Determination of Ground State Term Symbol. —

The ground state of any electronic configuration has many microstates. In microstates the energy levels are found to be different. To obtain the order of lowest to highest energy level Hund's rule is followed.

Hund's Rule -

(1) The term symbols are arranged in decreasing order of their multiplicity $(2S+1)$. It is related to the value of S. Greater the value of S greater will be the multiplicity. Thus the term symbols may be arranged in decreasing order of the values of S.

For example - For carbon p^2 configuration has 3 and 1 multiplicity. For multiplicity 3 and 1 values of S are 1 and 0 respectively. Hence according to this rule, the term symbol of 3 multiplicity will have the lowest energy.

(2) For the given values of S the highest value of L, will be more stable i.e. will have lowest energy. Two term symbols ^1D and ^1S of p^2 configuration of carbon have zero value of resultant S. For D and S the values of L are 2 and 0. Hence the term symbol ^1D having the highest value of L i.e 2 will have lowest energy.

(3) If Suborbit is less than half filled, lowest value of J and if the suborbit is more than half filled, the highest value of J gives most stable states.

The above rule can be explained taking ex. of p^2 configuration of carbon.

For carbon ^3P, ^1D and ^1S three term symbols. According Hund's first law ^3P state will be most stable as its multiplicity is maximum 3. Hence it will be assumed as a true ground state or lowest energy state. According to second law in ^1D and ^1S the value of L for ^1D is 2 which is greater than the zero value of L for ^1S. Hence the energy of ^1D will be lower than ^1S. The multiplicity of ^3P is 3. Hence for the three states related to 0, 1 and 2 three values of J will be $^3P_0$, $^3P_1$ and $^3P_2$.

The p suborbit of carbon is less than half filled.
Than according third law the term symbol having zero
value of J will have the lowest energy.

$$^3P_0 < ^3P_1 < ^3P_2$$

Hence the order according to energy of obtained term
symbols can be given as below :—

$$^3P < ^1D < ^1S$$

Thus the order of energy of the triplet state ^3P and
singlet state of ^1D and ^1S will be.

$$^3P_0 < ^3P_1 < ^3P_2 < ^1D_2 < ^1S_0$$
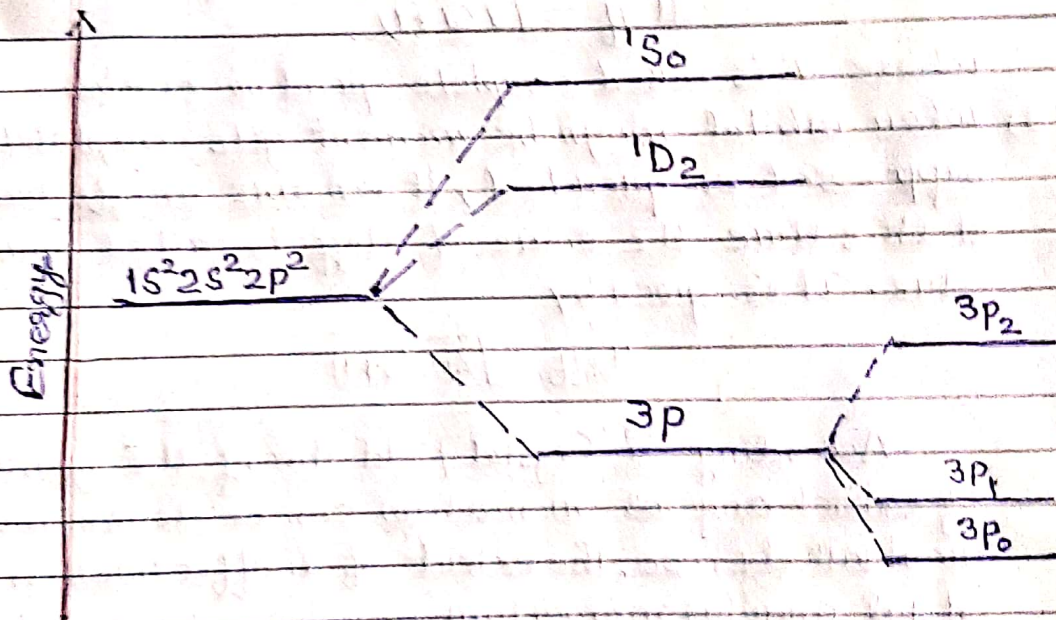
These states of carbon can be shown in Fig —

Fig — The order of energy of states obtained by L-S coupling
of carbon

Correlation of μ_s and μ_{eff} values —

μ_s is spin only and μ_{eff} is effective magnetic moment.
The spin magnetic moment (μ_s) is produced due to spin
of electron on its axis in an atom. Effective moment is
the resultant magnetic moment, then

$$\mu_{L+s} = \sqrt{L(L+1) + 4S(S+1)} \quad B.M.$$

According to VBT there are three relations conditions
for obtaining the effective magnetic moment.

