6. Anorganic Molecules: From Atoms to Complexes

6.1 Two important cases

Tetrahedral complex AB₄

e.g. Ni(CO)₄

Symmetry group: T₄

Octahedral complex AB₆

e.g. [CoF₆]³⁻

Symmetry group: O₄

6.2 Symmetry of central atom orbitals

We classify the AO basis of the central atom with respect to its symmetry within the point group of the molecules (note: (a) all symmetry elements must contain the central atom; (b) only the angular part of the wave function is relevant for its symmetry properties).

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>angular dependent part (cartesian coordinates)</th>
<th>angular dependent part (spherical coordinates)</th>
<th>T₄ (AB₄ tetr.)</th>
<th>O₄ (AB₆ oct.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>s</td>
<td>1</td>
<td>1</td>
<td>A₁</td>
<td>A₁g</td>
</tr>
<tr>
<td>1</td>
<td>px</td>
<td>x</td>
<td>cos(θ)</td>
<td>T₂</td>
<td>T₁u</td>
</tr>
</tbody>
</table>
The corresponding irreps can be found as usual by setting up the representation matrices and calculating their characters and analysing them in terms of the irreps of the group. In general, however, the corresponding irreps can be looked up in the character table.

6.3 Symmetry of ligand atom orbitals – \( \sigma \)-Bonding

**Tetrahedral complex \( AB_4 \)**

Application of all symmetry operations to the set of ligand AOs and determination of the characters of the 4 dimensional representation:
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<table>
<thead>
<tr>
<th>Operation</th>
<th>$\varphi_1, \varphi_2, \varphi_3, \varphi_4$</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>$\varphi_1, \varphi_2, \varphi_3, \varphi_4$</td>
<td>4</td>
</tr>
<tr>
<td>$C_3$ (8)</td>
<td>$\varphi_1, \varphi_4, \varphi_2, \varphi_3$</td>
<td>1</td>
</tr>
<tr>
<td>$C_2$ (3)</td>
<td>$\varphi_3, \varphi_4, \varphi_1, \varphi_2$</td>
<td>0</td>
</tr>
<tr>
<td>$S_4$ (6)</td>
<td>$\varphi_4, \varphi_1, \varphi_2, \varphi_3$</td>
<td>0</td>
</tr>
<tr>
<td>$\sigma_d$ (6)</td>
<td>$\varphi_1, \varphi_4, \varphi_3, \varphi_2$</td>
<td>2</td>
</tr>
</tbody>
</table>

Analysis (section 3.13):

\[
n_{A1} = \frac{1}{24} \left( 1*4*1+ 8*1*1+ 3*0*1+ 6*0*1+ 6*2*1 \right) = 1
\]

\[
n_{A2} = \frac{1}{24} \left( 1*4*1+ 8*1*1+ 3*0*1+ 6*0*(-1)+ 6*2*(-1) \right) = 0
\]

\[
n_E = \frac{1}{24} \left( 1*4*2+ 8*1*(-1)+ 3*0*2+ 6*0*0+ 6*2*0 \right) = 0
\]

\[
n_{T1} = \frac{1}{24} \left( 1*4*3+ 8*1*0+ 3*0*(-1)+ 6*0*1+ 6*2*(-1) \right) = 0
\]

\[
n_{T2} = \frac{1}{24} \left( 1*4*3+ 8*1*0+ 3*0*(-1)+ 6*0*(-1)+ 6*2*1 \right) = 1
\]

$\Gamma_{\text{Ligand } \sigma-\text{AOs}} = A_1 + T_2$

MO diagram for tetrahedral $\sigma$-bonded ML$_4$ complex of 3d transition metal:
Octahedral complex $AB_6$

Application of all symmetry operations to the set of ligand AOs and determination of the characters of the 6 dimensional representation:

<table>
<thead>
<tr>
<th>Operation</th>
<th>$\varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_5, \varphi_6$</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (1)</td>
<td>$\varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_5, \varphi_6$</td>
<td>6</td>
</tr>
<tr>
<td>$C_3$ (8)</td>
<td>$\varphi_2, \varphi_3, \varphi_4, \varphi_5, \varphi_1$</td>
<td>0</td>
</tr>
<tr>
<td>$C_2$ (6)</td>
<td>$\varphi_2, \varphi_1, \varphi_4, \varphi_5, \varphi_6$</td>
<td>0</td>
</tr>
<tr>
<td>$C_4$ (6)</td>
<td>$\varphi_2, \varphi_3, \varphi_4, \varphi_1, \varphi_5, \varphi_6$</td>
<td>2</td>
</tr>
<tr>
<td>$C_2'$ (6)</td>
<td>$\varphi_3, \varphi_4, \varphi_1, \varphi_2, \varphi_5, \varphi_6$</td>
<td>2</td>
</tr>
<tr>
<td>$i$ (1)</td>
<td>$\varphi_3, \varphi_4, \varphi_1, \varphi_2, \varphi_6, \varphi_5$</td>
<td>0</td>
</tr>
<tr>
<td>$S_4$ (6)</td>
<td>$\varphi_2, \varphi_3, \varphi_4, \varphi_1, \varphi_6, \varphi_5$</td>
<td>0</td>
</tr>
<tr>
<td>$S_6$ (8)</td>
<td>$\varphi_4, \varphi_5, \varphi_2, \varphi_6, \varphi_1, \varphi_3$</td>
<td>0</td>
</tr>
</tbody>
</table>
Analysis (analogous to tetrahedral case):

\[
\Gamma_{\text{Ligand } \sigma-\text{AOs}} = A_{1g} + E_g + T_{1u}
\]

MO diagram for octahedral $\sigma$-bonded ML$_6$ complex of 3d transition metal:
6.4 Symmetry of ligand atom orbitals – σ- and π-Bonding

Tetrahedral complex $AB_4$

Determination of characters of 8 dimensional reducible representation:

E: $\chi(E) = 8$

$C_3$: $\chi(C_3) = -1$

Because

$$C_3\begin{pmatrix} p_x \\ p_y \end{pmatrix} = \begin{pmatrix} \cos \frac{2\pi}{3} & \sin \frac{2\pi}{3} \\ -\sin \frac{2\pi}{3} & \cos \frac{2\pi}{3} \end{pmatrix} \begin{pmatrix} p_x \\ p_y \end{pmatrix}$$

$C_2$: $\chi(C_2) = 0$

$S_4$: $\chi(S_4) = 0$

$\sigma$: $\chi(\sigma) = 0$

All characters with exception of $\chi(C_3)$ can be directly derived by inspection of the effect of the symmetry elements.
Analysis (section 3.13):

\[ n_{A1} = \frac{1}{24} \left( 8(-1)*1+ 3*0*1+ 6*0*1+ 6*0*1 \right) = 0 \]

\[ n_{A2} = \frac{1}{24} \left( 8(-1)*1+ 3*0*1+ 6*0*(-1)+ 6*0*(-1) \right) = 0 \]

\[ n_{E} = \frac{1}{24} \left( 8(-1)*(-1)+ 3*0*2+ 6*0*0+ 6*0*0 \right) = 1 \]

\[ n_{T1} = \frac{1}{24} \left( 8(-1)*0+ 3*0*(-1)+ 6*0*1+ 6*0*(-1) \right) = 1 \]

\[ n_{T2} = \frac{1}{24} \left( 8(-1)*0+ 3*0*(-1)+ 6*0*(-1)+ 6*0*1 \right) = 1 \]

\[ \Gamma_{\text{Ligand } \pi-AOs} = E + T_1 + T_2 \]

MO diagram for tetrahedral σ- and π-bonded ML₄ complex of 3d transition metal:
Octahedral complex $AB_6$

Determination of characters of 8 dimensional reducible representation:

