

Crystal Field Theory History

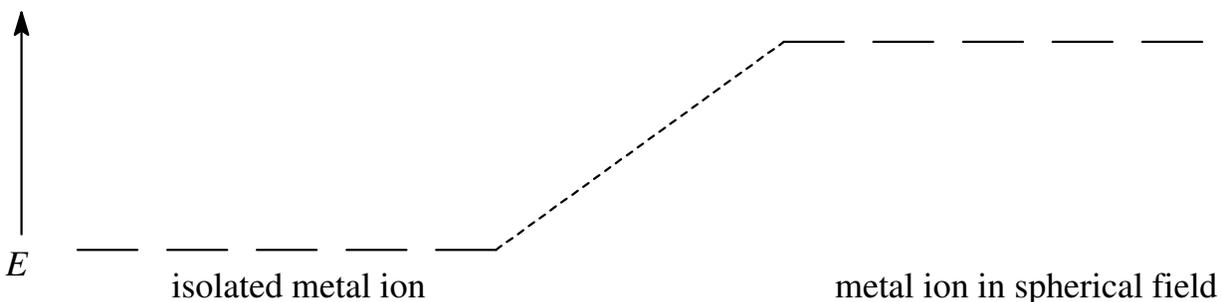
- 1929 Hans Bethe - Crystal Field Theory (CFT)
- Developed to interpret color, spectra, magnetism in crystals
- 1932 J. H. Van Vleck - CFT of Transition Metal Complexes
- Champions CFT to interpret properties of transition metal complexes
 - Show unity of CFT, VB, and MO approaches
- 1932 L. Pauling 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.

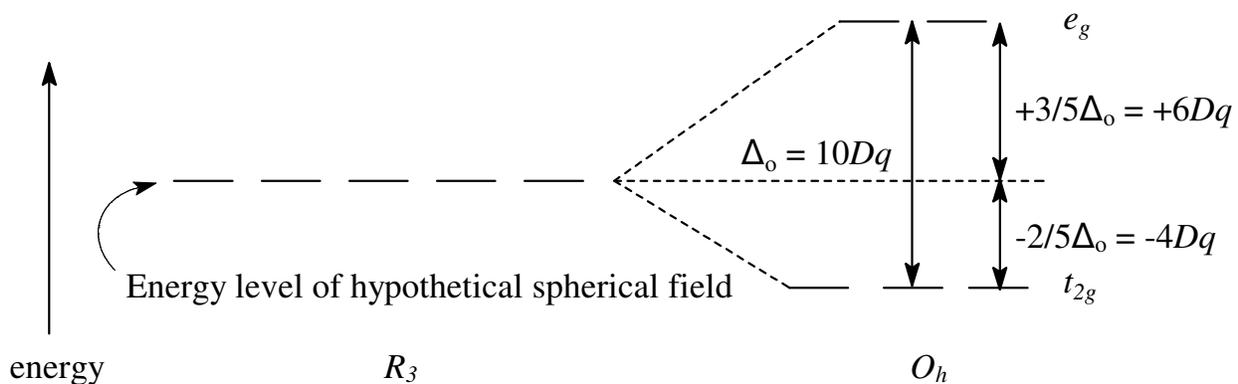
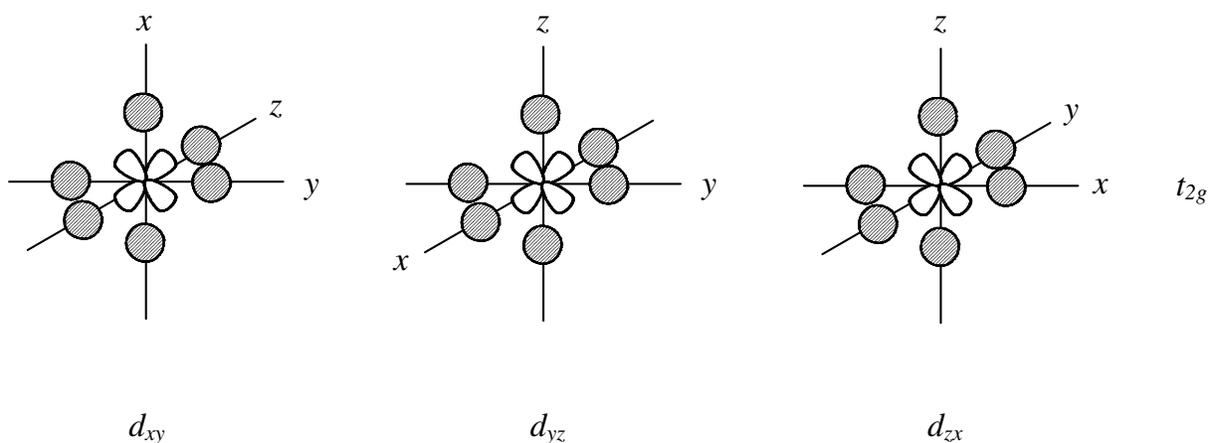
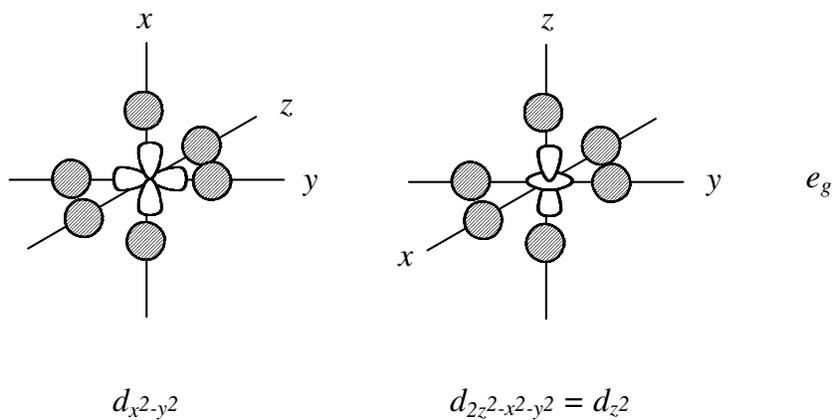


