(\frac{3}{2}, \frac{5}{2}\right) \text{ gives } J = 1, 2, 3, 4$$

Hence each level of the above four levels is further splitted by the electrostatic interaction and spin-spin interaction into a no of J -vals



input level \rightarrow spin-orbit energy \rightarrow splittable \rightarrow spin-spin energy

Selection rules for J-J Coupling

① $\Delta J = 0, \pm 1$ for the dipole & quadrupole transitions
 at $\Delta J = 0$ for other dipoles

② For dipoles as a whole
 $\Delta J = 0, \pm 1$, but $J = 0 \leftarrow J = 0$

L-S Coupling

Atom with two or more equivalent electrons

For two equivalent electrons (same n and l values) the values of at least one of the remaining quantum no. (m_l & m_s) must differ to satisfy Pauli's exclusion principle.

Therefore, certain terms which were possible for two non-equivalent electrons are now not allowed.

Ex. Example two non-equivalent p -electrons, such as $2p$ & $3p$ give rise the terms $1S, 1P, 1D, 3S, 3P, 3D$; But if the two electrons are equivalent. Only $3P^2$ then the terms $3D, 3S$ and $1P$ do not exist and we have only the terms $1S, 1D$ and $3P$.

Let us now see how to obtain terms from combination involving equivalent electrons.

Before we do so, we must mention two important facts:

- (i) A closed sub shell, such as s^2, p^6, d^{10} always form $1S_0$ term only. The closed sub-shell consists of maximum no. $2(2l+1)$ of equivalent electrons.

So that

$\Sigma m_l = 0$	}	For example p^6 - electron ($l=1$)	
$\Sigma m_s = 0$		<table style="margin-left: 20px;"> <tr> <td>$m_l = 1, 1, 0, 0, -1, -1$</td> </tr> <tr> <td>$m_s = \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}$</td> </tr> </table>	$m_l = 1, 1, 0, 0, -1, -1$
$m_l = 1, 1, 0, 0, -1, -1$			
$m_s = \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}$			

This means that $m_l = 0$ & $m_s = 0$
 $l = 0$ (s -shell)
 $2s^2$ ($2s^2$) ($2s^2$) = $1, 0, 0$ the possible terms $1S_0$

Here we conclude that when a subshell is completely filled the only allowed state is only one i.e. total spin angular momentum, total angular momentum (M_L) and total angular momentum (M_S) is equal to zero. This also shows that the subshell has no net magnetic dipole moment.

i) The terms of a configuration $(nl)^q$ are the same as the terms of the configuration $(nl)^{r-q}$, where r is the maximum no. of electrons i.e. $2(2l+1)$. For example the term of p^5 are the same as those of p^1 , the term of p^4 as the same as the term of p^2 .

We now calculate the spectral term arising from two equivalent p-electrons (p^2) let us imagine the atom to be placed in a very strong magnetic field where all the internal couplings are broken down.

The values of L & S vector, their process is independently found the magnetic field with quantized components M_L & M_S respectively.

The value of l for a p-electron is 1. Here the values of m_l are 1, 0, -1. m_s has the values $+\frac{1}{2}$ & $-\frac{1}{2}$.

Now, all the possible combinations of m_2 & m_3 are
 $2 \times (2^4) = 2 \times (16) = 32$

$$m_2 = \begin{matrix} 1 & 0 & -1 & 1 & 0 & -1 \\ m_3 & \frac{1}{2} & +\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} \end{matrix}$$

(a) (b) (c) (d) (e) (f)

the possible states of the cabinet

$${}^6C_2 = \frac{6 \times 5}{2 \times 1} = 15$$

$$\left| \begin{matrix} 3 & 4 \\ 6 \times 5 + 3 \times 2 \\ 2 \times 4 + 3 \times 2 \end{matrix} \right|$$

