Advanced Physical Chemistry (fizkemhk17em)
Electronic Structure

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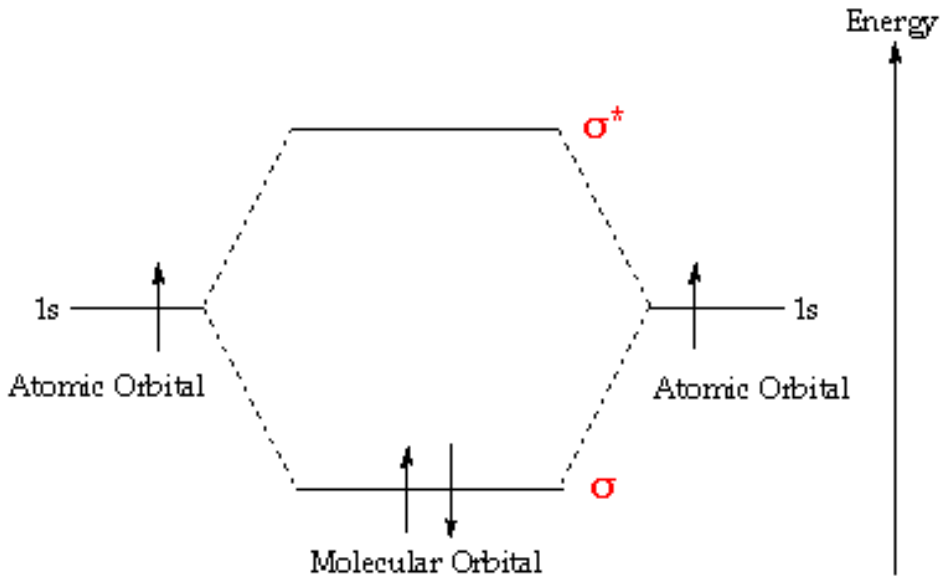
Electronic structure of diatomic molecules

Character table for point group $D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}$	...	$\infty\sigma_v$	i	$2S_{\infty}$	...	$\infty C'_2$	linear functions, rotations	quadratic functions	cubic functions
$A_{1g}=\Sigma^+_g$	+1	+1	...	+1	+1	+1	...	+1	-	x^2+y^2, z^2	-
$A_{2g}=\Sigma^-_g$	+1	+1	...	-1	+1	+1	...	-1	R_z	-	-
$E_{1g}=\Pi_g$	+2	$+2\cos(\phi)$	...	0	+2	$-2\cos(\phi)$	...	0	(R_x, R_y)	(xz, yz)	-
$E_{2g}=\Delta_g$	+2	$+2\cos(2\phi)$	...	0	+2	$+2\cos(2\phi)$	...	0	-	(x^2-y^2, xy)	-
$E_{3g}=\Phi_g$	+2	$+2\cos(3\phi)$	...	0	+2	$-2\cos(3\phi)$	...	0	-	-	-
E_{ng}	+2	$+2\cos(n\phi)$	...	0	+2	$(-1)^n 2\cos(n\phi)$	...	0	-	-	-
...	...	...	...	...	...	...	...	...	-	-	-
$A_{1u}=\Sigma^+_u$	+1	+1	...	+1	-1	-1	...	-1	z	-	z^3, $z(x^2+y^2)$
$A_{2u}=\Sigma^-_u$	+1	+1	...	-1	-1	-1	...	+1	-	-	-
$E_{1u}=\Pi_u$	+2	$+2\cos(\phi)$	...	0	-2	$+2\cos(\phi)$	...	0	(x, y)	-	(xz^2, yz^2) $[x(x^2+y^2), y(x^2+y^2)]$
$E_{2u}=\Delta_u$	+2	$+2\cos(2\phi)$	...	0	-2	$-2\cos(2\phi)$	...	0	-	-	$[xyz, z(x^2-y^2)]$
$E_{3u}=\Phi_u$	+2	$+2\cos(3\phi)$	...	0	-2	$2\cos(3\phi)$	...	0	-	-	$[y(3x^2-y^2), x(x^2-3y^2)]$
E_{nu}	+2	$+2\cos(n\phi)$	...	0	-2	$(-1)^{n+1} 2\cos(n\phi)$	...	0	-	-	-
...	...	...	...	...	...	...	...	...	-	-	-

