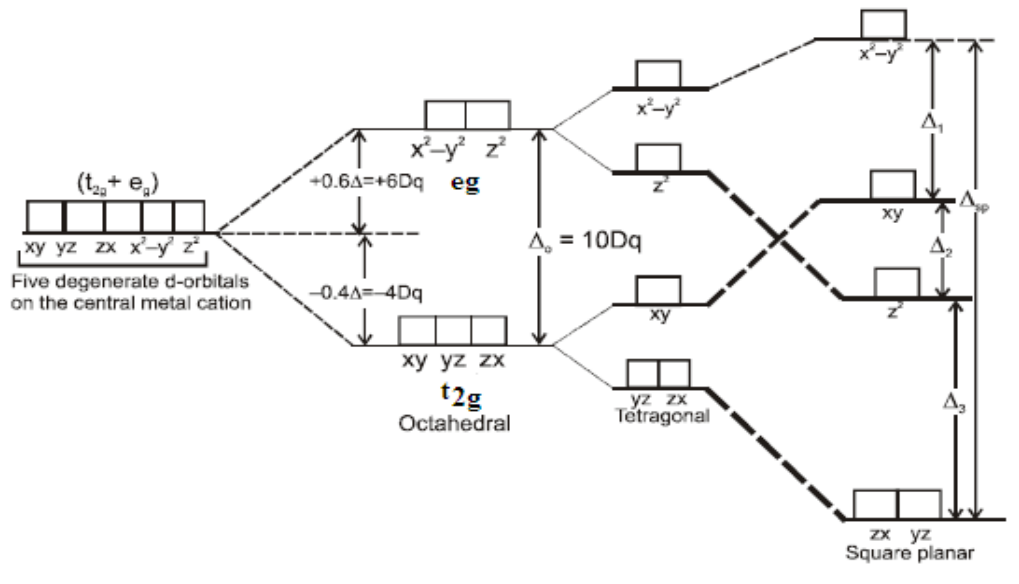
Metal-Ligand Bonding in Transition Metal Complexes

(Lecture-5)

B.Sc. 5th Semester (Pass Course)

INORGANIC CHEMISTRY

(As per MDU, Rohtak Syllabus)



