M.Sc Semester-II, Paper: CC-06 (Inorganic Chemistry)

Unit: 1 Electronic spectra of Transition metal complexes.

⇒ L-S/Russel-Saunders/Spin-orbit coupling?

In spectroscopy, Russel-Saunders (L-S) Coupling specifies a coupling scheme of electronic spin and orbital angular momentum. It is useful mainly for the higher atoms roughly for atoms with atomic number less than 57. For light atoms, the spin-orbit interaction or coupling is small so that the total/resultant orbital angular momentum (L) and total/resultant spin angular momentum (S) are good quantum numbers. The interaction between L & S is known as L-S coupling or Russel-Saunders coupling. The main points of L-S Coupling scheme are:

1. The S term is one with maximum spin multiplicity $(2S+1)$ or, maximum number of unpaired of electrons.
2. If there are more than one term with same multiplicity ground state term will one with lowest L-value.
3. The lowest energy term (Ground state) will one with highest spin multiplicity.
4. For half filled/more than half filled, ground state term symbol will be of high J-value (i.e., $|L+S|$). For less than half filled, the ground state term symbol will be of low J-value (i.e., $|L-S|$).

⇒ Russel-Saunders Symbol or Term?

It is an abbreviated description of the total angular momentum quantum numbers in a multi-electronic system. However, even a single electron can be described by a term symbol. The Russel-Saunders symbol or Term of a given system is represented as $^{(2S+1)}L_J$, where S = Total/Resultant spin angular momentum quantum no (Σm_s, m_s = spin Q. No.); $2S+1$ = Spin multiplicity; L = Total/Resultant orbital angular momentum quantum no. $= \Sigma m_l$ (m_l = magnetic quantum no.); J = Total/Resultant angular momentum $= |L+S|$ to $|L-S|$.

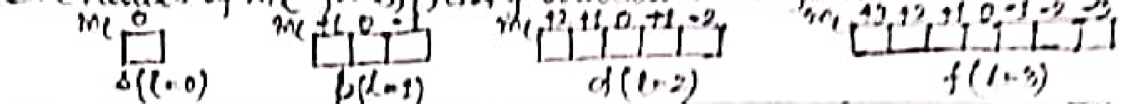
* Ground state term symbol for less than half filled orbital $= {}^{2S+1}L_{J_{min}}$ (i.e., $|L-S|$)
* Ground state term symbol for half/more than half filled orbital $= {}^{2S+1}L_{J_{max}}$ (i.e., $|L+S|$

⇒ Determination of Russel-Saunders Terms/Symbols:

The determination of Russel-Saunders terms for a given system involves following steps:

1. First of all electronic configuration (outer) of given system is shown in box-representation according to Hund's rule. e.g., d^5 conf. as $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$
2. The total/resultant spin angular momentum quantum no. (S) is known by Σm_s (where m_s = spin quantum no, generally unpaired electrons are taken consideration) S arises due to s-s coupling (i.e., spinning motion of electron in orbital). $m_s = +\frac{1}{2}$ for clockwise spin (↑) and $m_s = -\frac{1}{2}$ for anticlockwise spin (↓).
3. Then spin multiplicity is known by $(2S+1)$. e.g. for d^5 system, $S = 5 \times (+\frac{1}{2}) = +\frac{5}{2}$
   Spin multiplicity $= 2S+1 = 2 \times (+\frac{5}{2}) + 1 = 6$.
4. The total/resultant orbital angular momentum quantum no. (L) is known by Σm_l (where m_l = magnetic quantum no.). L arises due to l-l coupling (i.e., angular motion of electron in orbital). The value of L ranges from $(l_1 + l_2)$ to $(l_1 - l_2)$. L value will decide spectroscopic symbol.

The values of m_l for s, p, d & f orbitals are as follows:



L value:	0	1	2	3	4	5
Spectroscopic Symbol:	S	P	D	F	G	H.

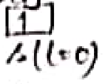
e.g. for d^5 conf., L = +2+1+0-1+2 = 0, So spectroscopic symbol is S.

5. Now, total/resultant angular momentum quantum no. (J) is known. J arises due to L-S coupling in multi electronic system. J can have the values ranging from (L+S) to (L-S) or S-L whichever is positive. For half filled or more than half filled, high J value, i.e., |L+S|, and for less than half-filled less J value, i.e., |L-S| is used in writing Russel-Saunders ground state term symbol.

6. Finally, spin multiplicity (2S+1) is written as superscript on LHS and total/resultant angular momentum (J) as subscript on RHS of spectroscopic symbol corresponding to L value as follows: $^{(2S+1)}L_J$.

⇒ Q. Determine ground state term symbol of following: (a) Mg^+ (b) P^{3+} (c) V^{2+} (d) Ni^{2+}

Ans. (a) Mg^+ : It has $2s^1$ Conf. or,

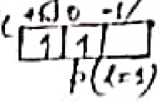


; $S = \Sigma m_s = +1/2$; $2S+1 = 2(+1/2)+1 = 2$.

$L = 0 (S)$; $J = |0+1/2|$ to $|0-1/2| = 1/2$

Spectroscopic term: ^2S ; Term Symbol/G.S. Term Symbol: $^2S_{1/2}$.

(b) P^{3+} : It has $2p^2$ Conf. or



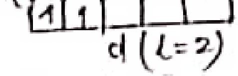
$S = \Sigma m_s = +1/2+1/2 = 1$; $2S+1 = 2\times1+1 = 3$

$L = +1+0 = 1 (P)$; $J = |1+1|$ to $|1-1|$ or 2 to 0 = 2, 1, 0

Spectroscopic term: ^3P

Term symbol: $^3P_2$, $^3P_1$, $^3P_0$; G.S. Term Symbol: $^3P_0$.

(c) V^{3+} : It has $3d^2$ Conf. or,



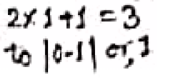
$S = \Sigma m_s = +1/2+1/2 = 1$; $2S+1 = 2\times1+1 = 3$

$L = +2+1 = 3 (F)$; $J = |3+1|$ to $|3-1|$ or, 4 to 2 = 4, 3, 2

Spectroscopic term: ^3F ; Term Symbol: $^3F_4$, $^3F_3$, $^3F_2$.

Ground state term Symbol: $^3F_2$

(d) Ni^{2+} : It has d^8 conf. or,



$S = \Sigma m_s = +1/2+1/2 = 1$; $2S+1 = 2\times1+1 = 3$

$L = +2+1+0-1+2 = 0$; $J = |1+0|$ to $|0-1|$ or, 1

Spectroscopic Symbol: ^3S

Term symbol/Ground state term Symbol: $^3S_1$

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