Lecture Series on 'Crystal Field Theory'

By
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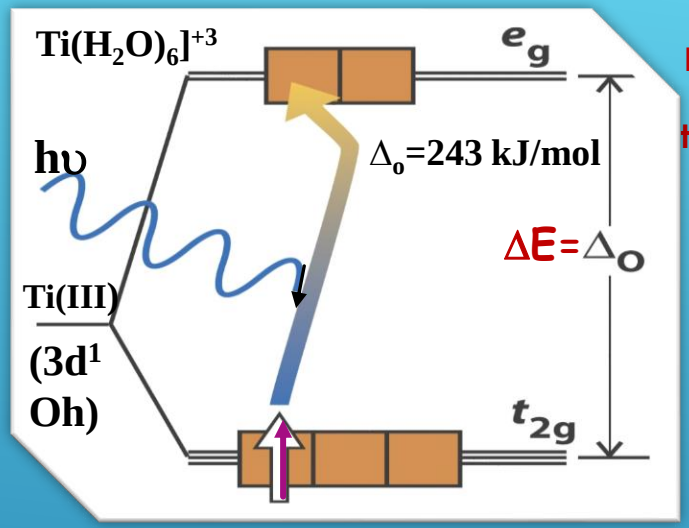
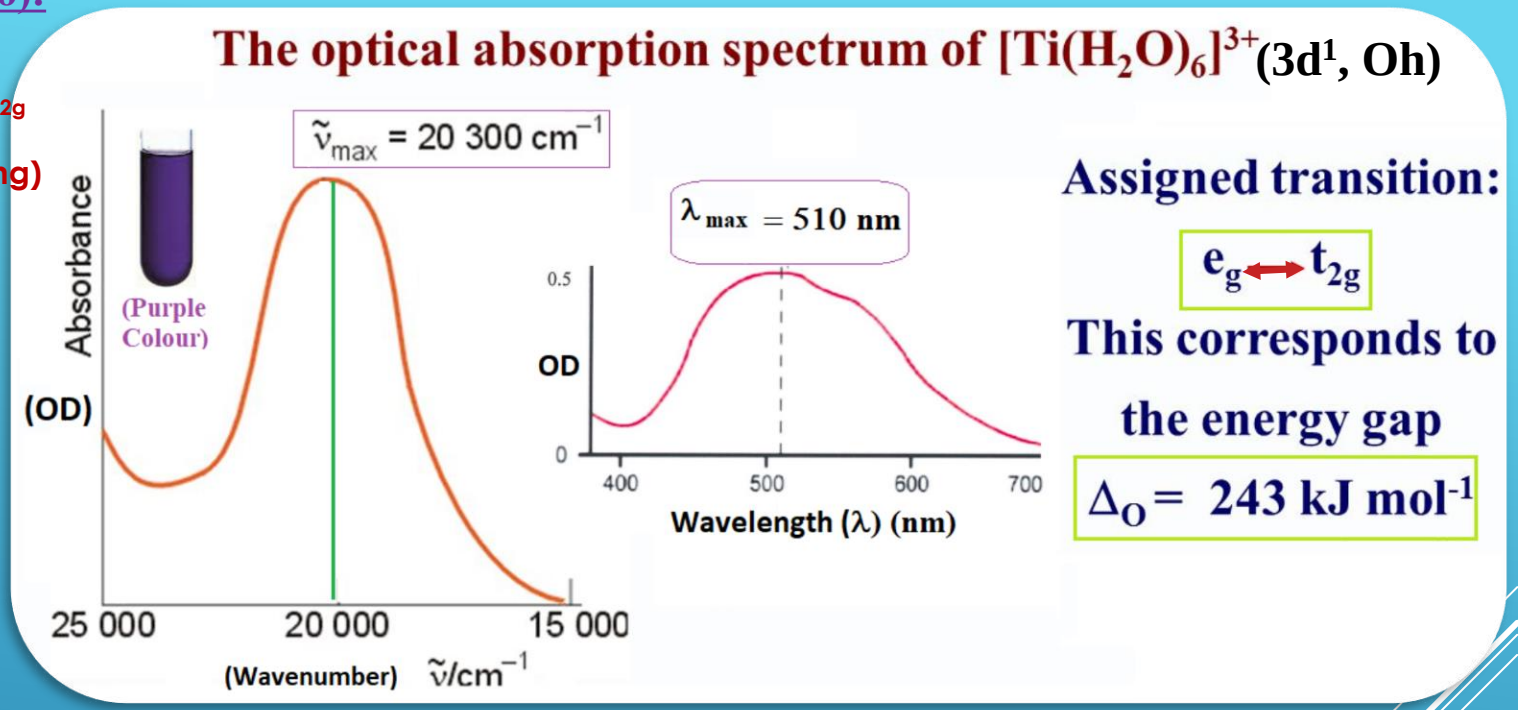
For M.Sc., NET, GATE.

Lecture-III

Experimental determination of Crystal field splitting (Δo):



The energy gap between the e_g and t_{2g} orbitals, Δ_0, the crystal field splitting) equals the energy of a photon: $10Dq_o=\Delta_0 = \Delta E = h\nu = h(c/\lambda)$



- Δ_{oct} is a measurable quantity (experimentally)
- In this case, Ti^{3+} (d^1) has a λ_{max} = 20,300 cm^{-1} or 243 kJ mol^{-1} for the energy required to promote an electron from the **t_{2g} to e_g set**.
- After splitting of d-orbital in Oh field, this complex is stabilized to the extent of 97 kJ/mol [243 x (-0.4)=-97 kJ/mol] wrt hypothetical spherical field. This extra stabilization of the complex is called crystal field stabilization energy (CFSE).

Here, wave-number $(1/\lambda) = 20{,}300\ cm^{-1} = 20{,}300 \times 100\ m^{-1} = 2.03 \times 10^6\ m^{-1}$.

Hence, $\Delta E = h\upsilon = h(c/\lambda) = (6.625 \times 10^{-34}\ j\text{-}s\text{-}molecule^{-1}) \times (3.0 \times 10^8\ m/s) \times (2.03 \times 10^6\ m^{-1}) = 4.034 \times 10^{-19}\ J\text{-}molecule^{-1} = (4.034 \times 10^{-19}) \times (6.023 \times 10^{23}\ J\text{-}mol^{-1}) = 243\ KJ/mol. = \Delta_{oct}$

***(1000 cm^{-1} = 11.96 kJ/mol or 2.86 kcal/mol or 0.124 eV.)*

❖ **The UV-Vis absorption spectrum reveals that this transition occurs with a maximum at 20300 cm^{-1} which corresponds to Δ_o ($10Dq_o$) 243 kJ/mol. However, this is applicable for one-electron transition which reflects the energy difference between t_{2g} & e_g. For more than one electronic systems electron-electron repulsion must be taken into consideration and hence calculation becomes may more difficult.**

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Lecture-3

❖Significance of Dq_0:

The term Dq is the product of two terms D and q required in the quantitative treatment of CFT to describe the Hamiltonian operator of the system. Thus, D and q are the potential energy terms and in the Oh-crystal field, these are given by:

$D=35 * Ze/4a^5$ and $q= 2e\ r^4/105$

Hence,

$$Dq = ze^2\ r^4/\ 6\ a^5$$

If **point dipole** of ligands is considered then, 10 Dq is given by:

$Dq= 5\mu\ r^4/6\ a^6.$

Here Z= charge on the ligand, e= charge of the electron, a= M-L distance and r^4 = mean fourth power radius of d-electron (i.e the distance from the nucleus). However, here Dq is the energy difference between the t_{2g} and e_g set is 10 Dq for Oh-ligand field. This term indicates the extra stabilization of the complex which is called crystal field stabilization energy (CFSE).

