Advanced Physical Chemistry (fizkemhk17em)
Electronic Structure

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Electronic structure of diatomic molecules
### Character table for point group D\(^{\infty}h\)

<table>
<thead>
<tr>
<th>(D^{\infty}h)</th>
<th>E</th>
<th>(2C^\infty)</th>
<th>(\infty \sigma_v)</th>
<th>i</th>
<th>(2S^\infty)</th>
<th>(\infty C_2)</th>
<th>linear functions, rotations</th>
<th>quadratic functions</th>
<th>cubic functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_{1g} = \Sigma^+_g)</td>
<td>+1</td>
<td>+1</td>
<td>...</td>
<td>+1</td>
<td>+1</td>
<td>...</td>
<td>+1</td>
<td>-</td>
<td>(x^2+y^2, z^2)</td>
</tr>
<tr>
<td>(A_{2g} = \Sigma^-_g)</td>
<td>+1</td>
<td>+1</td>
<td>...</td>
<td>-1</td>
<td>+1</td>
<td>...</td>
<td>-1</td>
<td>(R_x)</td>
<td>-</td>
</tr>
<tr>
<td>(E_{1g} = \Pi_g)</td>
<td>+2</td>
<td>+2cos((\phi))</td>
<td>...</td>
<td>0</td>
<td>+2</td>
<td>-2cos((\phi))</td>
<td>...</td>
<td>0</td>
<td>((R_x, R_y))</td>
</tr>
<tr>
<td>(E_{2g} = \Lambda_g)</td>
<td>+2</td>
<td>+2cos(2(\phi))</td>
<td>...</td>
<td>0</td>
<td>+2</td>
<td>+2cos(2(\phi))</td>
<td>...</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>(E_{3g} = \Phi_g)</td>
<td>+2</td>
<td>+2cos(3(\phi))</td>
<td>...</td>
<td>0</td>
<td>+2</td>
<td>-2cos(3(\phi))</td>
<td>...</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>(E_{ng})</td>
<td>+2</td>
<td>+2cos(n(\phi))</td>
<td>...</td>
<td>0</td>
<td>+2</td>
<td>(-1)^n2cos(n(\phi))</td>
<td>...</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(A_{1u} = \Sigma^+_u)</td>
<td>+1</td>
<td>+1</td>
<td>...</td>
<td>+1</td>
<td>-1</td>
<td>...</td>
<td>-1</td>
<td>(z)</td>
<td>-</td>
</tr>
<tr>
<td>(A_{2u} = \Sigma^-_u)</td>
<td>+1</td>
<td>+1</td>
<td>...</td>
<td>-1</td>
<td>-1</td>
<td>...</td>
<td>+1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(E_{1u} = \Pi_u)</td>
<td>+2</td>
<td>+2cos((\phi))</td>
<td>...</td>
<td>0</td>
<td>-2</td>
<td>+2cos((\phi))</td>
<td>...</td>
<td>0</td>
<td>((x, y))</td>
</tr>
<tr>
<td>(E_{2u} = \Lambda_u)</td>
<td>+2</td>
<td>+2cos(2(\phi))</td>
<td>...</td>
<td>0</td>
<td>-2</td>
<td>-2cos(2(\phi))</td>
<td>...</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>(E_{3u} = \Phi_u)</td>
<td>+2</td>
<td>+2cos(3(\phi))</td>
<td>...</td>
<td>0</td>
<td>-2</td>
<td>2cos(3(\phi))</td>
<td>...</td>
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<td>-</td>
</tr>
<tr>
<td>(E_{nu})</td>
<td>+2</td>
<td>+2cos(n(\phi))</td>
<td>...</td>
<td>0</td>
<td>-2</td>
<td>(-1)^n+12cos(n(\phi))</td>
<td>...</td>
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<td>-</td>
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<tr>
<td>...</td>
<td>...</td>
<td>...</td>
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<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Configuration: $1\sigma^2_g$

Symmetry of the state: $\Sigma^+_g \otimes \Sigma^+_g = \Sigma^+_g$

Notation for the state: $^1\Sigma^+_g$

Bond-order: 1, since one bonding orbital is occupied by two electrons
**He$_2$ molecule**

Configuration: \( 1\sigma_g^2 1\sigma_u^2 \)