<table>
<thead>
<tr>
<th>Operation</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (1)</td>
<td>12</td>
</tr>
<tr>
<td>$C_3$ (8)</td>
<td>0</td>
</tr>
<tr>
<td>$C_2$ (6)</td>
<td>0</td>
</tr>
<tr>
<td>$C_4$ (6)</td>
<td>0</td>
</tr>
<tr>
<td>$C_2'$ (6)</td>
<td>-4</td>
</tr>
<tr>
<td>i (1)</td>
<td>0</td>
</tr>
<tr>
<td>$S_4$ (6)</td>
<td>0</td>
</tr>
<tr>
<td>$S_6$ (8)</td>
<td>0</td>
</tr>
<tr>
<td>$\sigma_h$ (3)</td>
<td>0</td>
</tr>
<tr>
<td>$\sigma_d$ (6)</td>
<td>0</td>
</tr>
</tbody>
</table>

Analysis (section 3.13):

$$\Gamma_{\text{Ligand } \pi-\text{AOs}} = T_{1g} + T_{2g} + T_{1u} + T_{2u}$$
6.5 The direct product group (outer direct product)

We would like to investigate the symmetry properties of atoms in some more detail. One more definition from group theory is needed for this purpose.

We consider two groups $A=\{A_1, A_2, \ldots, A_n\}$ and $B=\{B_1, B_2, \ldots, B_m\}$, which (1) have no common element except $E$ and (2) for which $A_i B_j = B_j A_i$ for all $A_i, B_j$. The set of products of all elements of $A$ and $B$ is called the direct product group $A \otimes B = \{A_i B_j, A_1 B_2, \ldots, A_n B_m\}$.

(proof that $A \otimes B$ is a group and of direct product group properties: see textbooks, e.g. Wherrett; the product is called the outer direct product (i.e. between two groups) in contrast to the inner direct product (i.e. within one group) defined in section 4.3)

Direct product groups have some specific properties:

• The number of classes of $A \otimes B$ is equal to the product of the number of classes in $A$ and $B$. 
• The number of irreps of $A \otimes B$ is equal to the product of the number of irreps in $A$ and $B$.

• The irreps of the direct product group are given by the direct matrix product of the representations (This is in analogy to section 4.3, but outer direct product i.e. two different groups with commuting elements in this case. Note that the inner direct product may yield reducible representations, in contrast to the present case):

$$
\Gamma^A \otimes \Gamma^B = \left\{ \begin{array}{c}
\Gamma^A_{11} \quad \Gamma^B_{11} \\
\Gamma^A_{21} \quad \Gamma^B_{21} \\
\vdots \\
\Gamma^A_{12} \quad \Gamma^B_{12} \\
\Gamma^A_{22} \quad \Gamma^B_{22} \\
\vdots
\end{array} \right\} \times \left\{ \begin{array}{c}
\Gamma^A_{11} \quad \Gamma^B_{11} \\
\Gamma^A_{21} \quad \Gamma^B_{21} \\
\vdots \\
\Gamma^A_{12} \quad \Gamma^B_{12} \\
\Gamma^A_{22} \quad \Gamma^B_{22} \\
\vdots
\end{array} \right\}
$$

• The characters are given by the product of the individual characters (in analogy to section 4.3):

$$\chi_{A \otimes B} = \chi_A \cdot \chi_B$$

The construction of direct product groups e.g. provides an efficient method of deriving the character tables for more complex groups.

(6.1 Example: $O_h$ is the direct product group of which groups? Inspect the character tables).

6.6 Atomic symmetry: the rotation inversion group $R_3 \otimes S_1$

We inspect the symmetry operations of a H atom:

• Identity element: $E$.

• Rotations $C(\alpha, \xi)$ by an arbitrary angle $2\pi/\alpha$ around some arbitrary axis $\xi$.

Note: all rotations by a given angle $2\pi/\alpha$ around different axes $\xi$ and $\xi'$ fall into the same class, as there is a third rotation which transforms the coordinate systems accordingly:
All rotations by different angles belong to different classes.

