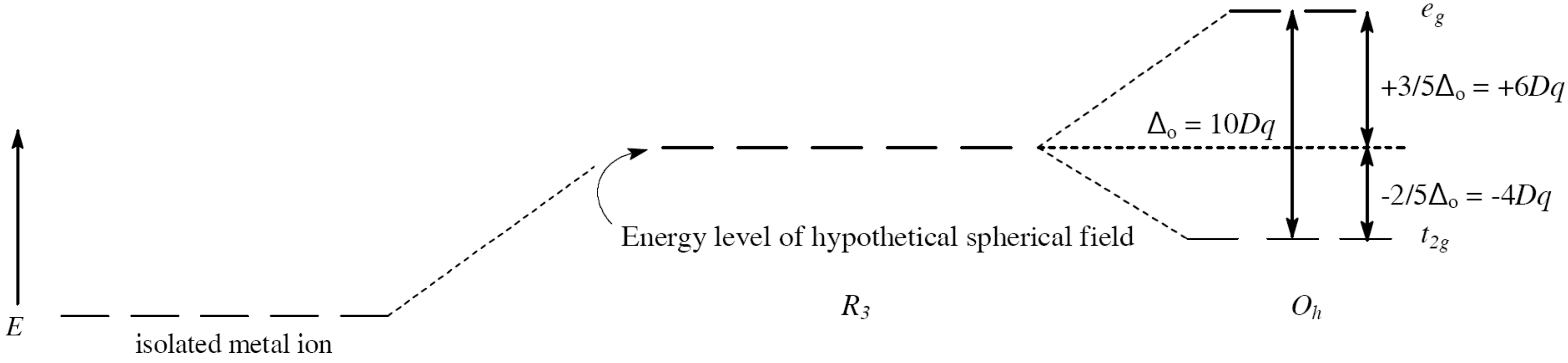
Metal *d* orbitals in an O_h crystal field

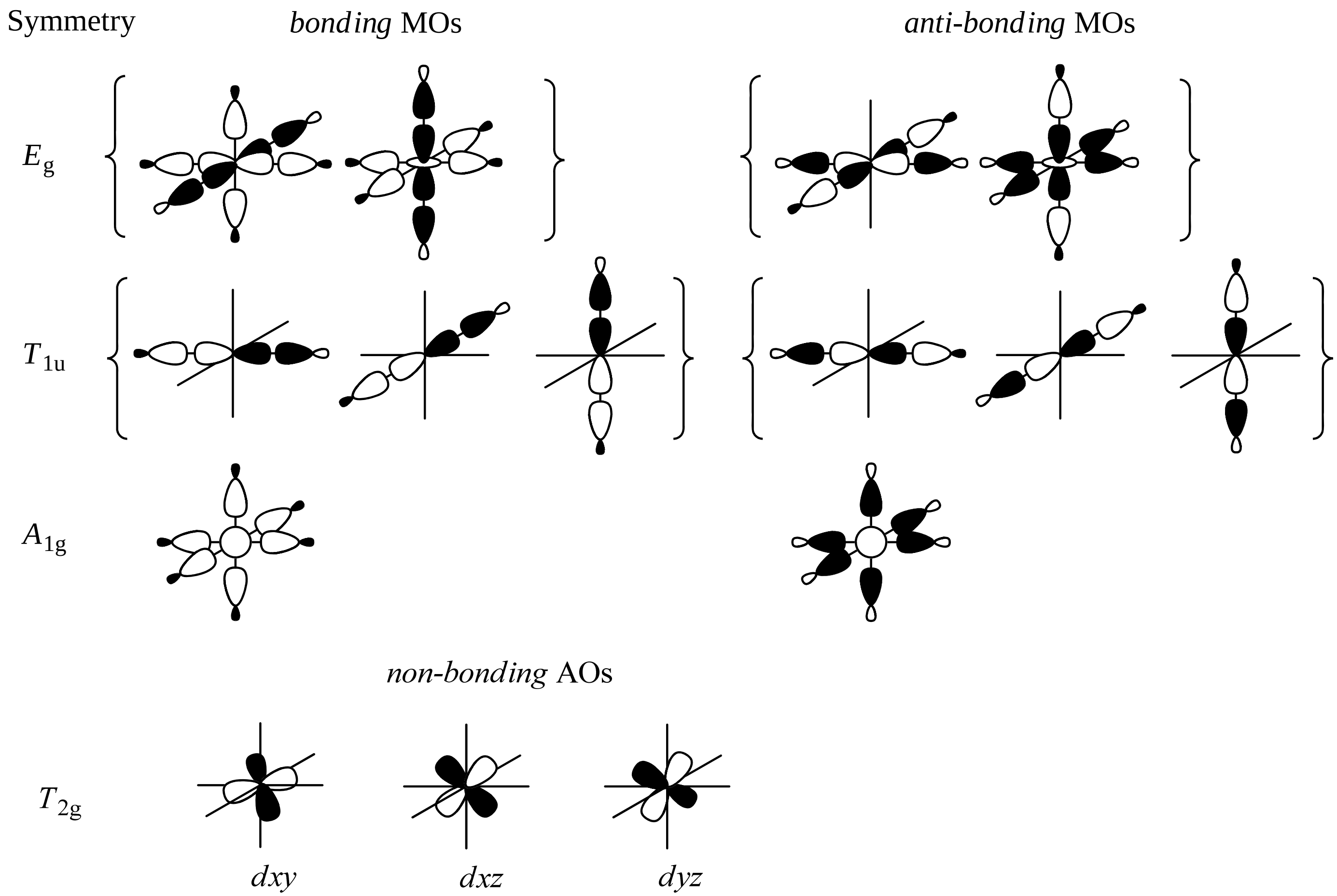
- If a transition metal ion is placed in a spherical field equivalent to the charges on six ligands, the energies of all five *d* orbitals would rise together (degenerately) as a result of the repulsions between the negative charges on the ligands and the negative charges of the electrons in the metal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