H_2 molecule



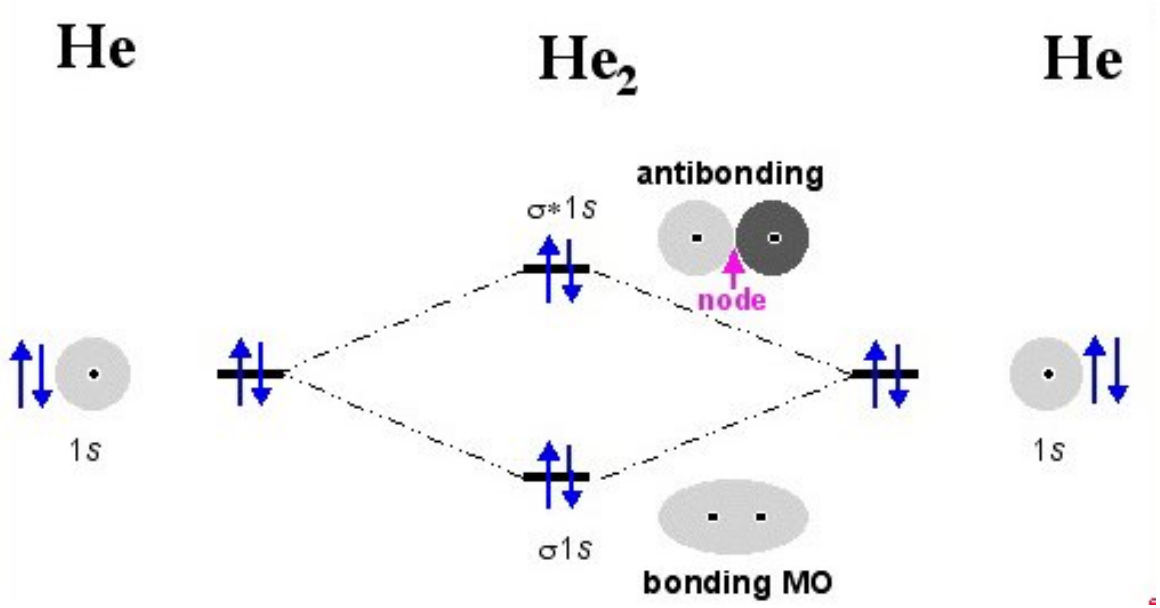
Configuration: $1\sigma_g^2$

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



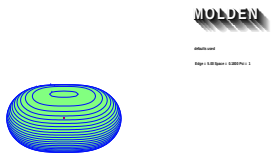
Configuration: $1\sigma_g^2 1\sigma_u^2$

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

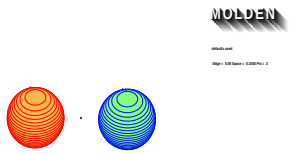
Notation for the state: ${}^1\Sigma_g^+$

