

Co-Ordination compound
or
Complex Compound

Crystal Field Theory (CFT) :-

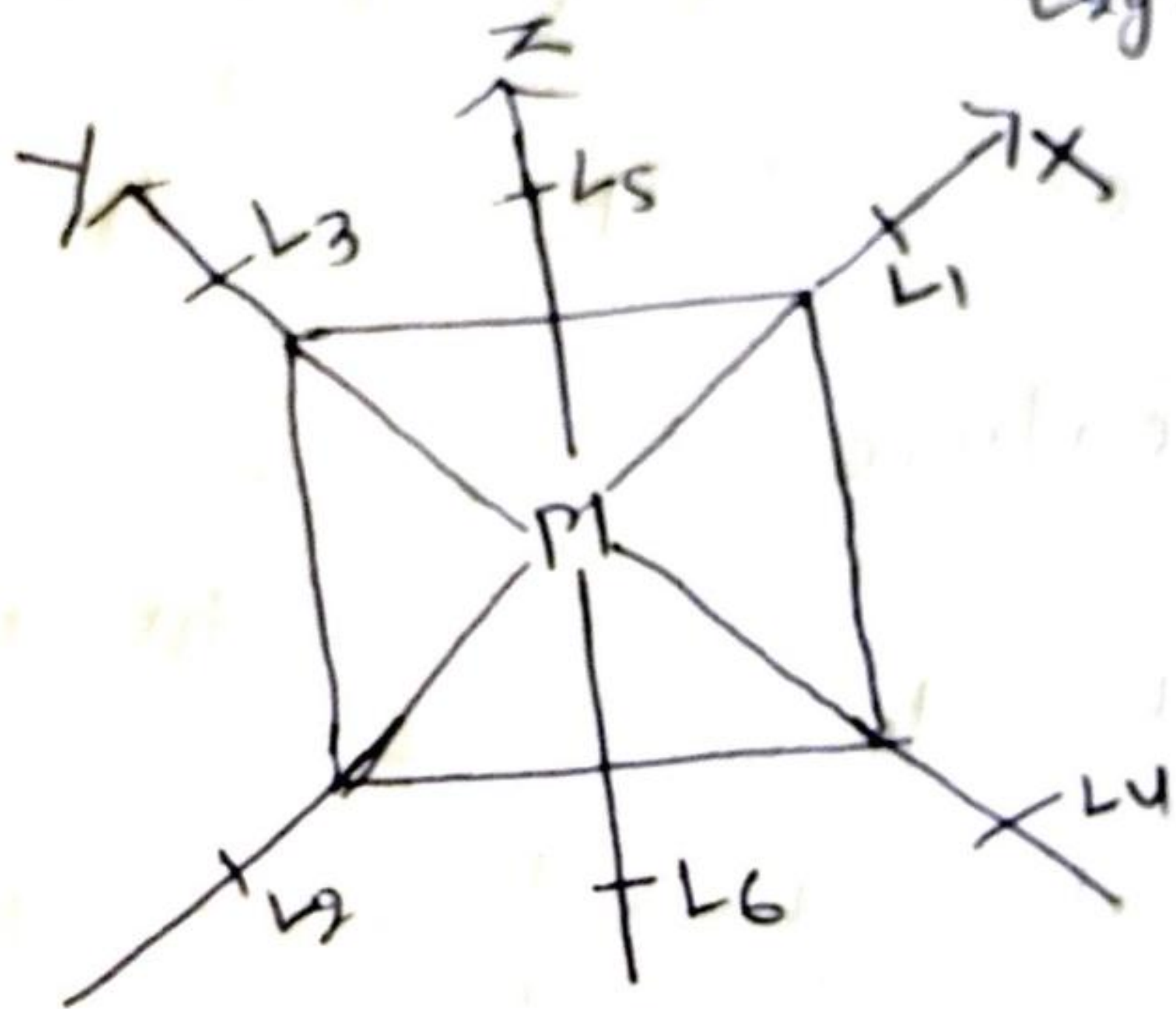
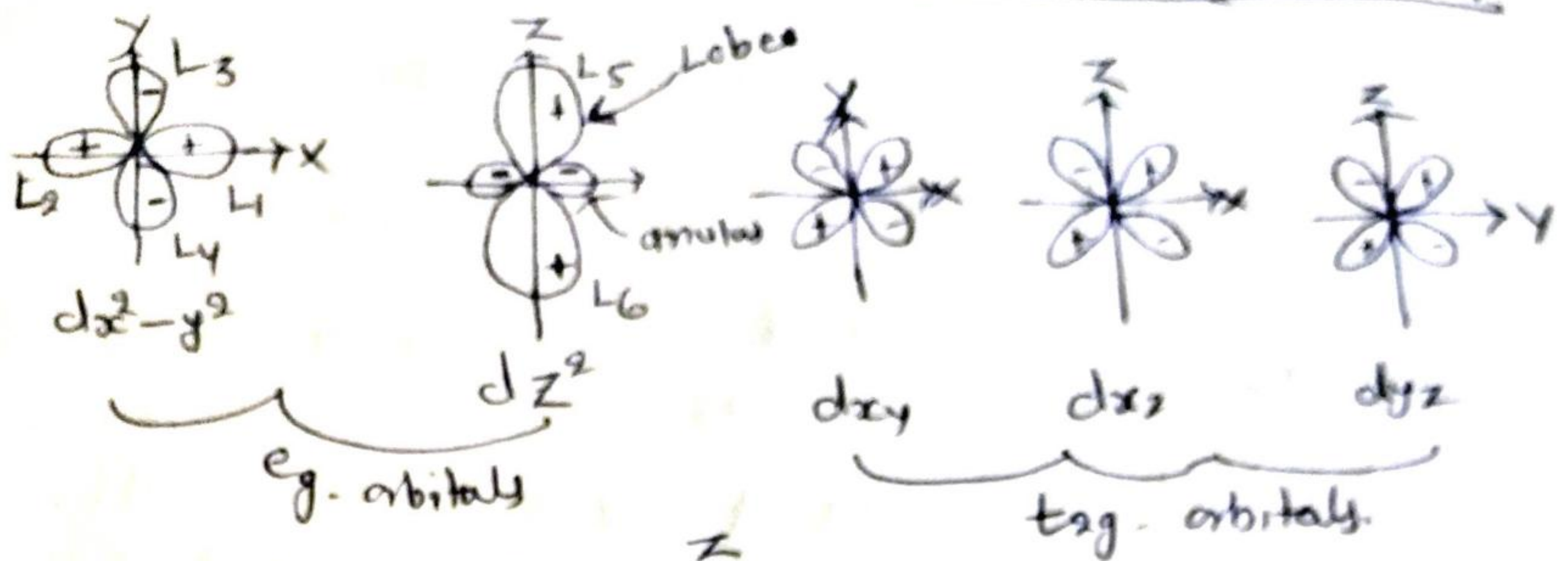
The theory was given by van Vleck and Bethe and it was applied to Co-ordination compounds by Nyholm. The theory deals with electro-valent nature of bonds between the central metal ion and the ligands.