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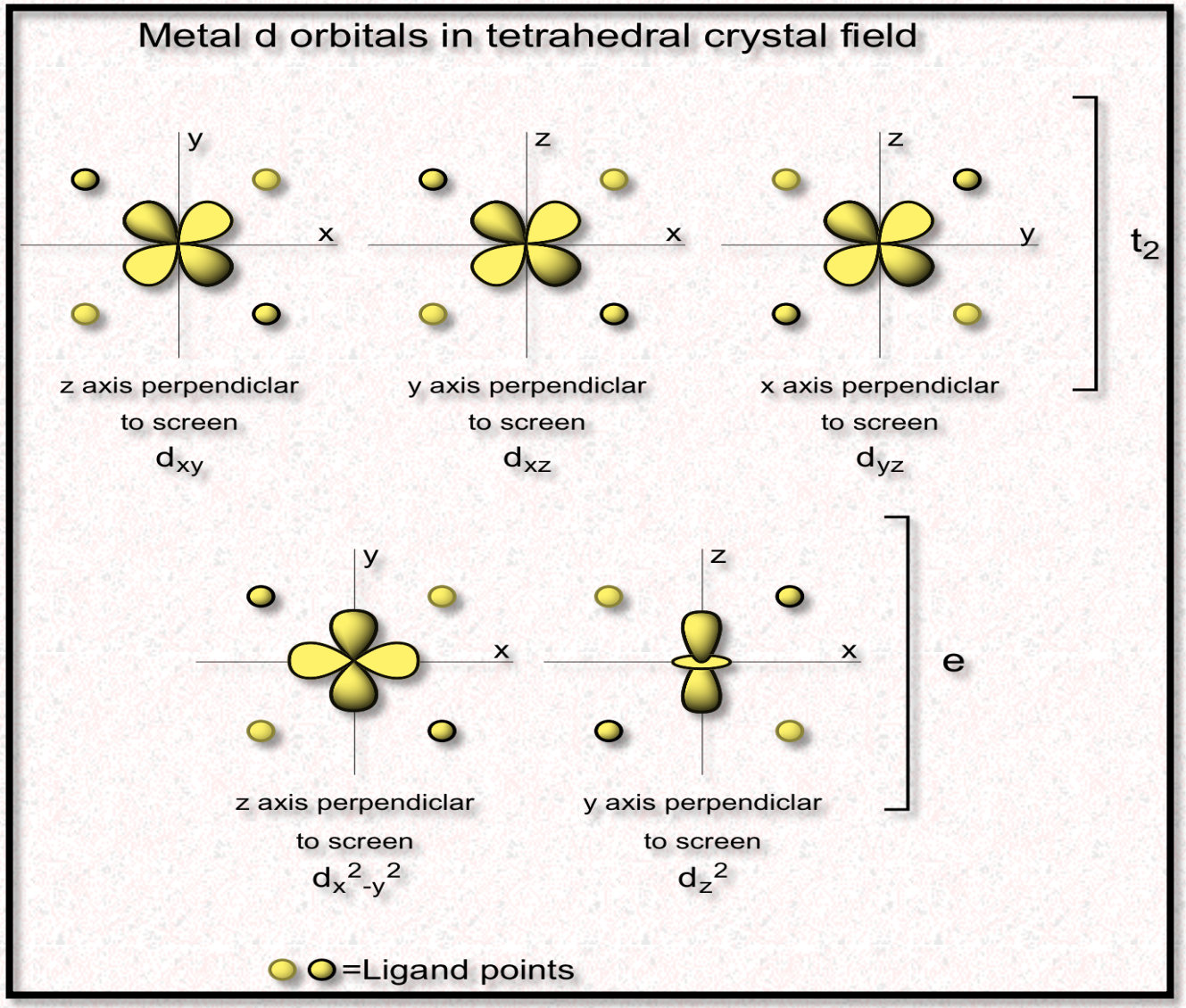
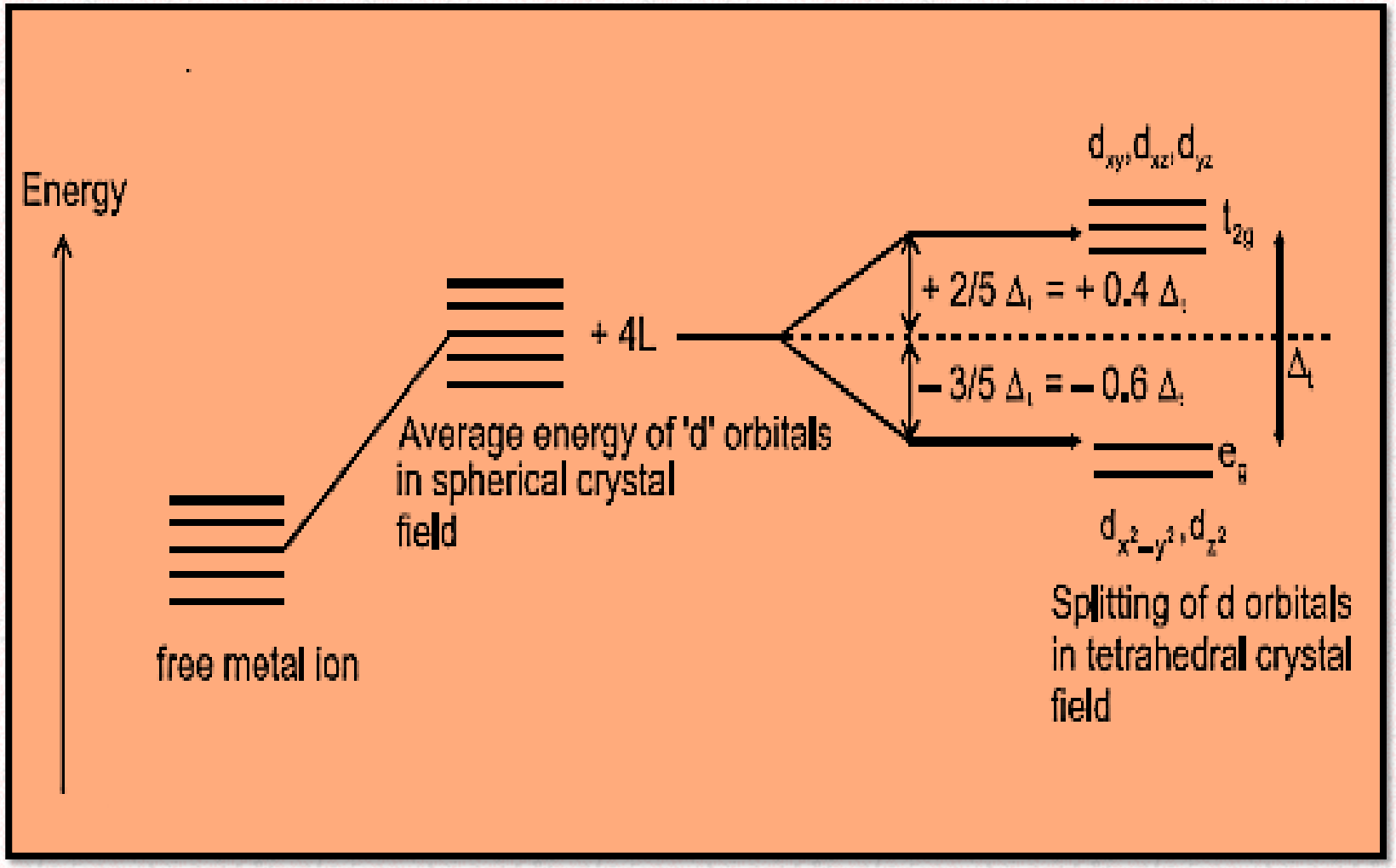
CONTENT