- ab, ac, ad, ae, af
- b.c, bd, be, bf
- cd, ce, cf
- de, df, ef

	ab	ac	ad	ae	af	bc	bd	be	bf	cd	ce	cf	de	df	ef
m_2	1	0	2	1	0	-1	1	0	-1	0	-1	-2	1	0	-1
m_3	1	1	0	0	0	0	0	0	0	0	0	0	-1	-1	-1

the highest rank of M_2 is 2, \Rightarrow 0 terms

$$m_2 = \begin{matrix} ad & ae & af & bf & cf \\ 2 & 1 & 0 & -1 & -2 \\ m_3 & 0 & 0 & 0 & 0 \end{matrix} \Rightarrow \Delta \neq 0$$

$$m_2 = \begin{matrix} ab & ac & bc & bd & cd & ce & de & df & ef \\ 1 & 0 & -1 & 1 & 0 & -1 & 1 & 0 & -1 \\ m_3 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & -1 & -1 \end{matrix} \Rightarrow 3P$$

only one combination $M_L=0, M_S=0$ which can give only 1S term ($L=0, S=0$)

$$\left. \begin{matrix} M_L = 0 \\ M_S = 0 \end{matrix} \right\} 1S \text{ term}$$

this two equivalent p-electron give rise to $1D, 3P, 1S$ terms and no others.

$$1D_2, 3P_{0,1,2} \text{ and } 1S_0$$

Berit's scheme

The above terms may also be calculated by a scheme is called the Berit's scheme for two equivalent p-electrons.

In this scheme we write in a table all the possible values of M_L , which can be formed by the combination of m_{l_1} and m_{l_2} of the two electrons as shown in the following table:

m_{l_1, l_2}	1	0	-1	
$M_L = 2$	2	0	1	1
$M_L = 1$	1	0	-1	0
$M_L = 0$	0	-1	-2	-1
	S	P	D	m_{l_2}

(Table for two-equivalent p-electrons)

from the Betti's table, we have nine

values of M_L . These values can be divided into three sets by the L-shaped (dotted) lines. These sets are:

$$\begin{array}{cccc} 2 & 1 & 0 & -1 & -2 \end{array} \quad (\text{Set I})$$

$$\begin{array}{cccc} 2 & 1 & 0 & -1 & -2 \end{array}$$

$$\begin{array}{cccc} 2 & 1 & 0 & -1 & -2 \end{array} \quad (\text{Set II})$$

$$\begin{array}{ccc} & 1 & 0 & -1 \end{array} \quad (\text{Set III})$$

$$\begin{array}{ccc} & & 0 \end{array} \quad (\text{Set III})$$

from these sets we have $L = 2, 1, 0$ and gives

the D, P, and S terms.

The spins of the two electrons can be combined to form $S=0$ and $S=1$ (doublet) (doublet)

For $S=1$, both electrons have the same spin quantum nos, hence they must differ in their values m_l .

Also we can not combine the any values of m_l lying on the diagonal lines, because the diagonal corresponds to the equal values of m_l and m_l .

Thus for $S=1$ (triplet), are ~~allowed~~ limited to the following M_L values.

$$\begin{array}{ccc} 1 & 0 & -1 \end{array} \quad (\text{II Set}), \quad \text{which is corresponds to } 3P \text{ terms or } 3P_{0,1,2} \text{ terms.}$$

When $S=0$, the electrons are differ in their spin quantum nos, hence there is no restriction on the values of M_L , which may be combined

with first value of S . At first the remaining sets E and T_2 sub combine with $S=0$. These sets are corresponds of the term with $L=2$ and $L=0$ respectively and gives 1D 1S and or 1D_2 1S_0

\therefore two ~~electrons~~ equivalent p-electrons gives 1S_0 , 1D_2 and ${}^3P_{0,1,2}$ terms respectively

There will also be the terms for p^4 configuration

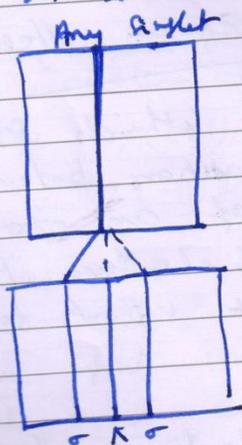
Now let us consider the two d-electrons
i. $(nd)^2$ configuration

$m_1 =$	2	1	0	-1	-2		
$m_2 =$	2	3	2	1	0	2	2
$m_2 =$	3	2	1	0	-1	0	1
$m_2 =$	2	1	0	1	-2	-1	0
$m_2 =$	1	0	-1	-2	-3	-2	-1
$m_2 =$	0	-1	-2	-3	-4	-2	-2
	S	P	D	F	G		

Zeeeman Effect [(Normal) & Anomalous]

In 1896, Zeeeman observed that when an atom is placed in an external magnetic field, the spectral ~~lines~~ emitted lines are split into several polarized components. The splitting is proportional to the strength of the field. This effect of magnetic field on the ~~spectral~~ atomic spectral lines is called the ~~Normal~~ Zeeeman effect.