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C. K. Jørgensen's (notation) *f* and *g* factors

$$\Delta_o = f(\text{ligand}) \cdot g(\text{metal})$$

g -factors			*f* -factors	
$3d^5$	Mn(II)	8.0	Br^-	0.72
$3d^8$	Ni (II)	8.7	SCN^-	0.73
$3d^7$	Co(II)	9.0	Cl^-	0.78
$3d^3$	V(II)	12.0	N_3^-	0.83
$3d^5$	Fe(III)	14.0	F^-	0.90
$3d^3$	Cr(III)	17.4	$oxalate^{2-}$	0.99
$3d^6$	Co(III)	18.2	H_2O	1.00
$3d^9$	Cu(II)	9.5	NCS^-	1.02
$3d^4$	Cr(II)	9.5	CH_3CN	1.22
$4d^6$	Ru(II)	20.0	pyridine	1.23
$3d^3$	Mn(IV)	23.0	NH_3	1.25
$3d^3$	Mo(III)	24.6	en (ethylenediamine)	1.28
$4d^6$	Rh(III)	27.0	bipy (2,2'-bipyridine)	1.33
$4d^3$	Tc(IV)	30.0	Phen (1:10-phenanthroline)	1.34
$5d^6$	Ir(III)	32.0	CN^-	1.70
$5d^6$	Pt(IV)	36.0		

Concept of Pairing Energy

Spin Pairing Energy (P) is an increase in **Energy** (due to electrostatic repulsions) when an e^- is put into an **occupied orbital**.

(This is not an experimentally determined quantity)

Pairing energy (P) = [Inherent coulombic repulsion (Πc) + Loss of exchange energy (Πe)]

N.B.- If the orbitals (4d, 5d) become bigger and diffuse so that the distance between the two electrons in the orbitals increase and hence the repulsion may decreases.

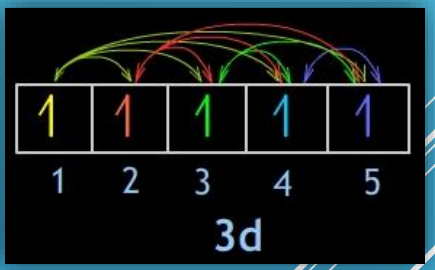
Πc = destabilizing energy for the Coulombic repulsion associated with putting two electrons into the same orbital.

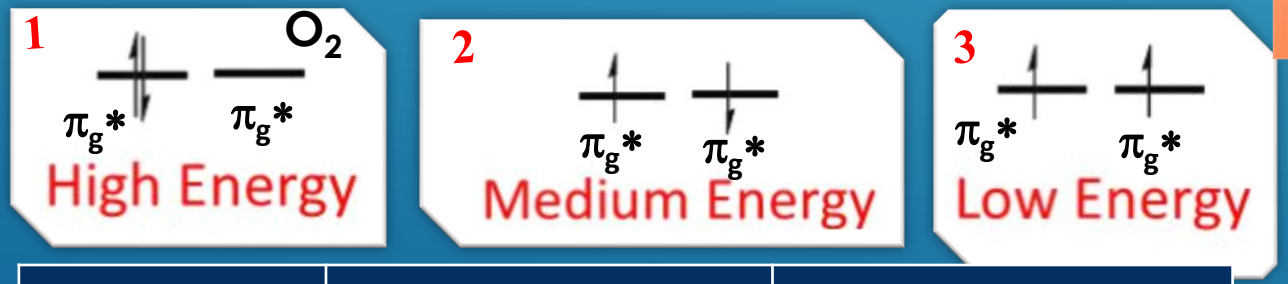
Πe = Stabilizing energy for electron exchange associated with two degenerate electrons having parallel (same) spin [Key factor is Hund's rule).

$$E_{ex} = \sum \frac{n(n-1)}{2} K \quad (K=\text{constant})$$

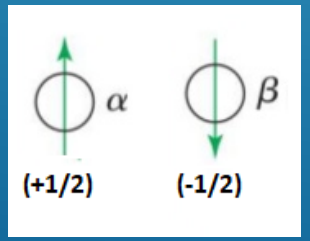
[n= number of unpair-electron in the (parallel) same spin]

Electron exchange in degenerate orbitalis.





E(ex)= 0 (With higher repulsion) Singlet O_2 highly reactive	E(ex)= 0 (with moderate repulsion wrt first one)	E(ex)= 1K (Higher stability) triplet O_2 kinetically inert



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Lecture-3

Concept of High Spin and Low spin

High spin and low spin are two possible classifications of spin states that occur in coordination compounds. These classifications come from either the ligand field theory, which accounts for the energy differences between the orbitals for each respective geometry, or the crystal field theory, which accounts for the breaking of degenerate orbital states, compared to the pairing energy.

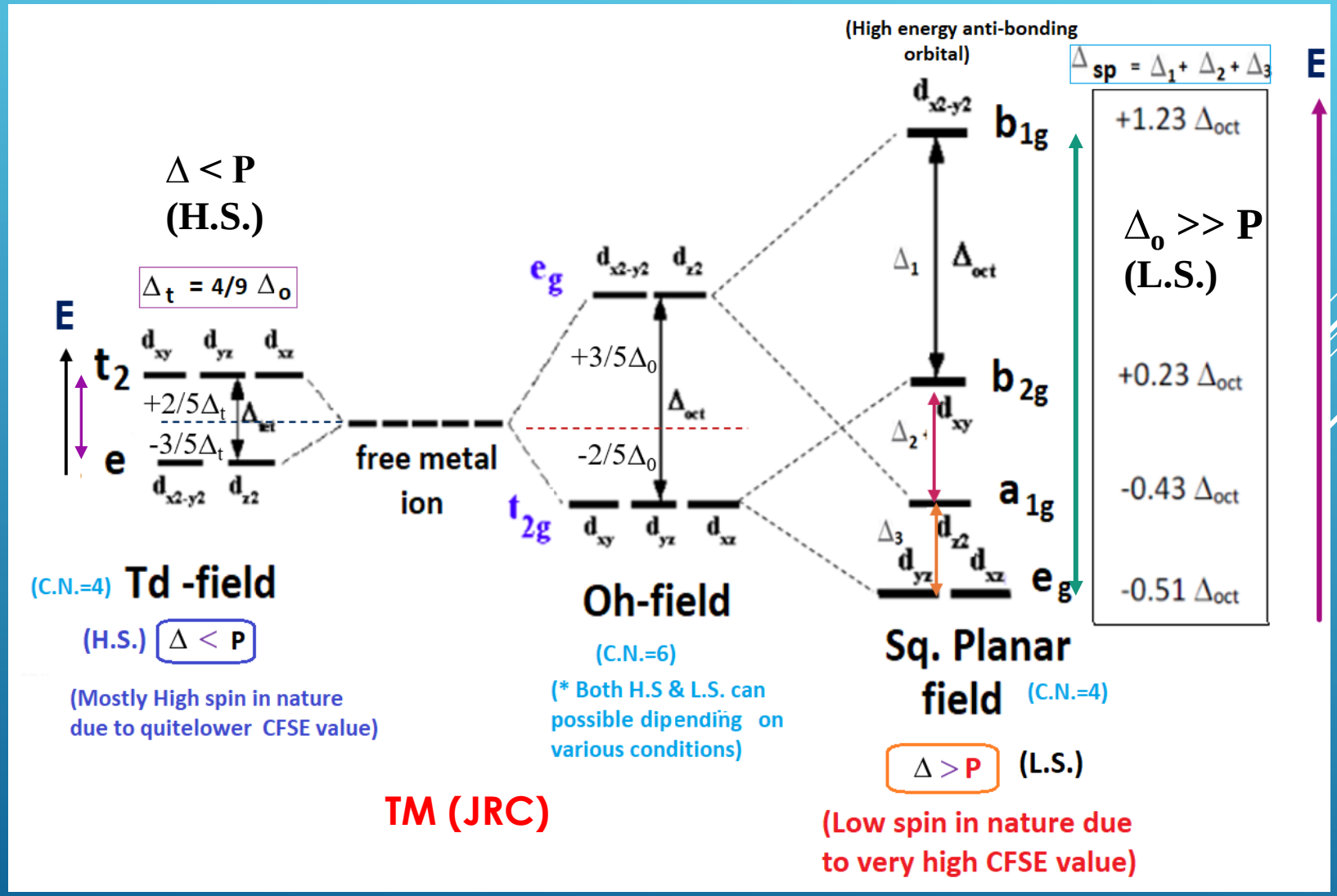
- Low spin complex:
  (L.S) =Complex containing lowest number of unpaired electrons
  High spin complex:
  (H.S.)= Complex containing higher number of unpaired electrons (**lower electrostatic interaction/ field or low field**)

