Theories for Interpreting Bonding, Magnetism, and Spectra of Transition Metal Complexes

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

Crystal Field Theory

☞ What are the effects on the energies of the *d* orbitals on a central transition metal ion, M, if we surround it by a certain number of nucleophilic ligands, L, arranged in a particular geometry?

- In free space, isolated metal ions are spherical, R_3, symmetry ($h = \infty$).
    - Any degree of degeneracy is permitted in R_3.
    - Orbitals in any subshell, defined by a certain value of *n* and a certain value of *l*, are degenerate in R_3.

- In a transition metal complex, ML_n, symmetry descends to a finite point group.
    - A finite point group places limits on the highest permitted dimension of degeneracy.
    - Degeneracies among orbitals in the same subshell may be lifted as a result of the descent in symmetry.

- For octahedral ML_6 (O_h) the five-fold degeneracy among *nd* orbitals must be lifted.
    - Maximum degeneracy in O_h is equivalent to the maximum degeneracy of the irreducible representations; viz., $d_i = 3$.
    - In the same subshell, *nd* orbitals can be no more than three-fold degenerate.

Splitting of *nd* orbitals in ML_6 (O_h)

- From the direct product listings in the O_h character table, the symmetries of *d* orbitals are

$$T_{2g} = (d_{xz}, d_{yz}, d_{xy}) \qquad E_g = (d_{2z^2-x^2-y^2}, d_{x^2-y^2})$$

☞ Note: $d_{2z^2-x^2-y^2} = d_{z^2}$ in O_h

○ *nd* orbital energies must spit in an octahedral field to form a two-fold degenerate set $e_g = (d_{2z^2-x^2-y^2}, d_{x^2-y^2})$ and a three-fold degenerate set $t_{2g} = (d_{xz}, d_{yz}, d_{xy})$.

Symmetry Test of Orbital Degeneracy

- The effect of a symmetry operation on an orbital is merely a change in coordinates without a change in energy.

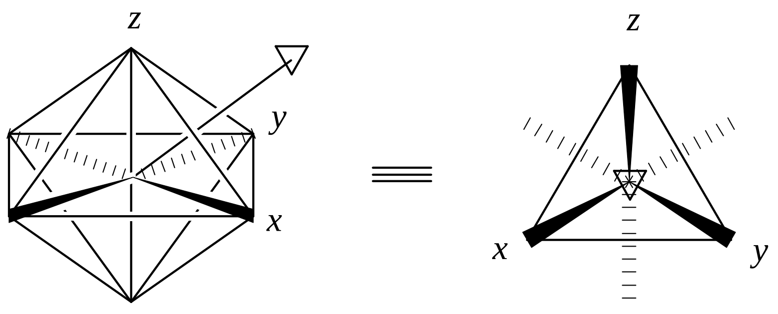
- If some operation of the group converts two or more orbitals into each other, they must be energetically equal.

- Any orbitals that are not related to each other by any symmetry operation of the group cannot be degenerate (except, rarely, as an accidental degeneracy).

☞ To determine which *d* orbitals are degenerate in O_h, apply various operations of the group to see which specific *d* orbitals are related to which other *d* orbitals.

Relationships Between *x*, *y*, and *z* in O_h

- In this case, the operations C_3 and C_3^2 performed about any three-fold axis will show the degeneracies among *d* orbitals.



(a) (b)

- First, note the effects of C_3 and C_3^2 on the *x*, *y*, and *z* axes.

	C_3	C_3^2
$x \rightarrow$	z	y
$y \rightarrow$	x	z
$z \rightarrow$	y	x

☞ This shows that (*x*, *y*, *z*) are degenerate in O_h and indicates that the orbitals (p_x, p_y, p_z) form a degenerate set. (T_{1u} in O_h)

Deducing the Degeneracies Among *d* Orbitals

- Using these *x*, *y*, *z* transformations, deduce the transformations of the five *d* orbitals by making the appropriate substitutions in the subscripts of their notations:

	C_3	$C_3^{\,2}$
d_{xy} →	d_{zx}	d_{yz}
d_{yz} →	d_{xy}	d_{zx}
d_{zx} →	d_{yz}	d_{xy}
$d_{2z^2-x^2-y^2}$	$d_{2y^2-z^2-x^2}$	$d_{2x^2-y^2-z^2}$
$d_{x^2-y^2}$	$d_{z^2-x^2}$	$d_{y^2-z^2}$

☞ The d_{xy}, d_{yz}, and d_{zx} interchange among themselves and must be degenerate. (T_{2g} in O_h)

☹ What are the orbitals generated from $d_{2z^2-x^2-y^2}$ and $d_{x^2-y^2}$?