Symmetry of the state: \( \Sigma_g^+ \otimes \Sigma_g^+ \otimes \Sigma_u^+ \otimes \Sigma_u^+ = \Sigma_g^+ \)

Notation for the state: \( ^1\Sigma_g^+ \)

Bond-order: 0, since one bonding and one anti-bonding orbital is occupied by two electrons each.
Diatomic molecules: molecular orbitals

$1\sigma_g$ \hspace{1cm} $1\sigma_u$

$2\sigma_g$ \hspace{1cm} $2\sigma_u$
Diatomic molecules: molecular orbitals

To construct the next orbitals, the $2p$ orbital of the atoms can be used. Considering also the symmetry ($z$ is the main axis of the molecule):

![Diagram of molecular orbitals]
Diatomic molecules: molecular orbitals

$1\pi_u$

$1\pi_g$

$3\sigma_g$

$3\sigma_u$
Li$_2$ molecule

Configuration: $1\sigma^2_1 \sigma^2_u 2\sigma^2_g$

Symmetry of the states: $\Sigma^+_g$

Notation for the state: $^1\Sigma^+_g$

Bond-order: 1, since two bonding and one anti-bonding orbitals are occupied by two electrons each.
**O₂ molecule**

Configuration: $1\sigma_g^2 \ 1\sigma_u^2 \ 2\sigma_g^2 \ 2\sigma_u^2 \ 1\pi_u^4 \ 3\sigma_g^2 \ 1\pi_g^2$, i.e. open shell

Possible symmetry of the state: $\Pi_g \otimes \Pi_g = \Sigma_g^+ \oplus \Sigma_g^- \oplus \Delta_g$

Possible states considering also Pauli-principle: $^3\Sigma_g^- \ 1\Sigma_g^+ \ 1\Delta_g$

In order of energy: $E_{3\Sigma_g^-} < E_{1\Delta_g} < E_{1\Sigma_g^+}$
$O_2$ molecule

Configuration: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 1\pi_g^2$, i.e. open shell

Bond-order: $\approx 2$, since three bonding orbitals ($3\sigma_g, 1\pi_u$) are occupied by six electrons, while there are only two electrons on the anti-bonding $1\pi_g$ orbital.

Az oxygen is paramagnetic since its ground state is a triplet!!!
Electronic structure of the AB-type diatomic molecules

Example: CO molecule:
Electronic structure of water molecule
Molecular orbitals of water

Orbitals are obtained from IEM, these will be occupied according to increasing orbital energy (Aufbau-principle)

Implementation: IEM with LCAO-MO\(^3\)

\[ \phi_i = \sum_a C_{ai} \chi_a \]

where \( \chi_a \) is a basis function.

The so-called minimal basis set will be used, which includes one function for each occupied subshell:

- **H**: 1s\(_A\), 1s\(_B\)
- **O**: 1s, 2s, 2p\(_x\), 2p\(_y\), 2p\(_z\)

\(^3\text{we show the results of Hartree-Fock-Roothan calculations}\)
Consideration of symmetry for water molecule

Basis of the representation: H: 1s\textsubscript{A}, 1s\textsubscript{B}, O: 1s, 2s, 2p\textsubscript{x}, 2p\textsubscript{y}, 2p\textsubscript{z}

Character table for \(C_{2v}\) point group with the characters of the above representation (the molecule is in the \(xz\) plane):

\[
\begin{array}{c|cccc}
C_{2v} & E & C_2 & \sigma_v(xz) & \sigma_v(yz) \\
\hline
A_1 & 1 & 1 & 1 & 1 \\
A_2 & 1 & 1 & -1 & -1 \\
B_1 & 1 & -1 & 1 & -1 \\
B_2 & 1 & -1 & -1 & 1 \\
\hline
\Gamma_{basis} & 7 & 1 & 5 & 3
\end{array}
\]

(The characters of the representation in the seven dimensional space (\(\Gamma_{basis}\)) will be evaluated on the blackboard.)
Consideration of symmetry for water molecule