- Inversion: $i$.
- Improper rotations: $C(\alpha, \xi)$ (same arguments as for rotations).

As all $C(\alpha, \xi)$ and $i$ commute, this group can be considered to be the direct product group of the pure rotational groups in three dimensions $C_3$ and the group $S_2$ (or $C_i$), therefore denote the rotation inversion group as $R_s \otimes S_2$.

We look up the character table of $R_s \otimes S_2$:

<table>
<thead>
<tr>
<th>$R_s \otimes S_2$</th>
<th>$E$</th>
<th>$\infty R(\alpha, \xi)$</th>
<th>$i$</th>
<th>$\infty i R(\alpha, \xi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^{lbg}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$D^{lgu}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$D^{lg}$</td>
<td>3</td>
<td>$\frac{\sin(\frac{1}{2} l \pi \alpha)}{\sin \frac{1}{2} \alpha}$</td>
<td>1</td>
<td>$\frac{\sin(\frac{1}{2} l \pi \alpha)}{\sin \frac{1}{2} \alpha}$</td>
</tr>
<tr>
<td>$D^{lg}$</td>
<td>$2l+1$</td>
<td>$\frac{\sin(\frac{1}{2} l \pi \alpha)}{\sin \frac{1}{2} \alpha}$</td>
<td>$2l+1$</td>
<td>$\frac{\sin(\frac{1}{2} l \pi \alpha)}{\sin \frac{1}{2} \alpha}$</td>
</tr>
<tr>
<td>$D^{lu}$</td>
<td>$2l+1$</td>
<td>$\frac{\sin(\frac{1}{2} l \pi \alpha)}{\sin \frac{1}{2} \alpha}$</td>
<td>-(2l+1)</td>
<td>$\frac{\sin(\frac{1}{2} l \pi \alpha)}{\sin \frac{1}{2} \alpha}$</td>
</tr>
</tbody>
</table>

The group $R_s \otimes S_2$ is a group involving continuous parameters. We call this type of group a continuous group or Lie group. In principle we could now generate the symmetry adapted
function by the use of projection operators (replacing the summation by integrations). In fact, we will follow a simpler strategy: We will show that the eigenfunctions of the H atoms correspond to certain irreps of $R_i \otimes S_z$.

H atom:

$$\hat{H}\psi(r, \vartheta, \phi) = E\psi(r, \vartheta, \phi)$$ with $\hat{H} = -\frac{\hbar^2}{2\mu r^2} \nabla^2 - \frac{e^2}{r}$

Solution: $\psi_{n,j,m}(r, \vartheta, \phi) = R_{m}(r) \cdot Y_{m}^{j}(\theta, \phi)$

with $R_{m}(r)$ : radial part

$$Y_{m}^{j}(\theta, \phi) = N \cdot P_{m}^{j}(\cos \theta)e^{im\phi}$$ : angular part, spherical harmonics

$P_{m}^{j}$ : associated Legendre functions

We determine the characters with respect to the operations of $R_i \otimes S_z$ choosing a set of functions for a given $l$ as a basis:

- $E$: $(2l+1)$ $m$ values, $(2l+1)$ functions, $\chi^{E}(E) = 2l + 1$
  - $C(\alpha, \xi)$: Same class for rotations by given angle around different axes. We choose $z$ axis: $R_{z}(\alpha)\psi_{n,j,m}(r, \vartheta, \phi) = \psi_{n,j,m}(r, \vartheta, \phi - \alpha) = e^{-i\alpha m}\psi_{n,j,m}(r, \vartheta, \phi)$