Old Orbitals from New

- The new, unfamiliar d orbitals that C_3 and $C_3^{\ 2}$ generate from $d_{2z^2\text{-}x^2\text{-}y^2}$ and $d_{x^2\text{-}y^2}$ are linear combinations of the two original orbitals:

$$d_{2y^2\text{-}z^2\text{-}x^2} = -\ (1/2)\ d_{2z^2\text{-}x^2\text{-}y^2} - (3/2)\ d_{x^2\text{-}y^2}$$

$$d_{2x^2\text{-}y^2\text{-}z^2} = -\ (1/2)\ d_{2z^2\text{-}x^2\text{-}y^2} + (3/2)\ d_{x^2\text{-}y^2}$$

$$d_{z^2\text{-}x^2} = +\ (1/2)\ d_{2z^2\text{-}x^2\text{-}y^2} - (1/2)\ d_{x^2\text{-}y^2}$$

$$d_{y^2\text{-}z^2} = -\ (1/2)\ d_{2z^2\text{-}x^2\text{-}y^2} - (1/2)\ d_{x^2\text{-}y^2}$$

Demonstration of first equation:

$$\begin{array}{rcl} -1/2\ (2z^2 - x^2 - y^2) & = & -z^2 + (1/2)x^2 + (1/2)y^2 \\ -3/2\ (x^2 - y^2) & = & -\ (3/2)x^2 + (3/2)y^2 \\ \hline & & -z^2 \quad -x^2 \quad + 2y^2 \ = \ 2y^2 - z^2 - x^2 \end{array}$$

☞ These combinations must have the same energy as the original orbitals comprising them, so the starting orbitals must have identical energies to each other, too.
  - ○ Thus, $d_{2z^2\text{-}x^2\text{-}y^2}$ and $d_{x^2\text{-}y^2}$ are degenerate. (E_g in O_h)

- Note that the transformations of the t_{2g} orbitals do not involve the e_g orbitals and vice versa.
  - ○ There is no operation of O_h that relates any of the orbitals in one set to those in the other.
    - ☞ The t_{2g} and e_g sets are not degenerate with each other and therefore should have distinct energies.

Symmetry Species of Degenerate Orbitals

To find the symmetry of any wave functions (orbitals, electronic states, etc.) in any group:

- Take the wave functions as a basis for a reducible representation in the point group of the system, and then decompose this representation into its component irreducible representations.

- The reducible representation can be constructed by using relationships that give the characters, $\chi[R]$, for operations in spherical symmetry (the group R_3) as a function of the angular momentum quantum number, j, of the wave function or state under consideration.

- These relationships can be used with O_h or any other point group, because all point groups are subgroups of R_3, and the character for a group operation that is retained in a subgroup is the same in the lower-order group.

Equations for Characters for Representations of Wave Functions

$$\chi(E) = 2j + 1$$

$$\chi[C(\theta)] = \frac{\sin(j + 1/2)\theta}{\sin\theta/2}$$

$$\chi(i) = \pm(2j + 1)$$

$$\chi[S(\theta)] = \pm\frac{\sin(j + 1/2)(\theta + \pi)}{\sin(\theta + \pi)/2}$$

$$\chi(\sigma) = \pm\sin(j + 1/2)\pi$$

In these equations

- E, C, i, S, and σ indicate the operations, where θ is the rotation angle for C and S, and $\pi = 180^{\circ}$.
- The quantum number j can be replaced by l when considering an orbital or L when considering the total orbital angular momentum of a Russell-Saunders term. Likewise, j can be replaced by s when considering electron spin or S when considering the spin state of a term.
- The variable sign (±) in the last three equations is taken as +1 for *gerade* states and –1 for *ungerade* states. In the case of one-electron wave functions, orbitals with even-valued l (s, d, g, etc.) are *gerade* (no sign change with inversion), so the positive value is used. Orbitals with odd-valued l (p, f, h, etc.) are *ungerade* (sign changes with inversion), so the negative value is used.

