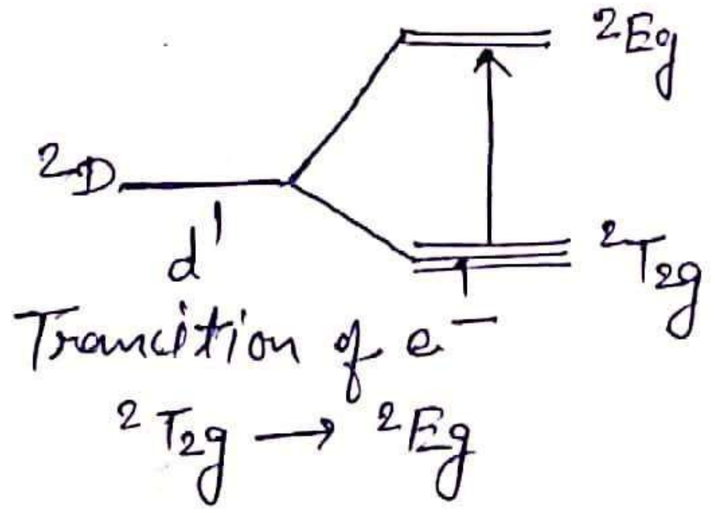
A more appropriate description of colour and electronic spectra, can be given by the splitting of ground energy terms of different configuration and transition between newly formed ground term and newly formed excited terms. Following splitting diagrams explain the electronic transitions involved in different cases of d^1 to d^9 configurations.

For d^5 configuration, the ground energy term is 6S. It will not split in octahedral field. The transition in this case takes place from sixtet term into quartet term. (eg. Mn^{2+} and Fe^{3+} in octahedral field)

① Splitting of D-term $\longrightarrow$ $T_{2g} + E_g$

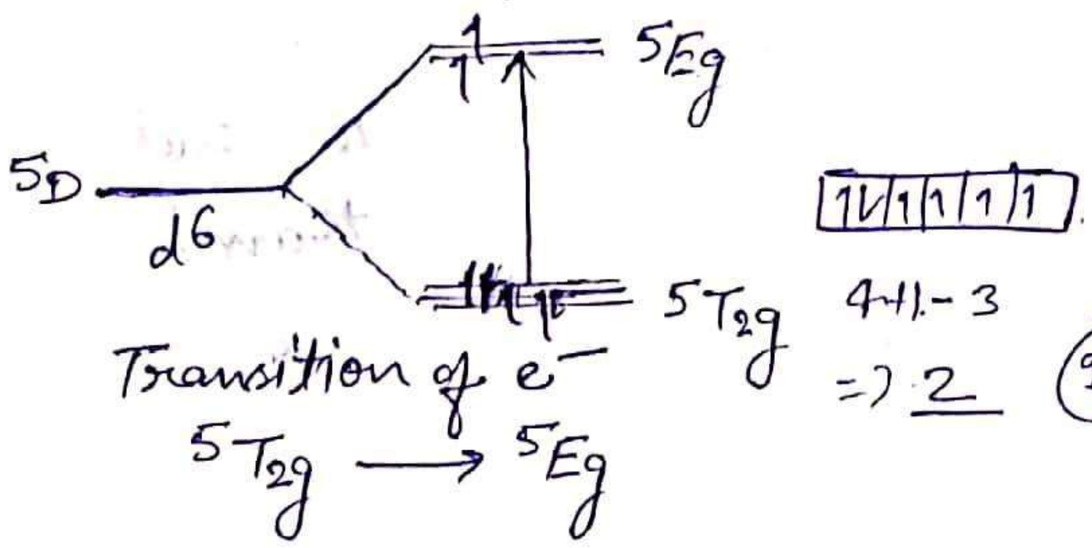
(i) For d^1 configuration



Transition of e^-

$^2T_{2g} \rightarrow {}^2E_g$

(ii) For d^6 - configuration.