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

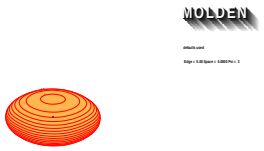
Diatomic molecules: molecular orbitals



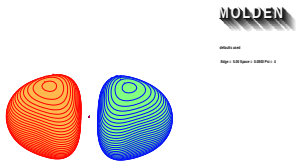
$1\sigma_g$



$1\sigma_u$



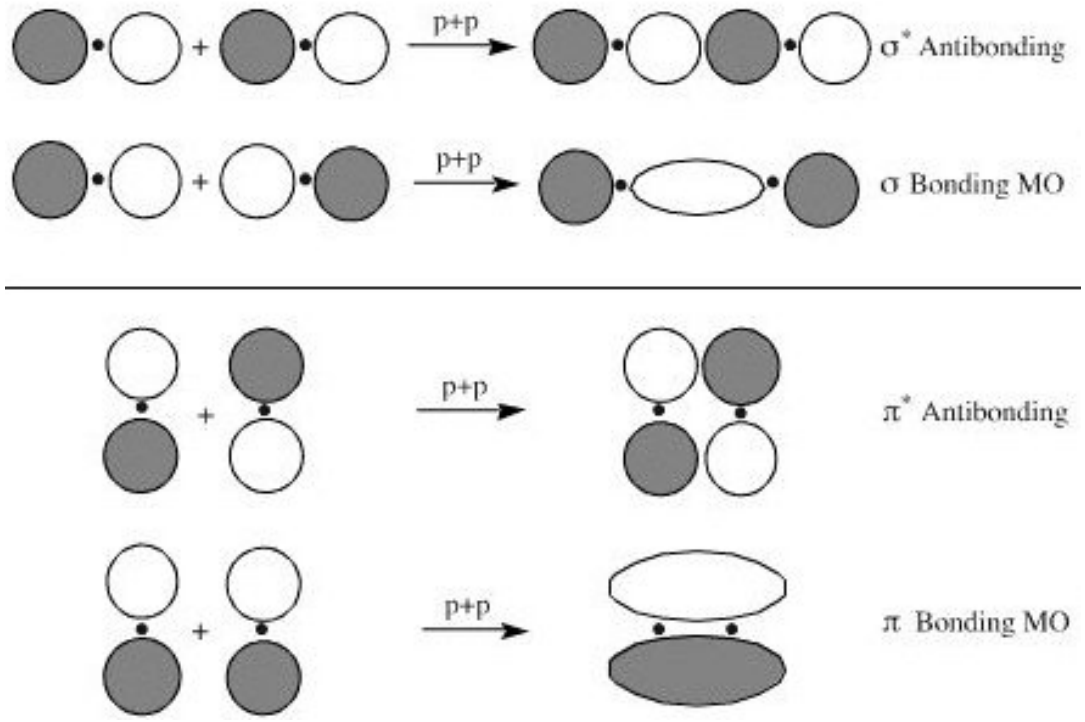
$2\sigma_g$



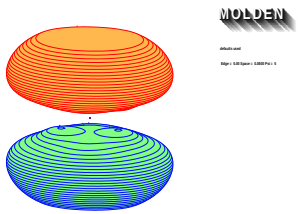
$2\sigma_u$

Diatomic molecules: molecular orbitals

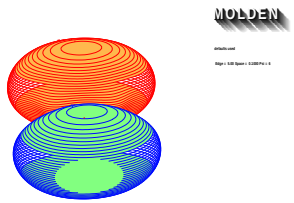
To construct the next orbitals, the $2p$ orbital of the atoms can be used. Considering also the symmetry (z is the main axis of the molecule):