Representation for *d* Orbitals in O_h
Calculating the Characters

☞ Apply the preceding equations, using $l = 2$ in place of j.

$$\chi(E) = 2l + 1 = 2(2) + 1 = 5$$

$$\chi[C_3] = \frac{\sin(l + 1/2)\theta}{\sin\theta/2} = \frac{\sin(2.5 \times 120^\circ)}{\sin 60^\circ} = -1$$

$$\chi[C_2] = \frac{\sin(l + 1/2)\theta}{\sin\theta/2} = \frac{\sin(2.5 \times 180^\circ)}{\sin 90^\circ} = 1$$

$$\chi[C_4] = \frac{\sin(l + 1/2)\theta}{\sin\theta/2} = \frac{\sin(2.5 \times 90^\circ)}{\sin 45^\circ} = -1$$

$$\chi(i) = +(2l + 1) = 2(2) + 1 = 5$$

$$\chi[S_4] = +\frac{\sin(l + 1/2)(\theta + \pi)}{\sin(\theta + \pi)/2} = \frac{\sin(2.5\times 270^\circ)}{\sin(135^\circ)} = -1$$

$$\chi[S_6] = +\frac{\sin(l + 1/2)(\theta + \pi)}{\sin(\theta + \pi)/2} = \frac{\sin(2.5\times 240^\circ)}{\sin(120^\circ)} = -1$$

$$\chi(\sigma) = +\sin(l + 1/2)\pi = \sin(2.5 \times 180^\circ) = 1$$

Representation for *d* Orbitals in O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_d	5	-1	1	-1	1	5	-1	-1	1	1

$$\Gamma_d = E_g + T_{2g}$$

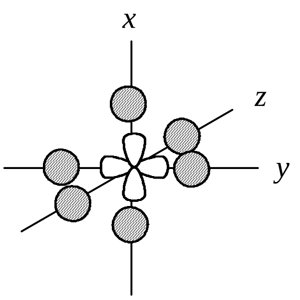
- As we have shown by our considerations of the effects of C_3 and C_3^2, the $d_{2z^2-x^2-y^2}$ and $d_{x^2-y^2}$ orbitals are doubly degenerate, and so must constitute the e_g set.

- Likewise, the d_{xy}, d_{yz}, and d_{zx} orbitals were shown to be triply degenerate, and so must constitute the t_{2g} set.

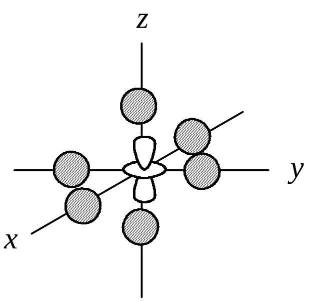
Metal *d* Orbitals in a Six-Ligand Field

- If a transition metal ion were placed in a spherical field equivalent to the charges on six ligands, the energies of all five *d* orbitals would rise together (degenerately) as a result of the repulsions between the negative charges on the ligands and the negative charges of the electrons in the metal orbitals.

- Imagine localizing the ligand charges equidistant from the metal ion along the axes of a Cartesian coordinate system, an octahedral arrangement.

