Our focus will be on the physical consequences that follow from the symmetry of transition metal complexes not the standard coordination chemistry or inorganic chemistry.

<table>
<thead>
<tr>
<th>7.1 Crystal Field Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2 Jahn-Teller Distortions and other Crystal Fields</td>
</tr>
<tr>
<td>7.3 Molecular Orbital Approach to Bonding in Complexes</td>
</tr>
<tr>
<td>7.4 Terms of Free Ions with dⁿ Configurations</td>
</tr>
<tr>
<td>7.5 Splitting of Terms</td>
</tr>
<tr>
<td>7.6 Electronic Structure of Transition Metal Complexes</td>
</tr>
</tbody>
</table>
Verify the fact that the d orbitals in an $O_h$ field must divide into two degenerate sets.

The effect of a symmetry operation on an orbital is only a change in coordinates without a change in energy. Thus, if some operation converts two or more orbitals into each other, they must be energetically equal (degenerate).

Three $p$ orbitals must be degenerate.
7.1 Crystal Field Theory

in the case of five d orbitals

<table>
<thead>
<tr>
<th></th>
<th>$C_3$</th>
<th>$C_3^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{xy}$ $\rightarrow$</td>
<td>$d_{yx}$</td>
<td>$d_{yz}$</td>
</tr>
<tr>
<td>$d_{yz}$ $\rightarrow$</td>
<td>$d_{xy}$</td>
<td>$d_{zx}$</td>
</tr>
<tr>
<td>$d_{zx}$ $\rightarrow$</td>
<td>$d_{yz}$</td>
<td>$d_{xy}$</td>
</tr>
<tr>
<td>$d_{2x^2-y^2-z^2}$ $\rightarrow$</td>
<td>$d_{2y^2-z^2-x^2}$</td>
<td>$d_{2x^2-y^2-z^2}$</td>
</tr>
<tr>
<td>$d_{x^2-y^2}$ $\rightarrow$</td>
<td>$d_{z^2}$</td>
<td>$d_{y^2-x^2}$</td>
</tr>
</tbody>
</table>

Interchange among themselves and must be degenerate

Not transformed directly into each other, they are transformed into functions that are linear combinations of each other. Must have the same energy

(7.1a) $d_{2y^2-z^2-x^2} = -(1/2)d_{2z^2-x^2-y^2} - (3/2)d_{x^2-y^2}$

(7.1b) $d_{2x^2-y^2-z^2} = -(1/2)d_{2z^2-x^2-y^2} + (3/2)d_{x^2-y^2}$

(7.1c) $d_{x^2-z^2} = +(1/2)d_{2z^2-x^2-y^2} - (1/2)d_{x^2-y^2}$

(7.1d) $d_{y^2-z^2} = -(1/2)d_{2z^2-x^2-y^2} - (1/2)d_{x^2-y^2}$
Now, we know that the d orbitals in an octahedral complex divide into a triply degenerate set and a doubly degenerate set.

We do not know yet about the symmetries. For this take the five wave functions as a basis.

We can obtain the following reducible representation.

\( \Gamma_d = E_g + T_{2g} \)
7.1 Crystal Field Theory

\[ \chi(E) = 2j + 1 \quad (7.2) \]
\[ \chi[C(\theta)] = \frac{\sin(j + 1/2)\theta}{\sin \theta/2} \quad (7.3) \]
\[ \chi(i) = \pm (2j + 1) \quad (7.4) \]
\[ \chi[S(\theta)] = \pm \frac{\sin(j + 1/2)(\theta + \pi)}{\sin(\theta + \pi)/2} \quad (7.5) \]
\[ \chi(\sigma) = \pm \sin(j + 1/2)\pi \quad (7.6) \]

Give the characters for operations in spherical symmetry (the group \( R_3 \)). These relationships can be used with \( O_h \) or any other point group, because all point groups are subgroups of \( R_3 \).

