B.Sc-III, Paper-VII, group-A

L-S Coupling

The L-S Coupling is also known as Russell-Saunders Coupling after the two astronomers who first used it in studying atomic spectra emitted by stars. In atoms which obey this Coupling we introduce the various perturbations in the order (a) spin spin Correlation (b) residual electrostatic interaction (c) spin-orbit interaction.

$$S = \left|\vec{s_1}+\vec{s_2}+\vec{s_3}+ \cdots\right|_{min},\ \left|\vec{s_1}+\vec{s_2} \cdots\right|_{min+1} \cdots$$

$$\cdots (s_1+s_2+s_3+\cdots)$$

Multiplicity $= (2s+1)$

For one electron $\rightarrow S = s = 1/2$ (doublets)

" 2 " $\rightarrow s_1 = 1/2,\ s_2 = 1/2$

$$S = |s_1 - s_2| + \cdots (s_1 - s_2 + 1) \cdots$$

$$= \left|1/2 - 1/2\right|,\ (1/2 - 1/2 + 1)$$

$$= 0, 1 \longrightarrow \text{Triplet } (-1, 0, 1)$$

$\downarrow$ singlet

~~For 3 ē :- $s_1 = 1/2,\ s_2 = 1/2\ s_3 = 1/2$~~

~~$S = |s_1 - s_2 - s_3|,\ (s_1 - s_2 - s_3 + 1),\ (s_1 - s_2 + s_3 + 2)$~~

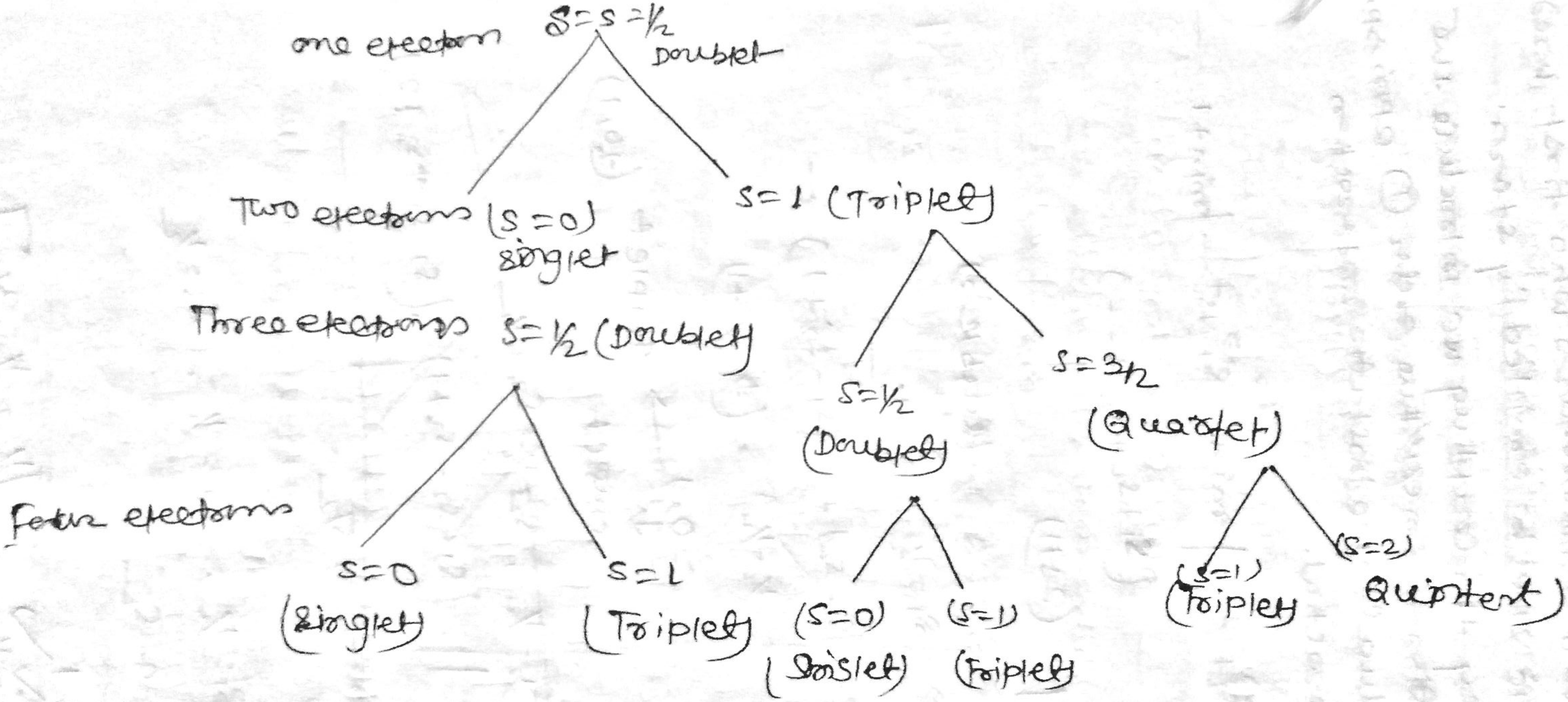
~~$= 1/2,\ 3/2,\ 5/2 \cdots$~~

For 3 ē $\rightarrow s_1 = 1/2,\ s_2 = 1/2,\ s_3 = 1/2$

we know s_1 & s_2

$$S = 0, 1 = [1/2, 1/2, 3/2]$$

again $s_3 = 1/2$


one electron
S=s=½
Doublet
Two electrons (S=0)
singlet
S=1 (Triplet)
Three electrons S=½ (Doublet)
S=½
(Doublet)
S=3/2
(Quartet)
Four electrons
S=0
(Singlet)
S=1
(Triplet)
(S=0)
(Singlet)
(S=1)
(Triplet)
(S=1)
(Triplet)
(S=2)
Quintet)

$L = |\vec{l_1} + \vec{l_2} + \vec{l_3} - |_{min}, \; |\vec{l_1} + \vec{l_2} + \vec{l_3} - |_{min+1} \ldots$

$\ldots (l_1 + l_2 + l_3 + \ldots)$

The states with different values of L have fairly large energy differences, ~~of~~ the one of largest L value being of lowest energy.