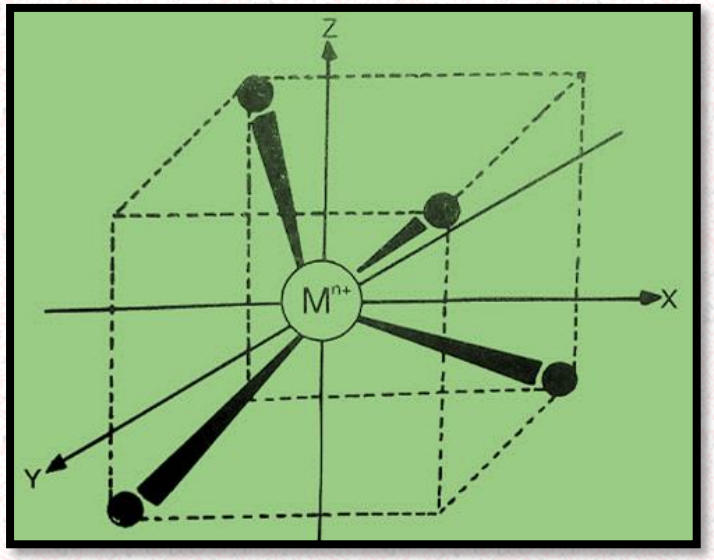
- Crystal field splitting of Tetrahedral ML_4 complexes
- Crystal field splitting of Square Planar ML_4 complexes

Crystal field splitting in a Tetrahedral complex




Energy
free metal ion
+ 4L
Average energy of 'd' orbitals in spherical crystal field
d_{xy}, d_{xz}, d_{yz}
t_{2g}
+ 2/5 Δ_t = + 0.4 Δ_t
– 3/5 Δ_t = – 0.6 Δ_t
Δ_t
e_g
$d_{x^2-y^2}, d_{z^2}$
Splitting of d orbitals in tetrahedral crystal field