The quantum number \( j \) can be replaced by \( l \) when considering an orbital, \( L \) when considering Russell-Saunders term. For the sign, orbitals with even-value (s, d, g, ...) are gerade (+) and orbitals with odd-value (p, f, ...) are ungerade (-).
7.1 Crystal Field Theory

The relative energy order to determine.

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.

However in octahedral arrangement.

More repulsions because the lobes of the orbitals in the e_g set point directly at the ligands.
7.1 Crystal Field Theory

This results in no net energy change for the system.

\[ \Delta E = E(e_g) + E(t_{2g}) = (2)(+3/5\Delta o) + (3)(-2/5\Delta o) \]
\[ = (2)(+6Dq) + (3)(-4Dq) \]
\[ = 0 \]

The magnitude of \( \Delta o \) depends upon both the metal ion and the attaching ligands.
Crystal field stabilization energy (CFSE); the actual distribution vs the uniform field. Good for the concept of the repulsion of orbitals by the ligands but no explanation for bonding in coordination complexes.

7.1 Crystal Field Theory

Free ion

$\text{R}_3$

$\text{O}_h$
The relative magnitudes of $\Delta_o$ and the mean pairing energy, $P$, determine which spin state results.
7.1 Crystal Field Theory

CFT considerations to tetrahedrally structured complexes

\[ \Gamma_d = E + T_2 \]

More repulsions in the \( t_2 \) set
7.2 Jahn-Teller Distortion and Other Crystal Fields

Group-subgroup

Splitting as a result of stretching

Figure 7.7 Two examples of a tetragonal distortion on an octahedral complex: (a) a stretch along \( z \), and (b) a compression along \( z \).

Figure 7.8 Crystal field effects of a tetragonal distortion on an octahedral \( ML_6 \) complex, deformed by stretching the two M–L bonds along \( z \).
7.2 Jahn-Teller Distortion and Other Crystal Fields

Splitting as **a result of removing two axial ligands**

**Figure 7.9** Crystal field splitting of $d$ orbitals for a square planar ML$_4$ complex and its relationship to the splitting for an octahedral ML$_6$ complex.
7.3 Molecular Orbital Approach to Bonding in Complexes

Unlike CFT and LFT models, we will include consideration of interactions with metal ion s and p orbitals.

We take six vectors pointing toward the center of a Cartesian coordination system as our basis for a reducible representation of SALCs $\Gamma_\sigma$.

To identify the symmetries of metal ion AOs, investigate the character table.

$\Gamma_\sigma = A_{1g} + E_g + T_{1u}$, six SALCs with three different symmetries.
7.3 Molecular Orbital Approach to Bonding in Complexes

SALC with $A_{1g}$ symmetry and s orbital of the central metal

SALCs with $E_g$ symmetry and $d_{z^2}$ and $d_{x^2-y^2}$ orbitals of the central metal

SALCs with $T_{1u}$ symmetry and three p orbitals of the central metal

Figure 7.11 Ligand SALCs and their matching symmetry metal ion AOs.

SALCs with $E_g$ symmetry and $d_{z^2}$ and $d_{x^2-y^2}$ orbitals of the central metal
7.3 Molecular Orbital Approach to Bonding in Complexes

MO diagram with only sigma bonding

Figure 7.12 Molecular orbital diagram for an octahedral complex with only sigma bonding between metal ion and ligands.
7.3 Molecular Orbital Approach to Bonding in Complexes

Delocalization of $e_g^*$ electron density and $\Delta_0$.

**Figure 7.13** Relationship between the relative energies of metal ion $d$ orbitals and ligand sigma orbitals to the delocalization of $e_g^*$ electrons toward either metal ion or ligands.
7.3 Molecular Orbital Approach to Bonding in Complexes

To include pi-bonding in our MO

Identify the symmetries of metal ion AOs, investigate the character table.