(1) When L-S coupling occurs, new quantum number J are obtained. The energy level J of ground state obtained by L-S coupling are very close to each other, Then

$$\mu_{eff} = \sqrt{L(L+1) + 4S(S+1)}$$

(2) When energy levels J produced by L-S coupling have too much difference with each other in ground state J-J coupling takes place. At this time the L-S coupling is found to be uneffective. The value of μ_{eff} is determined by the following formula —

$$\mu_{eff} = \sqrt{J(J+1)}$$

where J is called complete quantum number.

(3) When orbital magnetic moment gets completely suppressed or quenched, it remains uneffected. At this time the value of μ_{eff} is called spin only value. It is given by

$$\mu_{eff} = \sqrt{4S(S+1)}$$

According to Crystal field theory, the quenching of orbital angular momentum can be determined quantitatively also. The extent of ineffectiveness of orbital angular momentum can be determined by this theory. In this way the contribution of μ_L (orbital) magnetic moment to μ_{eff} value can be determined.

Orbital Contribution to Magnetic Moments

In free ions the orbitals of sub orbit have same energy i.e. show degeneracy. Equivalent orbitals are the orbitals having identical shape, size and energy. If on revolving the $d_{x^2-y^2}$ orbital of d suborbit along z axis it gets changed into its equivalent d_{xy} orbital after 45° rotation. Hence the electron of $d_{x^2-y^2}$ orbital will have angular moments relative to z axis. The value of this orbital momentum can be determined by the

following formula :-

$$\text{Orbital momentum} = \frac{90}{\text{angle required to change into equivalent orbital}}$$

The orbital momentum has $\frac{h}{2\pi}$ unit.

For example dx^2-y^2 orbital gets converted into dxy after $45°$ rotation. Orbital momentum of dx^2-y^2 relative to z axis,

$$= \frac{90}{45} = 2$$

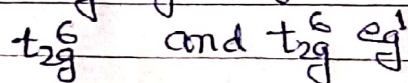If dxz orbital is rotated along the z axis, it gets converted into equivalent dyz orbital after $90°$ rotation. Hence the orbital momentum of dxz will be $90/90 = 1$. dz^2 orbital does not have its equivalent orbital. Hence it will have zero orbital angular momentum relative to z axis.

The equivalence of d orbitals is not found, in tetrahedral and octahedral complexes metal ions are in contact of 4 and 6 ligands respectively. In octahedral complexes if t_{2g} orbitals are either half filled or full filled, orbital angular momentum is found to be zero. Hence in this condition the contribution of orbital magnetic moment will be zero, and following configuration to μ_{eff} value is 0.

In presence of weak ligand field —

$$t_{2g}^3 \, , \, t_{2g}^3 e_g^1 \, , \, t_{2g}^3 e_g^2 \, , \, t_{2g}^6 e_g^2 \text{ and } t_{2g}^6 e_g^3$$
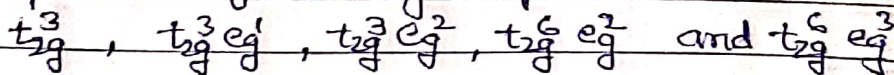
In presence of Strong ligand field —

$$t_{2g}^6 \text{ and } t_{2g}^6 e_g^1$$

But in the octahedral complexes the following configuration

$$t_{2g}^1 \, , \, t_{2g}^2 \, , \, t_{2g}^4 \text{ and } t_{2g}^5$$

We can say in octahedral complexes metal ions having A or E ground state do not contribute orbital magnetic moment to μ_{eff}. In these complexes the metal ions with T ground state contribute orbital magnetic moment to μ_{eff}. μ_{eff} depends on the extent of mixing of ground state and excited state

$$\mu_{eff} = \mu_s \, (1 - \alpha\lambda/\Delta)$$