- ☛ Localize the six ligand pairs into the positions of an octahedron ($R_3 \rightarrow O_h$).
 - Five-fold degeneracy among d orbitals will be lifted, in keeping with the direct product listings in the O_h character table.
 - The d_{xy} , d_{yz} , d_{xz} orbitals constitute a triply degenerate set of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

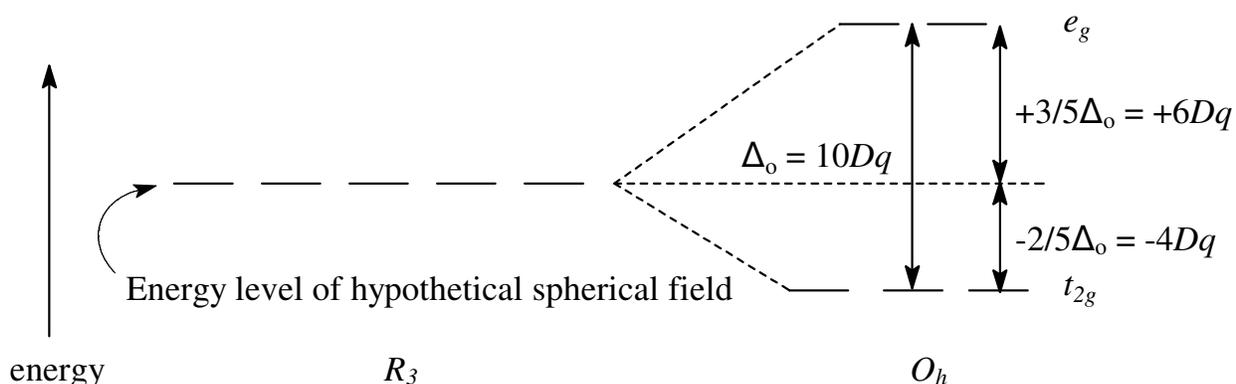
¹The vector product $2z^2 - x^2 - y^2$ indicates the d orbital more commonly labeled z^2 .

***d* Orbitals in an Octahedral Field**

- 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.