$\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}$, twelve SALCs with four different symmetries.
7.3 Molecular Orbital Approach to Bonding in Complexes

SALCs with $T_{2g}$

Will interact three $d$ orbitals ($d_{xy}$, $d_{yz}$, $d_{xz}$)

\[
\Pi_{xz} = \frac{1}{2}(\pi_1 + \pi_2 + \pi_3 + \pi_4) \\
\Pi_{yz} = \frac{1}{2}(\pi_5 + \pi_6 + \pi_7 + \pi_8) \\
\Pi_{xy} = \frac{1}{2}(\pi_9 + \pi_{10} + \pi_{11} + \pi_{12})
\]

SALCs with $T_{1u}$

Will interact three $p$ orbitals ($p_x$, $p_y$, $p_z$)

\[
\Pi_z = \frac{1}{2}(\pi_1 - \pi_3 + \pi_5 - \pi_7) \\
\Pi_x = \frac{1}{2}(\pi_2 - \pi_4 + \pi_{10} - \pi_{12}) \\
\Pi_y = \frac{1}{2}(\pi_6 - \pi_8 + \pi_9 - \pi_{11})
\]
7.3 Molecular Orbital Approach to Bonding in Complexes

Figure 7.12 Molecular orbital diagram for an octahedral complex with only sigma bonding between metal ion and ligands.

Figure 7.17 Simplified qualitative MO scheme for an octahedral ML₆ complex with pi-bonding.
7.3 Molecular Orbital Approach to Bonding in Complexes

For tetrahedrally structured complexes, sigma bonding

\[ s = a_1 \]
\[ p_x, p_y, p_z = t_2 \]
\[ d_{x^2 - y^2}, d_{z^2} = e \]
\[ d_{xy}, d_{xz}, d_{yz} = t_2 \]

\[ \Gamma_\sigma = A_1 + T_2. \]

\[ \begin{array}{c|ccccc}
T_d & E & 8C_3 & 3C_2 & 6S_4 & 6\sigma_d \\
\hline
\Gamma_\pi & 8 & -1 & 0 & 0 & 0 \\
\end{array} \]

\[ \Gamma_\pi = E + T_1 + T_2. \]
7.3 Molecular Orbital Approach to Bonding in Complexes

\[ s = a_1 \]
\[ p_x, p_y, p_z = t_2 \]
\[ d_{x^2-y^2}, d_{z^2} = e \]
\[ d_{xy}, d_{xz}, d_{yz} = t_2 \]

Figure 7.19 Simplified qualitative MO scheme for a tetrahedral ML₄ complex.
In the case of a single electron in a degenerate set of five d orbitals, the electron can have any of the values $m_l = +2, +1, 0, -1, -2$ and either of the values $m_s = +1/2, -1/2$. Thus, there are 10 ways of arranging the electron, making a total of 10 microstates.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$d^1$</th>
<th>$d^2$</th>
<th>$d^3$</th>
<th>$d^4$</th>
<th>$d^5$</th>
<th>$d^6$</th>
<th>$d^7$</th>
<th>$d^8$</th>
<th>$d^9$</th>
<th>$d^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microstates</td>
<td>10</td>
<td>45</td>
<td>120</td>
<td>210</td>
<td>252</td>
<td>210</td>
<td>120</td>
<td>45</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

Both the individual orbital magnetic moments and spin magnetic moments will interact with one another, resulting in an energy state or term for the configuration.

The Russell-Saunders coupling scheme usually gives an adequate approximation of observed behavior.
Carbon atom
Energy levels for the \( p^2 \) electrons → Five energy levels
Each energy levels can be described as a combination of the \( m_l \)
and \( m_s \) values of the 2p electrons.

\[
2p \text{ electrons} \\
n = 2, \ l = 1 \\
m_l = +1, 0, \text{ or } -1 \\
m_s = +1/2 \text{ or } -1/2
\]

The orbital angular momenta and the spin angular momenta of
the 2p electrons interact in a manner called Russell-Saunders
coupling (LS coupling).
How many possible combinations of $m_l$ and $m_s$ values?