- **Rule of Thumb:** **[Δ=CFSE or LFSE]**

✓ ***If 10 Dq (Δ_0) > P, then the corresponding complex will be Low-spin (L.S.).***

✓ ***If 10 Dq (Δ_0) < P, then the corresponding complex will be High-spin (H.S.)***

✓ ***If 10 Dq_o = P, then Low-spin ↔ High-spin (Δ_o =kT) will be in equilibrium i.e here spin-state isomerism appears.***



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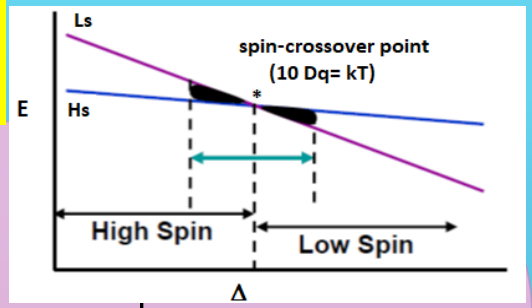
High spin (H.S.) or Low spin (L.S.) in Complex (3d-series). (Oh)



H.S.: $\Delta_0 < P$

H.S & L.S not applicable

[Ti(III),d^1]

$t_{2g}^1 e_g^0$

[Ti(II),d^2]

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

[V(II),d^3]

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

d^1 - d^3

[Cr(II),d^4]

$t_{2g}^3 e_g^1$

[Mn(II),d^5]

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

[Fe(II),d^6]

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

[Co(II),d^7]

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

L.S.: $\Delta_0 > P$

[Cr(II),d^4]

$t_{2g}^4 e_0^0$

[Mn(II),d^5]

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

[Fe(II),d^6]

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

[Co(II),d^7]

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

$d^4 - d^7$

(Spin state isomerism /spin state equilibrium may possible for $d^4 - d^7$ in Oh field).

H.S & L.S not applicable

[Ni(II),d^8]

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

[Cu(II),d^9]

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

[Zn (II),d^{10}]

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

$d^8 - d^{10}$

H.S & L.S Applicable*

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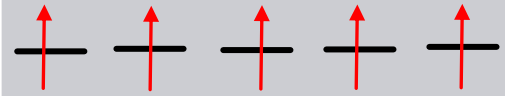
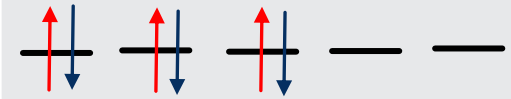
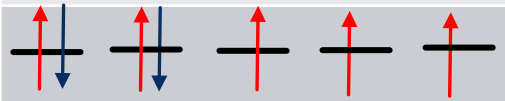
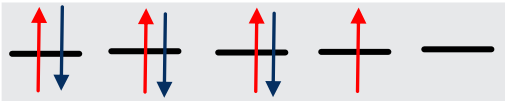
What can explain with the help of $E_{exchange}$?

Exchange Energy	d^5		d^6		d^7		Comments
$E_{ex}= \Sigma n(n-1)/2$	H.S (high spin)	L.S (low spin)	H.S (high spin)	L.S (low spin)	H.S (high spin)	L.S (low spin)	Form the value of loss of E_{ex}, as it is minimum for d^6,d^7 system, so they has a tendency to form L.S-complex. So, **Co(II) & **<u>Co(III) complexes are most of the cases L.S in nature.</u> While d^5complexes [Mn(II), **Fe(III)]** are usually H.S as loss of E_{ex} is maximum which is not compensated by the CFSE value of d^5 system. **<u>Exceptional:</u> $CoF_6]^{-3}$ **H.S. complex of Co(III) due to very weak field F-ligands.**
E_{ex}(α–spin)	10K	3K	10K	3K	10K	6K	
E_{ex} (β -spin)	0	1K	0	3K	1K	3K	
E_{ex} (total)	10K	4K	10K	6K	11K	9K	
Difference in exchange energy E_{ex} (From H.S to L.S)	(10-4)k =6K (maximum loss) [can't be compensated easily by CFSE]		(10-6)k =4K (#moderate loss)		(11-9)K =2K (minimum loss) [#can be compensated easily by High CFSE]		

Fe(III)	Co(III)	Co(II)
$3d^5$	$3d^6$	$3d^7$

d^n	Electron Arrangements
d^5 (H.S.)	
d^5 (L.S.)	
d^6 (H.S.)	
d^6 (L.S.)	
d^7 (H.S.)	
d^7 (L.S.)	

<u>(Considering degenerate orbitals)</u>

[N.B.- $Co(NH_3)_6]^{2+}$, $Co(NH_3)_6]^{3+}$, $Co(en)_3]^{3+}$, $Co(NH_3)_4F_2]^{3+}$: <u>L.S. Oh Complexes.</u>]

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Lecture-3

Ion has 4-7 d-electron?

(Oh)

No

Yes

H.S/ L.S. Same

1st Row T.S metal?

Yes

No

3d-series

Strong field
Ligand like pi-acceptor?

No

Very higher oxidation State (≥ 4)

No

H.S. (Except Co(III)

Yes

L.S.

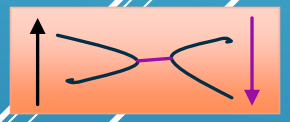
Yes

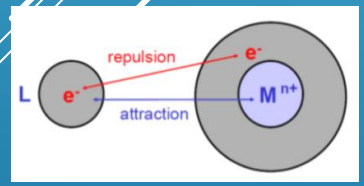
L.S.

3d
4d
5d

L.S.

(4d, 5d series)





Bigger diffuse size d-orbital have minimum electronic repulsion; hence the cost of electron-pairing an be easily compensated by Higher CFSE due to increased in Z-eff (higher M-L Interaction)

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Lecture-3

High spin (H.S.) or Low spin (L.S.)?

Q.1) What is the C.N. & Geometry of complex?

Td (C.N.=4)

Mostly H.S. in nature

Δ_o < Pairing energy : High Spin

✓ N.B.: *3d mostly H.S but 4d/5d some times may give exceptional depending on steric factor.

Oh (C.N.=6)

Q.2) What is the periodic Position of that transition metal?

Sq. Planar (C.N.=4)

L.S. in nature

Δ_o > Pairing Energy : Low Spin

1st Row (3d series)

❖ **Will depend on: (*Both possible)**

✓ **Ligand field strength**

[Weak filed (H.S.) & strong field ligand (L.S.)]

✓ **Oxidation state of metal**

✓ **'d' election configuration**

2nd or 3rd Row (4d or 5d series)

L.S. in nature

(Diffuseness as well as Z_{eff} key factor for 4d & 5d series)