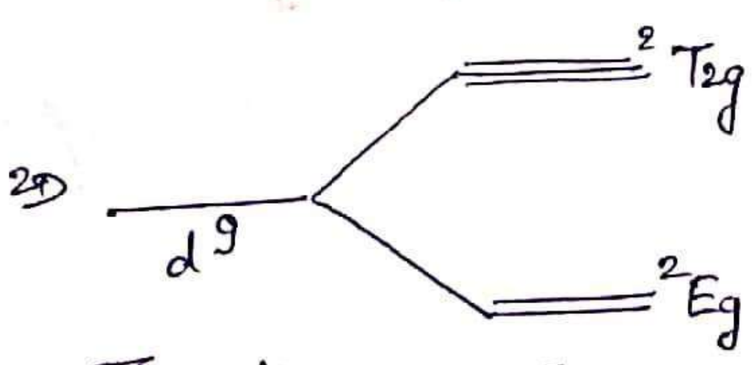


Transition of e^-

$^5T_{2g} \longrightarrow {}^5E_g$

4+1-3
=> 2 (D)

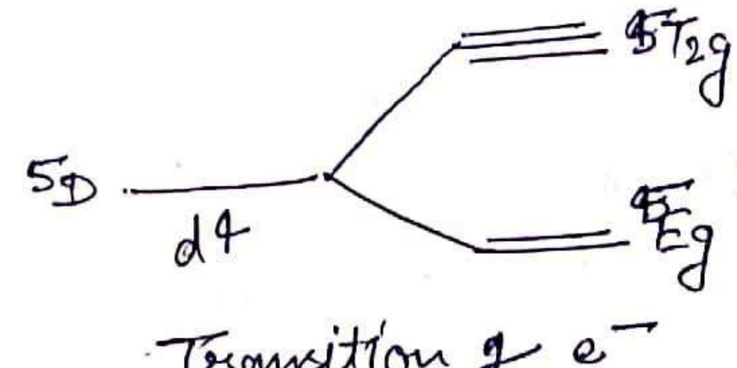
(iii) For d^9 configuration



Transition of e^-

$^2E_g \rightarrow {}^2T_{2g}$

(iv) For d^4 configuration.



Transition of e^-

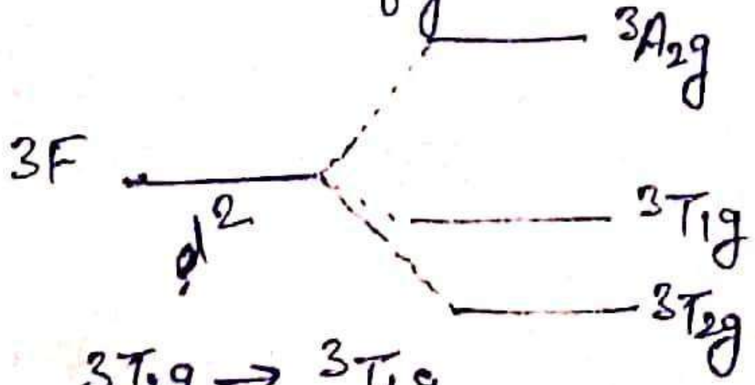
$^5E_g \rightarrow {}^5T_{2g}$

In d^1, d^6, d^4, d^9 configurations spectrum shows single band. The energy term of d^1 and d^6 split alike and energy term of d^4 and d^9 configuration split alike.

② Splitting of F-term.

F-term $\longrightarrow$ $T_{2g} + T_{1g} + A_{2g}$.

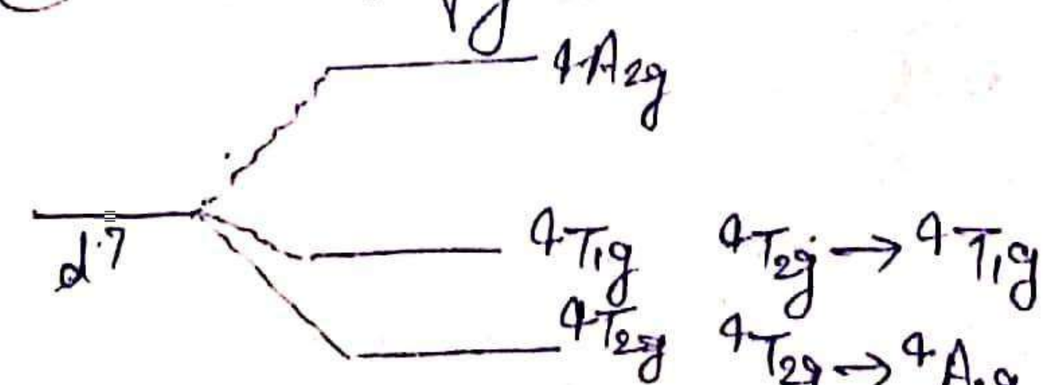
(i) For d^2 - Configuration.