A single spectral line viewed Normal to the field splits into three plane-polarized components; A central unshifted line with the electric vector vibrating parallel to the field is called the π -component, and two other lines equally displaced one ~~on~~ on either side with electric vector perpendicular to the field is called the σ -components. This is shown in Fig(1). This effect is called the Normal Zeeeman effect.



Fig(1): Normal triplet.

The fine-structure components of a multiplet spectral line, shows a complex Zeeman pattern.

For example, the D_1 and D_2 components of sodium yellow doublet gives four and six lines respectively (Fig 2) is called the anomalous Zeeman effect.

Sodium Principal doublet

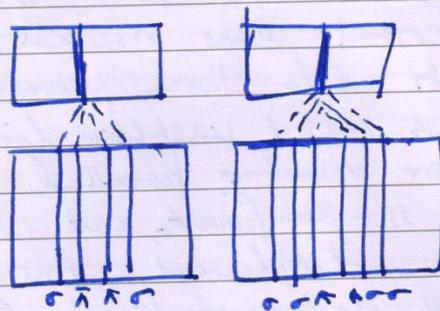


Fig 2: ~~Auto~~ Anomalous Zeeman effect

Explanation of Normal Zeeman effect

The normal Zeeman effect which shows by all lines due to the transitions between the singlet ($S=0$) states of an atom, can be explained by classical electron theory and also from the quantum theory without taking the note of electron spin.

In quantum theory, a polyelectronic atom possesses an orbital angular momentum \vec{L} and an orbital magnetic moment $\vec{\mu}$.

with the gyromagnetic ratio, given by

$$\frac{\vec{\mu}_L}{|\vec{L}|} = \frac{e}{2mc} \quad \text{--- (1)}$$

where $e \rightarrow$ charge (in esu)

$m \rightarrow$ mass (in gm)

$c \rightarrow$ velocity of light.

The $\vec{\mu}_L$ is directed opposite to the \vec{L} because e is negatively charged.

When the atom is placed in an external magnetic field \vec{B} , it is directed along the z-axis, then the vector \vec{L} precesses around the field direction.

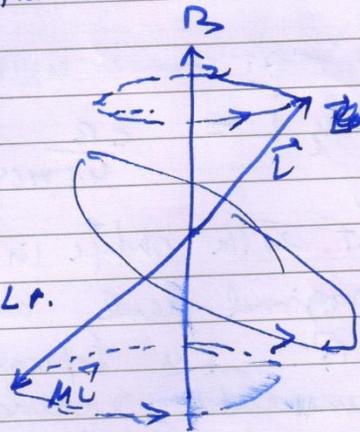
as shown in Fig. 3, the quantized components of \vec{L} is given by

$$L_z = M_L \hbar = M_L \frac{h}{2\pi} \quad \text{--- (2)}$$

where $M_L =$ (magnetic orbital quantum no)

$$= L, (L-1), \dots, -L.$$

$$= (2L+1) \text{ values.}$$



It means that in a magnetic field \vec{B} each

L -level splits into $(2L+1)$

levels, and each level is characterized by M_L value.

By the Larmor's theorem, the angular velocity of the precession is given by

$$\omega = \frac{\mu_B}{\hbar} B$$

$$\omega = \frac{e}{2mc} B \quad \text{--- (3)}$$

The interaction energy of such precession along \vec{B} is given by

$$\Delta E = \omega L_z = \left(\frac{e}{2mc} B \right) M_L \frac{\hbar}{2\pi}$$

$$\Delta E = \frac{eh}{4\pi mc} B M_L \quad \text{--- (4)}$$

in wave no.

$$-\Delta T = \frac{\Delta E}{hc} = \frac{eB}{4\pi mc^2} M_L \text{ cm}^{-1}$$

$$-\Delta T = M_L L \quad \text{--- (5)}$$

$$\text{Where } L = \frac{eh}{4\pi mc^2} \rightarrow \text{Lorentz Units}$$

ΔT is the change in energy for M_L level from the original level and shift is proportional to the B . The separation between any two consecutive Zeeman levels is $L \text{ cm}^{-1}$ whatever the value of L .

