Calculation of CFSE in octahedral crystal field:

(I) d^1 system:-

$Sc_{21} \rightarrow [Ar]\, 3d^1 4s^2$

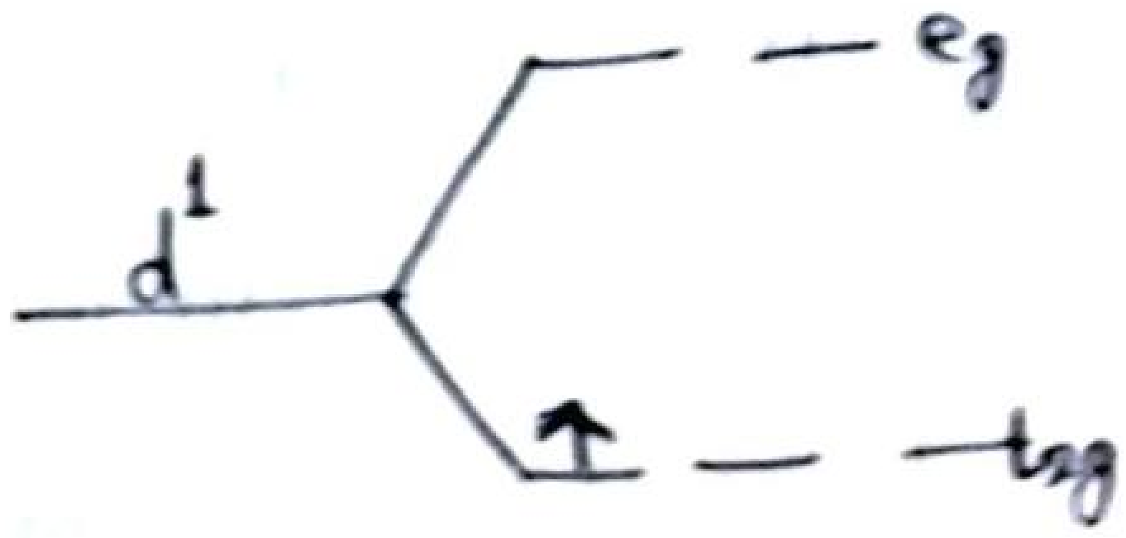
$Sc^{+2} \rightarrow [Ar]\, 3d^1$

$Ti_{22} \rightarrow [Ar]\, 3d^2 4s^2$

$Ti^{+3} \rightarrow [Ar]\, 3d^1$

$V_{23} \rightarrow [Ar]\, 3d^3 4s^2$

$V^{+4} \rightarrow [Ar]\, 3d^1$



m = No. of electron in t2g
n = No. of electrons in eg.

$$CFSE = [m \times (-4Dq) + (n \times +6Dq)]$$
$$= [m \times (-0.4\Delta_0) + n \times (0.6\Delta_0)]$$
$$= 1 \times -4Dq + 0 \times +6Dq$$
$$= -4Dq$$

* d-d transition: By the absorption of energy = Δ_0 or 10 Dq, the electron of t2g may jump to eg, this is called d-d transition of electrons. So octahedral complexes of d^1 system are coloured due to d-d transition.