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

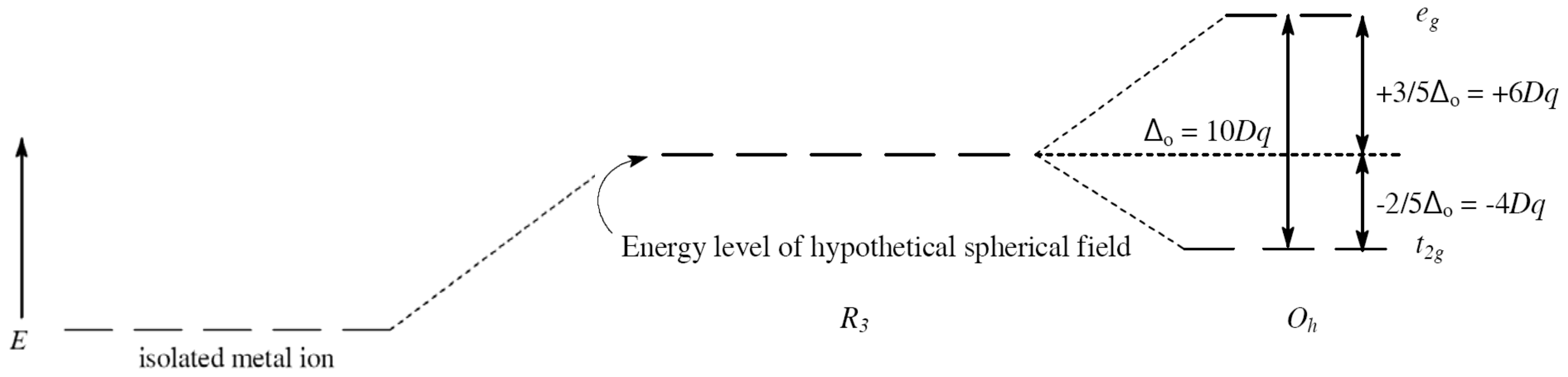
- In an octahedral (O_h) environment, the fivefold degeneracy among the *d* orbitals is lifted.

- 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 10 *Dq* between the two sets of *d* orbitals.





- The t_{2g} orbitals point between ligands.
- The e_g orbitals point directly at the ligands.
- Thus, the t_{2g} set is stabilized and the e_g set is destabilized *(relative to the energy of a hypothetical spherical octahedral field)*.



- 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 (*aka* the barycenter).
- The energy of each of the two orbitals of the e_g set rises by +3/5 Δ_o (+6 *Dq*) while the energy of each of the three t_{2g} orbitals falls by -2/5 Δ_o (-4 *Dq*).
- This results in no net energy change for the system:

$$\Delta E = E(e_g) + E(t_{2g})$$

$$= (2)(+3/5\ \Delta_o) + (3)(-2/5\ \Delta_o)$$

$$= (2)(+6\mathrm{Dq}) + (3)(-4\mathrm{Dq}) = 0$$

(The magnitude of Δ_o depends upon both the metal ion and the attaching ligands)

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 $<$ bpy $<$ phen $< NO_2^- < CN^- < CO$

- In the ***crystal field theory (CFT)*** model, the spectrochemical series is an empirical result that cannot be rationalized in terms of simple point charges.

  - ➢ For example, CO is a neutral ligand but produces the largest Δ_o splitting.

- The spectrochemical series can be rationalized in terms of the ***ligand field theory model*** which incorporates the quantum mechanical concepts of ***molecular orbital theory*** on top of the fundamental CFT model thus acknowledging metal-ligand (SALC) wavefunction combinations.

High-Spin and Low-Spin Configurations

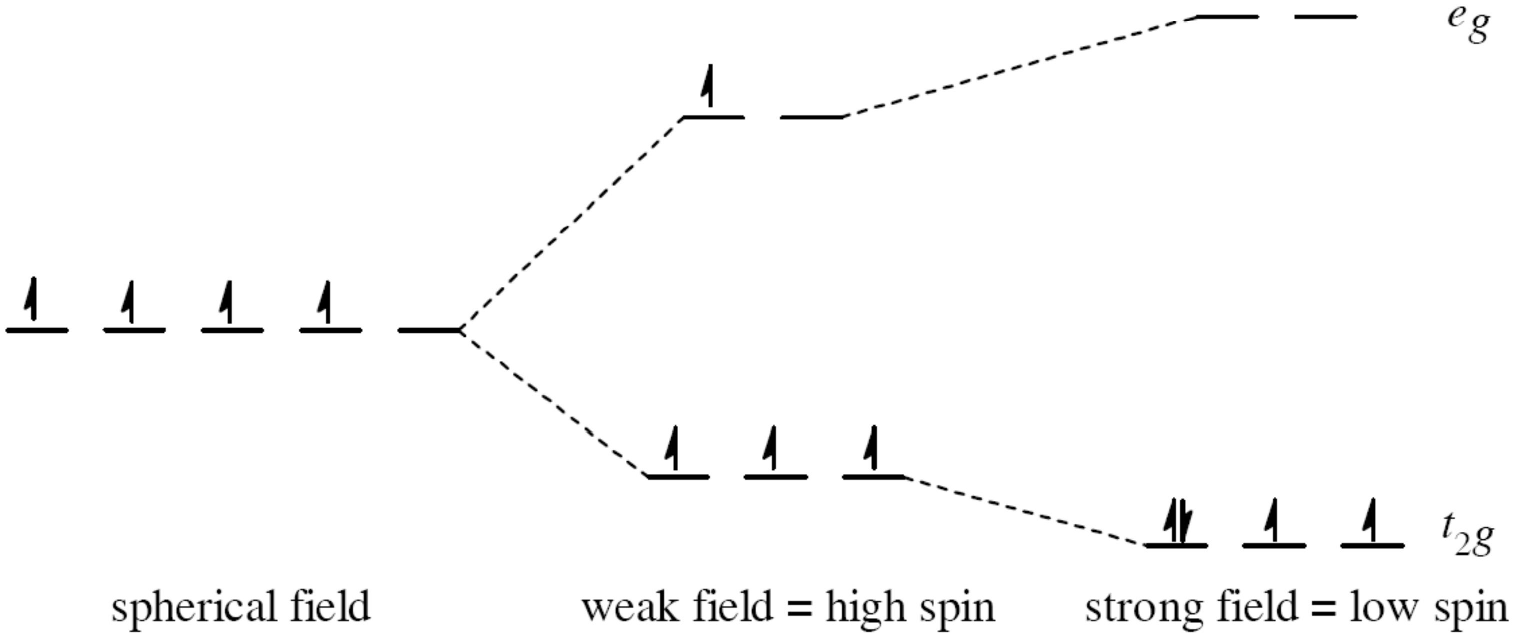
- In an octahedral complex, electrons fill the t_{2g} and e_g orbitals in an aufbau manner, but for configurations $d^4 – d^7$ there are two possible filling schemes depending on the magnitude of Δ_o .
- The relative magnitudes of Δ_o and the mean pairing energy, *P*, determine whether a high spin or low spin state is observed in octahedral complexes.
- *P* 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.
- When two electrons are forced to occupy the same orbital, they both experience interelectronic repulsion which increases the total energy of the orbital. The greater this repulsion effect, the greater the energy of the orbital.
- Thus, the coulombic contribution to the pairing energy tends to fall off in the order 3*d* > 4*d* > 5*d*, 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.