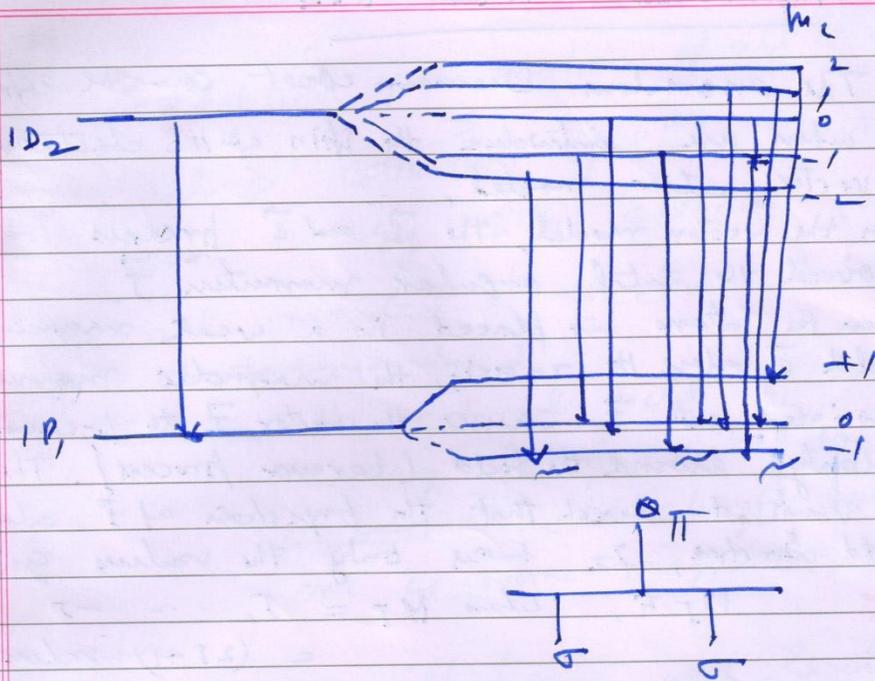
Let us consider the transition $1D_2 - 1P_1$.

These lines correspond to $L=2, L=1$ in a weak magnetic field it breaks into $(2L+1) = 5$ or 3 equispaced components respectively. The M_L values are $2, 1, 0, -1, -2$ and $1, 0, -1$ respectively.

as shown in Fig. 4.

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Ans selection rule for the magnetic quantum no. is

$$\Delta m_l = 0, \pm 1$$

Anomalous Zeeman effect

The anomalous Zeeman effect can be explained when we introduce the spin of the electron in vector atom model.

In the vector model, the \vec{L} and \vec{S} precess rapidly around the total angular momentum \vec{J} .

When the atom is placed in a weak magnetic field \vec{B} along the z-axis, the magnetic moment associated with \vec{J} causes the vector \vec{J} to precess slowly around the field (Larmor precession). The motion is quantized such that the projection of \vec{J} along the field direction, J_z takes only the values given by

$$M_J \hbar, \text{ where } M_J = J, \dots, -J \\ = (2J+1) \text{ values.}$$

Let us consider the simplest case of a single-valued electron atom. Classically the ratio of $|\vec{M}_L|$ to $|\vec{L}|$ is

$$\frac{e}{2mc} \text{ i.e. } \frac{|\vec{M}_L|}{|\vec{L}|} = \frac{e}{2mc} \quad \text{--- (1)}$$

in anomalous Zeeman effect,

$$\frac{|\vec{M}_S|}{|\vec{S}|} = 2 \times \frac{e}{2mc} \quad \text{--- (2)}$$

$$\therefore \vec{M} = \vec{M}_L + \vec{M}_S \quad \text{--- (3)}$$

Since \vec{J} is invariant, the \vec{L} , \vec{S} , \vec{M}_L , \vec{M}_S , and \vec{M} precess around the \vec{J} as shown in the Fig. (1). Here the component parallel to \vec{J} remains a constant of magnitude M_J which contributes to the magnetic moment of the atom. Thus

$$M_J = \text{Component of } \vec{M}_L \text{ along } \vec{J} + \text{Component of } \vec{M}_S \text{ along } \vec{J}$$

$$M_J = |\vec{M}_L| \cos(\vec{L}, \vec{J}) + |\vec{M}_S| \cos(\vec{S}, \vec{J}) \quad \text{--- (4)}$$