* Magnetic Property: Paramagnetic

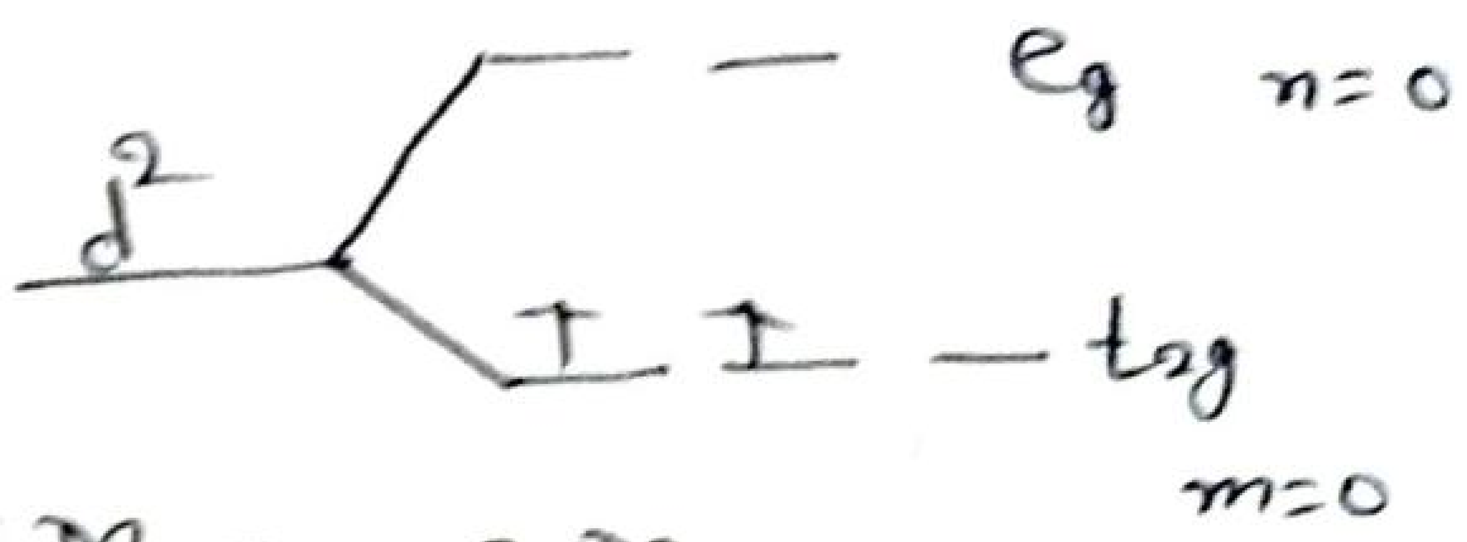
$$\text{Mag. Moment, } \mu_s = \sqrt{n(n+2)} \text{ BM}$$
$$= \sqrt{1(1+2)} \text{ BM}$$
$$= \sqrt{3} \text{ BM} = 1.73 \text{ BM}$$

* Q. Why the colour due to d-d transition is faint?
→ d-d transition is Laporte forbidden transition and hence the colour due to d-d transition is faint.

(II) d^2 system   Ti (II), V(III), Cr (IV)

$Ti_{22} \rightarrow [Ar]\, 3d^2\, 4s^2$

$Ti^{+2} \rightarrow [Ar]\, 3d^2$



CFSE = $2 \times -4Dq + 0 \times 6Dq = -8Dq$.

Paramagnetic

$\mu_s = \sqrt{2(2+2)}$ BM $= \sqrt{8}$ BM $= 2\sqrt{2}$ BM $= 2 \times 1.414$ BM
$= 2.828$ BM

Coloured due to d-d transition.

(III) d^3 system   V(II), Cr(III), Mn(IV)

CFSE = $3 \times -4Dq + 0 \times +6Dq$.
$= -12Dq$.

Paramagnetic

$\mu_s = \sqrt{3(3+2)}$ BM $= \sqrt{15}$ BM $= 3.8$ BM.

Complexes are coloured due to d-d-transition.

(IV) d^4 system   Cr(II), Mn(II)