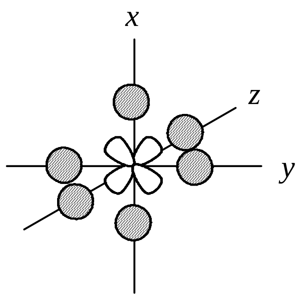


$d_{x^2-y^2}$

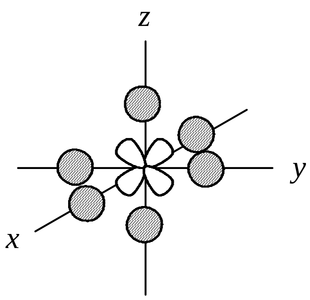


$d_{2z^2-x^2-y^2} = d_{z^2}$

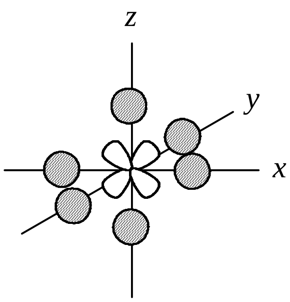
e_g



d_{xy}



d_{yz}



d_{zx}

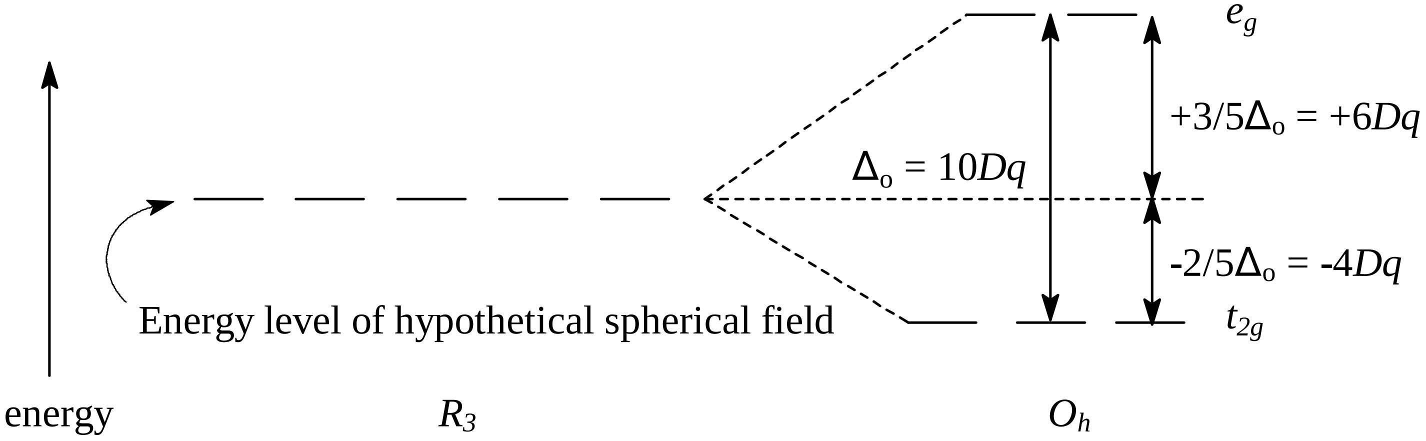
t_{2g}

- Rearranging the charges in this manner should not cause any ***net*** change in the energy of the system.

Relative Energies of the t_{2g} and e_g Orbitals

- In the octahedral field, the metal *d* orbitals of the e_g set will experience greater repulsions than those of the t_{2g} set.
  - The lobes of the orbitals in the e_g set point directly at the ligands, making greater repulsions.
  - The lobes of the orbitals in the t_{2g} set point between ligands, making lesser repulsions.

- Relative to the energy of the hypothetical spherical field, the e_g set will rise in energy and the t_{2g} set will fall in energy, creating an energy separation of Δ_o or $10Dq$ between the two sets of *d* orbitals.



- 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 each of the two orbitals of the e_g set rises by $+3/5\Delta_o = +6Dq$ while the energy of each of the three t_{2g} orbitals falls by $-2/5\Delta_o = -4Dq$. This results in no net energy change for the system; i.e.,

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

Magnitude of Δ_o

- The magnitude of Δ_o depends upon both the metal ion and the attaching ligands.

- Δ_o increases for similar transition metal ions in successive periods (i.e., first row < second row < third row).

- Δ_o increases as the charge on the metal ion increases (i.e., $M^{2+} < M^{3+}$).

- For the same metal ion, Δ_o increases for common ligands according to the ***spectrochemical series***:

  $I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < OH^- <$ *ox* $< H_2O < NCS^- <$
  $CH_3CN < NH_3 <$ *en* < *dipy* < *phen* $< NO_2^- < CN^- < CO$

- In the CFT model, the spectrochemical series is an empirical result that cannot be rationalized in terms of simple point charges.
  - Note, for example, CO is a neutral ligand but produces the largest Δ_o splitting.
  - The spectrochemical series can be rationalized in terms of models that acknowledge orbital interactions between metal and ligands.