Salient Feature of CFT :-

The following are the salient features of CFT.

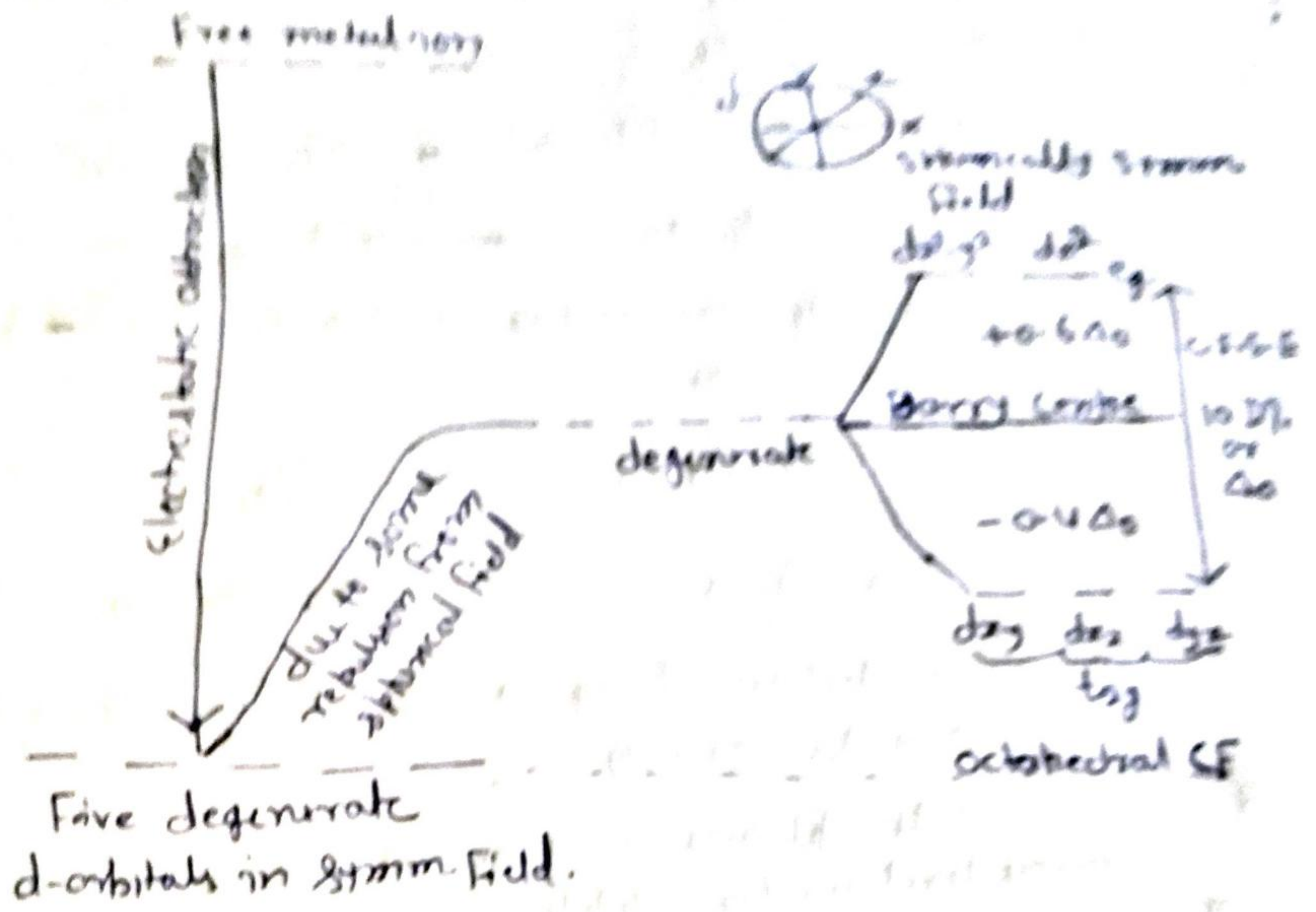
- 1) Ligands are assumed to be negatively charged point or point dipole.
- 2) When such ligands approach to the central metal ion, a force of attraction becomes operative between the two.
- 3) d-orbitals being the outermost orbitals in the metal ion their electrons experience repulsion from the -vely charged points or dipole.
- 4) Due to peculiar and different shape of ~~d-orbitals~~ 5-d-orbitals do not experience the same repulsion. Subsequently their degeneracy is lost and they undergo splitting, the phenomenon is called splitting of d-orbitals.
- 5) The mode of splitting of d-orbitals depends on the geometry of the complex.

Splitting of d-orbitals in octahedral field:



It is obvious from the diagram that dx^2-y^2 and dz^2 orbitals have their lobes directly pointed towards the ligands and hence experience greater repulsion and subsequently they get destabilised and so go higher in energy. The rest 3-d-orbitals i.e., dxy , dxz and dyz have their lobes between the two ligands hence they experience less repulsion than dx^2-y^2 and dz^2 . Subsequently they get stabilised and go lower in energy, thus in octahedral complexes, the degeneracy of d-orbitals is lost and they undergo ~~in~~ splitting.

