SIMPLE MODEL FOR COMPARISON OF CFT AND MOT APPROACH.

Consider a simple system consisting of a Lewis base ligand L, with one lone pair to donate to Lewis acid metal M+ that has two orbitals M1and M2with a single unpaired electron.

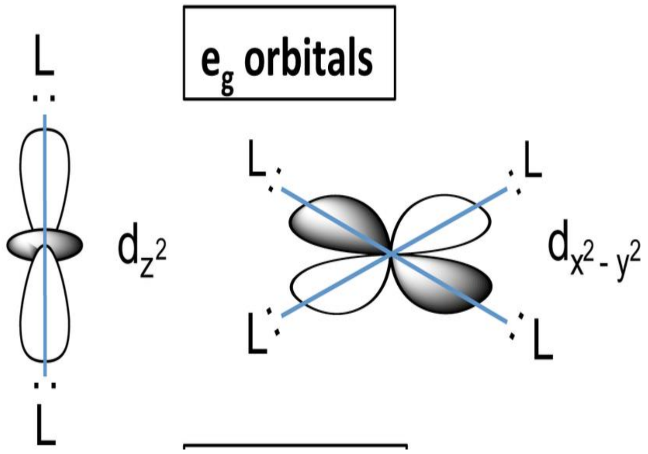
Crystal Field Theory is based on ionic model.

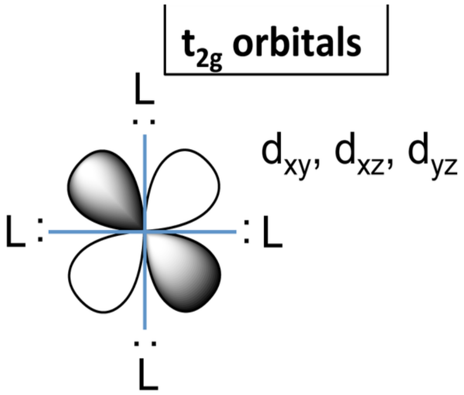
The metal (M) has a positive charge, equivalent to its oxidation state. Ligands negatively charged, e.g Cl Ion-Ion attraction

or if neutral molecule, e.g water, Ammonia, then negative end of the dipole, is oriented towards the metal. Ion- dipole attraction.

In addition there is repulsive forces between the electrons of metal and ligands.

There is no overlap between the orbitals of metal and ligand.





It is purely an electrostatic bond. There is no overlap between the metal and the ligand orbitals. The orbitals are held at a suitable distance from each other.

The tip of the ligand orbital, where there is maximum angular probability distribution of electronic charge, does not coincide with the tip of the t_{2g} orbital, hence less repulsion.

The tip of the ligand and metal orbitals are in one line. Repulsion is greater.

If the two orbitals had overlapped, repulsions would have ceased due to neutralization of spins and formation of sigma bond.

However, CFT is not based on overlap model.

The d-orbitals of the metals, $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{xz},, d_{yz} are degenerate. When the ligands approach the metal ion the energy is initially raised, forming a spherically symmetrical field. As the ligands approach further to form the octahedral complex, the d-orbitals split, on the bases of their lobes lying along the axis, $d_{x^2-y^2}$, d_{z^2} experience more repulsion (e_g orbitals). Lobes lying in between the axis d_{xy}, d_{xz},, d_{yz} (t_{2g}) less repulsion, hence lower energy.

The t_{2g} orbitals are stabilized by an amount, $-2/5\ \Delta_o$, while the e_g orbitals are destabilized by an amount of $+3/5\ \Delta_o$.

The splitting is higher for strong ligands and less for weak ligands. Hence $[Co(NH_3)_6]^{+3}$ is diamagnetic and $[CoF_6]^{-3}$ is paramagnetic.

1. CFT explains orbital energy. It is the sum of the energies of all the metal ion electrons. CFSE can be easily calculated, using simple calculations.

CFSE = X $(-2/5\ \Delta_o)$ + Y $(+3/5\ \Delta_o.)$ + (Z)Δ

MOT is based on covalent model, overlap of metal orbitals with ligand orbitals. Overlap possible if, Orbitals have appropriate energy and symmetry (orientations). For ex: 1s can combine with 1s and not with 2s as they have energy gap. Similarly, s-orbital can combine with p_z but not with p_x or p_y as the z-axis is inter nuclear axis and so oriented in line of s-orbital but others are perpendicular.

2. CFT is not used to predict or describe bonding, rather it is used to predict or understand spectra for a particular molecule. This includes the concepts of high spin and low spin which are used to predict and explain properties of a molecule due to the orbital positions of electrons. For instance, a 6 electron high spin complex would be paramagnetic because some electrons would remain unpaired. Meanwhile a 6 electron low spin complex would be diamagnetic because all electrons would be paired.

MOT on the other hand is used to explain bonding and reactivity.

A classic example of this is with pericyclic reactions. MOT is used to predict the phase of lobes in an MO diagram which in turn allows one to predict whether a reaction will proceed thermodynamically of photochemically based on the overlap of lobes.

3. CFT: The difference in energy between e_g and t_{2g} orbitals, arises because t_{2g} orbitals are repelled less than the e_g orbitals. A strong ligand (Spectrochemical series) will cause the two sets to be separated by a greater gap than a weaker ligand.

   MOT: Delta O represents the energy difference between non-bonding t_{2g} atomic orbitals and anti bonding e_g^* (σ^*_d) molecular orbitals.

   In MOT, a strong ligand is one whose orbitals overlap more efficiently with the metal orbitals, giving a larger value of Δo.

   The orbitals of a weaker ligand overlap poorly with the metal orbitals, resulting in a smaller value of Δo

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7. MOT is heavily based on mathematical equations and these equations are used in computational studies.

CFT on the other hand is almost entirely qualitative. One can calculate the Crystal Field Stabilization Energy (CFSE).

8. CFT involves only sigma bonding. MOT Sigma as well as Pi bonding are involved

9. CFT explains only electrostatic, MOT says bonding some transition elements can be explained by electrostatic some by covalent.

10. CFT does not explain charge transfer.

MOT does, example KMnO4 is coloured due to presence of anti bonding Molecular orbitals.