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma_v(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_{basis}$</td>
<td>7</td>
<td>1</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

\[ n_i = \frac{1}{h} \sum_{k=1}^{r} N_k \chi^i(k) \chi(k) \]

\[ n_{A1} = \frac{1}{4}(1 \cdot 1 \cdot 7 + 1 \cdot 1 \cdot 1 + 1 \cdot 1 \cdot 5 + 1 \cdot 1 \cdot 3) = 4 \]

\[ n_{A2} = \frac{1}{4}(1 \cdot 1 \cdot 7 + 1 \cdot 1 \cdot 1 + 1 \cdot (-1) \cdot 5 + 1 \cdot (-1) \cdot 3) = 0 \]

\[ n_{B1} = \frac{1}{4}(1 \cdot 1 \cdot 7 + 1 \cdot (-1) \cdot 1 + 1 \cdot 1 \cdot 5 + 1 \cdot (-1) \cdot 3) = 2 \]

\[ n_{B2} = \frac{1}{4}(1 \cdot 1 \cdot 7 + 1 \cdot (-1) \cdot 1 + 1 \cdot (-1) \cdot 5 + 1 \cdot 1 \cdot 3) = 1 \]

Thus: $\Gamma_{basis} = 4 \ A_1 \oplus 2 \ B_1 \oplus B_2$

This means, there are four $a_1$, two $b_1$ and one $b_2$ orbitals.
Bonding orbitals of water

\[
1a_1 : 1s \\
2a_1 : 2s(-2p_z) + 1s_A + 1s_B \\
1b_1 : 2p_x + 1s_A - 1s_B
\]

\[
3a_1 : 2p_z(+2s) \\
1b_2 : 2p_y
\]

Configuration: \((1a_1)^2 (2a_1)^2 (1b_1)^2 (3a_1)^2 (1b_2)^2\)

State: \(^1A_1\) (orbitals are fully occupied \(\Rightarrow\) total symmetric singlet state)
Anti-bonding orbitals of water

\[ 4a_1 : 2s + 2p_z - 1s_A - 1s_B \quad \quad 2b_1 : 2p_x \]
Localized orbitals of water

In this procedure we obtain two bonding orbitals corresponding to chemical intuition.
Localized orbitals of water

$3a_1$  $1b_2$

$3a_1 + 1b_2$  $3a_1 - 1b_2$

In this procedure we obtain two non-bonding pairs corresponding to chemical intuition.
Electronic structure of transition metal complexes
Electronic structure of transition metal complexes

System:

• „transition metal”: atom or positively charged ion
  → open shell, can take additional electrons

• „ligands”: negative ion, or strong dipole, usually closed shell
  → donate electrons (non-bonding pair, $\pi$-electrons)

Two theories:

• Cristal field theory: only symmetry

• Ligand field theory: simple MO theory
Electronic structure of transition metal complexes

Questions to answer:

• why are they stable?

• why is the typical color?

• why do they have typical ESR spectrum?
Cristal field theory (Bethe, 1929)

Basic principle:

- the ligands (bound by electrostatic interaction) perturb the electronic structure of the central atom (ion)
- electrons of the ligands are absolutely not considered

Denomination comes from the theory of crystals where the field of neighboring ions has similar effect on the electronic structure of an ion considered.

<table>
<thead>
<tr>
<th>pointgroup</th>
<th>atom $O_3^+$</th>
<th>complex lower symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>orbitals</td>
<td>degenerate $d$</td>
<td>(partial) break off of the degeneracy</td>
</tr>
</tbody>
</table>

The theory is purely based on symmetry!!
$\text{Ti}^{3+}(\text{H}_2\text{O})_6$

Pointgroup: $O_h$

Lower symmetry, the five d functions form a reducible representation:

$$\Gamma(5\,\text{functions}) = T_{2g} + E_g$$

$T_{2g} : d_{z^2}, d_{x^2-y^2}$

$E_g : d_{xy}, d_{xz}, d_{yz}$
**Character table of point group $O_h$**

<table>
<thead>
<tr>
<th>$O_h$</th>
<th>$I$</th>
<th>$8C_3$</th>
<th>$6C_2$</th>
<th>$6C_4$</th>
<th>$3C_2=(C_4^2)$</th>
<th>$i$</th>
<th>$6S_4$</th>
<th>$8S_6$</th>
<th>$3\sigma_h$</th>
<th>$6\sigma_d$</th>
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</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>$A_{2g}$</td>
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<td>-1</td>
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<td>-1</td>
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<td>-1</td>
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<td>$T_{2g}$</td>
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<td>-1</td>
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<td>$A_{2u}$</td>
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<tr>
<td>$T_{1u}$</td>
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<tr>
<td>$T_{2u}$</td>
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<td>-3</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>-1</td>
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</tbody>
</table>