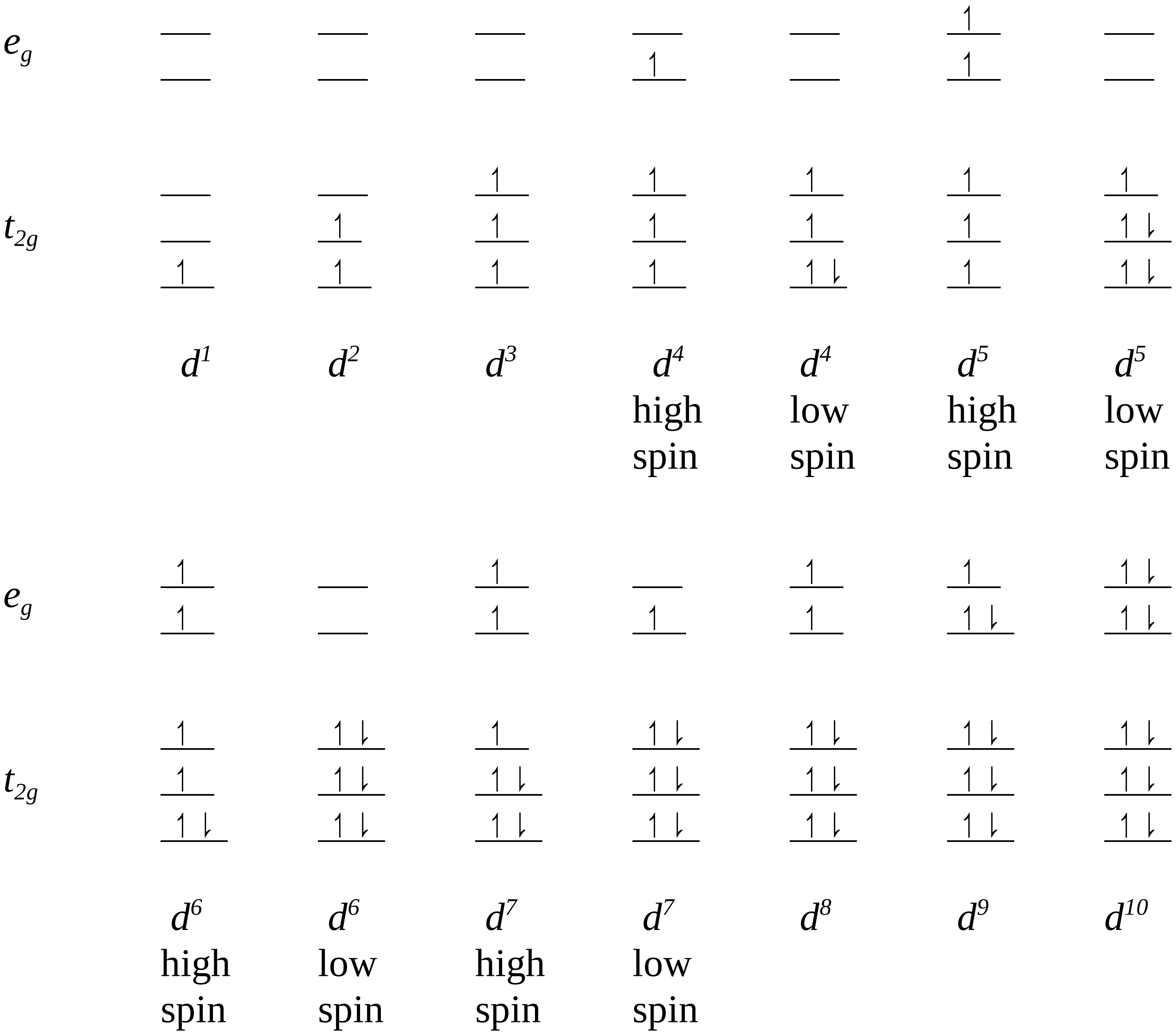
Δ_o and Spin State

- The ground state electronic configurations of transition metal ions in octahedral complexes can be determined by filling the *d* orbitals in the two levels according to the usual Aufbau process.

- For the configurations d^1, d^2, d^3, d^8, d^9, and d^{10} there is no ambiguity to the assignments.

- For configurations d^4 through d^7 both *high spin* or *low spin* configurations are possible.

High- and Low-Spin Configurations for MX_6 O_h



Factors Affecting High-Low Spins

- The relative magnitudes of Δ_o and the *mean pairing energy*, *P*, determine which spin state results in octahedral complexes.
    - The mean pairing energy results from coulombic repulsions between electrons in the same orbital, and from the loss of *exchange energy* produced by distributing electrons across multiply degenerate orbitals.
    - The coulombic contribution to the pairing energy tends to fall off in the order $3d > 4d > 5d$, as the orbitals become larger and the electron interactions are lessened.