One possible set of values for the two electrons in the $p^2$ configuration would be

First electron: $m_l = +1$ and $m_s = +1/2$ \textit{Notation 1+0-}
Second electron: $m_l = 0$ and $m_s = -1/2$

Russell-Saunders coupling (LS coupling)

\textbf{Orbit-orbit coupling}
$M_L = \sum m_l \rightarrow L$: total orbital angular momentum quantum number

\textbf{Spin-spin coupling}
$M_S = \sum m_s \rightarrow S$: total spin angular momentum quantum number

\textbf{Spin-orbit coupling}
$J = L + S$: total angular momentum quantum number

2p electrons
$n = 2$, $l = 1$
$m_l = +1$, 0, or -1
$m_s = +1/2$ or $-1/2$

microstate
Tabulate the possible microstates

1. No two electrons in the same microstate have identical quantum numbers (the Pauli exclusion principle)
2. Count only the unique microstates ($1^+0^-$ and $0^-1^+$)

Electronic quantum # ($m_l$ and $m_s$) to atomic quantum # ($M_L$ and $M_S$)

<table>
<thead>
<tr>
<th>$M_L$</th>
<th>$M_S$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-1</td>
<td>0</td>
<td>+1</td>
<td></td>
</tr>
<tr>
<td>+2</td>
<td>1^-</td>
<td>1+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+1</td>
<td>1^-</td>
<td>0^-</td>
<td>1^+</td>
<td>0^+</td>
</tr>
<tr>
<td>0</td>
<td>-1^-</td>
<td>-1^-</td>
<td>-1^+</td>
<td>1^-</td>
</tr>
<tr>
<td>-1</td>
<td>-1^-</td>
<td>0^-</td>
<td>-1^+</td>
<td>0^-</td>
</tr>
<tr>
<td>-2</td>
<td>-1^-</td>
<td>-1^-</td>
<td>-1^+</td>
<td>0^-</td>
</tr>
</tbody>
</table>

2p electrons

$n = 2$, $l = 1$

$m_l = +1$, 0, or -1

$m_s = +1/2$ or $-1/2$
$L$ and $S$ describe collections of microstates. $M_L$ and $M_S$ describe the microstates themselves.

<table>
<thead>
<tr>
<th>Atomic States</th>
<th>Individual Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_L = 0, \pm 1, \pm 2, \ldots, \pm L$</td>
<td>$m_l = , \pm 1, \pm 2, \ldots, \pm l$</td>
</tr>
<tr>
<td>$M_S = S, S-1, \ldots, -S$</td>
<td>$m_s = +1/2, -1/2$</td>
</tr>
</tbody>
</table>

Term symbol

<table>
<thead>
<tr>
<th>Term</th>
<th>$L$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1S$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^2S$</td>
<td>0</td>
<td>$1/2$</td>
</tr>
<tr>
<td>$^3P$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$^4D$</td>
<td>2</td>
<td>$3/2$</td>
</tr>
<tr>
<td>$^5F$</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

Term Symbol

$2S+1L_J$

$L = 0, 1, 2, 3 \rightarrow S, P, D, F$
Electronic quantum \# \((m_l \text{ and } m_s)\) to atomic quantum \# \((M_L \text{ and } M_S)\) → describe states of multielectron atoms

Free-ion terms are very important in the interpretation of the spectra of coordination compounds.