Crystal Field Splitting Energy, Δ_o



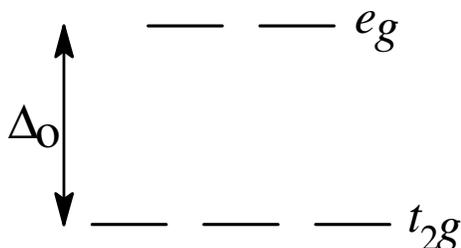
- The energy gap between t_{2g} and e_g levels is designated Δ_o or $10Dq$.
- The energy increase of the e_g orbitals and the energy decrease of the t_{2g} orbitals must be balanced relative to the energy of the hypothetical spherical field (sometimes called the *barycenter*).
 - The energy of the e_g 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.

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

- The magnitude of Δ_o depends upon both the metal ion and the attaching ligands.
- Magnitudes of Δ_o are typically $\sim 100 - 400$ kJ/mol ($\sim 8,375 - 33,500$ cm⁻¹).²

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 Δ_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 Δ_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, Δ_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 $ML_6 O_h$

e_g	<u>—</u> <u>—</u>	<u>—</u> <u>—</u>	<u>—</u> <u>—</u>	<u>—</u> <u>1</u>	<u>—</u> <u>—</u>	<u>1</u> <u>1</u>	<u>—</u> <u>—</u>
t_{2g}	<u>—</u> <u>—</u> <u>1</u>	<u>—</u> <u>1</u> <u>1</u>	<u>1</u> <u>1</u> <u>1</u>	<u>1</u> <u>1</u> <u>1</u>	<u>1</u> <u>1</u> <u>1↓</u>	<u>1</u> <u>1</u> <u>1</u>	<u>1</u> <u>1↓</u> <u>1↓</u>
	d^1	d^2	d^3	d^4 high spin	d^4 low spin	d^5 high spin	d^5 low spin
e_g	<u>1</u> <u>1</u>	<u>—</u> <u>—</u>	<u>1</u> <u>1</u>	<u>—</u> <u>1</u>	<u>1</u> <u>1</u>	<u>1</u> <u>1↓</u>	<u>1↓</u> <u>1↓</u>
t_{2g}	<u>1</u> <u>1</u> <u>1↓</u>	<u>1↓</u> <u>1↓</u> <u>1↓</u>	<u>1</u> <u>1↓</u> <u>1↓</u>	<u>1↓</u> <u>1↓</u> <u>1↓</u>	<u>1↓</u> <u>1↓</u> <u>1↓</u>	<u>1↓</u> <u>1↓</u> <u>1↓</u>	<u>1↓</u> <u>1↓</u> <u>1↓</u>
	d^6 high spin	d^6 low spin	d^7 high spin	d^7 low spin	d^8	d^9	d^{10}

Crystal Field Stabilization Energy (CFSE)³

- Occupancy of electrons in t_{2g} and e_g orbitals results in an overall *crystal field stabilization energy* (CFSE), defined for octahedral complexes as⁴

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

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

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

- For d^n cases that could be high- or low-spin, the configuration that results in the lower CFSE for the Δ_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:

$$\text{CFSE}(d^7 \text{ low}) = -1.8\Delta_o + 3P = -1.8\Delta_o + 3\Delta_o = 1.2\Delta_o$$

$$\text{CFSE}(d^7 \text{ high}) = -0.8\Delta_o + 2P = -0.8\Delta_o + 2\Delta_o = 1.2\Delta_o$$
 - There are no cases for which $\Delta_o = P$.

³CFSE is also called Ligand Field Stabilization Energy (LFSE).

⁴Meissler & Tarr use Π_c for the Δ_o term and Π_e for the P term in the defining equation. Some sources do not include pairing energy in calculating CFSE.

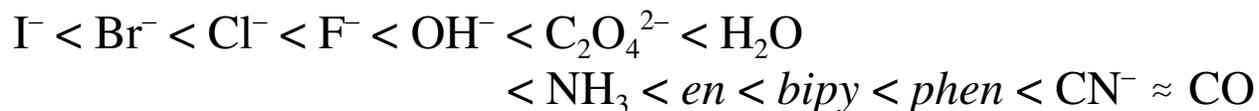
Values of Δ_o , P , CFSE and Resulting Spin State

