Crystal Field Theory History

1929  Hans Bethe - Crystal Field Theory (CFT)
      • Developed to interpret color, spectra, magnetism in crystals

1932  J. H. Van Vleck - CFT of Transition Metal Complexes
      • Champions CFT to interpret properties of transition metal complexes
      • Show unity of CFT, VB, and MO approaches

1932  L. Pauling and J. C. Slater - VB theory
      • Apply hybrid orbital concepts to interpret properties of transition metal complexes
      • Becomes dominant theory to explain bonding and magnetism until 1950s
      • Can't explain colors and visible spectra

1952  L. E. Orgel - Revival of CFT and development of Ligand Field Theory (LFT)
      • Slowly replaces VB theory
      • Explains magnetism and spectra better

1954  Y. Tanabe and S. Sugano - Semi-quantitative term splitting diagrams
      • Used to interpret visible spectra

1960s  CFT, LFT, and MO Theories
      • Used in conjunction with each other depending on the level of detail required
      • MO used for most sophisticated and quantitative interpretations
      • LFT used for semi-quantitative interpretations
      • CFT used for everyday qualitative interpretations
CFT Principles

- CFT takes an electrostatic approach to the interaction of ligands and metal ions.
  - In purest form it makes no allowances for covalent M–L bonding.

- CFT attempts to describe the effects of the Lewis donor ligands and their electrons on the energies of $d$ orbitals of the metal ion.

- We will consider the case of an octahedral $ML_6$ ($O_h$) complex first and then extend the approach to other complex geometries.
Energies of $d$ orbitals in an Octahedral Complex

Consider a spherical field ($R_3$) equivalent to six electron pairs surrounding a central metal ion, M.
- Ligand-metal electron repulsions will perturb the energies of the five degenerate $d$ orbitals, making them rise in energy.

Localize the six ligand pairs into the positions of an octahedron ($R_3 \rightarrow O_h$).
- Five-fold degeneracy among $d$ orbitals will be lifted, in keeping with the direct product listings in the $O_h$ character table.
- The $d_{xy}$, $d_{yz}$, $d_{xz}$ orbitals constitute a triply degenerate set of $t_{2g}$ symmetry.
- The $d_{x^2-y^2}$, $d_{z^2}$ orbitals constitute a doubly degenerate set of $e_g$ symmetry.$^1$

The energies of the $t_{2g}$ orbitals and $e_g$ orbitals relative to the perturbed energy of the hypothetical spherical field depend upon their orientation to the six ligand coordination positions.

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$^1$The vector product $2z^2 - x^2 - y^2$ indicates the $d$ orbital more commonly labeled $z^2$. 
The $e_g$ orbitals have lobes that point at the ligands and so will ascend in energy.

The $t_{2g}$ orbitals have lobes that lie between ligands and so will descend in energy.
The energy gap between $t_{2g}$ and $e_g$ levels is designated $\Delta_o$ or $10Dq$.

The energy increase of the $e_g$ orbitals and the energy decrease of the $t_{2g}$ orbitals must be balanced relative to the energy of the hypothetical spherical field (sometimes called the barycenter).
- The energy of the $e_g$ set rises by $+3/5\Delta_o = +6Dq$ while the energy of the $t_{2g}$ set falls by $-2/5\Delta_o = -4Dq$, resulting in no net energy change for the system.

$$\Delta E = E(e_g)\uparrow + E(t_{2g})\downarrow$$
$$= (2)(+3/5\Delta_o) + (3)(-2/5\Delta_o)$$
$$= (2)(+6Dq) + (3)(-4Dq) = 0$$

The magnitude of $\Delta_o$ depends upon both the metal ion and the attaching ligands.

Magnitudes of $\Delta_o$ are typically $\sim 100 – 400$ kJ/mol ($\sim 8,375 – 33,500$ cm$^{-1}$).

$^21$ kJ/mol = 83.7 cm$^{-1}$
Electron Filling of $t_{2g}$ and $e_g$ Orbitals

- Electrons fill $t_{2g}$ and $e_g$ orbitals in an aufbau manner, starting with the $t_{2g}$ set, in accord with the Pauli exclusion principle and Hund’s rule.
  - Spins of successively added electrons are parallel so long as the Pauli exclusion principle allows.
  - At the point when the set of $t_{2g}$ orbitals is half filled, an additional electron must pair if it is to occupy one of the orbitals of the degenerate set.
  - But if the mean pairing energy ($P$) is greater than $\Delta_o$, a lower energy state will result by putting the electron in the higher $e_g$ level.