Lecture-3

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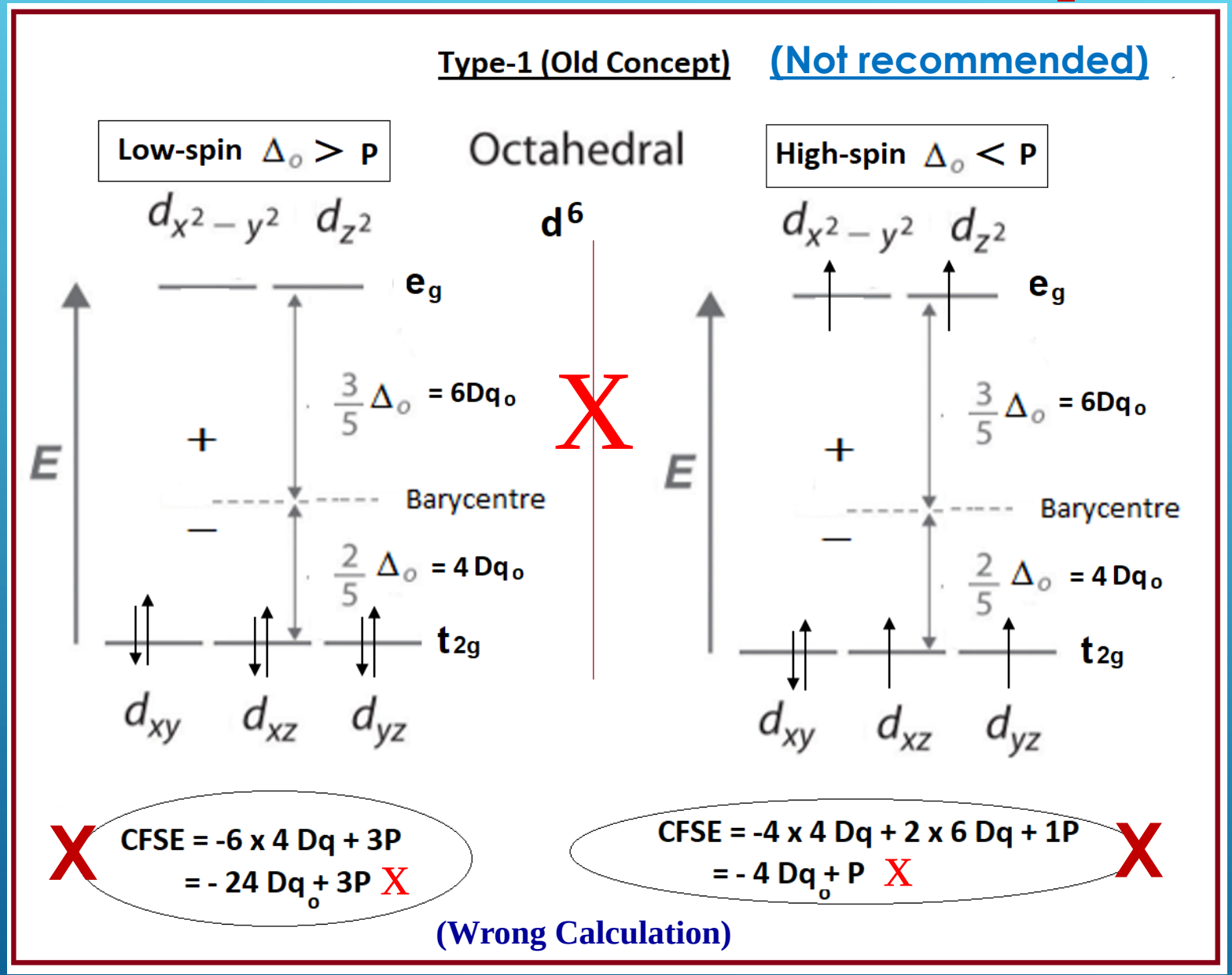
CFSE Calculation for Octahedral System (Δ_0):



Definition of CFSE:

The crystal field stabilization energy (CFSE) is the gain in the energy (EXTRA STABILIZATION) achieved by d^n systems due to preferential filling up of orbitals (resulting by non spherical interactions) by electrons. Actually it refers to the energy differences between the energy of electron configuration of the ligand filed and the energy of the electron configuration in the isotropic field. It determines the energy differences between the two sets of orbital splitting.

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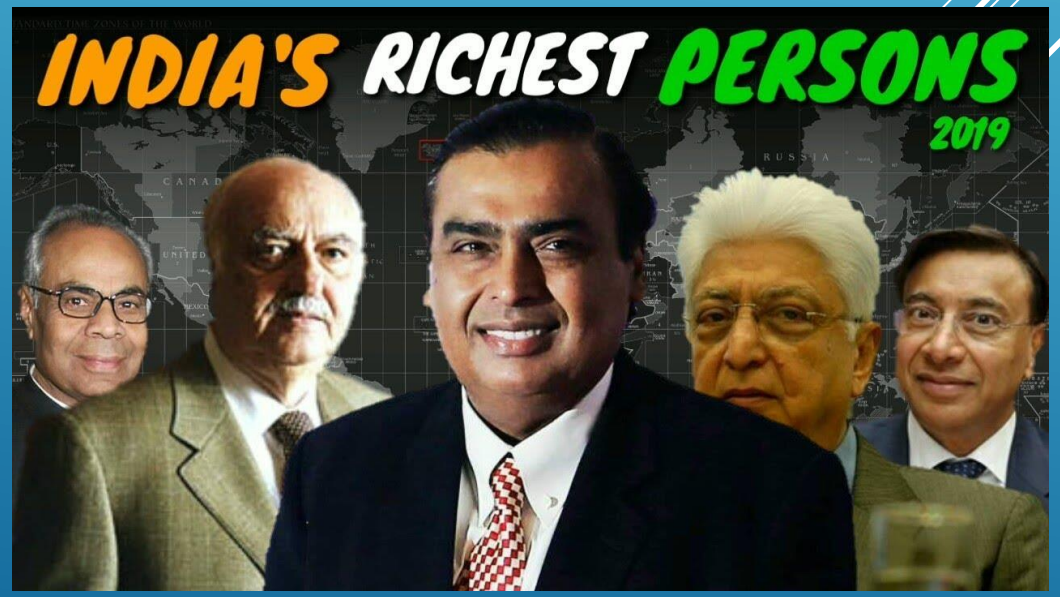
Understanding of CFSE



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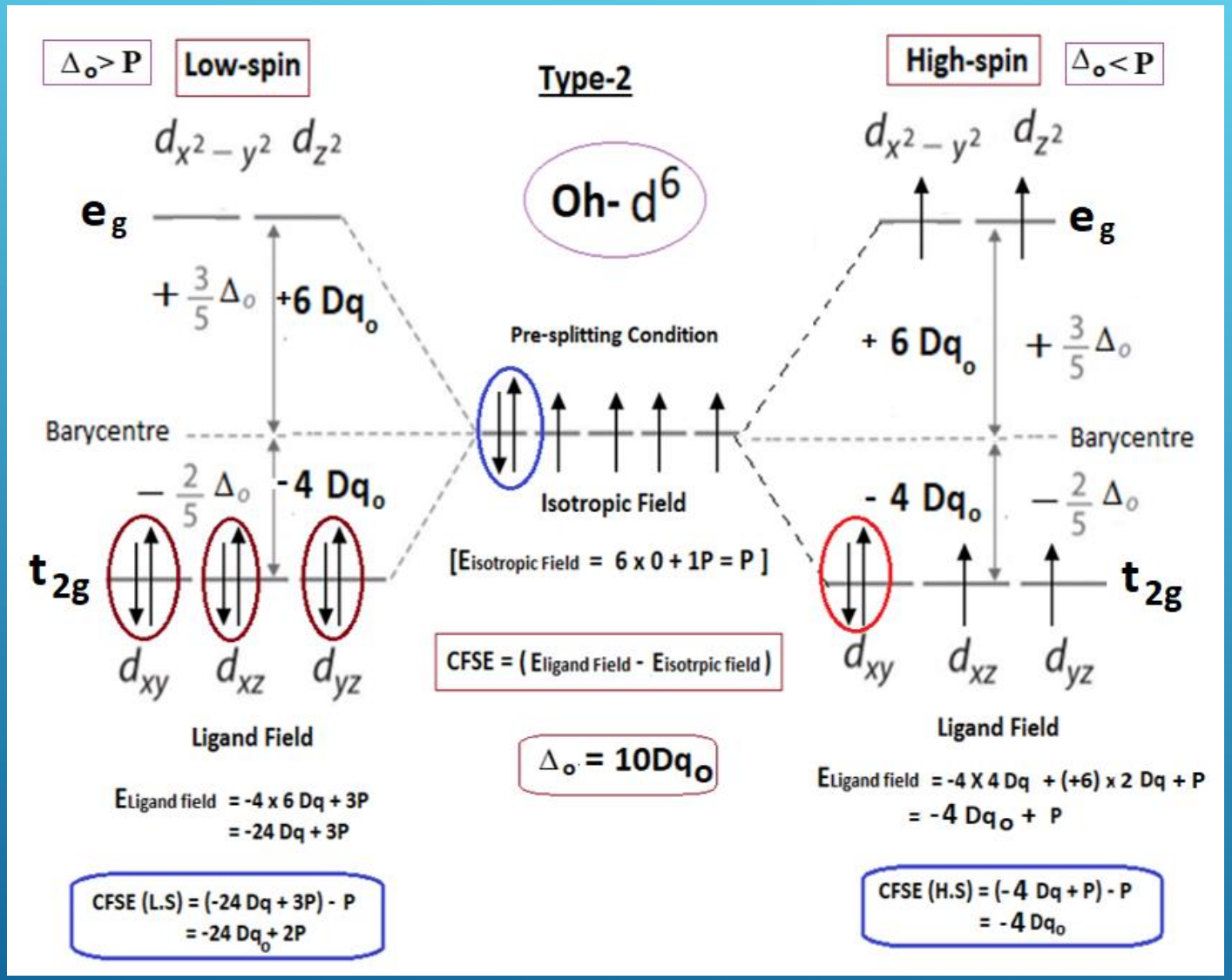
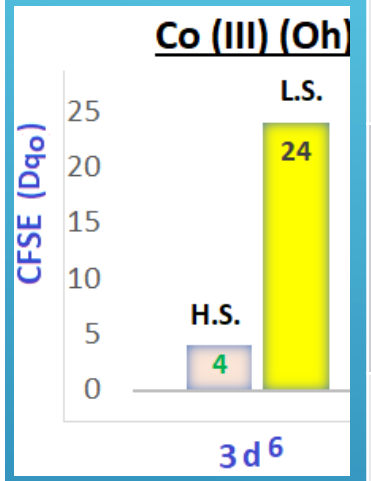