- A high spin configuration avoids pairing by spreading the electrons across both the t_{2g} and e_g levels.

- A low spin configuration avoids occupying the higher energy e_g level by pairing electrons in the t_{2g} level.

- Unlike free ions, the Δ_o energy gap in octahedral complexes of transition metals is relatively small and is comparable to typical pairing energies.

    - In d^{4-7} O_h cases a weak crystal field (small Δ_o) favors the high spin configuration, and a strong crystal field (large Δ_o) favors the low spin configuration.

    - For a given first-row transition metal ion, the magnitude of the field depends largely on the nature of the ligand; i.e., where it falls in the spectrochemical series.

    - Second and third row transition metal tend to have larger Δ_o and smaller *P* values, which favor low spin configurations.

Tetrahedral ML_4 Complexes

- C_3 and C_3^2 make the orbitals d_{xy}, d_{yz}, and d_{zx} triply degenerate and the orbitals $d_{2z^2-x^2-y^2}$ and $d_{x^2-y^2}$ doubly degenerate.

- Applying the equations for characters of a representation of a wave function:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_d	5	-1	1	-1	1

$$\Gamma_d = E + T_2$$

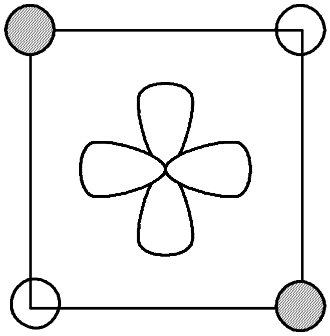
(as shown in the direct product listings in the T_d character table).

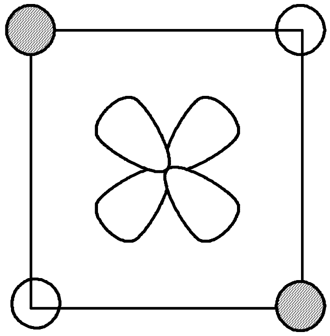
  - Thus the d_{xy}, d_{yz}, and d_{zx} orbitals are labeled t_2.

  - The $d_{2z^2-x^2-y^2}$ and $d_{x^2-y^2}$ orbitals are labeled e.

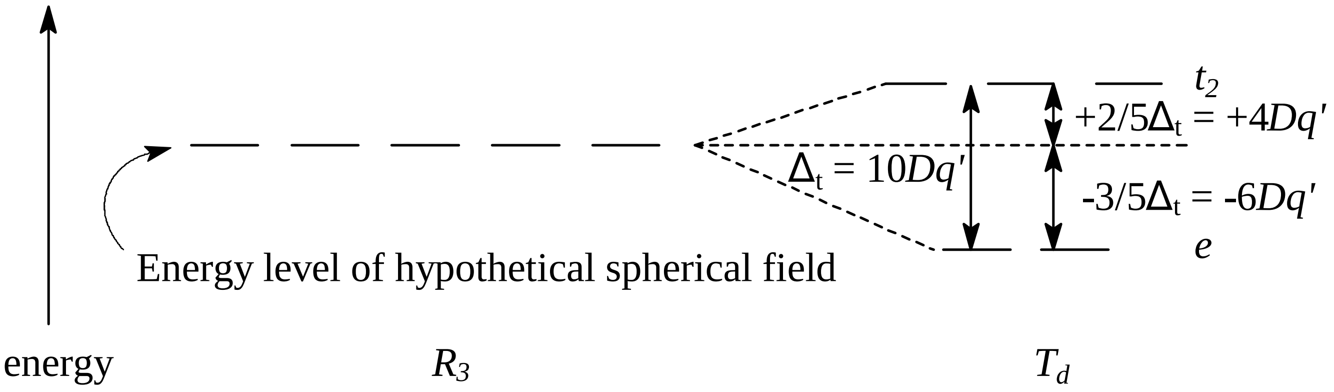
Relative Energies of t_2 and e Orbitals in ML_4 (T_d)

- 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 of 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 $+2\Delta_t/5 = +4Dq'$



High-Spin/Low-Spin Tetrahedral Complexes?

- 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 $\Delta_t = (4/9)\Delta_o$.
    - $\Delta_t << P$ in ordinary complexes, so high spin is favored.