\(^1S\) (singlet S):
\[
S \rightarrow L = 0 \rightarrow M_L = 0,
\]
\[
2S+1 = 1 \rightarrow S = 0 \rightarrow M_S = 0
\]

The minimum configuration of two electrons:

\[
\begin{array}{c|c}
M_S & \hline
0 & \hline
\end{array}
\]

\[
\begin{array}{c|c}
M_L & \hline
0 & \hline
0^+0^- & \hline
\end{array}
\]
$^2P$ (doublet P):

- $P \rightarrow L = 1 \rightarrow M_L = +1, 0, -1$
- $2S + 1 = 2 \rightarrow S = 1/2 \rightarrow M_S = +1/2, -1/2$

The minimum configuration of one electron

<table>
<thead>
<tr>
<th>$M_L$</th>
<th>$M_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>1&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
<tr>
<td>0</td>
<td>0&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
<tr>
<td>-1</td>
<td>-1&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Six microstates
The spin multiplicity is the same as the number of microstates.
7.4 Terms of Free Ions with d\textsuperscript{n} Configuration

Term symbol \(2S+1L\)

L may be 0, 1, 2,…  
S may be 0, \(\frac{1}{2}\), 1, 2/3… \(2S+1\); multiplicity

The L values that result from the possible ways in which \(l\) values can be combined for the configurations \(p^2\) and \(d^2\).

**Figure 7.20** Vector addition of individual \(l\) vectors to give \(L\) for configurations \(p^2\) and \(d^2\).

<table>
<thead>
<tr>
<th>L value:</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>…</th>
</tr>
</thead>
<tbody>
<tr>
<td>State:</td>
<td>S</td>
<td>P</td>
<td>D</td>
<td>F</td>
<td>G</td>
<td>H</td>
<td>…</td>
</tr>
</tbody>
</table>

[Diagram showing vector addition for p\textsuperscript{2} and d\textsuperscript{2} configurations]
7.4 Terms of Free Ions with $d^n$ Configuration

$M_L = L, L-1, ... -L$

$M_S = S, S-1, ... -S$

**Figure 7.21** Possible orientations of the resultant orbital angular momentum vector for a $D$ term ($L = 2$). The magnitude of the vector is $\sqrt{6}(h/2\pi)$ and its projections on the $z$ axis have magnitudes of $M_L(h/2\pi)$.

**Figure 7.22** Possible orientations of the resultant spin angular momentum vector for a triplet term ($S = 1, 2S + 1 = 3$). The magnitude of the vector is $\sqrt{2}(h/2\pi)$, and its projections on the $z$ axis have magnitudes of $M_S(h/2\pi)$. 
### 7.4 Terms of Free Ions with $d^n$ Configuration

#### Table 7.1 Terms for Free-Ion $d^n$ Configurations

<table>
<thead>
<tr>
<th>$d^n$</th>
<th>Free-Ion Terms&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Total Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^0$, $d^{10}$</td>
<td>$^1S$</td>
<td>1</td>
</tr>
<tr>
<td>$d^1$, $d^9$</td>
<td>$^2D$</td>
<td>10</td>
</tr>
<tr>
<td>$d^2$, $d^8$</td>
<td>$^1S$, $^1D$, $^1G$, $^3P$, $^3F$</td>
<td>45</td>
</tr>
<tr>
<td>$d^3$, $d^7$</td>
<td>$^2P$, $^2D(2)$, $^2F$, $^2G$, $^2H$, $^4P$, $^4F$</td>
<td>120</td>
</tr>
<tr>
<td>$d^4$, $d^6$</td>
<td>$^1S(2)$, $^1D(2)$, $^1F$, $^1G(2)$, $^1I$, $^3P(2)$, $^3D$, $^3F(2)$, $^3G$, $^3H$, $^5D$</td>
<td>210</td>
</tr>
<tr>
<td>$d^5$</td>
<td>$^2S$, $^2P$, $^2D(3)$, $^2F(2)$, $^2G(2)$, $^2H$, $^2I$, $^4P$, $^4D$, $^4F$, $^4G$, $^6S$</td>
<td>252</td>
</tr>
</tbody>
</table>

<sup>a</sup> The terms denote the quantum numbers of the electronic states.
Reduce microstate table into its component free-ion terms.

The spin multiplicity is the same as the # of microstates.

Each terms has different energies; they represent three states with different degrees of electron-electron interactions.

Which term has the lowest energy. This can be done by using two of Hund’s rules.

