Dr. Ranjana Singh
Assistant Professor, Physics
Harprasad Das Jain College
Ara, Bihar, India

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MPHYCC10-08

Spectroscopic terms and their notations:-

The quantized energy state of an atomic electron can be described in terms of quantum numbers n, l, s, & J

n = principle quantum number = 1, 2, 3 - - - - -

orbital quantum number $l = 0, 1, 2, 3$ - - - are named as s, p, d, f, g electrons i.e.

$l = 0$	s
$l = 1$	p
$l = 2$	d
$l = 3$	f

~~n=1~~, for given n there are 0 to $n-1$, l values.

for $n = 1$, $l = 0$, electronic state = 1s
$n = 2$ $l = 0$ electronic " = 2s
$n = 3$ $l = 1$ electronic " = 3p

Terms:- The energy levels of electrons of an atom are called terms of the atom. The corresponding energy in wavenumbers are called term values.

for one e^- atom the energy level corresponding to $l = 0, 1, 2, 3$ - - - are called S, P, D, F, G terms respectively.

Due to spin orbit interaction energy energy level 'l' is splitted into two sublevels

$$J = l + s = l + \frac{1}{2} \quad \&$$

$$J = l - s = l - \frac{1}{2}$$

Multiplicity of the term = $2s+1$

Example:- Calculate the term symbol for $n = 2$, $l = 1$, $s = \frac{1}{2}$, $J = 3/2$

Term symbol = ${}^{2s+1}A_J$ where A = S, P, D, F, G for $l = 0, 1, 2, 3$ - -

$2s+1 = 2 \times \frac{1}{2} + 1 = 2$, A = P, $J = 3/2$ then term symbol = ${}^2P_{3/2}$

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L-S coupling: →

This coupling is also known as 'Russell-Saunders' coupling. The atoms obeying this coupling various perturbations are introduced in order.

(a) spin-spin correlation (b) residual electrostatic interaction & (c) spin orbit interaction.

(a) Due to spin-spin interaction, the individual spin angular momentum vectors of the optical electrons are strongly coupled with one-another to form a resultant spin angular momentum vector $\vec{S}$ of magnitude $\sqrt{S(S+1)}\,h/2\pi$.

S = quantum number = $|\vec{s}_1+\vec{s}_2+\vec{s}_3\cdots|_{min}$, $|\vec{s}_1+\vec{s}_2+\vec{s}_3\cdots|_{min}+1$ ------

The heighest S value will have lowest energy. The different levels are designated by their multiplicity (2S+1)

example for one electron $S=\frac{1}{2}$

then $2s+1 = 2\times\frac{1}{2}+1 = 2$ (doublet)

For 2 e⁻s $s_1=\frac{1}{2}$, $s_2=\frac{1}{2}$

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

→ singlet 1, 0

$S = 2s+1 = 1$ & 3 (triplet

for 3 e⁻s $s_1=\frac{1}{2}$, $s_2=\frac{1}{2}$, $s_3=\frac{1}{2}$

$s' = s_1 \pm s_2 = 0, 1$

$s = s' \pm s_3 = 0\pm\frac{1}{2} = \frac{1}{2}$

$1\pm\frac{1}{2} = \frac{1}{2}, \frac{3}{2}$

$S = \frac{1}{2}, \frac{1}{2}, \frac{3}{2} \Rightarrow 2s+1 = 2$ (doublet), 2(doublet), 4(quartets)

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(b) Due to result of residual electrostatic interaction the individual orbital angular momentum vectors of the optical electrons are strongly coupled with each other to form resultant orbital angular momentum vector $\vec{L}$ of magnitude $\sqrt{L(L+1)}\,h/2\pi$ which is constant of motion. L can take the following values

$L = |l_1+l_2+l_3 - \cdots|_{min}, |l_1+l_2+l_3+\cdots|_{min}+1 \cdots\cdots (l_1+l_2+l_3 \cdots)$