- The Δ_o energy gap in octahedral complexes of transition metals is relatively small and is comparable to typical pairing energies.
- For a given first-row transition metal ion, i.e. of a fixed oxidation state, the magnitude of Δ_o depends largely on the nature of the ligand, i.e., where it falls in the spectrochemical series:

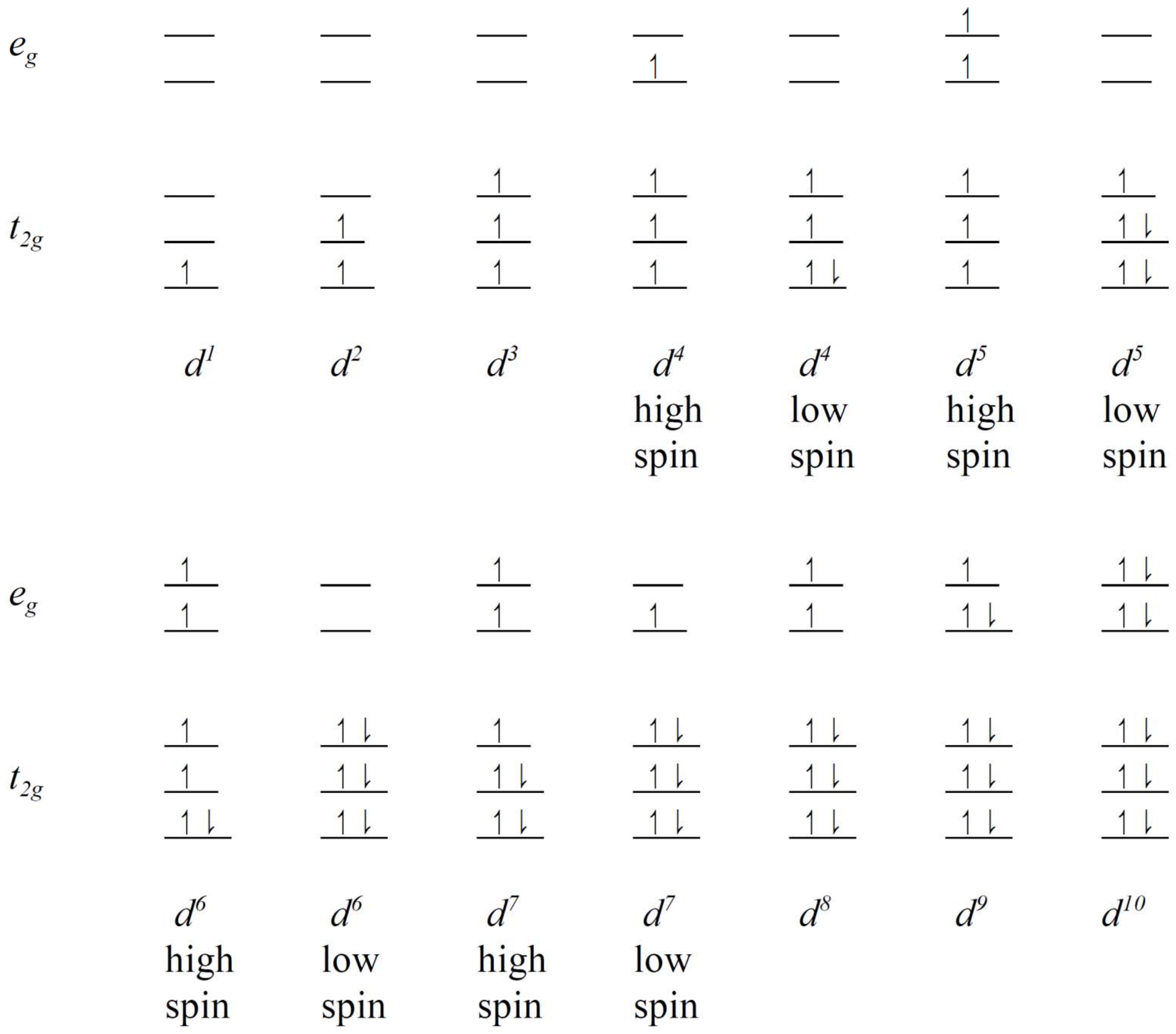
low field strength results in a high-spin state

high field strength results in a low-spin state

- Thus, 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 example, in a d^4 configuration, the high-spin state is $t_{2g}^3e_g^1$, and the low-spin state is $t_{2g}^4\,e_g^0$.
- ***Second and third row transition metal tend to have larger Δ_o and smaller P values, which favor low spin configurations.***



- Low field strength results in a high-spin state.
- High field strength results in a low-spin state.
- For example, in a d^4 configuration, the high-spin state is $t_{2g}{}^3\,e_g{}^1$, and the low-spin state is $t_{2g}{}^4\,e_g{}^0$.