Therefore:

$$\chi^{\alpha}(R_{z}(\alpha)) = \sum_{m=-l}^{l} e^{im\alpha} \left( \begin{array}{ccc}
\psi_{n,j,-l} \\
0 \\
0 \\
\vdots \\
0 \\
\psi_{n,j,l}
\end{array} \right) \left( \begin{array}{ccc}
e^{-il\alpha} & 0 & 0 \\
0 & e^{-i(-l+1)\alpha} & 0 \\
0 & 0 & \ddots \\
0 & 0 & 0 & e^{-i(l+1)\alpha} \\
\psi_{n,j,-l+1} \\
\psi_{n,j,-l+1} \\
\vdots \\
\psi_{n,j,l+1}
\end{array} \right) \left( \begin{array}{c}
\psi_{n,j,-l} \\
\psi_{n,j,-l+1} \\
\vdots \\
\psi_{n,j,l+1}
\end{array} \right)$$

$$\chi^{\alpha}(R_{z}(\alpha)) = \frac{\sin(l + \frac{\alpha}{2})}{\sin \frac{\alpha}{2}}$$

- $i$: $iY_{m}^{j}(\theta, \phi) = (-1)^{j} Y_{m}^{j}(\theta, \phi)$ (intuitively clear from the graphical representation of spherical harmonics; for proof see textbooks)
• $\chi' (i R_\alpha (\alpha)) = (-1)^l \frac{\sin (l + \frac{1}{2}) \alpha}{\sin \frac{\alpha}{2}}$; follows from the direct product group properties of $R_\alpha \otimes S_\alpha$.

Apparently, the $(2l+1)$-fold degenerate eigenfunctions of the H atom Hamiltonian span a basis for the following irreps of the rotation-inversion group $R_\alpha \otimes S_\alpha$:

- $l=0$: s functions; $D^{0g}$
- $l=1$: p functions; $D^{1u}$
- $l=2$: d functions; $D^{2g}$
- $l=3$: f functions; $D^{3u}$

... 

Note: The functions only span bases for half of the irreps existing in the group. Half of the irreps cannot be represented by single electron functions. These irreps can, however exist in case of many electron systems, as we will see in the following.

6.7 Symmetry of many electron atoms

We investigate a two electron atom, as usual describing the wave function by a product of single electron functions $\psi_{n_1, m_1, l_1, \sigma_1}(\vec{r}_1)$; $\psi_{n_2, m_2, l_2, \sigma_2}(\vec{r}_2)$.

$\psi(\vec{r}_1, \vec{r}_2) = \psi_{n_1, m_1}(\vec{r}_1) \cdot \psi_{n_2, m_2}(\vec{r}_2)$

Can we classify the possible two electron states in terms of symmetry? According to section 4.3 we have to determine the direct product of the corresponding sets of function belonging to the irreps $D^p$ and $D^{p'}$ (p, p’ denoting the parity, i.e. the symmetry behaviour with respect to i).

Considering $C(\alpha, \xi)$, the character of $D^p$ is (see 6.6):

$\chi’ (R(\alpha)) = \sum_{m} e^{im\xi}$

Accordingly the character of the direct product is
\[ \chi(R(\alpha)) \cdot \chi''(R(\alpha)) = (e^{-i\beta} + e^{-i(l-1)\alpha} + \ldots + e^{-i\beta}) (e^{-i\gamma} + e^{-i(l-1)\alpha} + \ldots + e^{-i\gamma}) \]
\[ = \sum_{l=1}^{l} e^{il\alpha} + \sum_{l=1}^{l-1} e^{il\alpha} + \ldots + \sum_{l=1}^{l'} e^{il\alpha} \]

(after some rearrangement of the terms in the last line). Thus, we obtain
\[ \chi(R(\alpha)) \cdot \chi''(R(\alpha)) = \chi^{l+l'}(R(\alpha)) + \chi^{l+l'}(R(\alpha)) + \ldots + \chi^{l-l'}(R(\alpha)) \]

or

\[ \Gamma^r(R(\alpha)) \otimes \Gamma^r(R(\alpha)) = \Gamma^{l+l'}(R(\alpha)) + \Gamma^{l+l'}(R(\alpha)) + \ldots + \Gamma^{l-l'}(R(\alpha)) \]

i.e. \( L = l + l', l + l' - 1, \ldots, l - l' \) (Clebsch-Gordan series)

Note:

(1) parity \( P \) of the product function:
\[ g \cdot g = u \cdot u = g \]
\[ g \cdot u = u \cdot g = u \]

(2) common notation \( S, P, D, F, G, H, \ldots \) for \( L = 0, 1, 2, 3, 4, 5, \ldots \) (corresponding \( \text{SALCs: } \psi_{l_1,l_2}^{l+M} = \sum_{m_{1,2}} C_{m_{1,2}} \psi_{l_1,m_1} \psi_{l_2,m_2} \)

with \( C_{m_{1,2}} \): Clebsch-Gordan coefficients, see textbooks)

Example:

As an example we consider an electron system with two d electrons:

\[ d^2: l_1 = 2; l_2 = 2 \]
\[ \Rightarrow L = 4, 3, 2, 1, 0 \text{ (G, F, D, P, S)} \]

Using the same coupling scheme for the electron spin, we obtain:

\[ s_1 = 1/2; s_2 = 1/2 \]
\[ \Rightarrow S = 1, 0 \]

Consequently, the possible configurations are:
The above is correct, if both electrons occupy different d shells, e.g. 3d$^1$4d$^1$. If, however, both electron occupy the same shell (3d$^2$) the Pauli principle excludes some of these states. The Pauli principle requires that a fermion wavefunction is antisymmetric with respect to particle exchange. Taking into account the particle spin $\alpha$ or $\beta$, the following wavefunction comply with the Pauli principle:

Singulett state (symmetric space function, antisymmetric spin function):

$$
\Psi_1 = \frac{1}{\sqrt{2}} (\psi(1,2) + \psi(2,1)) - \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \alpha(1)\beta(2))
$$

Triplett state (antisymmetric space function, symmetric spin function):

$$
\Psi_2 = \frac{1}{\sqrt{2}} (\psi(1,2) - \psi(2,1)) \alpha(1)\alpha(2)
$$

$$
\Psi_3 = \frac{1}{\sqrt{2}} (\psi(1,2) - \psi(2,1)) \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) + \alpha(1)\beta(2))
$$

$$
\Psi_4 = \frac{1}{\sqrt{2}} (\psi(1,2) - \psi(2,1)) \beta(1)\beta(2).
$$

It is apparent that $\Psi_1$ vanishes if the spatial part is symmetric with respect to particle exchange and that $\Psi_{2,3,4}$ vanish if the spatial part is antisymmetric. In some cases this classification is obvious. For $n_1s^2n_2s$, the coupled two-electron function is the simply the product and therefore symmetric. Therefore, the functions $\Psi_{2,3,4}$ can only exist, if the radial parts differ ($n_1 \neq n_2$). In general, however, the behavior of the functions has to be investigated in detail.

(6.2 General analysis of states that comply with the Pauli principle).
For the \( d^2 \) configuration, the following states, which are conform with the Pauli principle (energetically split by the electron-electron interaction):

\[ ^3F, \ ^1D, \ ^3P, \ ^1G, \ ^1S \]

Table of \( d_n \) states in L-S (Russell-Sounders) coupling (F. A. Cotton):

<table>
<thead>
<tr>
<th>( d^1 )</th>
<th>( 1(S, D, G) )</th>
<th>( ^3(D) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d^2 )</td>
<td>( 1(S, D, G) )</td>
<td>( ^3(P, F) )</td>
</tr>
<tr>
<td>( d^3 )</td>
<td>( 2(D) )</td>
<td>( ^2(P, D, F, G, H) )</td>
</tr>
<tr>
<td>( d^4 )</td>
<td>( 1(S, D, G) )</td>
<td>( ^3(P, F) )</td>
</tr>
<tr>
<td>( d^5 )</td>
<td>( 2(D) )</td>
<td>( ^2(P, D, F, G, H) )</td>
</tr>
</tbody>
</table>

\( d^6 \) Same as \( d^4 \)

\( d^7 \) Same as \( d^3 \)

\( d^8 \) Same as \( d^2 \)

\( d^9 \) Same as \( d^1 \)