- For configurations $d^1 – d^3$ and $d^8 – d^{10}$ there is only one ground state configuration.

- For configurations $d^4 – d^7$ there are two possible filling schemes depending on the magnitudes of $P$ and $\Delta_o$.
  - A high spin configuration minimizes pairing by spreading the electrons across both the $t_{2g}$ and $e_g$ levels.
  - A low spin configuration minimizes occupying the higher energy $e_g$ level by pairing electrons in the $t_{2g}$ level.

- For a given metal ion, the pairing energy is relatively constant, so the spin state depends upon the magnitude of the field strength, $\Delta_o$.
  - Low field strength ($\Delta_o < P$) results in a high-spin state.
  - High field strength ($\Delta_o > P$) results in a low-spin state.
## High- and Low-Spin Configurations for ML$_6$ $O_h$

<table>
<thead>
<tr>
<th></th>
<th>$e_g$</th>
<th>$t_{2g}$</th>
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<td>$t_{2g}$</td>
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<tr>
<td>$d^1$</td>
<td>high spin</td>
<td>high spin</td>
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<td>$d^2$</td>
<td>low spin</td>
<td>low spin</td>
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<tr>
<td>$d^3$</td>
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<td>high spin</td>
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<tr>
<td>$d^4$</td>
<td>low spin</td>
<td>low spin</td>
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<tr>
<th></th>
<th>$e_g$</th>
<th>$t_{2g}$</th>
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<tr>
<td>$d^6$</td>
<td>high spin</td>
<td>high spin</td>
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<td>$d^7$</td>
<td>low spin</td>
<td>low spin</td>
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<tr>
<td>$d^8$</td>
<td>high spin</td>
<td>high spin</td>
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<tr>
<td>$d^9$</td>
<td>low spin</td>
<td>low spin</td>
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<tr>
<td>$d^{10}$</td>
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Crystal Field Stabilization Energy (CFSE)\textsuperscript{3}

- Occupancy of electrons in $t_{2g}$ and $e_g$ orbitals results in an overall crystal field stabilization energy (CFSE), defined for octahedral complexes as\textsuperscript{4}

$$\text{CFSE} = (-0.4n_{t_{2g}} + 0.6n_{e_g})\Delta_o + pP$$

where

- $n_{t_{2g}}$ = number of electrons in $t_{2g}$ orbitals
- $n_{e_g}$ = number of electrons in $e_g$ orbitals
- $p$ = total number of electron pairs
- $P$ = mean pairing energy

Examples of CFSE Calculations

<table>
<thead>
<tr>
<th>Free Ion</th>
<th>$O_h$</th>
<th>CFSE Calculation</th>
<th>CFSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^3$</td>
<td>$t_{2g}^3$</td>
<td>$(3)(-0.4\Delta_o)$</td>
<td>$-1.2\Delta_o$</td>
</tr>
<tr>
<td>$d^8$</td>
<td>$t_{2g}^6e_g^2$</td>
<td>$[(6)(-0.4) + (2)(+0.6)]\Delta_o + 3P$</td>
<td>$-1.2\Delta_o + 3P$</td>
</tr>
<tr>
<td>$d^7$ low</td>
<td>$t_{2g}^6e_g^1$</td>
<td>$[(6)(-0.4) + (1)(+0.6)]\Delta_o + 3P$</td>
<td>$-1.8\Delta_o + 3P$</td>
</tr>
<tr>
<td>$d^7$ high</td>
<td>$t_{2g}^5e_g^2$</td>
<td>$[(5)(-0.4) + (2)(+0.6)]\Delta_o + 2P$</td>
<td>$-0.8\Delta_o + 2P$</td>
</tr>
</tbody>
</table>

- For $d^n$ cases that could be high- or low-spin, the configuration that results in the lower CFSE for the $\Delta_o$ of the complex is the spin state that is observed.
  - For the hypothetical case $\Delta_o = P$, neither state would be preferred, as the two CFSEs for $d^7$ illustrate:
    - CFSE($d^7$ low) = $-1.8\Delta_o + 3P = -1.8\Delta_o + 3\Delta_o = 1.2\Delta_o$
    - CFSE($d^7$ high) = $-0.8\Delta_o + 2P = -0.8\Delta_o + 2\Delta_o = 1.2\Delta_o$
  - There are no cases for which $\Delta_o = P$.