$Cr_{24} \rightarrow [Ar]\, 3d^5\, 4s^1$

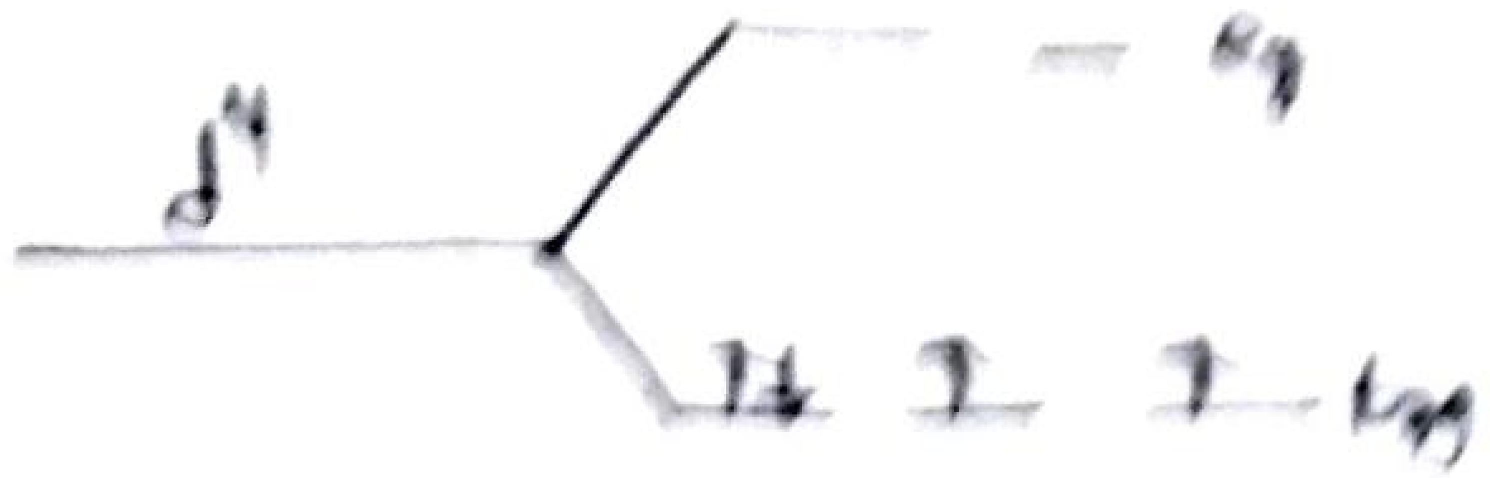
$Cr^{+2} \rightarrow [Ar]\, 3d^4$

$Mn_{25} \rightarrow [Ar]\, 3d^5\, 4s^2$

$Mn^{+2} \rightarrow [Ar]\, 3d^4$.

d^4 system

(a) If $\Delta_o > P$, the electrons prefer to pair up in t_{2g}, such complexes are called spin paired complexes or Low spin complexes