$L = 0, 1, 2, 3, 4 \ldots$

S, P, d, F, G

For 3P 3d :-

$l_1 = 1, \; l_2 = 2$

$L = (l_1 - l_2), (l_1 - l_2 + 1), (l_1 + l_2)$

$= \cancel{a}1, \; 2, \; l_1 + l_2 = 3$

1, 2, 3. i.e (P d F states)

For 2P 3P 4d electrons :→

$l_1 = 1, \; l_2 = 1$

$$\begin{tikzcd}[column sep=small]
L_1 = 0 \arrow[d] & 1 \arrow[dl] & 2 \arrow[dll] \\
l_3 = 2 & &
\end{tikzcd}$$

$L_2 = \cancel{2, 3, 4}$

$L_2 = l_1 = 0, \; l_3 = 2$

$L_2 = 2$ i.e D (States) ← (I)

$L_1 = 1, \; l_3 = 2$

then $L_2 = 1, 2, 3$, (P, d, f) States ← (II)

$L_1 = 2, \; l_3 = 2$ then

$L_2 = 0, 1, 2, 3, 4$ i.e (S, P, d, F, G States) (III)

Spin orbit interaction, the resultant orbital angular momentum vector $\vec{L}$ and the resultant spin angular momentum vector $\vec{S}$ are less strongly coupled with each other to form a vector $\vec{J}$

$$\boxed{\vec{J} = \vec{L} + \vec{S}}$$

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

$$J = |L-S|, |L-S+1| \ldots |L+S|$$

Lande interval Rule

L-S Coupling the spin-orbit interaction energy is of the form,

$$\Delta E_{l,s} = a(\vec{L} \cdot \vec{S})$$

where a is an interaction Constant

$$\vec{J} = \vec{L} + \vec{S}$$

Taking scalar self product

$$\vec{J} \cdot \vec{J} = (\vec{L} + \vec{S}) \cdot (\vec{L} + \vec{S})$$

$$\Rightarrow \vec{L} \cdot \vec{L} + \vec{L} \cdot \vec{S} + \vec{S} \cdot \vec{L} + \vec{S} \cdot \vec{S}$$

$$|\vec{J}|^2 = |\vec{L}|^2 + |\vec{S}|^2 + 2\vec{L} \cdot \vec{S}$$

$$\text{or } \vec{L} \cdot \vec{S} = \frac{|\vec{J}|^2 - |\vec{L}|^2 - |\vec{S}|^2}{2}$$

$$\Delta E_{l,s} = \frac{a}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]\frac{h^2}{4\pi^2}$$

but $|\vec{J}| = \sqrt{J(J+1}\,\frac{h}{2\pi}$

$$\boxed{\Delta E_{l,s} = A\left[J(J+1) - L(L+1) - S(S+1)\right]}$$

Fine structure seperation :-

$\left(\frac{0}{1} : \frac{1}{2}\right)$ ${}^3P_0, {}^3P_1, {}^3P_2 \longrightarrow 1:2$ $\left\{ J(J_1+1) : (\right.$

$\frac{2}{1} : \frac{3}{2}$ ${}^3D_1, {}^3D_2, {}^3D_3 \longrightarrow 2:3$

$\frac{3}{2}$ ${}^4D_{1/2}, {}^4D_{3/2}, {}^4D_{5/2}, {}^4D_{7/2} \rightarrow 3:5:7$

$L = 0, S = 1$ then $J = 1$

$L = 1$ $S = 1$ then $J = 2$

$L = 2, 1$ then $J = 3$

$$^3S_1,\ ^3P_2,\ ^3D_3.$$

i.e $^1S_0$, $^1D_2$, $^1P_1$, $^3S_0$, $^3P_2$, $^3D_3$

Order of terms and fine structure levels:-

electronic configuration may be deduced from a set of rules given by Hund. These rules are

(1) Of the terms arising from equivalent electrons those with largest multiplicity lie lowest.

(2) Of the terms, with given multiplicity and arising from equivalent electrons, that with largest L value lie lowest.

Selection Rules for multi electron atom

L-S Coupling

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

$$\Delta l = \pm 1$$

for two electron transition

$$\Delta l_1 = \pm 1, \quad \Delta l_2 = 0, \pm 2$$

Thus for the atom as a whole, the quantum number L-S & J must be follows

$$\boxed{\begin{array}{l} \Delta L = 0, \pm 1 \\ \Delta S = 0 \qquad \Delta J = 0, \pm 1 \quad \text{but } J = 0 \nleftrightarrow J\ 0 \end{array}}$$

J-J Coupling :-

The rules Lands holds only when the spin-orbit (Magnetic coupling is weak i.e when the splitting b/n the various fine structure levels of a Multiplet are very small compared with the seperations b/n the various multiplets themselves

J-J Coupling :-

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

$$J = |\vec{J_1} - \vec{J_2}| \ldots |J_1 + J_2|$$

Selection rules in J-J Coupling

① The parity of the configuration must change in an electric dipole transition (Laporte rule)

One electron jumps in the transition we must have $\Delta l = \pm 1$.

If two electron jumps then $\Delta l_1 = \pm 1$ & $\Delta l_2 = 0, \pm 2$

So, exactly J-J coupling

$\Delta J = 0, \pm 1$ but $J \leftrightarrow J = 0$