Crystal Field Theory (CFT) In Detail  
(H&S 3rd Ed. Chpt. 21.3)

CFT provides a simple model for d orbital splitting:

- works for several oxidation states and geometries
- allows prediction of properties such as structures, colours, magnetism

CFT examines relative d orbital energies when a $M^{n+}$ ion is placed in an ‘electrical field’ created by the ligand (donor) electrons:

- electrostatic attraction between $M^{n+}$ and L
- electrostatic repulsion between d electrons and L electrons (considered as point charges) destabilizes d electrons differentially depending upon their orientation in space

![Diagram showing energy levels and d orbitals in Oh field case]
CFT for an Oh complex:

size of $\Delta_{\text{oct}}$ or $(\Delta_0)$ is determined by the ‘crystal field strength’

$\Delta_{\text{oct}}$ (weak field) $<$ $\Delta_{\text{oct}}$ (strong field)

factors affecting the size of $\Delta_{\text{oct}}$ include:

- identity and Ox. St. of the metal (larger for $2^{\text{nd}}$/$3^{\text{rd}}$ row than $1^{\text{st}}$ row $d$ block)
- nature of the ligands ($\sigma$ and $\pi$ bonding ability)
Electronic spectra (UV-Vis) can provide a measure of $\Delta_{\text{oct}}$ because transitions between d orbitals ($t_{2g} \rightarrow e_g$) fall in this region:

\[ [\text{Ti(H}_2\text{O)}_6]^{3+} \]

* $\Delta_{\text{oct}}$ is a measurable quantity

* in this case, Ti$^{3+}$ has $\lambda_{\text{max}} = 20,300 \text{ cm}^{-1}$ or 243 kJ mol$^{-1}$ for the energy required to promote an electron from the $t_{2g}$ to $e_g$ set
Electronic spectroscopy of many Oh complexes gives a *relative* ranking of the crystal field strengths of ligands called the *spectrochemical series*:

\[ \text{I}^- < \text{Br}^- < \text{NCS}^- < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{ox}^{2-} \sim \text{H}_2\text{O} < \]

weak field \hspace{1cm} \rightarrow \hspace{1cm} \text{increasing} \hspace{1cm} \Delta_{\text{oct}} \hspace{1cm} \rightarrow \hspace{1cm}

\[ \text{NCS}^- < \text{py} < \text{NH}_3 < \text{en} < \text{bipy} < \text{phen} < \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- \sim \text{CO} \]

increasing \hspace{1cm} \Delta_{\text{oct}} \hspace{1cm} \rightarrow \hspace{1cm}

**strong field**

A few points about the spectrochemical series:

1. **For a given M^{n+} ion, varying L gives **predictable trends** BUT NOT absolute values for \( \Delta_{\text{oct}} \)**

2. **For a given ML\(_n\), higher ox. states give larger **\( \Delta_{\text{oct}} \)**
   smaller ionic radius, shorter M-L distance?**

3. **Heavier metals of a given triad (2\(^{nd}\) and 3\(^{rd}\) row) give greater **\( \Delta_{\text{oct}} \)** for a given ML\(_n\) type complex**

4. **For a given ML\(_n\) type of complex, \( \Delta_{\text{oct}} \) does NOT vary in a predictable way across the row**