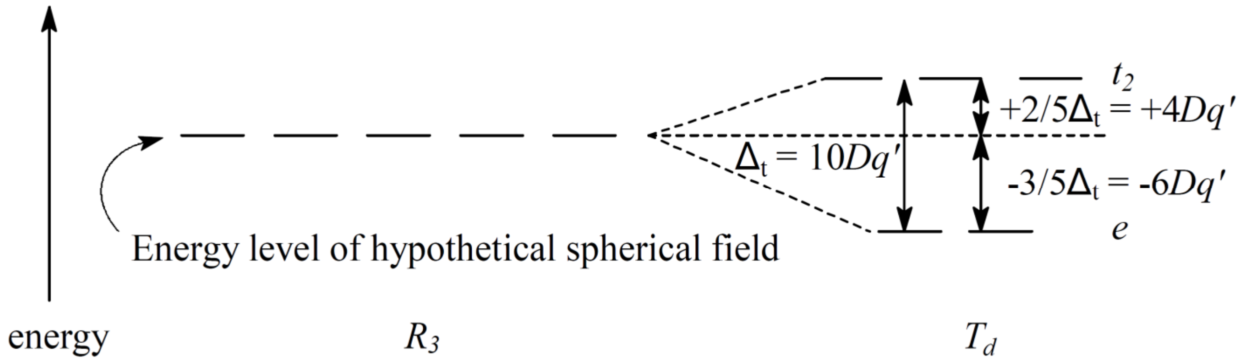


Low field strength results in a high-spin state - High field strength results in a low-spin state

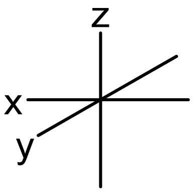
Energies of t_2 and e d-orbitals in ML_4 (T_d)

- 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 dx^2-y^2 orbital (e set) and dxy orbital (t_2 set) relative to the four ligands.
- The difference results in an energy split between the two levels of Δ_t or 10 Dq'.
- 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 $+2\Delta_t/5 = +4Dq'$

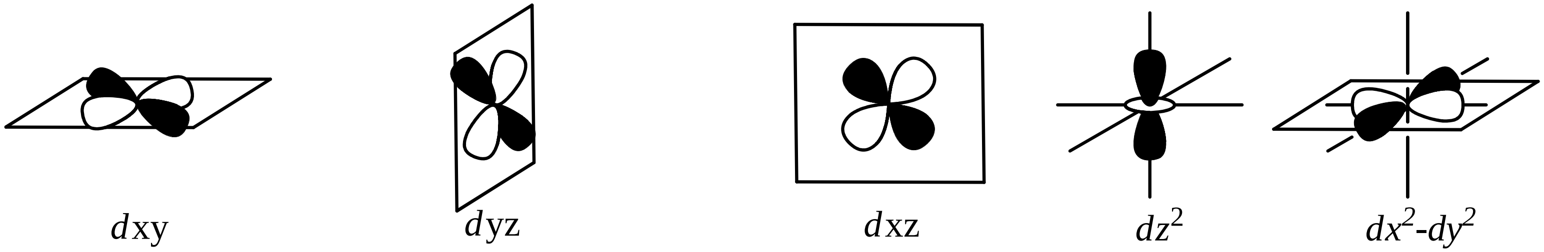
$$\begin{aligned}\Delta E &= E(e_g) + E(t_{2g}) \\ &= (2)(-3/5\ \Delta_o) + (3)(+2/5\ \Delta_o) \\ &= (2)(-6\ Dq) + (3)(+4\ Dq) = 0\end{aligned}$$



$$\Gamma_\sigma = A_1 + T_2$$

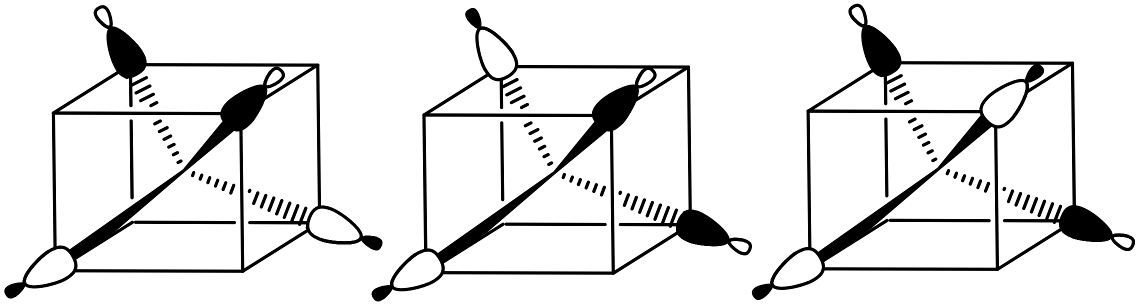


AOs



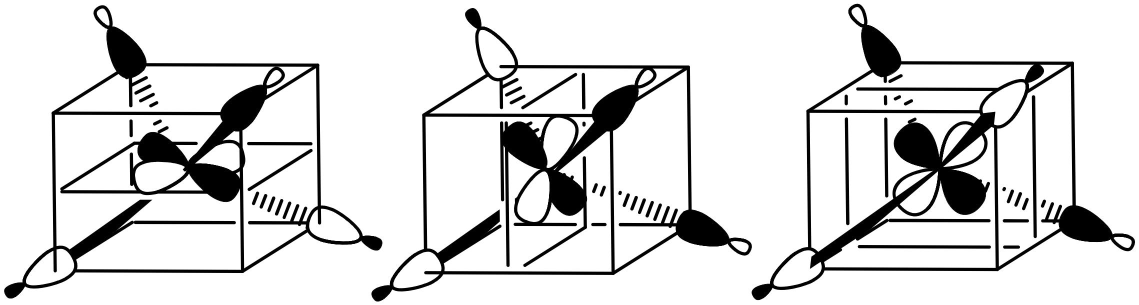
SALCs

T_2
(1 node)



MOs

T_2
(1 node)



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 and as a result *P* is typically greater than Δ_t
- $\Delta_t << P$ in ordinary complexes, so high spin is favored.
- For a given ligand at the same M-L distances, it can be shown that

$$\Delta_t = (4/9)\,\Delta_o$$

Other crystal fields

- We can deduce the 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 useful to begin with either the octahedral or tetrahedral results and consider the effects brought about by distorting the perfect geometry to bring about the new configuration.
- The results for the perfect and distorted geometries can be correlated through descent in symmetry, using the appropriate correlation tables.
- We can take this approach with distortions produced by ligand substitution or by intermolecular associations, if descent in symmetry involves a group-subgroup relationship.