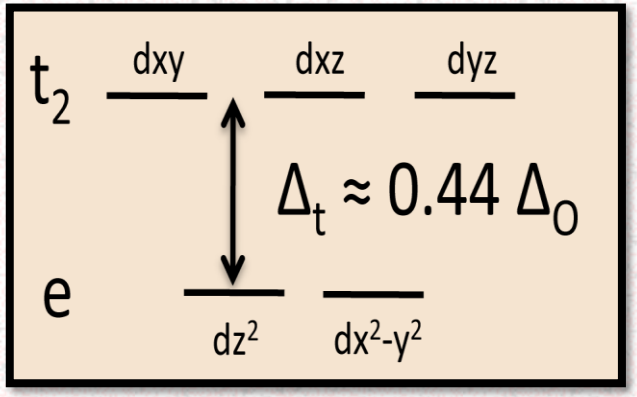
➢ Tetrahedral Field



- There are only 4 ligands in tetrahedral complex, so ligand field is roughly 2/3 of octahedral field.

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

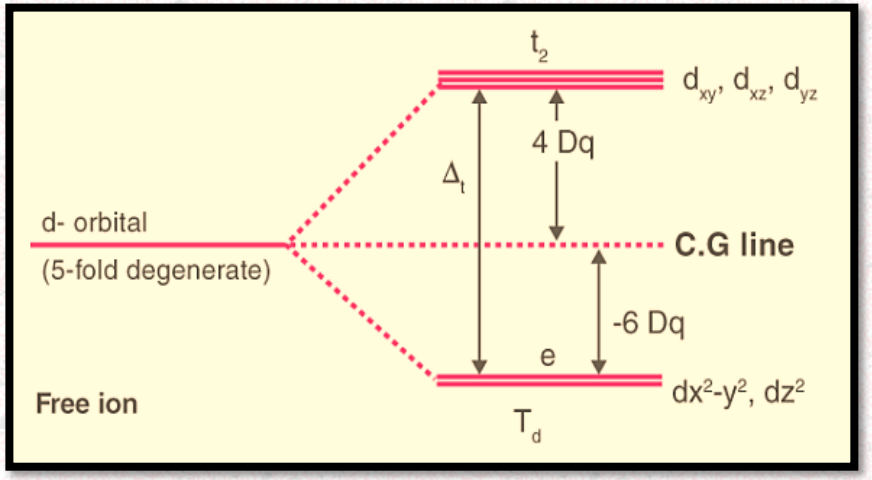
- All tetrahedral complexes are high spin since CFSE is normally smaller than pairing energy.
- If a very strong field ligand is present, square planar geometry will be favoured.



As Δ_t is less than half the size of Δ_o, then normally all tetrahedral complexes are high spin. This is because the pairing energy P is almost always larger than the splitting between the two energy levels.

➢ CFSE value of Tetrahedral Complex:

The procedure for working out the CFSEs for tetrahedral complexes is the same as that for octahedral complexes. However, as the energies of the two set of orbitals are reversed (the e set is lower in energy than the t_2 set) the CFSE for a $t_2^x e^y$ configuration is now:



In case of tetrahedral field, CFSE can be calculated in terms of Δ_t and Δ_o :

CFSE = {-0.6 (no. of electrons in e set) + 0.4 (no. of electrons in t_2 set)}Δ_t

Or

CFSE = {-0.6 (no. of electrons in e set) + 0.4 (no. of electrons in t_2 set)} $\frac{4}{9}\Delta_o$