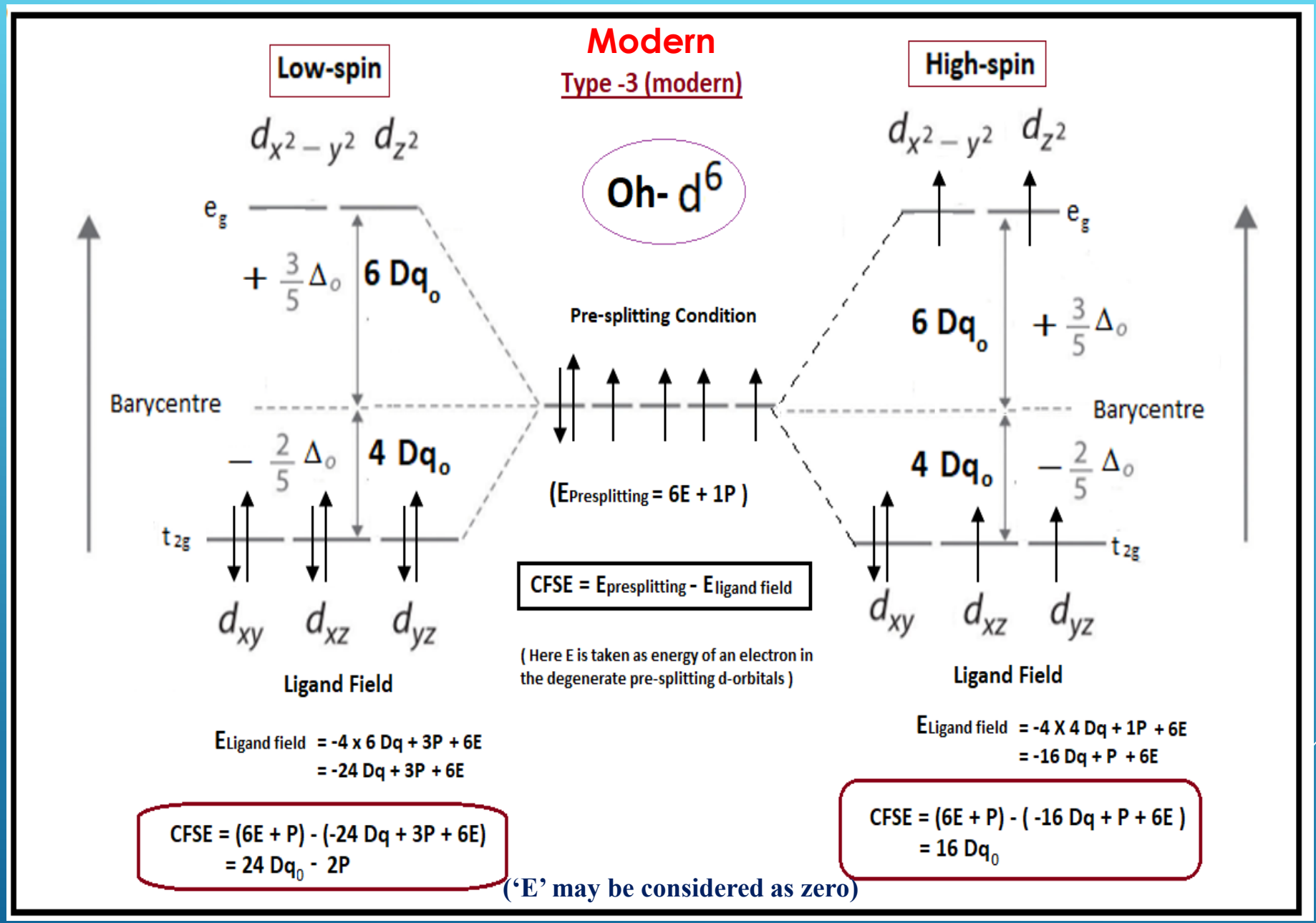
d^6 (Oh)	H.S.	L.S.
Configuration	$t_{2g}^4 e_g^2$	$t_{2g}^6 e_g^0$
$E_{after\ splitting}$	$(-4Dq_o) * 4 + (+ 6 Dq_o) * 2 + 1P$ $= - 4Dq_o + 1P$	$(-4) * 6 Dq_o + 0 + 3P$ $= -24Dq_o + 3P$
$E_{before\ splitting}$	1P	
CFSE	$= - 4Dq_o$	$= - 24Dq_o + 2P$

$\Delta_o (d^6 (Oh)_{L.S.} > \Delta_o (d^6 (Oh)_{H.S.}$

Co(III) (d^6) (Oh) is mostly L.S. in nature due to higher CFSE which can easily compensate the minimum loss of pairing energy.

*Exceptional: $CoF_6]^{-3}$ is found to be H.S. complex of Co(III) due to very weak field F-ligands.

[CFSE = E(ligand field)-E(Isotropic field)]



[CFSE = E(Isotropic field) - E(ligand field)-)]

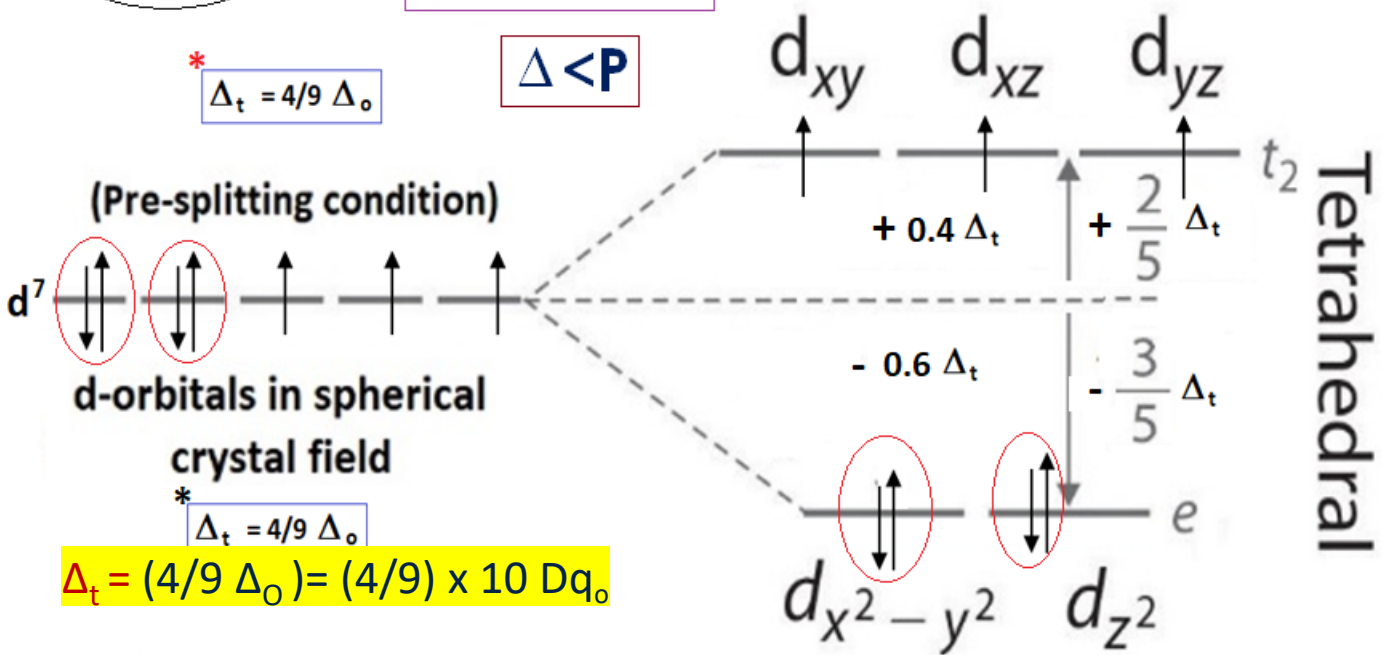
CFSE Calculation for Td System

d^7 (Td)