\( d^{10} \) \( ^1(S) \)

6.8 Many electron atoms in ligand fields

Now we investigate the behaviour of the many electron states in a weak ligand field of tetrahedral or octahedral symmetry. For this purpose we calculate the characters of the irreps of \( R_1 \otimes S_2 \) with respect to the characteristic rotations \( \chi'(R(\alpha)) = \frac{\sin(\frac{1}{2} \alpha)}{\sin(\frac{1}{2} \alpha)} \) and analyse these in terms of \( O \) and \( T \) (the \( O_h \) symmetry is obtained by adding the parity, see direct product group properties, sect. 6.5):

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>E</th>
<th>( R_2 )</th>
<th>( R_2 )</th>
<th>( R_2 )</th>
<th>Contained irreps in</th>
<th>( O )</th>
<th>( O_h )</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>( A_1 )</td>
<td>( A_{1g} )</td>
<td>( A_1 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>3</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>T_1</td>
<td>T_{1g}</td>
<td>T_2</td>
<td></td>
</tr>
</tbody>
</table>
Thus we obtain the following terms for $d^2$ in an octahedral ligand field, weaker than the electron-electron interaction:

$^3F \Rightarrow ^3A_{2g}, ^3T_{1g}, ^3T_{2g}$

$^1D \Rightarrow ^1E_g, ^1T_{2g}$

$^3P \Rightarrow ^3T_{1g}$

$^1G \Rightarrow ^1A_{1g}, ^1E_g, ^1T_{1g}, ^1T_{2g}$

$^1S \Rightarrow ^1A_{1g}$

In case of a very strong ligand field, it is more appropriate to consider the interaction with the field first, and then take into account the electron-electron interaction as a correction:

- Single $d$ electron in $O_h$ field: $e_g + t_{2g}$
- $d^2$: three configurations: $e_g^2$, $e_g t_{2g}$, $t_{2g}^2$

The three configurations are analysed as usual with respect to their direct products and its rotational symmetry in the subgroup $O$:

<table>
<thead>
<tr>
<th>O</th>
<th>E</th>
<th>$8C_3$</th>
<th>$3C_4$</th>
<th>$6C_4$</th>
<th>$6C_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$T_2$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$E^2$</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$T_2^2$</td>
<td>9</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$E \times T_2$</td>
<td>6</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

As before we would obtain the states
if the two electrons would occupy different d shells. With both electrons in the same shell, the Pauli principle excludes some states, for those configurations, in which more than one electron occupies the same set of orbitals (i.e. $e_g^2$ and $t_{2g}^2$).

These states can be identified by the method of descending symmetry, illustrated for the case of $e_g^2$:

Note: - spin is preserved during symmetry reduction
- from (1) to (2) and from (5) to (6) using correlation table:

from (A. F. Cotton):

Thus we obtain:
Summary:

It is noteworthy that many of these states are actually unstable with respect to a distortion. The Jahn-Teller theorem states that degenerate electronic states are unstable with respect to a deformation, which reduces the symmetry, lifts the degeneracy and lowers the total energy (this deformation can be described as a coupling of between the electronic and vibrational states of the system). In terms of group theory, this is easy to understand: If we for example reduce the symmetry of a $T_{2g}$ state by coupling to a $E_g$ vibrational mode to $D_{4h}$, $T_{2g}$ splits according to $T_{2g} (O_h) = B_{2g}(D_{4h}) + E_g(D_{4h})$, with one state being lower in energy than the energy of the symmetric state.
6.9 Tanabe-Sugano diagrams

(6.3 Tanabe Sugano diagrams for $d^2$ to $d^8$).

- ground state is defined as zero energy
- parameters: $\Delta$: parameter describing splitting between $t_{2g}$ and $e_g$ orbitals
  - $B$: parameter describing electron-electron repulsion

- Note: For some configurations, the ground state changes as a function of the strength of the ligand field.
  