Complex	d^n	P (cm ⁻¹)	Δ_o (cm ⁻¹)	State	CFSE
[Cr(H ₂ O) ₆] ²⁺	d^4	18,800	13,900	high	$-0.6\Delta_o$
[Fe(H ₂ O) ₆] ³⁺	d^5	24,000	13,700	high	0
[Fe(H ₂ O) ₆] ²⁺	d^6	14,100	10,400	high	$-0.4\Delta_o + P$
[Fe(CN) ₆] ⁴⁻	d^6	14,100	33,000	low	$-2.4\Delta_o + 3P$
[CoF ₆] ³⁻	d^6	16,800	13,000	high	$-0.4\Delta_o + P$
[Co(NH ₃) ₆] ³⁺	d^6	16,800	23,000	low	$-2.4\Delta_o + 3P$
[Co(H ₂ O) ₆] ²⁺	d^7	18,000	9,300	high	$-0.8\Delta_o + 2P$

- Values of Δ_o depend on both the metal ion and the ligand.
- Most aquo complexes are high spin, because H₂O is a weak-field ligand.
- Almost all Co³⁺ (d^6) complexes are low spin, including [Co(H₂O)₆]³⁺, except [CoF₆]³⁻, which is high spin.
- Second and third row transition metal ions tend to have low spin states.
 - These ions tend to have larger Δ_o values.
 - Larger $4d$ and $5d$ orbitals result in smaller P values, owing to lesser electronic repulsions.
 - $4d$ and $5d$ orbitals overlap with ligand orbitals, delocalizing electron density onto the ligands.

Spectrochemical Series

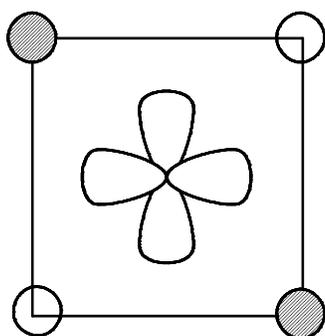
- For a given metal ion, the magnitude of Δ_o depends on the ligand and tends to increase according to the following *spectrochemical series*:



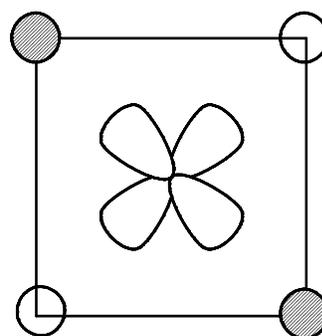
- *en* = ethylenediamine, *bipy* = 2,2'-bipyridine, *phen* = *o*-phenanthroline
- Ligands up through H_2O are *weak-field ligands* and tend to result in high-spin complexes.
- Ligands beyond H_2O are *strong-field ligands* and tend to result in low-spin complexes.

Tetrahedral Crystal Field Splitting

- The same considerations of crystal field theory can be applied to ML_4 complexes with T_d symmetry.
 - In T_d , d_{xy} , d_{yz} , d_{xz} orbitals have t_2 symmetry and $d_{x^2-y^2}$, d_{z^2} 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 t_2 orbitals are closer to ligands than are the e orbitals. This can be seen by comparing the orientations of the $d_{x^2-y^2}$ orbital (e set) and d_{xy} orbital (t_2 set) relative to the four ligands.



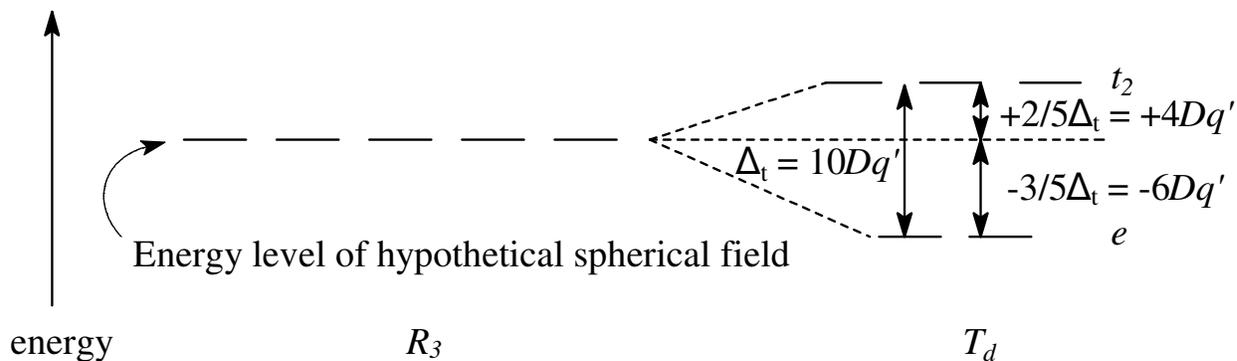
$d_{x^2-y^2}$



d_{xy}

- The difference results in an energy split between the two levels by Δ_t or $10Dq'$. Relative to the barycenter defined by the hypothetical spherical field
 - the e level is lower by $-3\Delta_t/5 = -6Dq'$
 - the t_2 level is higher by $+2\Delta_t/5 = +4Dq'$

Tetrahedral Crystal Field Splitting - cont.