H. S. (by virtue of low CFSE value)

$\Delta < P$

* $\Delta_t = 4/9\ \Delta_o$



* $\Delta_t = 4/9\ \Delta_o$

$\Delta_t = (4/9\ \Delta_O) = (4/9) \times 10\ Dq_o$

(Number of paired electrons in the pre-splitting and splitted conditions are same and hence their contribution cancelled during CFSE calculation)

CFSE (Td) = 4 x - 0.6 Δ_t + 3 x 0.4 Δ_t = (- 1.2 Δ_t)

= (- 1.2) x (4/9 Δ_o) = (- 1.2) x (4/9) x (10 Dq_o) = **- 5.33 Dq_o**

($\because \Delta_o = 10\ Dq_o$)

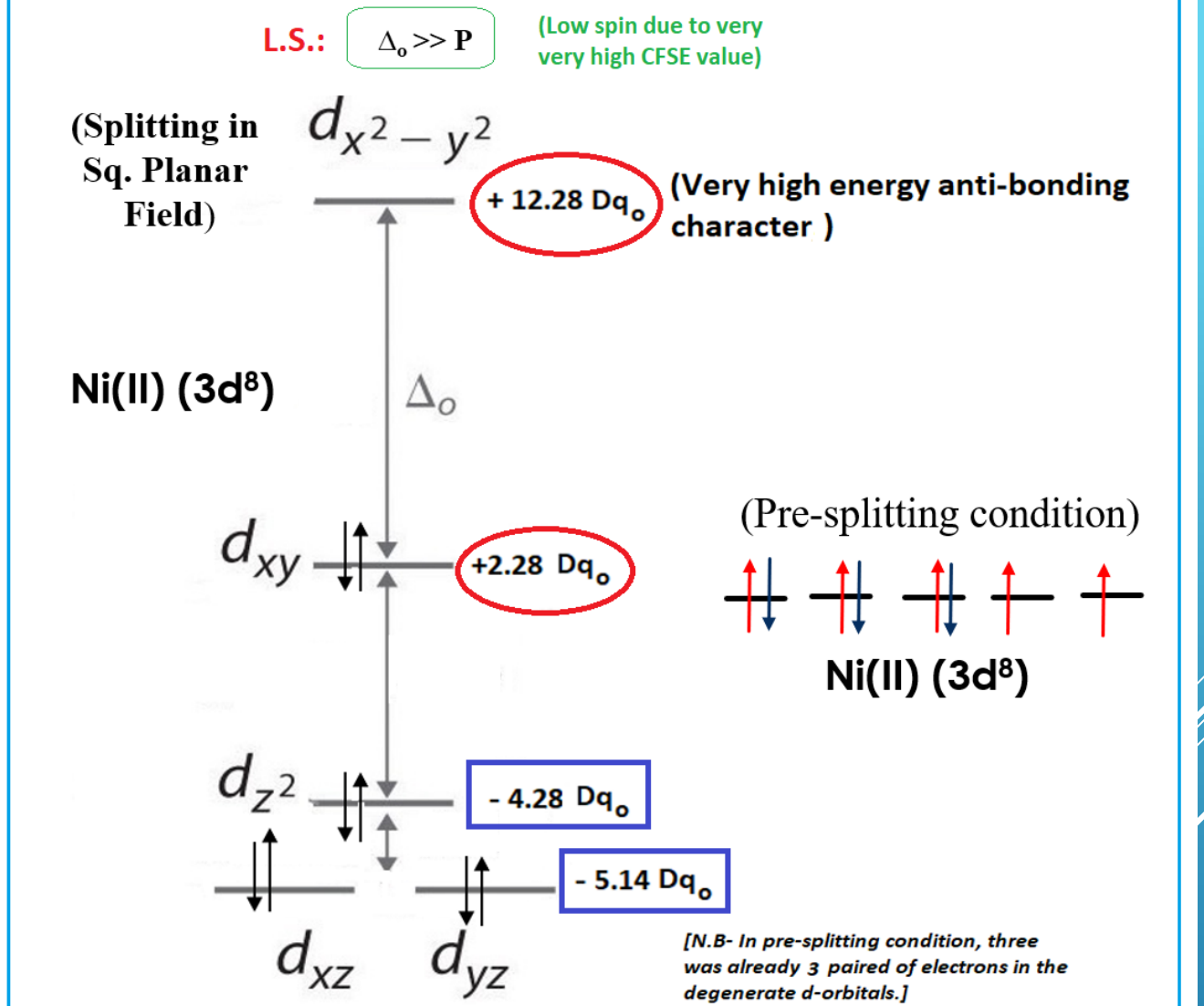
d^7	H.S. (by virtue of low CFSE)	
Configuration	$e^4\ t_2^3$	
$E_{after\ splitting}$	(4) * (-0.6Δ_t) + 3 * (+ 0.4 Δ_t) + 2P	= -1.2Δ_t+2P = - 1.2 *4/9Δ_o+ 2P =-0.533 Δ_o+ 2P = 0.533 * (10 Dq_o) +2P = [- 5.33 Dq_o + 2P]
$E_{before\ splitting}$	2P	
$CFSE_{(Td)}$	= E(ligand field) -E(Isotropic field)] = [- 5.33 Dq_o + 2P] –[2P] = - 5.33 Dq_o	

[CFSE = E(ligand field)-E(Isotropic field)]

CFSE Calculation for Sq. Planar System

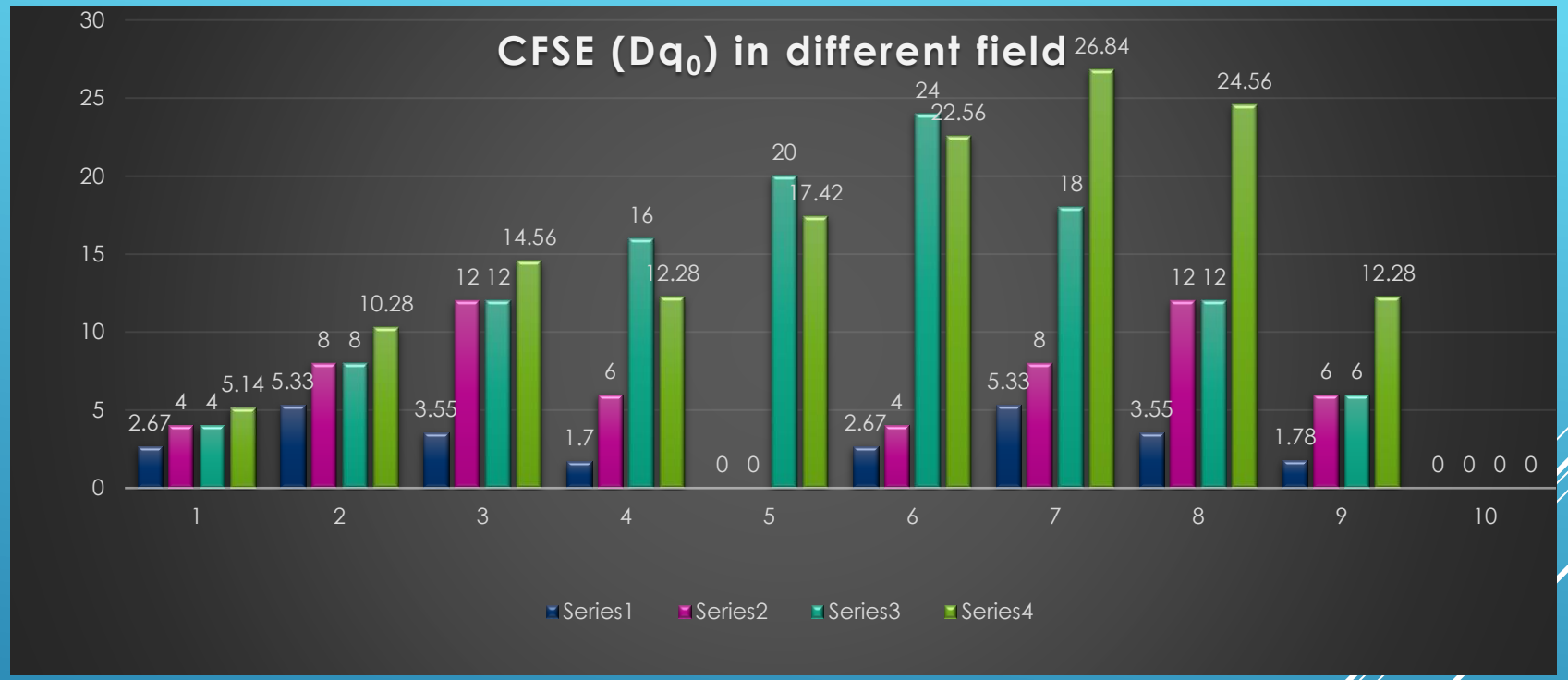
d- orbitals in Sq. Planar (D_{4h}) field	Energy in Dq_o	Corresponding symmetry
E $x^2 - y^2$	+ 12.28	b_{1g} (1)
xy	+ 2.28	b_{2g} (1)
z^2	- 4.28	a_{1g} (1)
xz, yz	- 5.14	e_g (2)