  Example: $d^4$, low field: $5E_g (t_{2g}^3 e_g)$, high spin complex
  
  high field: $3T_{1g} (t_{2g}^4)$, high spin complex

- Note: A given number of electrons or holes leads to the same set of states (i.e. $d^{10-n}$ and $d^n$), but the order changes as the sign of the interaction of the holes with the environment has the opposite sign.

- Note: In tetrahedral coordination the same states are generated as in octahedral coordination, but the order is reversed ($T_d$: $E(e_g) < E(t_{2g})$; $O_h$: $E(e_g) > E(t_{2g})$).

6.10 Spectroscopy of d-d transitions, vibronically allowed transitions

For many d-transition metal complexes, transitions between the d states discussed in the previous section are generally forbidden, e.g. in all centrosymmetric complexes due to the parity selection rule, which excludes $g \leftrightarrow g$ transition (the dipole operator always has parity $u$). Still, most transitions can be observed spectroscopically. The reason is that the transitions may be vibronically allowed, i.e. allowed due to the coupling to a molecular vibration. Accordingly we have to investigate the matrix element

$$\mu_\sigma = \langle \nu_f, \nu_i | \hat{p} | \nu_0, \nu_0 \rangle$$
which might be nonzero even if the pure electronic transition is forbidden. The fact can be interpreted in first order perturbation theory with

\[
\hat{H}_e = \hat{H}_e^0 + \sum \left( \frac{\partial \hat{H}}{\partial Q} \right)_{Q_0} Q_i + \ldots \quad (Q_i \text{ is the vibrational mode as discussed in chapter 7})
\]

as a mixing of the vibrationally excited electronic states with states of different symmetry by coupling to molecular vibrations:

\[
\langle \varepsilon, \nu \mid \hat{\mu} \mid \nu \rangle = \langle \varepsilon', \nu' \mid \hat{\mu} \mid \nu \rangle + \sum_{\nu', \nu} a_{\nu', \nu} \langle \varepsilon \mid \nu \rangle \langle \nu' \mid \hat{\mu} \mid \nu \rangle
\]

with

\[
a_{\nu, \nu'} = \frac{\sum_{\nu'} \left| \langle \nu' \mid \hat{\mu} \mid \nu \rangle \right|^2 \langle \nu \mid \frac{\partial H}{\partial Q} \rangle_{Q_0} \langle \nu' \rangle}{E_{\nu, \nu'} - E_{\nu}}.
\]

Thus the forbidden transition “borrows” intensity from the allowed transitions.

From the point of view of group theory the transition is vibronically allowed if

\[
A_i \in \Gamma(\varepsilon) \otimes \Gamma(\nu) \otimes \Gamma(\hat{\mu}) \otimes \Gamma(\nu_0) \otimes \Gamma(\nu_0)
\]

or, if we start from the vibrational ground state \((\nu_0 = 0, \ \Gamma(\nu_0) = A_i)\) the transition \(\varepsilon, \nu \leftrightarrow \varepsilon_0\) becomes vibronically allowed by coupling to a vibration which belongs to the same irrep as the pure electronic transition \(\Gamma(\varepsilon) \otimes \Gamma(\hat{\mu}) \otimes \Gamma(\nu_0)\).

Example:

\(\text{Co(NH}_3\text{)}_6^{3+}: d^6, \text{ low spin, ground state } ^1A_{1g}\)

excited state: \(^1T_{1g}\)

dipole operator: \(\Gamma(\hat{\mu}) = T_{1u}\)

\[
\Rightarrow \Gamma(\varepsilon \otimes \hat{\mu} \otimes \varepsilon) = T_{1g} \otimes T_{1u} \otimes A_{1g} = A_{1u} + E_u + T_{1u} + T_{2u}
\]

Analysis of vibrational modes: \(\Gamma_{vib} = A_{1g} + E_u + 2T_{1u} + T_{2g} + T_{2u}\)

\[
\Rightarrow \text{Vibronically allowed transition through coupling with modes } 2T_{1u} + T_{2u}.
\]