Splitting of d-orbitals in octahedral field



Five degenerate d-orbitals in spher. field.

CFSE (Crystal Field Splitting/Stabilisation) Energy

The energy gap between t_{2g} and e_g orbital in crystal field is called crystal field splitting energy. It is denoted by Δ_o or $10 Dq$.

(O - represents octahedral; $Dq =$ unit of P.E.)

$$D = \frac{35ze}{4a^5} \quad ; \quad z = \text{Nuclear charge}$$

$$a = \text{Bohr's constant} = 0.529 \text{ \AA} \quad (\text{for H atom})$$

$$q = \frac{ze r^{-4}}{105} \quad ; \quad r = \text{radial distance}$$

$$Dq = \frac{5 \mu r^4}{6 a^4}$$

In order to maintain the bary centre the decrease in energy of t_{2g} must be equal to the increase in energy of e_g .

$$t_{2g} = -\frac{2}{5} \Delta_0 = -0.4 \Delta_0 / \text{electron}$$

$$\text{or } t_{2g} = -\frac{2}{5} \Delta_0 = -0.4 \Delta_0 / \text{electron}$$

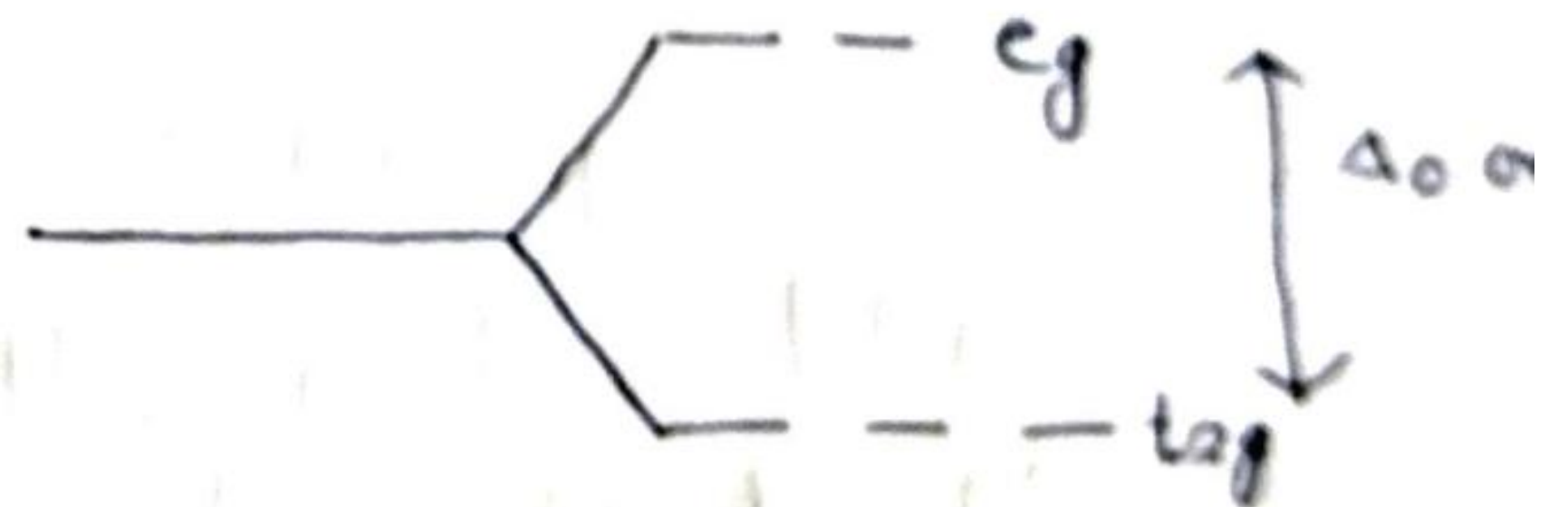
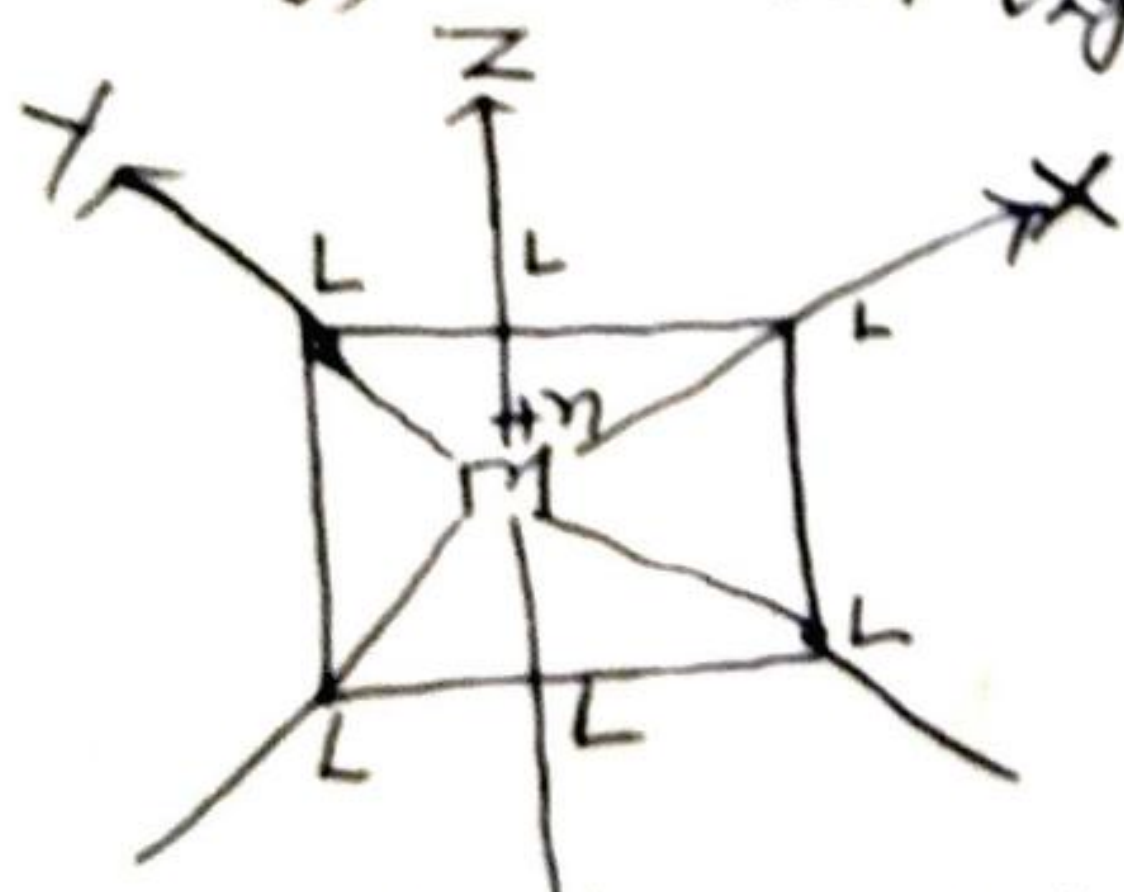
So, each electron in t_{2g} is stabilised by $-4Dq$ or $-0.4 \Delta_0$ energy

$$e_g = +\frac{3}{5} \Delta_0 = +0.6 \Delta_0 / \text{electron}$$

$$= +\frac{3}{5} \Delta_0 = +0.6 \Delta_0 / \text{electron}$$

So, each electron of e_g is destabilised by $+6Dq$ or $+0.6 \Delta_0$ energy.

d-orbitals splitting in octahedral field shows lower energy level for t_{2g} -orbitals than e_g -orbitals. Explain.



In octahedral crystal field, there are two ligands along axis (x, y and z-axis) and hence $d_{x^2-y^2}$ and d_{z^2} having 4 lobes in the direction of the ligand experience greater repulsion go higher in energy than the bary centre containing d_{xy} , d_{xz} and d_{yz} having their lobes in between two ligands experience less repulsion than e_g orbitals and hence lower in energy than bary centre containing t_{2g} . That's why in octahedral field t_{2g} orbitals are at lower energy than e_g orbitals.