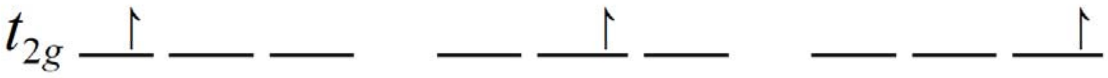
Jahn-Teller Distortion

- Jahn-Teller Theorem: *For any nonlinear system in a degenerate state, a distortion will occur that will lift the degeneracy.*
- The theorem does not predict the exact nature of the distortion
- A Jahn-Teller distortion results in partial or complete lifting of the degeneracies among some orbitals.
- In so doing, electrons may occupy lower-energy orbitals, resulting in a lower overall energy state for the system.
- The “perfect” geometries really cannot exist as stable species for certain electronic configurations, because the distorted molecule is the energetically preferred structure.
- Describing certain complexes as octahedral, tetrahedral, or square planar is often really an approximation of their true structure.
- Jahn-Teller Corollary: *If the system is centrosymmetric, the distorted configuration will also be centrosymmetric.*

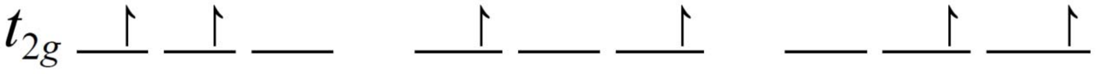
Degenerate ground states of ML_6 O_h complexes

- We can identify octahedral ground state configurations subject to the Jahn-Teller effect by considering the degeneracy of possible d^n electronic configurations.
- A degenerate electronic state results whenever the electrons in either the t_{2g} or e_g levels can be distributed in two or more ways among degenerate orbitals.

  Example: The d^1 ground-state configuration can have the single electron in any one of the three t_{2g} orbitals, so the electronic state is triply degenerate.



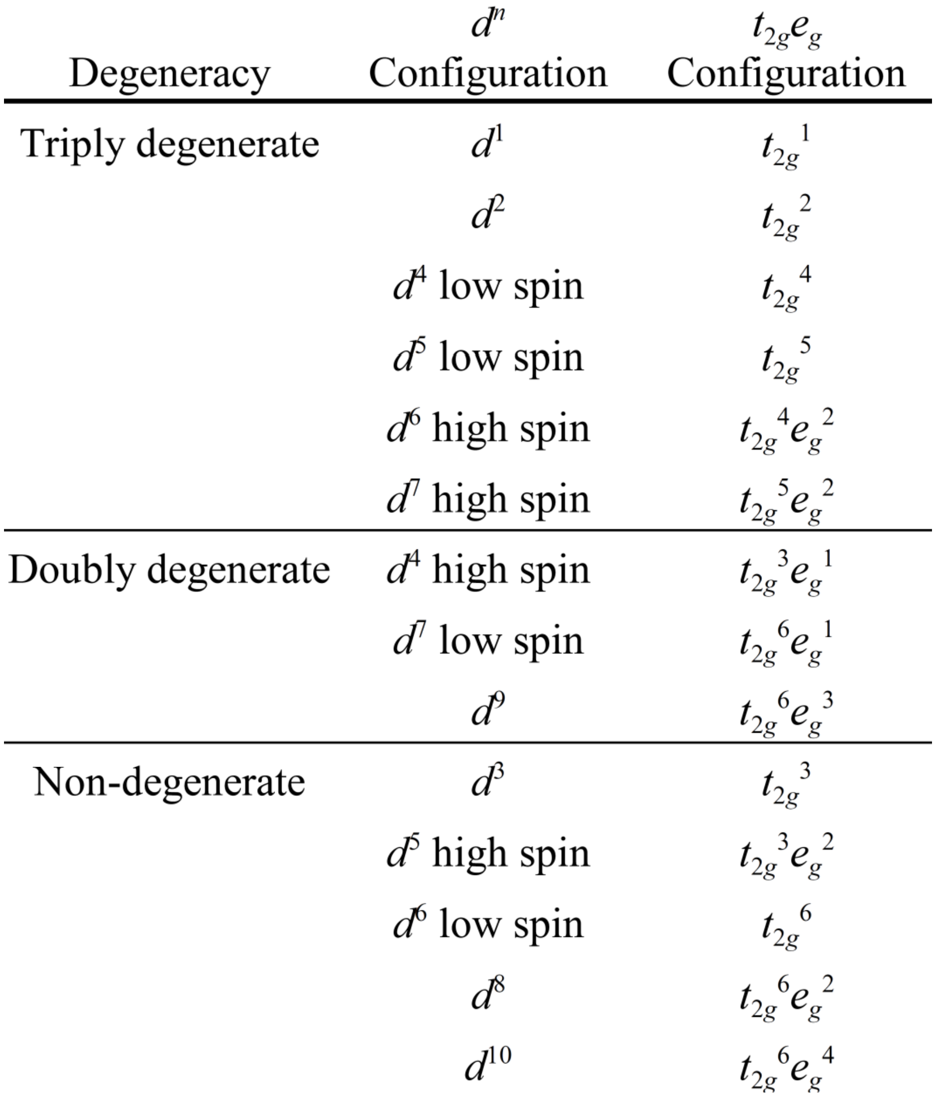
  Example: With equal probability, any one of the three t_{2g} orbitals could be vacant in the ground state for d^2 ($t_{2g}{}^2$), so this too is a triply degenerate state.



- Distortions will be more pronounced for the doubly degenerate configurations, which have an imbalance in the filling of the e_g level.
- Lesser distortions result from triply degenerate states, which have an imbalance in the distribution among t_{2g} orbitals.
- This difference is best understood by considering shielding effects and the orientations of the t_{2g} and e_g orbitals.

Degenerate and non-degenerate d^n ground states

- Only non-degenerate states are immune to Jahn-Teller Distortion !