1. The ground term (term of lowest energy) has the highest spin multiplicity. (Hund’s rule of maximum multiplicity)

2. If two or more terms share the maximum spin multiplicity, the ground term is one having the highest value of \( L \).
Reduce microstate table into its component free-ion terms.
\[ d^2 \]
\[ l = 2 \]
\[ m_l = +2, +1, 0, -1, -2 \]
\[ m_s = +1/2 \text{ or } -1/2 \]

<table>
<thead>
<tr>
<th></th>
<th>( M_L )</th>
<th>( M_S )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-4</td>
<td>x</td>
</tr>
<tr>
<td>+4</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>+3</td>
<td>x</td>
<td>XXX</td>
</tr>
<tr>
<td>+2</td>
<td>x</td>
<td>XXX</td>
</tr>
<tr>
<td>+1</td>
<td>XX</td>
<td>XXXXX</td>
</tr>
<tr>
<td>0</td>
<td>XX</td>
<td>XXXXX</td>
</tr>
<tr>
<td>-1</td>
<td>XX</td>
<td>XXXXX</td>
</tr>
<tr>
<td>-2</td>
<td></td>
<td>XXX</td>
</tr>
<tr>
<td>-3</td>
<td>x</td>
<td>XXX</td>
</tr>
<tr>
<td>-4</td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>
7.5 Splitting of Terms

The possible splitting of S, P, D, F terms:

- **S state is nondegenerate; no splitting**
- **P term from Eqs. 7.2 ~ 7.6**
  
  \[
  T_{1g}; \text{ in } O_h \text{ a } P \text{ term is not split, but becomes a triply degenerate } T_{1g} \text{ term}
  \]

- **D term has a fivefold orbital degenerate**
  from Eqs. 7.2 ~ 7.6
  
  \[
  \Gamma_D = E_g + T_{2g}
  \]

- **F term has a sevenfold orbital degenerate**
  from Eqs. 7.2 ~ 7.6
  
  \[
  \Gamma_F = A_{2g} + T_{1g} + T_{2g}
  \]
### Table 7.2  Splitting of Free-Ion Terms of \(d^n\) Configurations in an Octahedral Field

<table>
<thead>
<tr>
<th>Free-Ion Term</th>
<th>Terms in (O_h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S)</td>
<td>(A_{1g})</td>
</tr>
<tr>
<td>(P)</td>
<td>(T_{1g})</td>
</tr>
<tr>
<td>(D)</td>
<td>(E_g + T_{2g})</td>
</tr>
<tr>
<td>(F)</td>
<td>(A_{2g} + T_{1g} + T_{2g})</td>
</tr>
<tr>
<td>(G)</td>
<td>(A_{1g} + E_g + T_{1g} + T_{2g})</td>
</tr>
<tr>
<td>(H)</td>
<td>(E_g + 2T_{1g} + T_{2g})</td>
</tr>
<tr>
<td>(I)</td>
<td>(A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g})</td>
</tr>
</tbody>
</table>

for \(d^2\)
7.5 Splitting of Terms

We need to know the term symbols arising from 45 microstates in the slightly relaxed strong-field case.

Setup for preparation a correlation diagram for a d² ion in O₉ environment.
1. Sketch the energy levels, showing the d electrons.
2. Spin multiplicity of lowest-energy state = number of unpaired electrons + 1.
3. Determine the maximum possible value of $M_L$ for the configuration as shown. This determines the type of free-ion term.
4. Combine results of steps 2 and 3 to get ground term.

Spin multiplicity = 3 + 1 = 4
Max. of $M_L$: 2 + 1 + 0 = 3

$^4F$
7.5 Splitting of Terms

For the ground-state configuration $t_{2g}^2$ we take the direct product $t_{2g} \times t_{2g}$

\[
\Gamma(t_{2g}^2) = A_{1g} + E_g + T_{1g} + T_{2g}
\]

We need to know spin multiplicities. Here $D_t = 15$.

