Crystal field theory (**CFT**)

Crystal field theory (**CFT**) describes the breaking of degeneracies of electron orbital states, usually d or f orbitals, due to a static electric field produced by a surrounding charge distribution (anion neighbors). This theory has been used to describe various spectroscopies of transition metal coordination complexes, in particular optical spectra (colors). CFT successfully accounts for some magnetic properties, colors, hydration enthalpies, and spinel structures of transition metal complexes, but it does not attempt to describe bonding. CFT was developed by physicists Hans Bethe and John Hasbrouck van Vleckin the 1930s. CFT was subsequently combined with molecular orbital theory to form the more realistic and complex ligand field theory (LFT), which delivers insight into the process of chemical bonding in transition metal complexes.

According to crystal field theory, the interaction between a transition metal and ligands arises from the attraction between the positively charged metal cation and the negative charge on the non-bonding electrons of the ligand. The theory is developed by considering energy changes of the five degenerate *d*-orbitals upon being surrounded by an array of point charges consisting of the ligands. As a ligand approaches the metal ion, the electrons from the ligand will be closer to some of the *d*-orbitals and farther away from others, causing a loss of degeneracy. The electrons in the *d*-orbitals and those in the ligand repel each other due to repulsion between like charges. Thus the d-electrons closer to the ligands will have a higher energy than those further away which results in the *d*-orbitals splitting in energy. This splitting is affected by the following factors:

- The nature of the metal ion.
- The metal's oxidation state. A higher oxidation state leads to a larger splitting relative to the spherical field.

- The arrangement of the ligands around the metal ion.
- The coordination number of the metal (i.e. tetrahedral, octahedral...)
- The nature of the ligands surrounding the metal ion. The stronger the effect of the ligands then the greater the difference between the high and low energy *d* groups.

The most common type of complex is octahedral, in which six ligands form the vertices of an octahedron around the metal ion. In octahedral symmetry the *d*-orbitals split into two sets with an energy difference, $\boldsymbol{\Delta}_{\mathbf{oct}}$ (the crystal-field splitting parameter, also commonly denoted by **10*Dq*** for ten times the "differential of quanta" where the d_{xy}, d_{xz} and d_{yz} orbitals will be lower in energy than the $d_z{}^2$ and $d_x{}^2{}_{-y}{}^2$, which will have higher energy, because the former group is farther from the ligands than the latter and therefore experiences less repulsion. The three lower-energy orbitals are collectively referred to as $\mathbf{t_{2g}}$, and the two higher-energy orbitals as $\mathbf{e_g}$. These labels are based on the theory of molecular symmetry: they are the names of irreducible representations of the octahedral point group, O_h. Typical orbital energy diagrams are given below in the section High-spin and low-spin.

Tetrahedral complexes are the second most common type; here four ligands form a tetrahedron around the metal ion. In a tetrahedral crystal field splitting, the *d*-orbitals again split into two groups, with an energy difference of $\boldsymbol{\Delta}_{\mathbf{tet}}$. The lower energy orbitals will be $d_z{}^2$ and $d_x{}^2{}_{-y}{}^2$, and the higher energy orbitals will be d_{xy}, d_{xz} and d_{yz} - opposite to the octahedral case. Furthermore, since the ligand electrons in tetrahedral symmetry are not oriented directly towards the *d*-orbitals, the energy splitting will be lower than in the octahedral case. Square planar and other complex geometries can also be described by CFT.

The size of the gap Δ between the two or more sets of orbitals depends on several factors, including the ligands and geometry of the complex. Some ligands always produce a small value of Δ, while others always give a large splitting. The reasons behind this can be explained by ligand field theory. The spectrochemical series is an empirically-derived list of ligands ordered by the size of the splitting Δ that they produce

$I^- < Br^- < S^{2-} < SCN^-$ (S–bonded)
$< Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^-$ (N–bonded)
$< CH_3CN <$ py $< NH_3 <$ en $<$ 2,2'-bipyridine $<$ phen $< NO_2^- < PPh_3 < CN^- <$ CO.