CFSE of Td complex In terms of Δ_o

Tetrahedral

Fe^{2+} (d^6) e^3 t_2^3

$$CFSE = [-0.6\times3+0.4\times3]\ \frac{4}{9}\Delta_o = 0.27\Delta_o$$

Fe^{3+} (d^5) e^2 t_2^3

$$CFSE = [-0.6\times2+0.4\times3]\ \frac{4}{9}\Delta_o = 0$$

Tetrahedral

Ni^{2+} (d^8) e^4 t_2^4

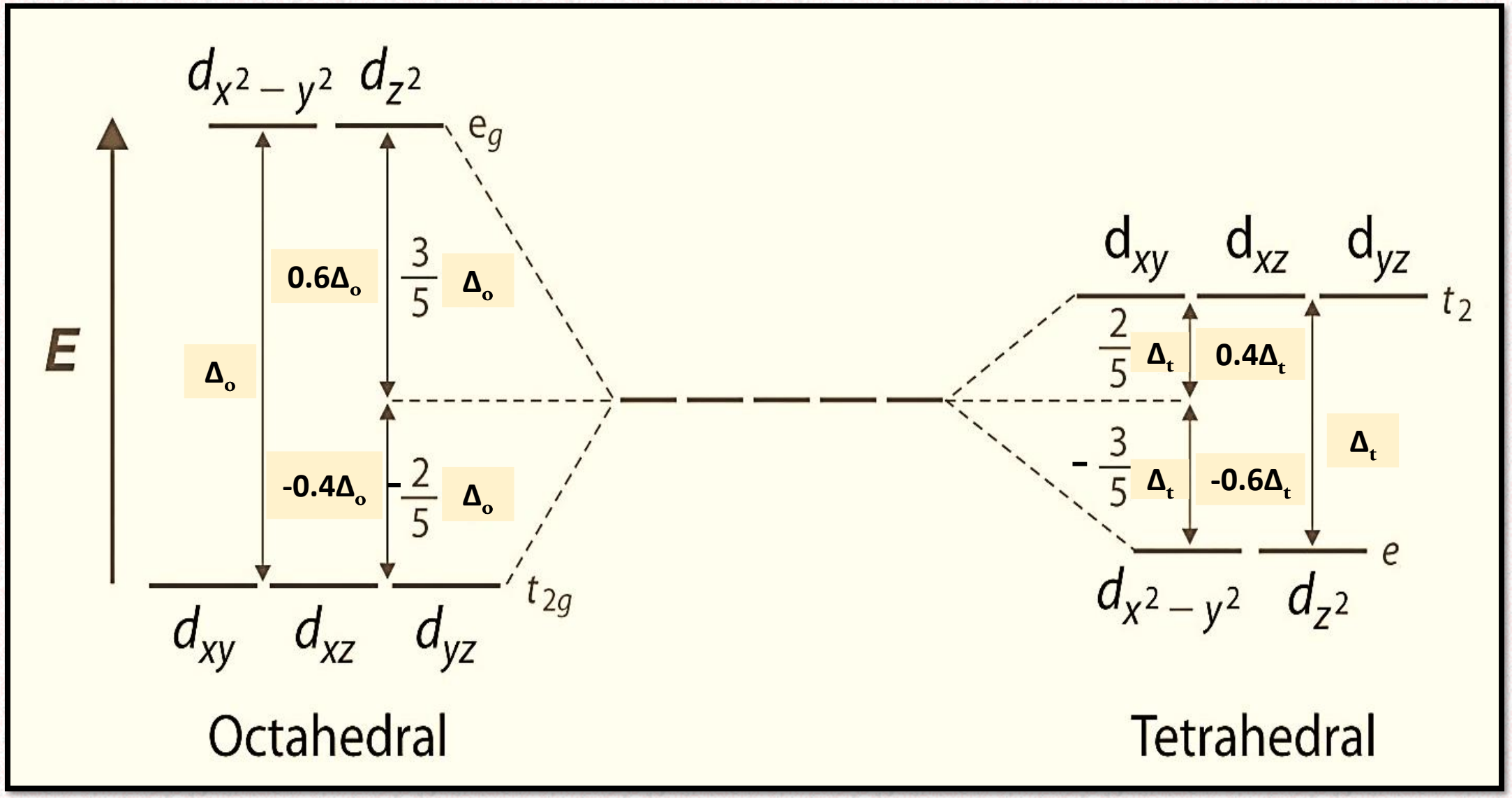
$$CFSE = [-0.6\times4+0.4\times4]\ \frac{4}{9}\Delta = -0.36\Delta_o$$