The state of largest L have lowest energy

The different levels are designated as S, P, D, F, G --- according to L = 0, 1, 2, 3, 4 --- values

example for 3P, 3d electron

$l_1 = 1,\ l_2 = 2$

$L = |l_1 \pm l_2| = 1 \pm 2 = 1, 2, 3$ (P, D, F) — states.

for 2P, 3P, 4d, $l_1 = 1,\ l_2 = 1,\ l_3 = 2$

$L' = |l_1 \pm l_2| = 0, 1, 2$

$L = |L' \pm l_3| = 2$ (D state)
$= 1, 2, 3$ (P, D, F states)
$= 0, 1, 2, 3, 4$ (S, P, D, F, G states)

(c) Due to result of smaller spin-orbit magnetic interaction the resultant orbital angular momentum vector $\vec{L}$ & the resultant spin angular momentum vector $\vec{S}$ are ~~less strongly~~ or weakly coupled with each other to form total angular momentum $\vec{J}$ of the atom. $\vec{J} = \vec{L} + \vec{S}$

magnitude of $\vec{J} = \sqrt{J(J+1)}\,h/2\pi$

$J = |L-S|, |L-S|+1 \cdots\cdots (L+S)$

If $L > S$ the number of J values $= 2S+1$
$S > L$ the ... ... $= 2L+1$

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Due to spin-orbit interaction level characterized by L and S is further broken up into comparative closer (2S+1) or (2L+1) level each having different J values. The group of these J values forms a fine structure multiplet their spacing are governed by Lande interval rule.

Lande interval rule :→

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

i.e. the energy spacing between consecutive levels J & J+1 of a fine structure multiplet is proportional to (J+1) i.e. larger of the two J values involved.

example 1:- fine structure levels $^3P_0$ $^3P_1$, $^3P_2$ have sepration in the ratio 1:2

$$E_1 - E_0 = 2A(1)$$
$$E_2 - E_1 = 2A(2)$$
$$\Rightarrow \frac{E_1 - E_0}{E_2 - E_1} = \frac{1}{2}$$

Q(1):- Fine structure levels are $^3D_1$, $^3D_2$, $^3D_3$ find out their sepration ratio.

Q(2):- Fine structure levels are $^4D_{1/2}$, $^4D_{3/2}$, $^4D_{5/2}$, $^4D_{7/2}$ find the sepration ratio.

Normal Multiplet :→ For a given multiplet the level with smallest J values lies lowest. Then this multiplet is called normal multiplet.

Inverted multiplet :→ The multiplet in which largest J value lies lowest is called inverted multiplet.

Dr. Ronjona Singh
Assistant Professor, Physics
Hariprasad Das Jain College
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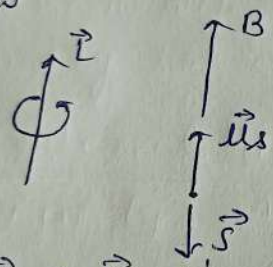
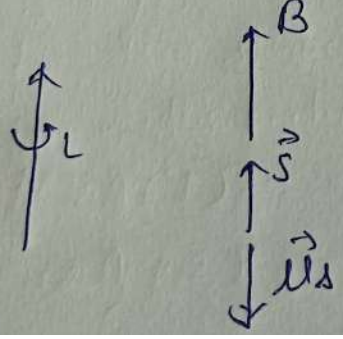
orbital motion of e^- produces magnetic field $\vec{B}$ whose direction is similar to $\vec{L}$ direction. In this field the most stable state (state with lowest energy) will have $\vec{\mu}_s$ directed along $\vec{B}$ we know $\vec{\mu}_s$ directed opposite to $\vec{S}$ as shown in the figure below



$\Rightarrow J = L - S$

$\left[\begin{array}{l} U = -\mu_s \cdot B \\ \text{energy} = -M \cdot B \end{array} \right]$

while $\vec{L}$ & $\vec{S}$ directed in the same direction gives largest J value $\nexists$ i.e. $\vec{\mu}_s$ will be opposite to $\vec{B}$ the state will be leas stable state.



$\Rightarrow J = L + S$

$\left[\begin{array}{l} U = \mu_s \cdot B \\ \text{energy} = M \cdot B \end{array} \right]$