- In principle, both high and low spin configurations are conceivable for d^3-d^6 $ML_4 T_d$ complexes.
- With extremely rare exceptions, only high spin configurations are observed.
 - Δ_t is much smaller than Δ_o .
 - For a given ligand at the same M-L distances, it can be shown that $\Delta_t = (4/9)\Delta_o$.
 - $\Delta_t \ll P$ in ordinary complexes, so high spin is favored.
- The crystal field stabilization energy for tetrahedral complexes is calculated from the following equation:

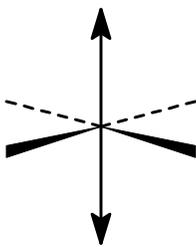
$$CFSE(T_d) = (-0.6n_e + 0.4n_{t_2})\Delta_t + pP$$

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 ML_6

- 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 ML_4 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

$$a_{1g} = d_{2z^2-x^2-y^2} (= d_{z^2})$$
$$b_{1g} = d_{x^2-y^2}$$

- 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

$$b_{2g} = d_{xy}$$
$$e_g = (d_{xz}, d_{yz})$$

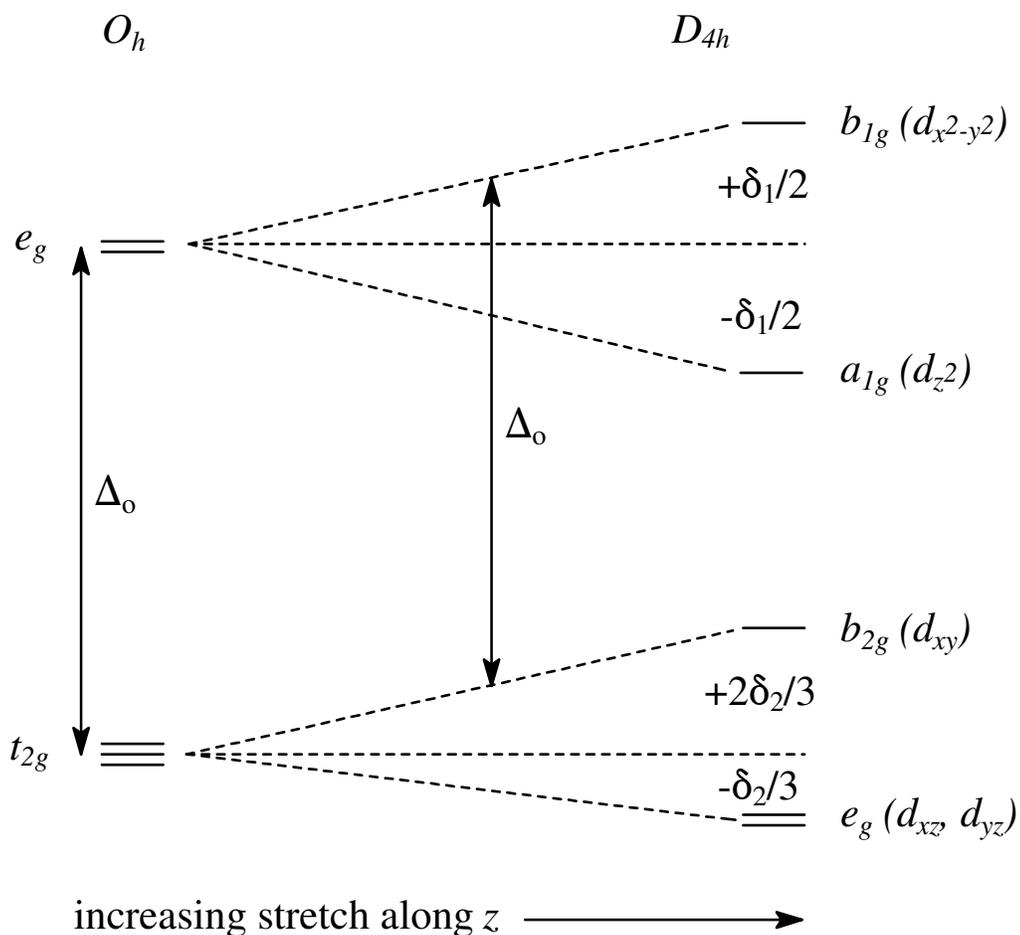
- Moving the two ligands away from the central metal ion lowers the repulsions between ligand electrons and the metal electrons in those d orbitals that have substantial electron distribution along z .