CFSE of Td complex In terms of Δ_t

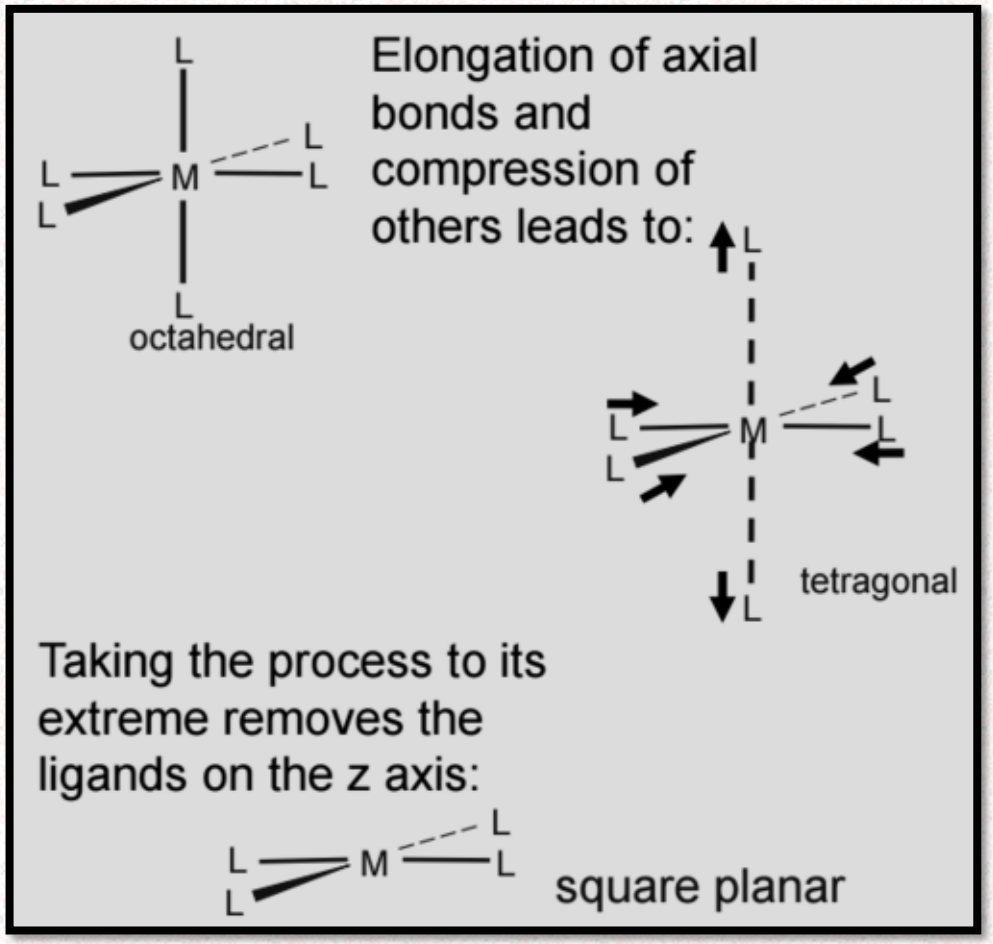
A table showing the crystal field stabilization energies for tetrahedral complexes with different numbers of d-electrons is given below:

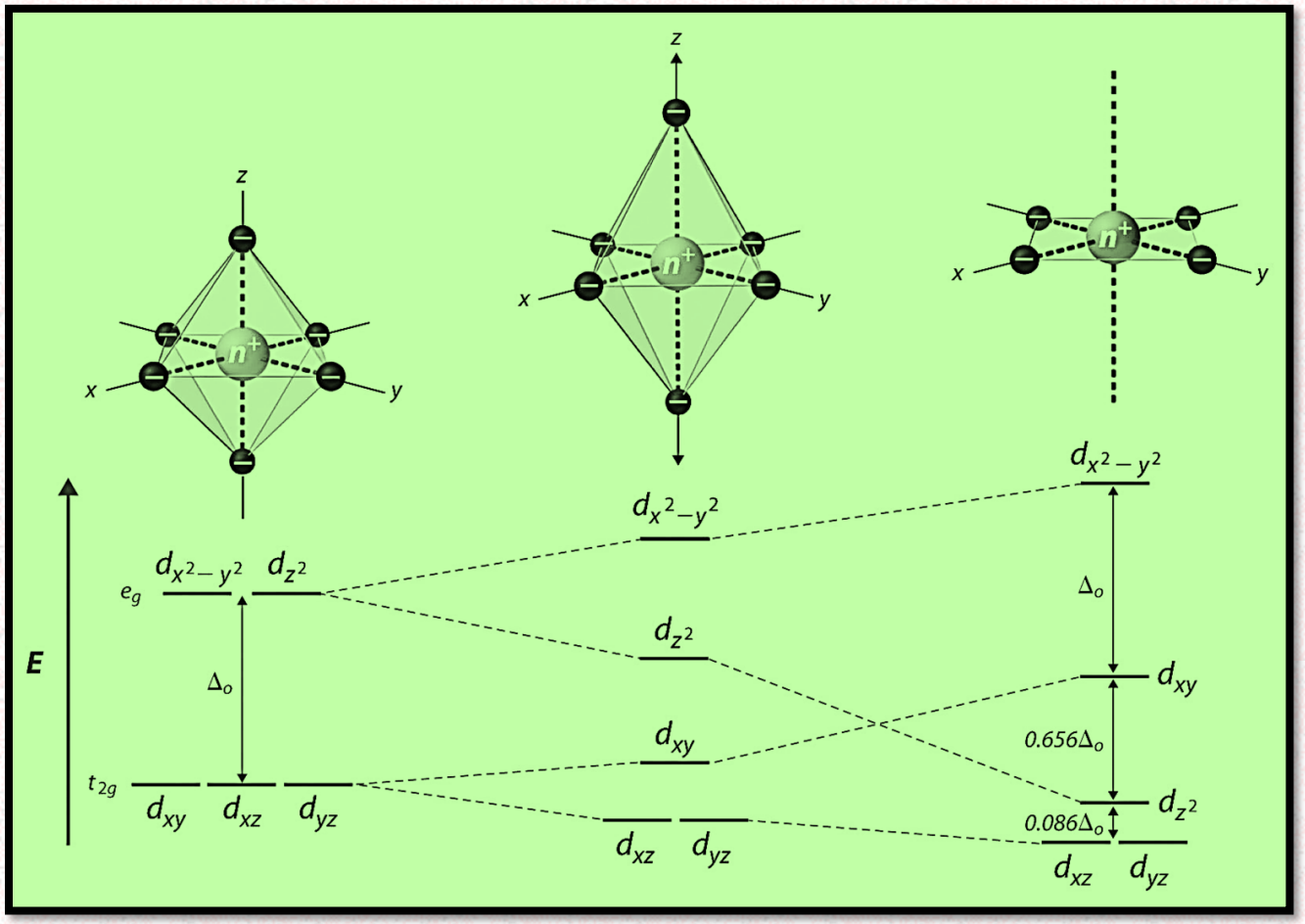
Crystal Field Stabilization Energies for Tetrahedral Complexes of d^1 - d^{10} Ions