Lecture-3



Summery of CFSE values in Oh, Td and Sq. Planar System

d^n	CFSE (Td)	CFSE (Oh)
1	-2.67 Dq_o	-4 Dq_o
2	-5.33 Dq_o	-8 Dq_o
3	-3.55 Dq_o	-12 Dq_o
4	-1.78 Dq_o	-6 Dq_o (h.s.) -16 Dq_o + 1 PE (l.s.)
5	0 Dq_o	0 Dq_o (h.s.) -20 Dq_o + 2 PE (l.s.)
6	-2.67 Dq_o	-4 Dq_o (h.s.) -24 Dq_o + 2 PE (l.s.)
7	-5.33 Dq_o	-8 Dq_o (h.s.) -18 Dq_o + 1 PE (l.s.)
8	-3.55 Dq_o	-12 Dq_o
9	-1.78 Dq_o	-6 Dq_o
10	0 Dq_o	0 Dq_o



No. of d electrons	*CFSE (Strong field)*	CFSE (Sq. Planar) (Dq_o)
1	-0.514Δ	- 5.14
2	-1.028Δ	-10.28
3	-1.456Δ	-14.56
4	-1.228Δ	-12.28
5	$-1.742\Delta + P$	-17.42 + P
6	$-2.256\Delta + P$	- 22.56 + P
7	$-2.684\Delta + P$	-26.84+ P
8	$-2.456\Delta + P$	-24.56 + P
9	-1.228Δ	- 12.28
10	-0Δ	0

Series-1: For Td (H.S.)
Series-2: **For Oh (H.S.)**
Series-3: **For Oh(L.S.)**
Series-4: **For Sq. Planar**

N.B.- 1. e-set acting as bonding/non-bonding where as t_2 set acting as anti-bonding for Td.

2. t_{2g} set acting as bonding/non-bonding where as e_g set acting as anti-bonding in Oh.
3. d^{1-3} (Oh) and d^{8-10} no spin-cross in Oh field.
4. dxz, yz and dz2 acting as bonding exclusively whereas dxy moderately bonding while dx2-y2 as very high energy anti-bonding orbital in Sq. Planar field.

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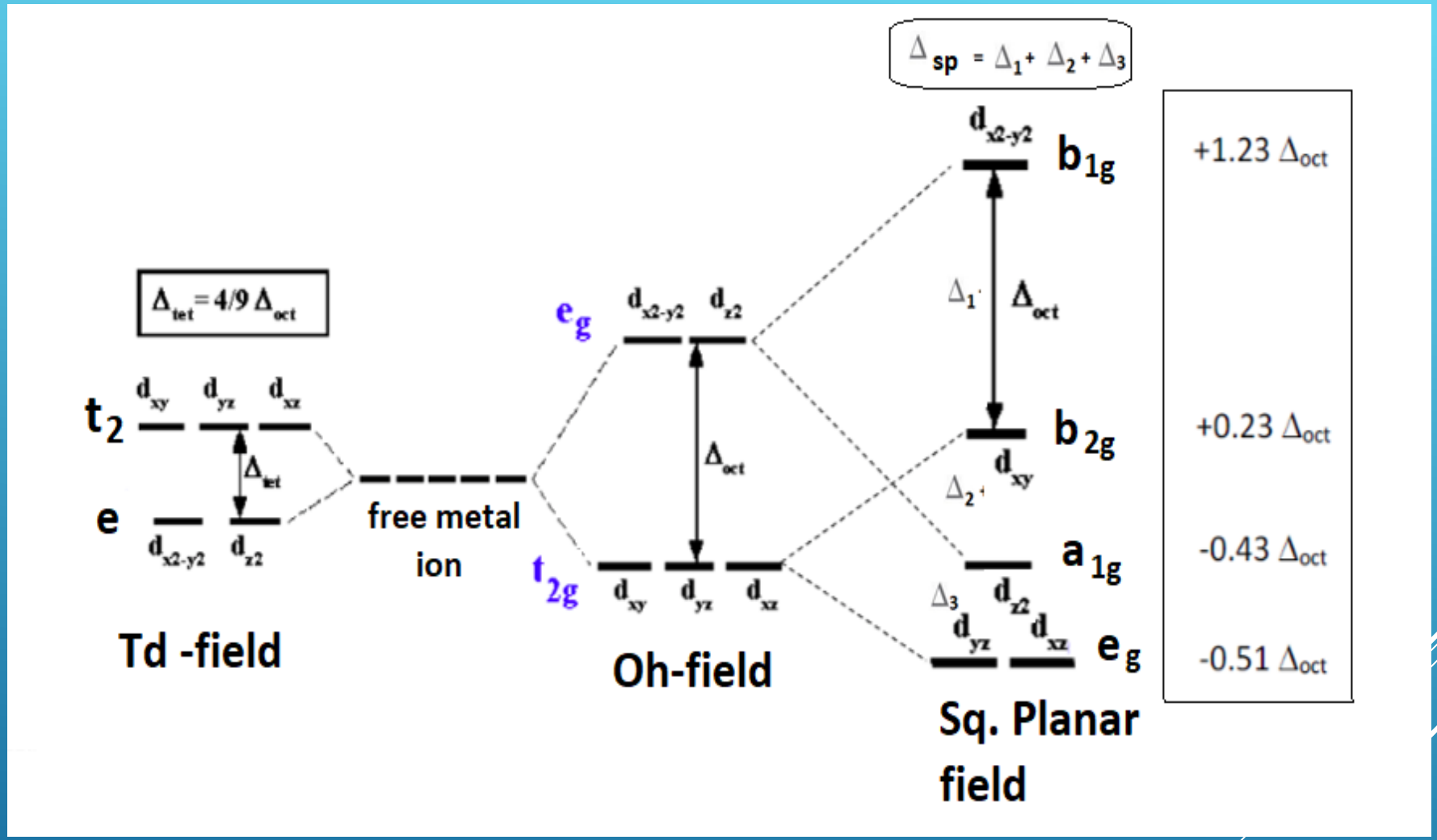
Lecture-3

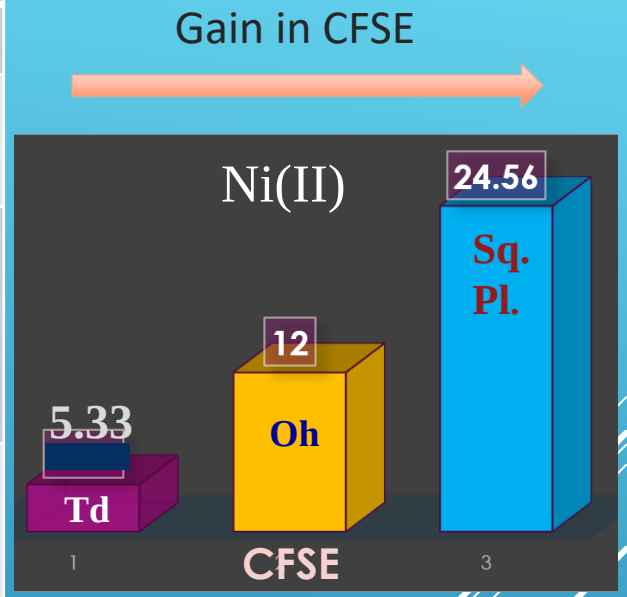


**CFSE Order:

$\Delta_{Sp} > \Delta_{Oh} > \Delta_{Cubic} > \Delta_{Td}$

Preferential geometry for Ni(II) (d^8) in general cases based on CFSE.