\textsuperscript{3}CFSE is also called Ligand Field Stabilization Energy (LFSE).

\textsuperscript{4}Meissler & Tarr use $\Pi_c$ for the $\Delta_o$ term and $\Pi_e$ for the $P$ term in the defining equation. Some sources do not include pairing energy in calculating CFSE.
Values of $\Delta_o$, $P$, CFSE and Resulting Spin State

<table>
<thead>
<tr>
<th>Complex</th>
<th>$d^n$</th>
<th>$P$ (cm$^{-1}$)</th>
<th>$\Delta_o$ (cm$^{-1}$)</th>
<th>State</th>
<th>CFSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cr(H}_2\text{O)}_6]^2^+$</td>
<td>$d^4$</td>
<td>18,800</td>
<td>13,900</td>
<td>high</td>
<td>$-0.6\Delta_o$</td>
</tr>
<tr>
<td>$[\text{Fe(H}_2\text{O)}_6]^3^+$</td>
<td>$d^5$</td>
<td>24,000</td>
<td>13,700</td>
<td>high</td>
<td>0</td>
</tr>
<tr>
<td>$[\text{Fe(H}_2\text{O)}_6]^2^+$</td>
<td>$d^6$</td>
<td>14,100</td>
<td>10,400</td>
<td>high</td>
<td>$-0.4\Delta_o + P$</td>
</tr>
<tr>
<td>$[\text{Fe(CN)}_6]^4^-$</td>
<td>$d^6$</td>
<td>14,100</td>
<td>33,000</td>
<td>low</td>
<td>$-2.4\Delta_o + 3P$</td>
</tr>
<tr>
<td>$[\text{CoF}_6]^3^-$</td>
<td>$d^6$</td>
<td>16,800</td>
<td>13,000</td>
<td>high</td>
<td>$-0.4\Delta_o + P$</td>
</tr>
<tr>
<td>$[\text{Co(NH}_3)_6]^3^+$</td>
<td>$d^6$</td>
<td>16,800</td>
<td>23,000</td>
<td>low</td>
<td>$-2.4\Delta_o + 3P$</td>
</tr>
<tr>
<td>$[\text{Co(H}_2\text{O)}_6]^2^+$</td>
<td>$d^7$</td>
<td>18,000</td>
<td>9,3000</td>
<td>high</td>
<td>$-0.8\Delta_o + 2P$</td>
</tr>
</tbody>
</table>

- Values of $\Delta_o$ depend on both the metal ion and the ligand.
- Most aquo complexes are high spin, because $\text{H}_2\text{O}$ is a weak-field ligand.
- Almost all Co$^{3+}$ ($d^6$) complexes are low spin, including $[\text{Co(H}_2\text{O)}_6]^3^+$, except $[\text{CoF}_6]^3^-$, which is high spin.
- Second and third row transition metal ions tend to have low spin states.
  - These ions tend to have larger $\Delta_o$ values.
  - Larger 4$d$ and 5$d$ orbitals result in smaller $P$ values, owing to lesser electronic repulsions.
  - 4$d$ and 5$d$ orbitals overlap with ligand orbitals, delocalizing electron density onto the ligands.
Spectrochemical Series

- For a given metal ion, the magnitude of $\Delta_0$ depends on the ligand and tends to increase according to the following spectrochemical series:

$$\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{bipy} < \text{phen} < \text{CN}^- \approx \text{CO}$$

- $\text{en} =$ ethylenediamine, $\text{bipy} = 2,2'$-bipyradine, $\text{phen} = o$-phenanthroline
- Ligands up through $\text{H}_2\text{O}$ are weak-field ligands and tend to result in high-spin complexes.
- Ligands beyond $\text{H}_2\text{O}$ are strong-field ligands and tend to result in low-spin complexes.
The same considerations of crystal field theory can be applied to ML₄ complexes with T_d symmetry.
- In T_d, d_xy, d_yz, d_xz orbitals have t₂ symmetry and dₓ²−y², d_z² orbitals have e symmetry.