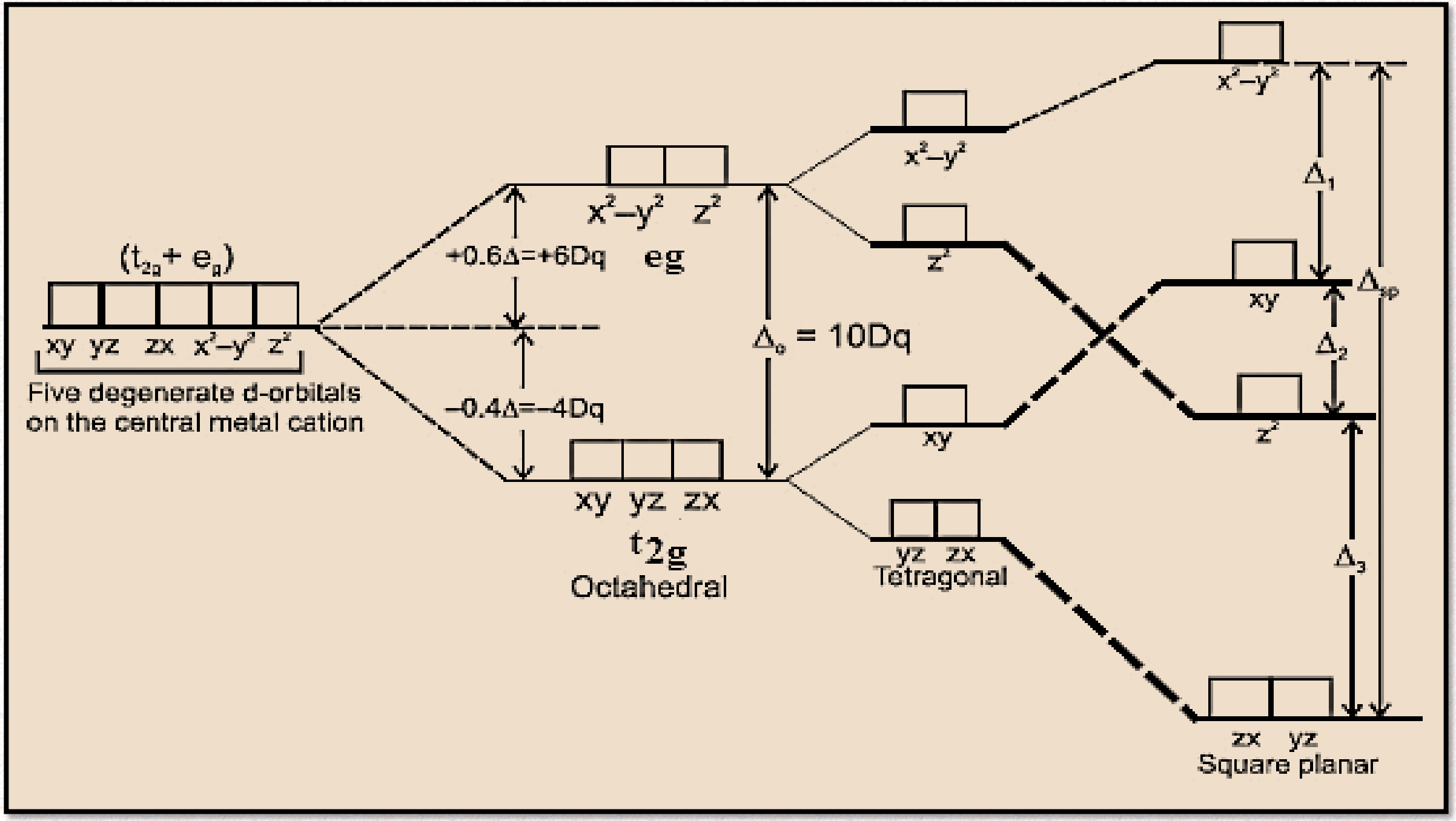
# of d-electrons	Tetrahedral CFSE	# of d-electrons	Tetrahedral CFSE
1	$-0.6\ \Delta_t$	6	$-0.6\ \Delta_t$
2	$-1.2\ \Delta_t$	7	$-1.2\ \Delta_t$
3	$-0.8\ \Delta_t$	8	$-0.8\ \Delta_t$
4	$-0.4\ \Delta_t$	9	$-0.4\ \Delta_t$
5	zero	10	zero


$d_{x^2-y^2}$ d_{z^2}
e_g
E
Δ_o
$0.6\Delta_o$
$\frac{3}{5}\Delta_o$
$-0.4\Delta_o$
$-\frac{2}{5}\Delta_o$
t_{2g}
d_{xy} d_{xz} d_{yz}
Octahedral
d_{xy} d_{xz} d_{yz}
t_2
$\frac{2}{5}\Delta_t$
$0.4\Delta_t$
Δ_t
$-\frac{3}{5}\Delta_t$
$-0.6\Delta_t$
e
$d_{x^2-y^2}$ d_{z^2}
Tetrahedral

Crystal field splitting in a square planar complex






$(t_{2g} + e_g)$
xy yz zx x^2-y^2 z^2
Five degenerate d-orbitals
on the central metal cation
+0.6Δ=+6Dq
eg
x^2-y^2 z^2
–0.4Δ=–4Dq
xy yz zx
t_{2g}
Octahedral
Δ_o = 10Dq
x^2-y^2
z^2
xy
yz zx
Tetragonal
x^2-y^2
Δ_1
xy
Δ_{sp}
Δ_2
z^2
Δ_3
zx yz
Square planar


Thank
you!!