Degeneracy	d^n Configuration	$t_{2g}e_g$ Configuration
Triply degenerate	d^1	t_{2g}^1
	d^2	t_{2g}^2
	d^4 low spin	t_{2g}^4
	d^5 low spin	t_{2g}^5
	d^6 high spin	$t_{2g}^4e_g^2$
	d^7 high spin	$t_{2g}^5e_g^2$
Doubly degenerate	d^4 high spin	$t_{2g}^3e_g^1$
	d^7 low spin	$t_{2g}^6e_g^1$
	d^9	$t_{2g}^6e_g^3$
Non-degenerate	d^3	t_{2g}^3
	d^5 high spin	$t_{2g}^3e_g^2$
	d^6 low spin	t_{2g}^6
	d^8	$t_{2g}^6e_g^2$
	d^{10}	$t_{2g}^6e_g^4$

Shielding effects and distortion for d^9

$$d^9 = t_{2g}^6 e_g^3 = t_{2g}^6 [(dx^2\text{-}y^2)^2(dz^2)^1] \text{ and } t_{2g}^6 [(dx^2\text{-}y^2)^1(dz^2)^2]$$

- $t_{2g}^6 [(dx^2\text{-}y^2)^2(dz^2)^1]$
  - The pair of electrons in the $dx^2\text{-}y^2$ orbital will more effectively shield ligands in the *xy* plane from the metal ion's charge than the single electron in the dz^2 orbital would shield ligands along the *z* axis.
  - If this were to occur, the ligands along the *z* axis will be **more strongly** attracted to the central metal and their M-L bond lengths would be **shortened relative to those in the *xy* plane.**
- $t_{2g}^6 [(dx^2\text{-}y^2)^1(dz^2)^2]$
  - The single electron in the $dx^2\text{-}y^2$ orbital would less effectively shield ligands in the *xy* plane from the metals charge than the pair of electrons in the dz^2 orbital would shield ligands along the *z* axis.
  - If this were to occur, the ligands along the *z* axis would be **less strongly** attracted to the central metal ion and their M-L bond lengths would be **lengthened relative to those in the *xy* plane.**
- Shielding effects are less pronounced for triply degenerate configurations, because the orbitals' lobes are oriented between the ligands. Thus, the resulting distortions are not as severe and often we can't tell which distortion will occur.

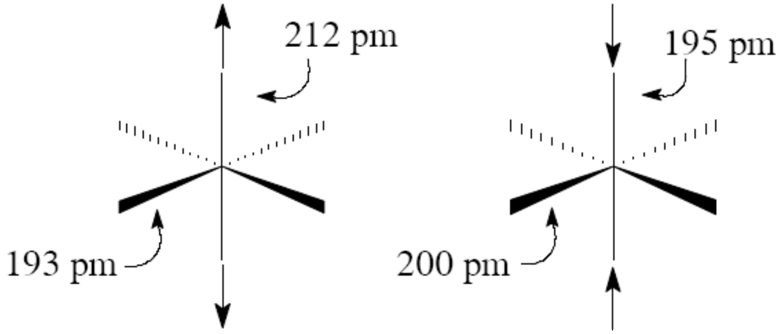
Tetragonal distortion

- Although the exact nature of the resulting distortion cannot be predicted from the Jahn-Teller theorem, the foregoing analysis of the d^9 case suggests that a **tetragonal distortion might result.**
- 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.
- Jahn-Teller tetragonal distortions must result in a centrosymmetric group, e.g., $D_{4\mathrm{h}}$.
- Tetragonal distortions to non-centrosymmetric groups, e.g., $C_{4\mathrm{v}}$, are possible, but not by the Jahn-Teller effect.
- A tetragonal distortion would occur if the M-L bonds of two ligands lying along the *z* axis were either stretched or compressed equally while maintaining equivalence among the four remaining ligands in the *xy* plane.
- By either process, the symmetry would descend from O_h to D_{4h} .
- The descent in symmetry causes a partial lifting of the degeneracies among the *d* orbitals in the octahedral field.

- For example, $Mn(acac)_3$ has a ^5E_g ground state, which has an imbalance in the filling of electrons in orbitals that point directly at ligands.

$$(t_{2g})^3\ (dx^2\text{–}y^2)^1(\mathrm{d}z^2)^0 \quad \textit{or} \quad (t_{2g})^3\ (dx^2\text{–}y^2)^0(dz^2)^1$$

- This results in significant distortion from ideal octahedral symmetry (O_h) as Jahn-Teller distortion results in partial or complete lifting of the *d*-orbital degeneracies.
- For $Mn(acac)_3$ this suggests tetragonal distortion, $O_h \rightarrow D_{4h}$.
- Most probable distortions are equally elongating or shortening two trans-related positions, relative to the four remaining equal positions in a plane. $Mn(acac)_3$ exists in two tetragonally distorted forms.



Splitting of *d* orbital degeneracies : $O_h \rightarrow D_{4h}$

- From the correlation table that links the groups O_h and D_{4h} we see that the two e_g orbitals of the octahedral field become non-degenerate as a_{1g} and b_{1g} in the tetragonal field.

- From the direct product listings in the D_{4h} character table we see

  a_{1g} = $d2z^2-x^2-y^2$ (= dz^2)