- 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.

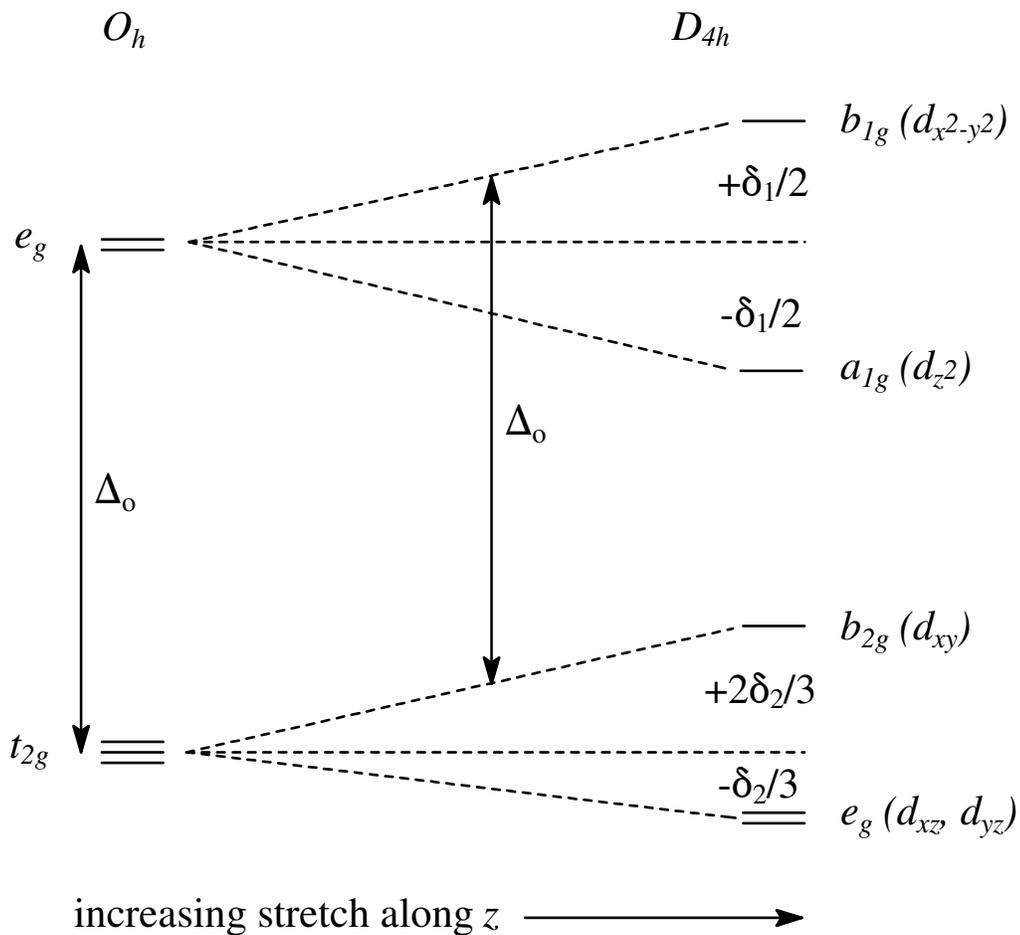
Orbital Splitting from a Stretching Tetragonal Distortion



- The upper e_g orbitals of the perfect octahedron split equally by an amount δ_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 δ_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 δ_1 and δ_2 Splittings