Relative energies of the two levels are reversed, compared to the octahedral case.
- No d orbitals point directly at ligands.
- The t₂ orbitals are closer to ligands than are the e orbitals. This can be seen by comparing the orientations of the dₓ²−y² orbital (e set) and d_xy orbital (t₂ set) relative to the four ligands.

The difference results in an energy split between the two levels by Δₜ or 10Dq'. Relative to the barycenter defined by the hypothetical spherical field
- the e level is lower by −3Δₜ/5 = −6Dq'
- the t₂ level is higher by +2Δₜ/5 = +4Dq'
In principle, both high and low spin configurations are conceivable for $d^3-d^6 \text{ML}_4 T_d$ complexes.

- With extremely rare exceptions, only high spin configurations are observed.
  - $\Delta_t$ is much smaller than $\Delta_o$.
  - For a given ligand at the same M-L distances, it can be shown that $\Delta_t = (4/9)\Delta_o$.
  - $\Delta_t << P$ in ordinary complexes, so high spin is favored.

- The crystal field stabilization energy for tetrahedral complexes is calculated from the following equation:
  $$\text{CFSE}(T_d) = (-0.6n_e + 0.4n_{t_2})\Delta_t + pP$$
Crystal Field Splitting for Other Geometries

- We can deduce the CFT splitting of $d$ orbitals in virtually any ligand field by
  - Noting the direct product listings in the appropriate character table to determine the ways in which the $d$ orbital degeneracies are lifted
  - Carrying out an analysis of the metal-ligand interelectronic repulsions produced by the complex’s geometry.

- Sometimes it is useful to begin with either the octahedral or tetrahedral splitting scheme, and then consider the effects that would result by distorting to the new geometry.
  - The results for the perfect and distorted geometries can be correlated through descent in symmetry, using the appropriate correlation tables.
  - Can take this approach with distortions produced by ligand substitution or by intermolecular associations, if descent in symmetry involves a group-subgroup relationship.
Crystal Field for Tetragonally Distorted ML₆

- A tetragonal distortion to an octahedron results from any change in geometry that preserves a $C_4$ axis.
  - Tetragonal distortion occurs whenever two *trans* related ligands are differentiated from the remaining four.

- A useful tetragonal distortion to consider involves equally stretching two *trans* related ligands, thereby causing a descent in symmetry $O_h \rightarrow D_{4h}$.

- The stretching occurs along the $z$ axis, leaving the four positions in the $xy$ plane equivalent to each other.
- Ultimately, such a stretching leads to removal of the two ligands, leaving a square planar ML₄ complex.
Splitting of $d$ Orbital Degeneracies – $O_h \rightarrow D_{4h}$

- From a correlation table that links the groups $O_h$ and $D_{4h}$ it can be determined that the two $e_g$ orbitals of the octahedral field become nondegenerate as $a_{1g}$ and $b_{1g}$ in the $D_{4h}$ tetragonal field.
  - From the direct product listings in the $D_{4h}$ character table
    \[
    a_{1g} = d_{2z^2-x^2-y^2} (= d_z) \\
    b_{1g} = d_{x^2-y^2}
    \]

- From the correlation table it can also be shown that the degeneracy among the $t_{2g}$ orbitals in $O_h$ is partially lifted to become $b_{2g}$ and $e_g$ in the $D_{4h}$ tetragonal field.
  - From the direct product listings in the $D_{4h}$ character table
    \[
    b_{2g} = d_{xy} \\
    e_g = (d_{xz}, d_{yz})
    \]

- Moving the two ligands away from the central metal ion lowers the repulsions between ligand electrons and the metal electrons in those $d$ orbitals that have substantial electron distribution along $z$.
  - Thus the energies of the $d_{xz}$, $d_{yz}$, and $d_{z^2}$ orbitals are lowered.