$t_{2g}^4 e_g^0$

$S = +\frac{1}{2} - \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 1$

Spin paired octahedral complex
or
Low spin octahedral complex

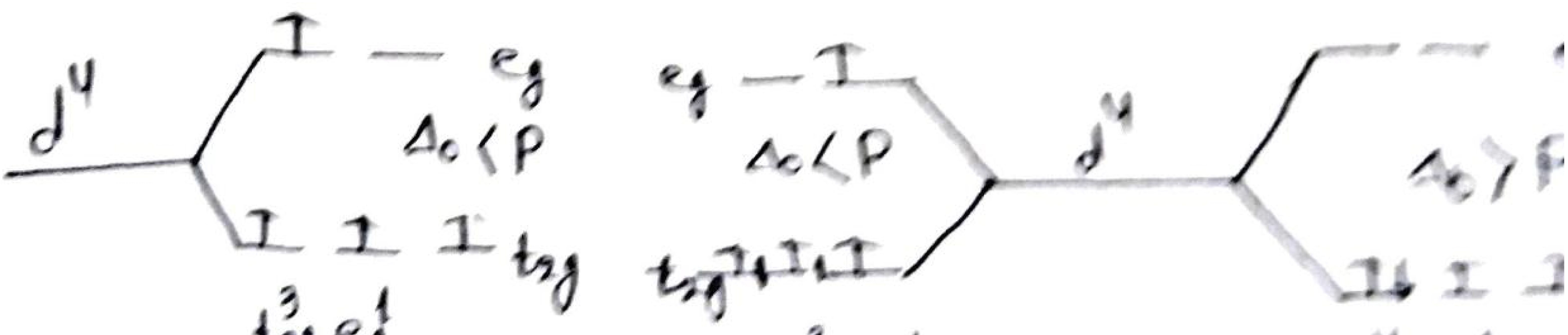
$CFSE = 4 \times -4Dq = -16Dq$

Paramagnetic

$\mu_s = \sqrt{n(n+2)} = \sqrt{8}\ BM = \sqrt{2 \times 4}\ BM = 2.83\ BM$
$= 2.828\ BM$

coloured due to d-d transition

(b) If $\Delta_o < P$, the electron prefers to go e_g orbital than to pair up in t_{2g} orbitals, such complexes are called high spin complexes or spin free complexes.



$t_{2g}^3 e_g^1$
High spin or spin free complex

$t_{2g}^4 e_g^0$
Low spin or paired complex

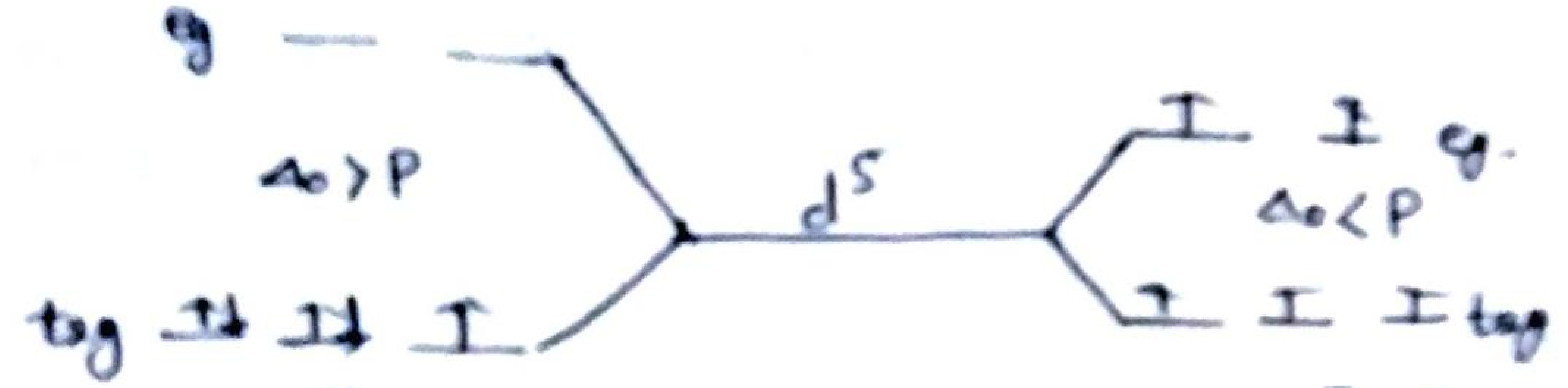
$CFSE = 3 \times -4Dq + 1 \times 6Dq$
$= -12Dq + 6Dq = -6Dq$

complexes: paramagnetic

$\mu_s = \sqrt{4(4+2)}\ BM = \sqrt{24}\ BM$

complexes are coloured due to d-d transition.

(V) d^5 system : Mn(II), Fe(III), Co(IV)