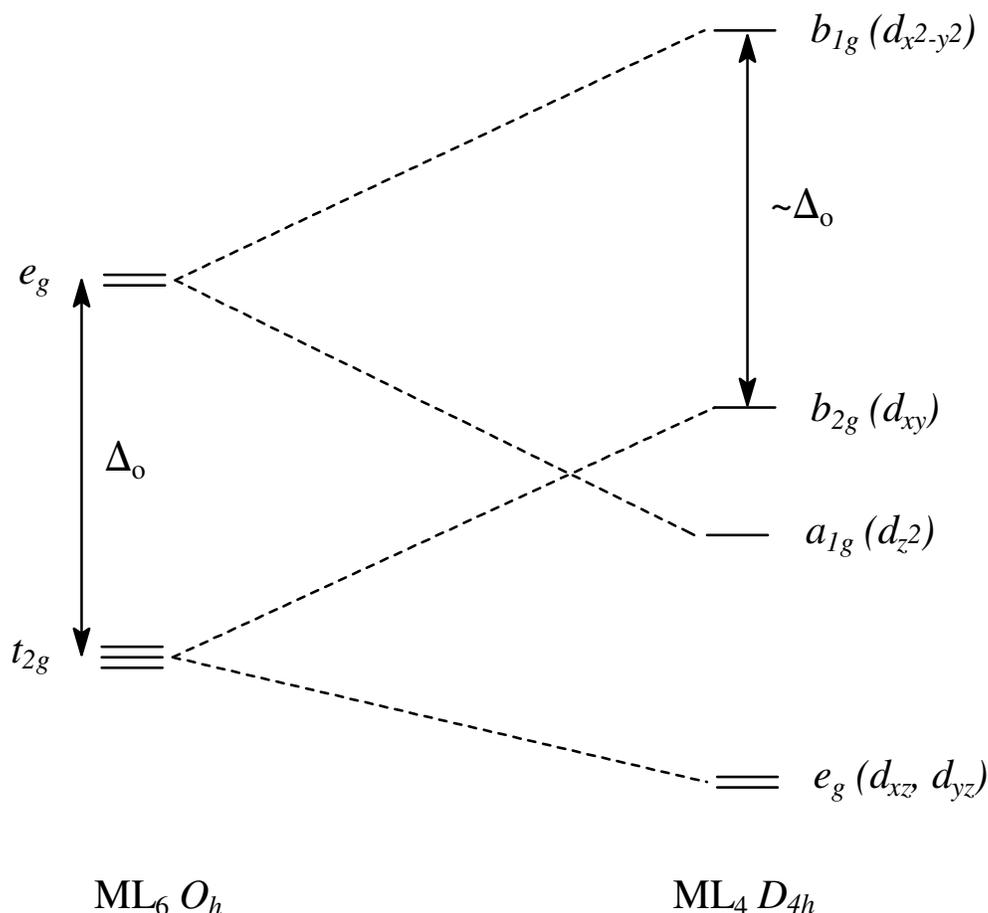
- Both the δ_1 and δ_2 splittings, which are very small compared to Δ_o , maintain the barycenters defined by the e_g and t_{2g} levels of the undistorted octahedron.
 - The energy gap δ_1 is larger than that of δ_2 , because the $d_{x^2-y^2}$ and d_{z^2} orbitals are directed at ligands.
 - The distortion 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 Δ_o of the undistorted octahedral field.



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

Square Planar ML_4 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 δ_1 and δ_2 .
- Eventually the two ligands will be removed, resulting in a square planar ML_4 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



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; and, J. Börgl, M. G. Campbell, and T. Ritter, *J. Chem. Educ.*, **2016**, *93*, 118.

ML₄ (D_{4h}) vs. ML₄ (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 Δ_o value.
 - The energy gap between the b_{2g} (d_{xy}) and b_{1g} ($d_{x^2-y^2}$) levels is equivalent to Δ_o .
 - ☞ A large Δ_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 $e^4t_2^4$.
 - ☞ ML₄ (D_{4h}) and ML₄ (T_d) can be distinguished by magnetic susceptibility measurements.
- Ni²⁺ 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., [NiCl₄]²⁻).
- With second and third row transition metal ions the Δ_o energies are inherently larger, and square planar geometry can occur even with relatively weak field ligands; e.g., square planar [PtCl₄]²⁻.