- $x^2 + y^2 + z^2$
- $(2z^2 - x^2 - y^2, x^2 - y^2)$
- $(R_x, R_y, R_z)$
- $(xz, yz, xy)$
- $(x, y, z)$
$\text{Ti}^{3+}(\text{H}_2\text{O})_6$
Energy levels:

\[ \text{Ti}^{3+}(\text{H}_2\text{O})_6 \]

Degree of splitting:

- The theory does not say a word about this

- However: \( 6 \cdot \Delta_{t_{2g}} = 4 \cdot \Delta_{e_g} \), i.e. the average energy does not change!
Ligand field theory

Basic principle: MO theory

- the orbitals of the central atom interact with the orbitals of the ligands → bonding and anti-bonding orbitals are formed

- symmetry is again important: which orbitals do mix?

Basis:

- atom (ion): 3d, 4s, 4p orbitals

- ligands (closed shell): s-type orbital per ligand ("superminimal basis") (sometimes eventually also $\pi$ orbitals)

Symmetrized basis:

according to the pointgroup of the complex, we split it into irreducible representations.
Character table of point group \(O_h\)

<table>
<thead>
<tr>
<th>(O_h)</th>
<th>(I)</th>
<th>(8C_3)</th>
<th>(6C_2)</th>
<th>(6C_4)</th>
<th>(3C_2=(C_4^2))</th>
<th>(i)</th>
<th>(6S_4)</th>
<th>(8S_6)</th>
<th>(3\sigma_h)</th>
<th>(6\sigma_d)</th>
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<tbody>
<tr>
<td>(A_{1g})</td>
<td>1</td>
<td>1</td>
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<tr>
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<tr>
<td>(E_g)</td>
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<tr>
<td>(T_{1g})</td>
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<tr>
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<tr>
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<td>(T_{2u})</td>
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<td>-1</td>
<td>-3</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

- \(x^2 + y^2 + z^2\)
- \((2z^2 - x^2 - y^2)\)
- \((\frac{x^2}{y^2} - y^2)\)
- \(R_x, R_y, R_z\)
- \((xz, yz, xy)\)
- \((x, y, z)\)
Octahedral complex ($O_h$)

Basis:

- atom (ion): 3d, 4s, 4p orbitals $\rightarrow$
  \[
  \Gamma(3d) = T_{2g} + E_g \\
  \Gamma(4s) = A_{1g} \\
  \Gamma(4p) = T_{1u}
  \]

- ligand:
  \[
  \Gamma(\lambda_1, \ldots \lambda_6) = A_{1g} + E_g + T_{1u}
  \]
$\text{Ti}^{3+}(\text{H}_2\text{O})_6$ – orbitals of the waters
$\text{Ti}^{3+}(\text{H}_2\text{O})_6$ – MO theory

\begin{align*}
\text{Fém} & \quad \text{Komplex} \\
\quad \text{(oktaedrikus)} & \quad \text{Ligandum} \\
4\sigma (t_{\text{in}}) \\
4s (e_g) \\
3d (t_{\text{in}}, e_g) \\
\end{align*}

\begin{align*}
\text{e}_g & \quad \text{t}_{\text{in}} \\
\text{a}_{1g} &
\end{align*}
$\text{Ti}^{3+}(\text{H}_2\text{O})_6$ – MO theory
$\text{Ti}^{3+}(\text{H}_2\text{O})_6$ – MO theory
$\text{Ti}^{3+}(\text{H}_2\text{O})_6$ – MO theory
$\text{Ti}^{3+}(\text{H}_2\text{O})_6$ – MO theory
Character table of pointgroup $T_d$

<table>
<thead>
<tr>
<th>$T_d$</th>
<th>$I$</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6S_4$</th>
<th>$6\sigma_d$</th>
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<tr>
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<td>-1</td>
<td>-1</td>
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<tr>
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<tr>
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</tbody>
</table>

$\Gamma \downarrow 4 \Lambda 0 \Sigma 2$
Tetrahedral complex – MO theory

Diagram showing the electronic configuration of a tetrahedral complex, with labels for 4p(t2), 4s(a1), 3d(t2g, eg), a1, t2, and ligandum.