Ni(II) ($3d^8$)	Geometry		
	Oh	**Td**	**Sq. Planar**
Electronic configuration	$t_{2g}^6 e_g^2$	$e^4\ t_2^3$	$d^2_{xz}, d^2_{yz} < d^2_{z2} < d^2_{xy} < d^0_{x2-y2}$
CFSE (Dq_o)	(-4 x 6+ 6 x 2) = - 12 Dq_o	[-6 x 4+ 4 x 3] x (4/9) Dq_o = - 5.33 Dq_o	[(-)5.14 x 4 + (-)4.28 x 2 + (+) 2.28 x 2 + (+) 12.28 x 0] Dq_o = -24.56 Dq_o
Stability Order of Ni(II) & Conclusion	**Sq. Planar>>Oh > Td** **Hence Ni(II) prefers Sq. Planar complex due to high gain in CFSE than Oh or Td.** To obtained such stable sq. planar geometry Ni(II) should associated with tertra coordinated (C.N.=4) *strong field ligand* ***preferably*** *with* ***negatively charged*** ***CN^-*** *pi-acid ligand.*		



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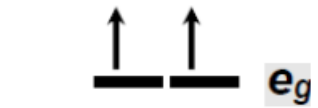
[N.B.- Similar observations also applicable for Cu(II) (d^9)]

CFSE Calculation in cm^{-1} unit.

If $\Delta_o = 9{,}350cm^{-1}$

(Oh, $3d^6$)

High Spin



(+) 3/5 Δ_o

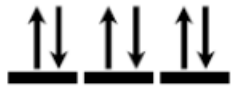
(-) 2/5 Δ_o

$$\text{CFSE} = 4(-0.4\Delta_o) + 2(0.6\Delta_o)$$
$$= -0.4(9350cm^{-1})$$
$$= -3740cm^{-1}$$

Low Spin

(+) 3/5 Δ_o

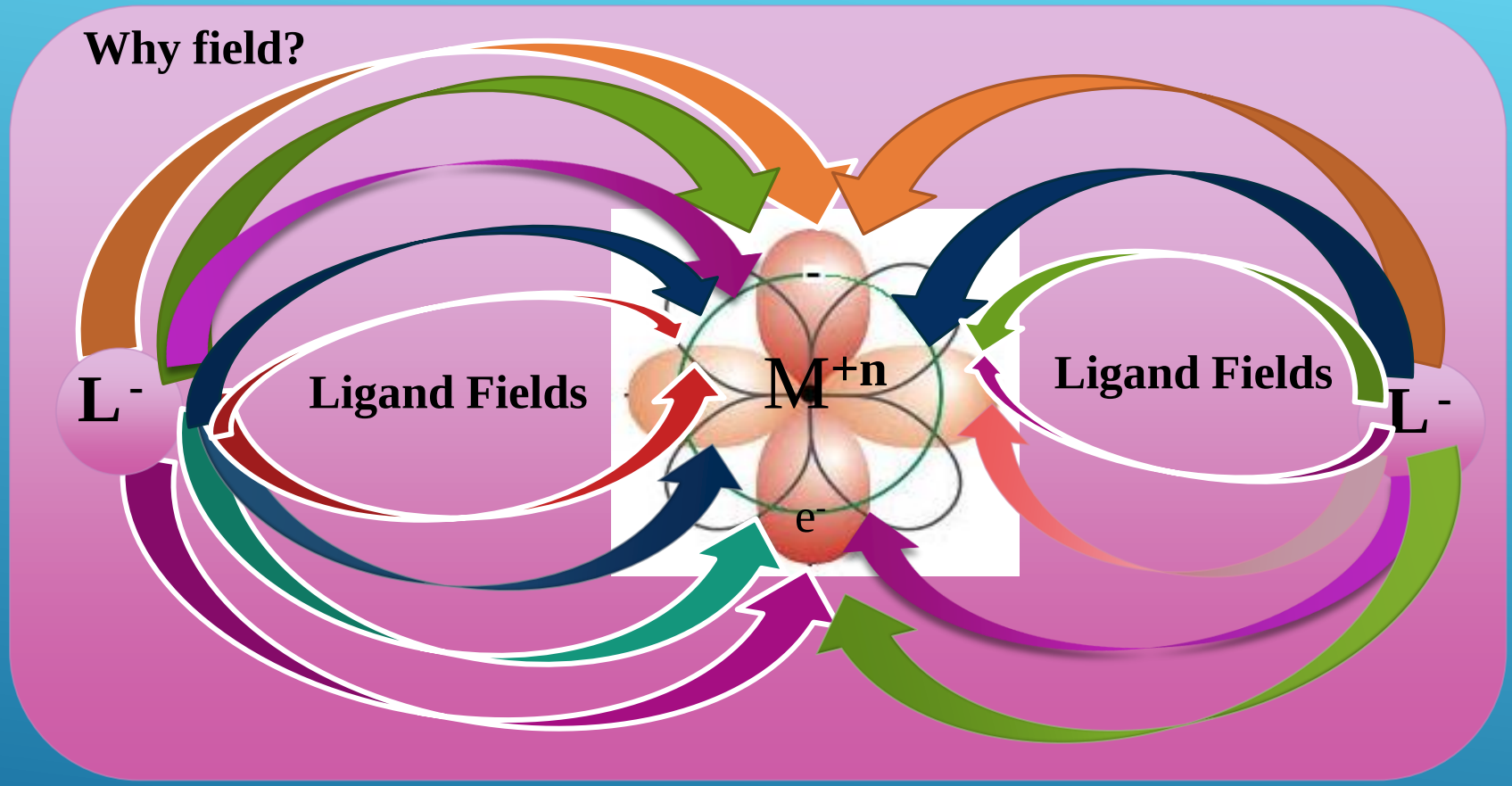
(-) 2/5 Δ_o



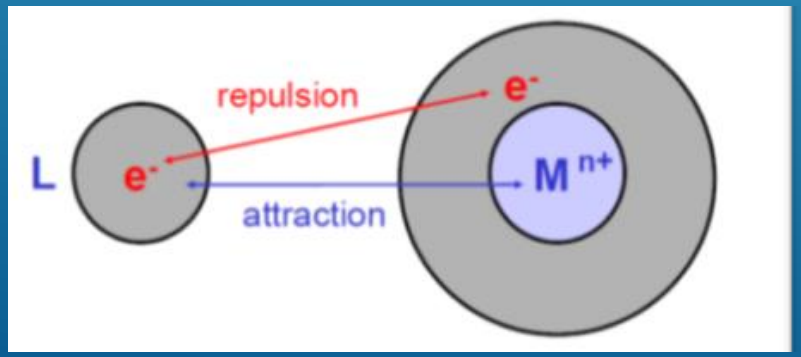
$$\text{CFSE} = 6(-0.4\Delta_o) + 0(0.6\Delta_o)$$
$$= -2.4(9350cm^{-1})$$
$$= -22,440cm^{-1}$$

[Excluding pairing energy (P)]

CFSE or LFSE (modern concept)??



Since there is an interactions between
the ligands with d-orbital of metal which
destroy the degeneracy of the metal
orbitals giving rise to redistribution of energy
levels with gain in energy (as a result of the
non-spherical interaction), so it is better to use
Ligand field stabilization energy (LFSE)
But however it is as same as CFSE
and its calculation
also remain unchained.



CFSE = LFSE

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