$^3T_{2g} \rightarrow {}^3T_{1g}$

$^3T_{2g} \rightarrow {}^3A_{2g}$

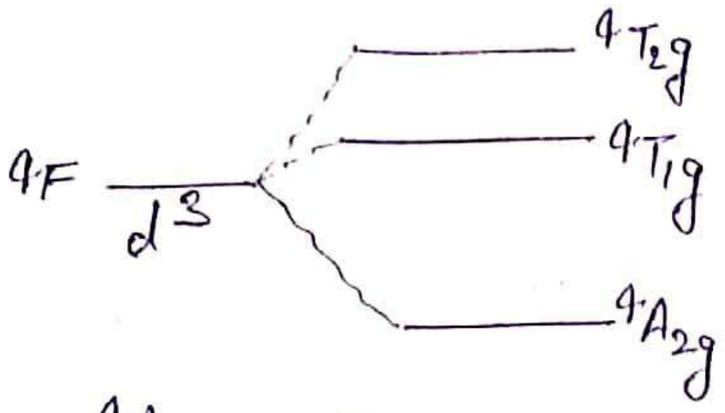
(ii) For d^7 configuration.



$^4T_{2g} \rightarrow {}^4T_{1g}$

$^4T_{2g} \rightarrow {}^4A_{2g}$

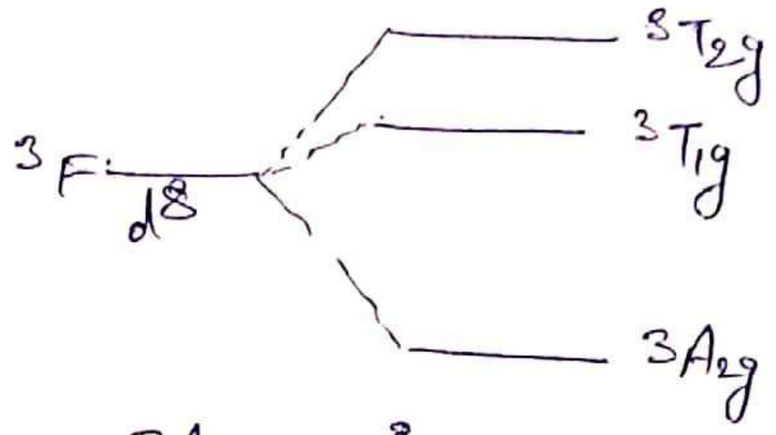
(iii) For d^3 configuration.



$^4A_2g \rightarrow {}^4T_1g$

$^4A_2g \rightarrow {}^4T_2g$

For d^8 configuration.



$^3A_2g \rightarrow {}^3T_1g$

$^3A_2g \rightarrow {}^3T_2g$

In case of d^2, d^7, d^3, and d^8, the spectrum show two bands. The splitting of energy terms of d^2 and d^7 and d^3 & d^8 are alike.

(2.) Charge Transfer — If there is no unpaired electron in d-subshell of transition metal ion and compound of this ion shows colour then it is due to charge transfer. Charge transfer bands are of two types -

(i) Ligand to Metal Charge Transfer band -

When the electronic transition takes place from a molecular orbital located primarily on the ligand to a non-bonding or antibonding molecular orbital located primarily on the metal atom, the ligand to metal ($L \rightarrow M$) charge transfer bands are observed. This cannot be explained by Crystal-field theory and represents the tendency of ligands to reduce the metal ion. CdS, HgI_2, MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$ are the examples of this type of compounds exhibiting charge transfer bands.

(ii) Metal to Ligand Charge Transfer Band — These involve the transition of electrons from an non-bonding or antibonding orbital concentrated on the metal ion to the antibonding orbital located primarily on the ligands and measures the tendency of metal ion to reduce the ligands. The $M \rightarrow L$ bands are observed generally for the metal ion in low oxidation state in the U.V. region but are seen many times in the tail of visible region. eg. $[Fe(dipy)_3]^{2+}$ and $[Fe(o\text{-phen})_3]^{2+}$

Note: (1.) d-d-transitions are forbidden transitions because $\Delta l = 0$ but this may take place as a result of breakdown of this selection rule (d-p mixing)

(2.) Charge transfer band is more intense than d-d transition band.

(3) Magnetic Properties -

Free transition metal ions frequently have unpaired d-electrons Many compounds having these ions with electronic configurations of unpaired d-electrons show paramagnetic behaviour.

Fe, Co, Ni are ferromagnetic and there ions show mainly paramagnetic behaviour.

However, certain ions are also there, which do not show configurations with unpaired electrons. rather have paired d-electrons. For eg. Sc(III), Ti(IV), Zn(II), Cu(I) etc.

The Cu^+ is diamagnetic.