$t_{2g}^5 e_g^0$ $t_{2g}^3 e_g^2$

(a) $\Delta_o > P$

Spin paired or Low spin complex

$CFSE = 5 \times -4Dq + 0 \times 6Dq$

$= -20 Dq$

Paramagnetic

$\mu_s = \sqrt{1(1+2)}$ BM

$= 1.73$ BM

colour due to d-d transition

(b) $\Delta_o < P$

Spin free or High spin complex

$CFSE = 3 \times -4Dq + 2 \times 6Dq$

$= 0 Dq.$

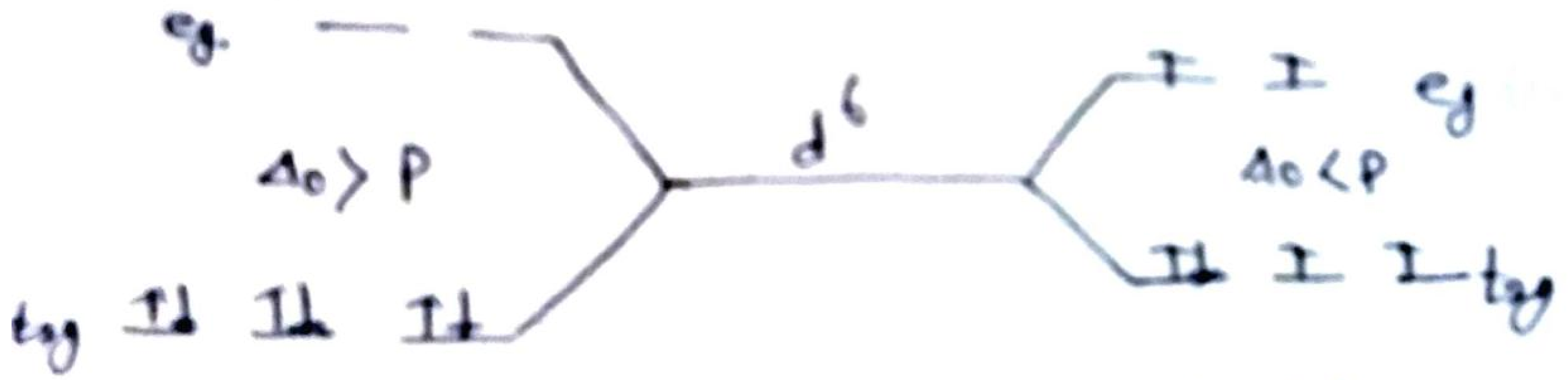
Paramagnetic

$\mu_s = \sqrt{5(5+2)}$ BM

$= \sqrt{35}$ BM

coloured due to d-d transition

VI) d^6 system : Fe(II), Co(III).