Three possible ways

\[
\begin{align*}
\frac{1}{2} A_{1g} + \frac{1}{2} E_g + \frac{1}{2} T_{1g} + \frac{3}{2} T_{2g} \\
\frac{3}{2} A_{1g} + \frac{1}{2} E_g + \frac{3}{2} T_{1g} + \frac{1}{2} T_{2g} \\
3 A_{1g} + 3 E_g + 1 T_{1g} + 1 T_{2g}
\end{align*}
\]

The triplet state must have a triply degenerate orbitals term
7.5 Splitting of Terms

For the ground-state configuration $e_g^2$ we take the direct product $e_g \times e_g$

\[
\Gamma(e_g^2) = A_{1g} + A_{2g} + E_g
\]

We need to know spin multiplicities. Here $D_t = 6$.

Two possible ways

\[
\Gamma_{(eg2)} = 3A_{1g} + 1A_{2g} + 1E_g
\]

\[
\Gamma_{(eg2)} = 1A_{1g} + 3A_{2g} + 1E_g
\]

The triplet state must have nondegenerate orbitals term
For the ground-state configuration $t_{2g}^1e_{g}^1$ we take the direct product $t_{2g} \times e_{g}$

\[ \Gamma = T_{1g} + T_{2g} \]

We need to know spin multiplicities. Here $D_t = 24$. The electrons in this configuration are unrestricted by the Pauli exclusion principle. And they can occur as both singlets and triplets

\[ \Gamma = 1T_{1g} + 1T_{2g} + 3T_{1g} + 3T_{2g} \]
Figure 7.23  Setup for preparing a correlation diagram for a $d^2$ ion in an octahedral environment. The spin multiplicities of strong field terms indicated with superscript (1,3) are yet to be determined.
7.5 Splitting of Terms

$\Gamma = 1^{A_1g} + 3^{T_2g} + 3^{A_1g} + 3^{T_2g}$

$\Gamma_{(eg2)} = 3^{A_1g} + 1^{A_2g} + 1^{E_g}$

$\Gamma_{(eg2)} = 1^{A_1g} + 3^{A_2g} + 1^{E_g}$

$\Gamma = 1^{T_{1g}} + 1^{T_{2g}} + 3^{T_{1g}} + 3^{T_{2g}}$

Correlation diagram for a $d^2$ ion in an $O_h$ environment.

Figure 7.24 Complete correlation diagram for a $d^2$ ion in an octahedral environment.
7.5 Splitting of Terms

Correlation diagram for a d$^8$ ion in O$_h$ environment

Figure 7.26 Correlation diagram for a d$^8$ ion in an octahedral environment.
The most striking feature of transition metal complexes is the array of colors they present.

Color results when a complex absorbs frequencies in the visible region of the spectrum, causing transitions from the ground electronic states to certain of the excited states of the configurations.

Since the electronic states arise from d-electron configurations on the metal ion, the absorptions are said to result d-d transitions.

1. Transitions between states of the same parity are forbidden (symmetry with respect to a center of inversion): Laporte selection rule

2. Transitions between states of different spin multiplicities are forbidden: spin selection rule

Forbidden; $g \rightarrow g$ transition allowed; $g \rightarrow u$ transition

$^4A_2$ and $^4T_1$: spin-allowed

$^4A_2$ and $^2T_2$: spin-forbidden
Some rules for relaxation of selection rules

1. Vibrations may temporarily change the symmetry (the center of symmetry is temporarily lost: vibronic coupling) relax the first selection rule: d-d transition

2. Tetrahedral complexes often absorb more strongly than $O_h$ complexes. Metal-ligand sigma bonds can be described as involving a combination of sp$^3$ and sd$^3$ hybridization of the metal orbitals: relax the first selection rule

3. Spin-orbit coupling provides a mechanism of relaxing the second selection rule
Correlation diagram for a $d^8$ ion in $O_h$ environment