3d [↑↓ ↑↓ ↑↓ ↑↓ ↑↓] 4s [↑↓]

The Cu^{2+} ion is paramagnetic.

3d [↑↓ ↑↓ ↑↓ ↑↓ ↑] 4s [ ]

The general equation for magnetic moment of the transition metal is —

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

Where S = Total spin angular momentum quantum No.

L = Total orbital angular momentum quantum No.

μ_{S+L} = Magnetic moment due to spin and orbital momentum.

For, 1st row transition metals the contribution of total orbital angular momentum quantum No. is zero i.e. $L = 0$.

Hence, $\mu_S = \sqrt{4S(S+1)}$

where μ_S ⇒ Magnetic moment due to spin only moment.

If the ions of compounds contains 'n' no. of electrons (unpaired).

$$S = \frac{n}{2}$$

Hence. $\mu_S = \sqrt{4S(S+1)} = \sqrt{\frac{2}{4} n\left(\frac{n}{2}+1\right)}$

$$\mu_S = \sqrt{n(n+2)} \quad \text{B.M.}$$

Where 1 BM = $\frac{eh}{4\pi mc}$

e = electronic charge
h = Plancks constt.
m = rest mass of e^-
c = velocity of e^- (light)

in n = 1, μ_S = 1.73
n = 2, μ_S = 2.83
n = 3, μ_S = 3.87
n = 4, μ_S = 4.92
n = 5, μ_S = 5.90.

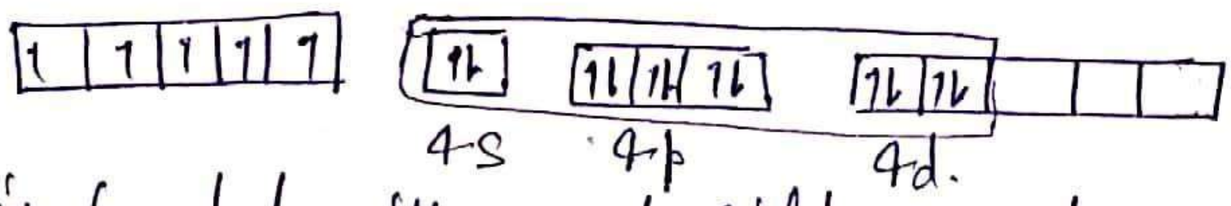
For 4d & 5d elements, the spin only moment becomes smaller but it seldom retains μ_{S+L} value.

For inner transition elements it is essential to combine spin and orbit motion & the results may be obtained by Russel-Saunder's Coupling Scheme. & evaluating the value.

$$\mu = g\sqrt{J(J+1)}$$

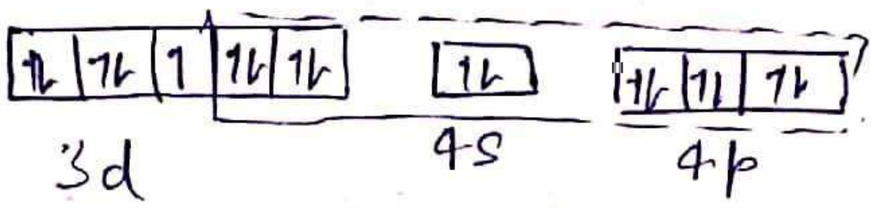
g = gyrometric ratio, i.e ratio of megnetic moment and angular momentum. (Lande's 'g' factor). $g = 2$ for d-electrons. For f-electrons with the help of S, L and J value.

In $FeCl_3 \cdot 6H_2O$. or $[Fe(H_2O)_6]^{3+}$, Fe^{3+} has 5 unpaired electrons.



B/c it is bonded with weak field ligand. sp^3d^2

For $[Fe(CN)_6]^{3-}$ – there is only 1 unpaired electron.



d^2sp^3

(9.) **Ability to form Complexes –**

Transition metals form a variety of co-ordination compounds This is due to the fact that T.E metal ions are small, highly charged ions and have vacant orbitals of approximately the correct energy to accept the lone-pair of e^- donated by other gps or ions. (ligands).

Several types of compounds varying from coordination No. 2-8 are known. The geometries of these complexes depend on the participation of different orbitals (hybrid orbitals).

C.No 2 → Linear.
C.No. 3 → Trigonal Planar.
C.No. 4 → Td & Sq. Planar
C.No. 5 → Sq. pyramidal
C.No. 6 → Octahedral.
C.No 7 → less common, trigonal prismatic, pentagonal bipyramidal and capped trigonal prism.
C.No. 8 → Square antiprism & dodecahedral e.