a) $\Delta_o > P$

$t_{2g}^6 e_g^0$

$CFSE = 6 \times -4Dq + 0 \times 6Dq$

$= -24 Dq$

Diamagnetic

$\mu_s = 0$

coloured due to d-d transition

(b) $\Delta_o < P$

$t_{2g}^4 e_g^2$

$CFSE = 4 \times -4Dq + 2 \times 6Dq.$

$= -16 Dq + 12 Dq$

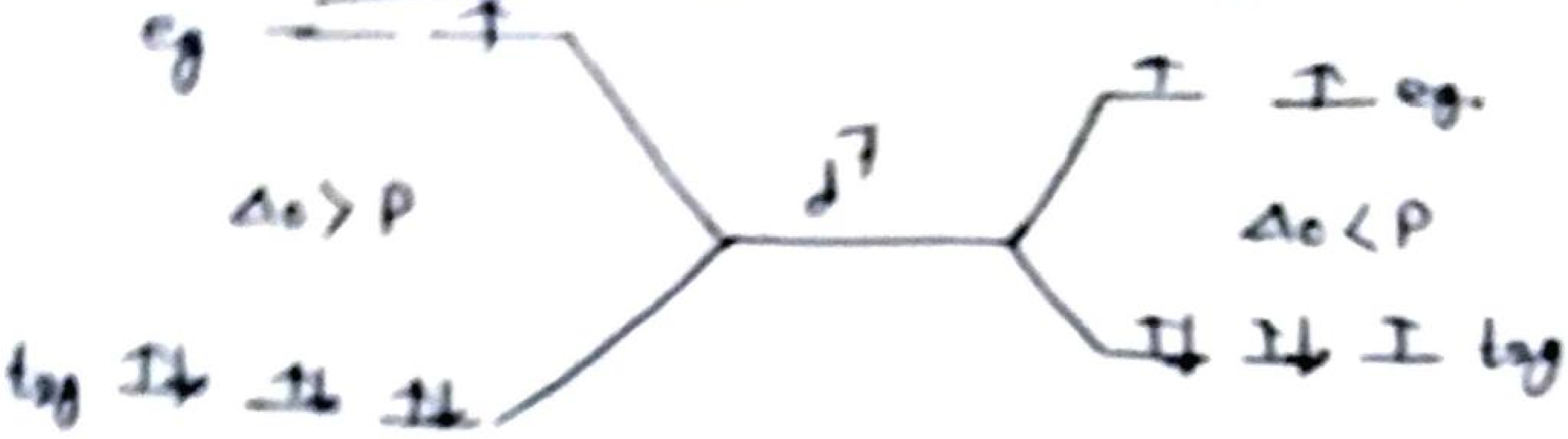
$= -4 Dq.$

Paramagnetic

$\mu_s = \sqrt{4(4+2)} = \sqrt{24}$ BM

coloured due to d-d transi[tion]

(VII) d^7 system : Co(II), Ni(III)



(a) $\Delta_o > P$

$t_{2g}^6 e_g^1$

CFSE = 6×-4 Dq + 1×6 Dq

= -18 Dq.

Paramagnetic

$\mu_s = \sqrt{1(1+2)}$ BM = 1.732 BM

coloured due to d-d transition

(b) $\Delta_o < P$

$t_{2g}^5 e_g^2$

CFSE = 5×-4 Dq + 2×6 Dq

= -8 Dq

Paramagnetic

$\mu_s = \sqrt{3(3+2)}$ BM = $\sqrt{15}$

(VIII) d^8 system : Ni(II)

(a) $\Delta_o > P$

$t_{2g}^6 e_g^2$

CFSE = 6×-4 Dq + 2×6 Dq

= -12 Dq.

Paramagnetic

$\mu_s = \sqrt{2(2+2)}$ BM = $\sqrt{2 \times 4}$ BM

= $2\sqrt{2}$ BM = 2×1.414 = 2.828 BM.

coloured due to d-d transition

(b) $\Delta_o < P$

$t_{2g}^6 e_g^2$

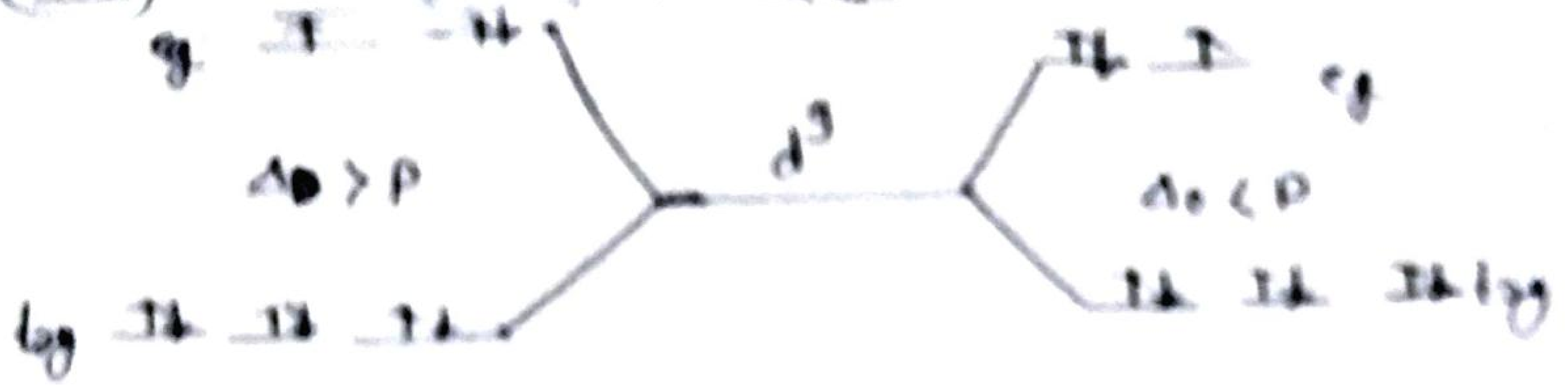
CFSE = -12 Dq

Paramagnetic

μ_s = 2.828 BM

coloured due to d-d transition

(IX) d^9 system : Cu(II)