- If we assume that the stretch along $z$ is accompanied by a counterbalancing contraction in the $xy$ plane, so as to maintain the overall energy of the system, then the orbitals with substantial electron distribution in the $xy$ plane will experience increased repulsions.
  - Thus, the $d_{xy}$ and $d_{x^2-y^2}$ orbitals rise in energy.
Orbital Splitting from a Stretching Tetragonal Distortion

- The upper $e_g$ orbitals of the perfect octahedron split equally by an amount $\delta_1$, with the $d_{x^2-y^2}$ orbital ($b_{1g}$ in $D_{4h}$) rising by $+\delta_1/2$ and the $d_{z^2}$ orbital ($a_{1g}$ in $D_{4h}$) falling by $-\delta_1/2$.

- The lower $t_{2g}$ orbitals of the perfect octahedron split by an amount $\delta_2$, with the $d_{xy}$ orbital ($b_{2g}$ in $D_{4h}$) rising by $+2\delta_2/3$, and the degenerate $d_{xz}$ and $d_{yz}$ orbitals ($e_g$ in $D_{4h}$) falling by $-\delta_2/3$. 
Magnitudes of the $\delta_1$ and $\delta_2$ Splittings

- Both the $\delta_1$ and $\delta_2$ splittings, which are very small compared to $\Delta_0$, maintain the barycenters defined by the $e_g$ and $t_{2g}$ levels of the undistorted octahedron.
  - The energy gap $\delta_1$ is larger than that of $\delta_2$, because the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals are directed at ligands.
  - The distortion has the same effect on the energies of both the $d_{x^2-y^2}$ and $d_{xy}$ orbitals; i.e. $\delta_1/2 = 2\delta_2/3$.

As a result, the energies of both the $d_{x^2-y^2}$ and $d_{xy}$ rise in parallel, maintaining a separation equal to $\Delta_0$ of the undistorted octahedral field.

- Note that $\delta_1/2 = 2\delta_2/3$ implies that $\delta_1 = (4/3)\delta_2$. 

![Energy Level Diagram](image_url)
Square Planar ML₄ Complexes

- If we imagine continuing the stretching of M-L bonds along \(z\), the orbital splittings will become progressively greater, producing successively larger values of \(\delta_1\) and \(\delta_2\).

- Eventually the two ligands will be removed, resulting in a square planar ML₄ complex.

- At some point before this extreme the \(a_{1g} (d_{z^2})\) level may cross and fall below the \(b_{2g} (d_{xy})\) level, resulting in the following splitting scheme.⁵

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⁵The ordering of the lower four \(d\) orbitals probably varies among square planar complexes and has been the subject of much debate. See A. B. P. Lever, *Inorganic Electron Spectroscopy*, 2nd ed., Elsevier, Amsterdam, 1984, p. 537ff. and references therein.
**ML\(_4\) (D\(_{4h}\)) vs. ML\(_4\) (T\(_d\))**

- Most square planar complexes are \(d^8\) and less often \(d^9\).
- In virtually all \(d^8\) cases a low spin configuration is observed, leaving the upper \(b_{1g} (d_{x^2-y^2})\) level vacant in the ground state.
  - This is expected, because square planar geometry in first-row transition metal ions is usually forced by strong field ligands.
  - Strong field ligands produce a large \(\Delta_o\) value.
  - The energy gap between the \(b_{2g} (d_{xy})\) and \(b_{1g} (d_{x^2-y^2})\) levels is equivalent to \(\Delta_o\).

  A large \(\Delta_o\) value favors pairing in the \(b_{2g} (d_{xy})\) level, a low-spin diamagnetic configuration for \(d^8\).

- Tetrahedral \(d^8\) is a high-spin paramagnetic configuration \(e^4t^2_2\).

- ML\(_4\) (D\(_{4h}\)) and ML\(_4\) (T\(_d\)) can be distinguished by magnetic susceptibility measurements.

- Ni\(^{2+}\) ion tends to form square planar, diamagnetic complexes with strong-field ligands (e.g., [Ni(CN)\(_4\)]\(^{2-}\)), but tends to form tetrahedral, paramagnetic complexes with the weaker-field ligands (e.g., [NiCl\(_4\)]\(^{2-}\)).

- With second and third row transition metal ions the \(\Delta_o\) energies are inherently larger, and square planar geometry can occur even with relatively weak field ligands; e.g., square planar [PtCl\(_4\)]\(^{2-}\).