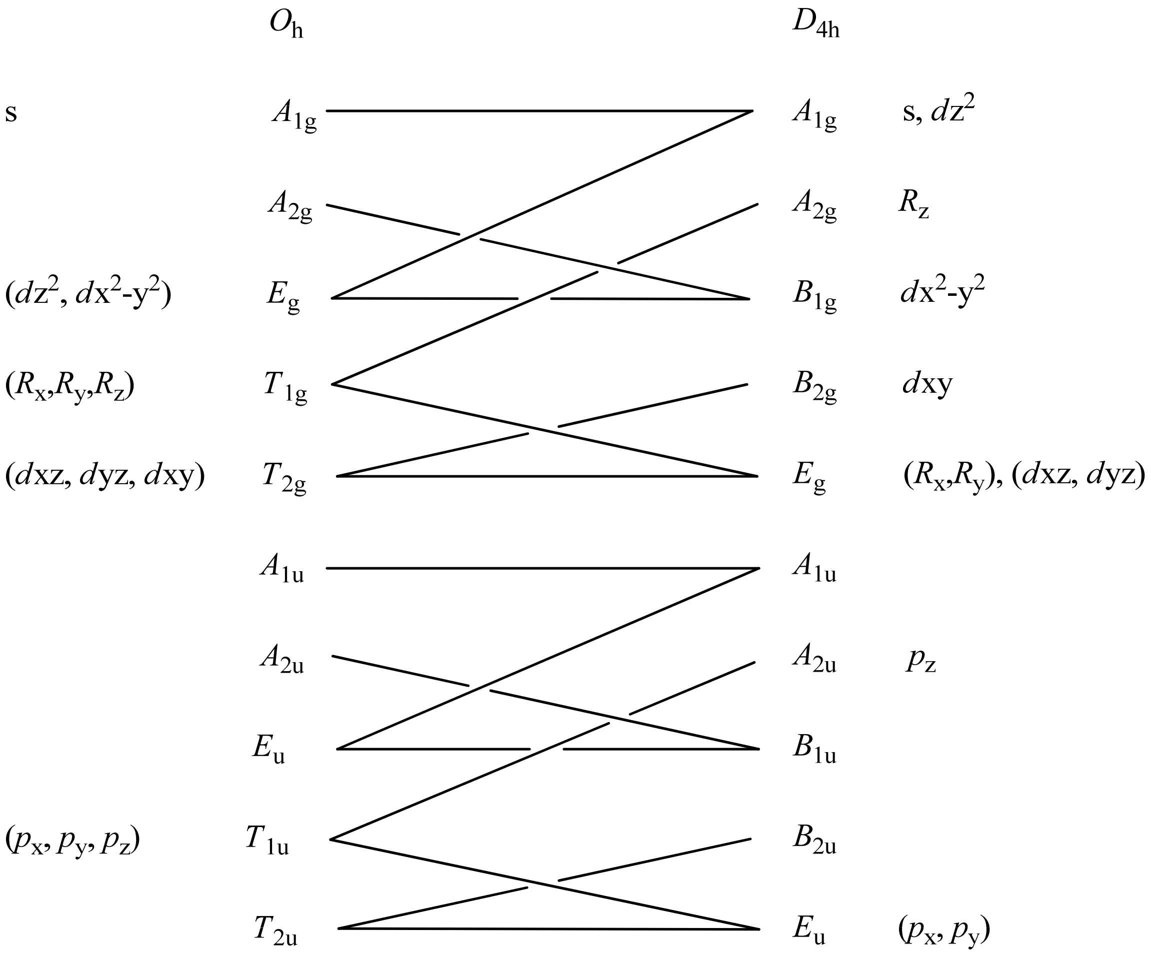
  b_{1g} = dx^2-y^2

- 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 we see

  b_{2g} = dxy

  e_g = (dxz, dyz)



	O_h	D_{4h}	
s	A_{1g}	A_{1g}	s, dz^2
	A_{2g}	A_{2g}	R_z
(dz^2, dx^2-y^2)	E_g	B_{1g}	dx^2-y^2
(R_x,R_y,R_z)	T_{1g}	B_{2g}	dxy
(dxz, dyz, dxy)	T_{2g}	E_g	(R_x,R_y), (dxz, dyz)
	A_{1u}	A_{1u}	
	A_{2u}	A_{2u}	p_z
	E_u	B_{1u}	
(p_x, p_y, p_z)	T_{1u}	B_{2u}	
	T_{2u}	E_u	(p_x, p_y)

Relative Energies of *d* orbitals in D_{4h}

- The relative energy ordering of the orbitals depends on the direction and magnitude of the tetragonal distortion.

- A distortion in which the two M-L bonds along *z* are progressively stretched is an interesting case to consider, because at its limit the two ligands would be removed, resulting in a square planar ML_4 complex.

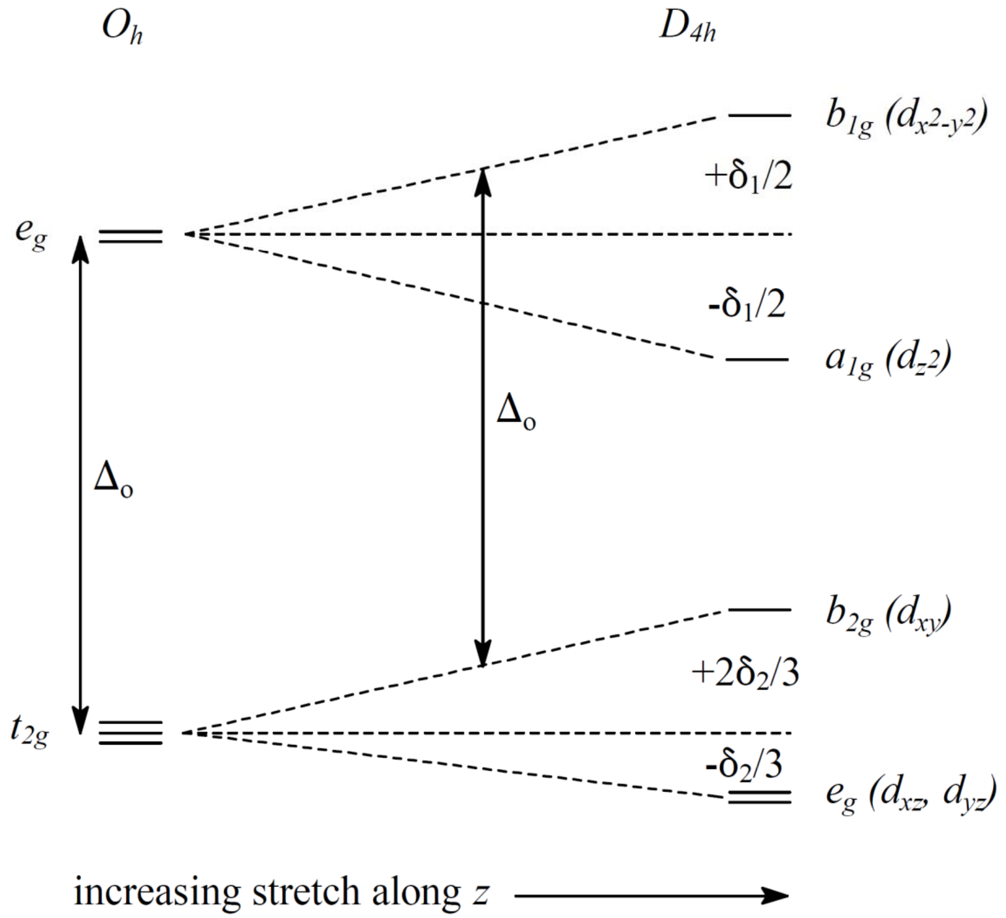
- Moving the two ligands away from the central metal ion lowers the repulsions between ligand electrons and the metal electrons in *d* orbitals that have substantial electron distribution along *z*.

- 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 stretching tetragonal distortion



- The upper e_g orbitals of the perfect octahedron split equally by an amount δ_1, with the dx^2-y^2 orbital (b_{1g} in D_{4h}) rising by $+\delta_1/2$ and the dz^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 $-\delta_2/3$.