(a) $\Delta_o > P$

$t_{2g}^6 \; e_g^3$

CFSE = $6 \times -4Dq + 3 \times 6Dq$

= $-6Dq$

Paramagnetic

$\mu_s = \sqrt{1(1+2)}$ BM = 1.732 BM

(b) $\Delta_o < P$

$t_{2g}^6 \; e_g^3$

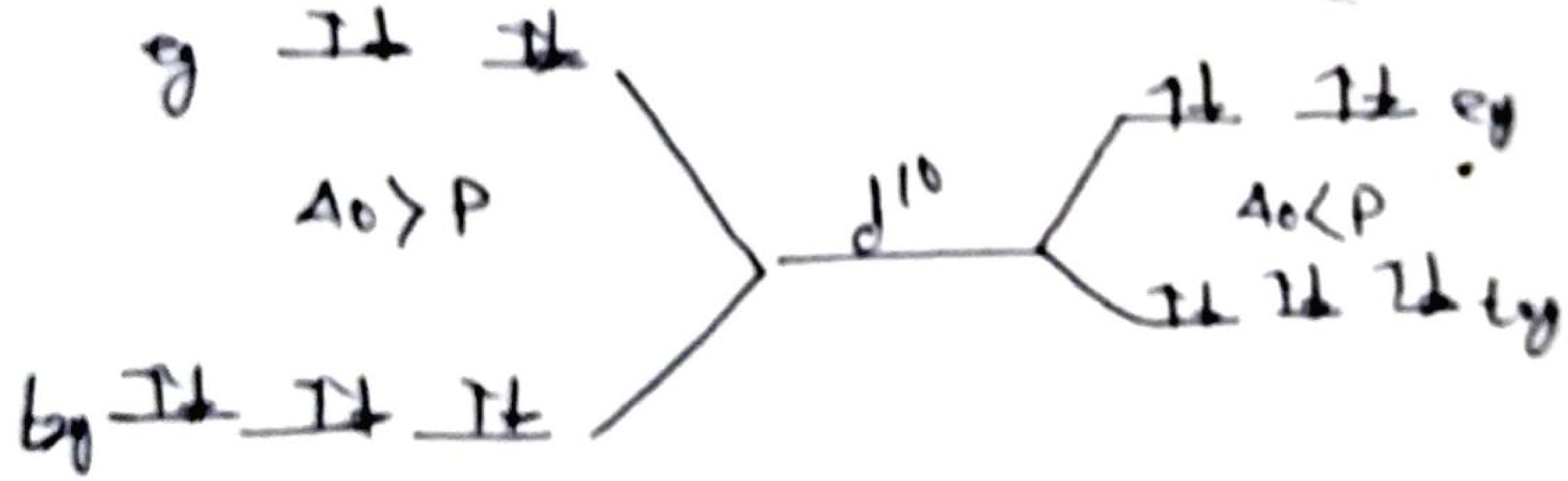
CFSE = $-6Dq$.

Paramagnetic

$\mu_s = 1.732$ BM

coloured due to d-d transition.

(X) d^{10} system ; Cu(I), Zn(II)



(a) $\Delta_o > P$

$t_{2g}^6 \; e_g^4$

CFSE = $6 \times -4Dq + 4 \times 6Dq$

= 0

(b) $\Delta_o < P$

$t_{2g}^6 \; e_g^4$

CFSE = 0

Diamagnetic

$\mu_s = \sqrt{0(0+2)}$ BM = 0

colourless due to lack of d-d transition