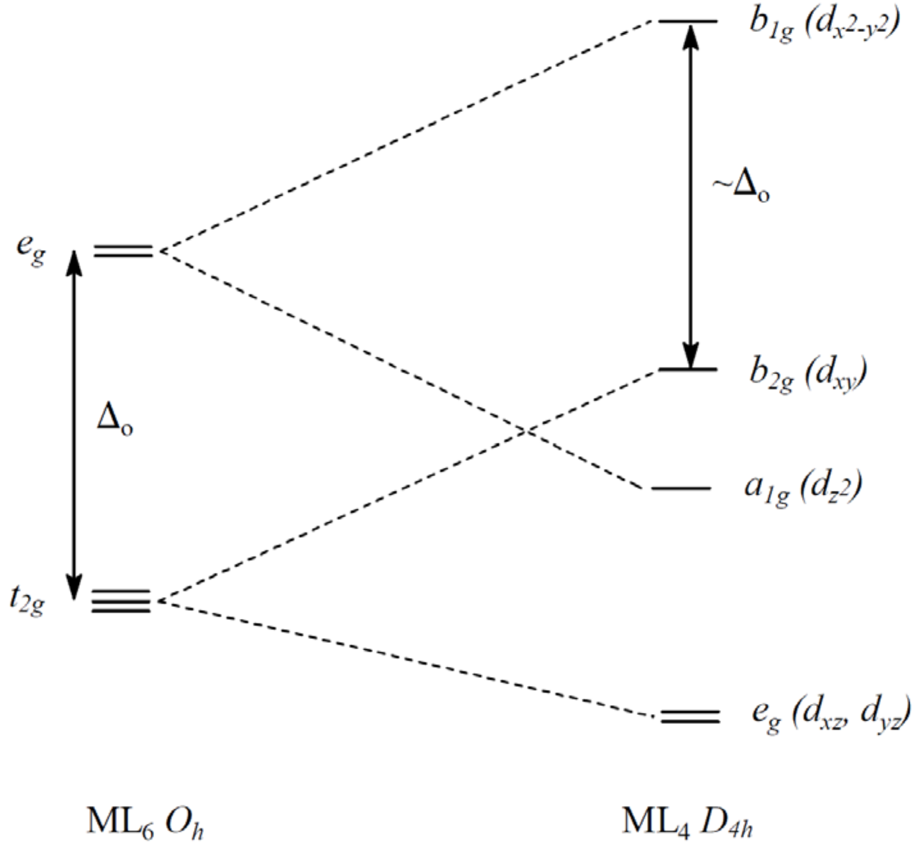
Magnitudes of the δ_1 and δ_2 splittings

- 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 $dx^2\text{-}y^2$ and dz^2 orbitals are directed at ligands.
- The distortion has the same effect on the energies of both the $dx^2\text{-}y^2$ and dxy orbitals;
  i.e. $\delta_1/2 = 2\delta_2/3$.
- As a result, their energies rise in parallel, maintaining a separation equal to the Δ_o of the undistorted octahedral field.

Tetragonal Compression Jahn-Teller Distortion

- If we carry out the opposite tetragonal distortion (compression along *z*), the octahedral degeneracies will be lifted in the same manner, as required by symmetry, but the ordering of the orbitals across both the δ_1 and δ_2 gaps will be reversed.
- The energy of the dx^2-y^2 orbital (b_{1g}) will fall by $-\delta_1/2$, and the energy of the orbital dz^2 (a_{1g}) will rise by $+\delta_1/2$.
- The energy of the dxy (b_{2g}) orbital will fall by $-2\delta_2/3$, and the energy of the dxz and dyz (e_g) orbitals will rise by $+\delta_2/3$.
- In this case, the energy of the dxy (b_{2g}) and dx^2-y^2 (b_{1g}) orbitals will fall equally with increasing compression along *z* (i.e., $-\delta_1/2 = -2\delta_2/3$), maintaining a separation equal to Δ_o .

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} (dz^2) level may cross and fall below the b_{2g} (*d*xy) level, resulting in the above splitting scheme.

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} (dx^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 which produce a large Δ_o value.
- The energy gap between the b_{2g} ($d$xy) and b_{1g} (dx^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 $e^4\ t_2^4$.
- 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 lands, e.g., $[NiCl_4]^{2-}$.
- 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 $[PtCl4]^{2-}$.

State Splitting in an Octahedral Field

- In the absence of the octahedral field (point group R_3), the ground state of a $3d^4$ configuration is ^5D.
- A weak O_h field causes this to split into two states:

  Ground state: $^5E_g = t_{2g}^3 e_g^1$

  Excited state: $^5T_{2g} = t_{2g}^2 e_g^2$

- The ^5E_g ground state is doubly-degenerate, because there are two ways of placing the e_g^1 electron:

  $(t_{2g})^3$ $(\mathrm{dx}^2\text{–}\mathrm{y}^2)^1(\mathrm{dz}^2)^0$

  $(t_{2g})^3$ $(\mathrm{dx}^2\text{–}\mathrm{y}^2)^0(\mathrm{dz}^2)^1$

- The $^5T_{2g}$ excited state is triply degenerate, because there are three ways of placing the vacant orbital:

  $(d\mathrm{xy})^1(d\mathrm{yz})^1(d\mathrm{xz})^0$ $(e_g)^2$

  $(d\mathrm{xy})^1(d\mathrm{yz})^0(d\mathrm{xz})^1$ $(e_g)^2$

  $(d\mathrm{xy})^0(d\mathrm{yz})^1(d\mathrm{xz})^1$ $(e_g)^2$

- ^5E_g state is paramagnetic from four unpaired electrons.

Absorption Spectra and State-to-State Transitions

- When a transition metal complex absorbs visible light, the energy absorbed (h<) causes a transition from the ground state to an excited state, corresponding to a change in electronic configuration.
- For a high-spin d^4 complex like $Mn(acac)_3$, only one same-spin state-to-state transition is possible: $^5E_g \rightarrow {}^5T_{2g}$
- The $^5E_g \rightarrow {}^5T_{2g}$ gives rise to a single absorption band in the visible spectrum at ~ 500 nm, absorbing red-orange light and transmitting green light.