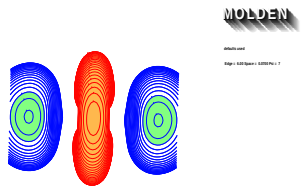


Diatomic molecules: molecular orbitals

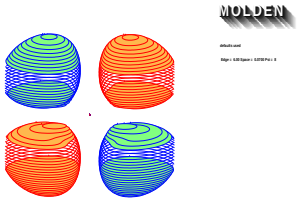


$1\pi_u$

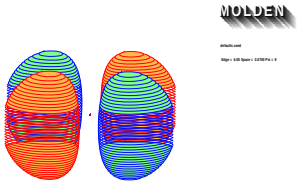


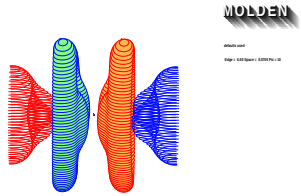


$3\sigma_g$



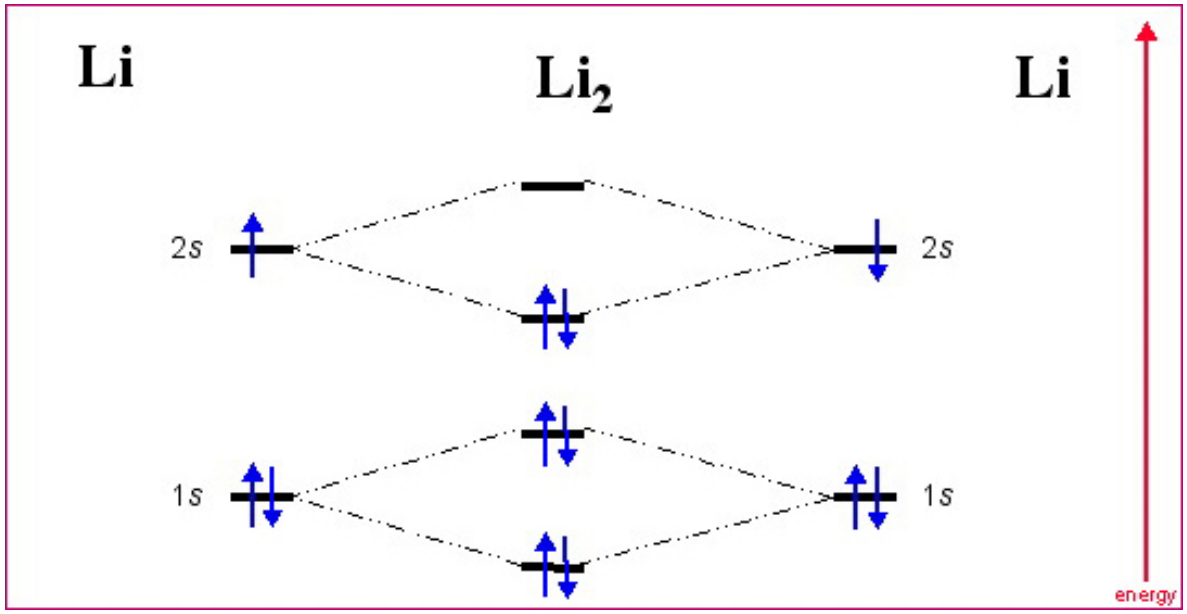
$1\pi_g$





$3\sigma_u$

Li_2 molecule



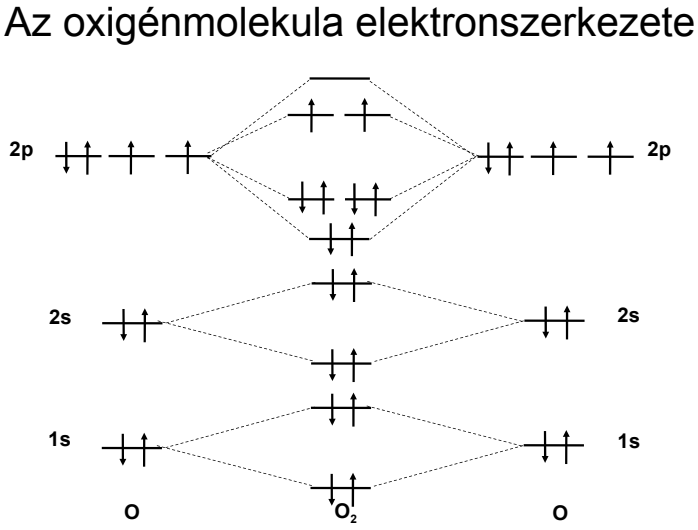
Configuration: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2$

Symmetry of the states: Σ_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.

O_2 molecule



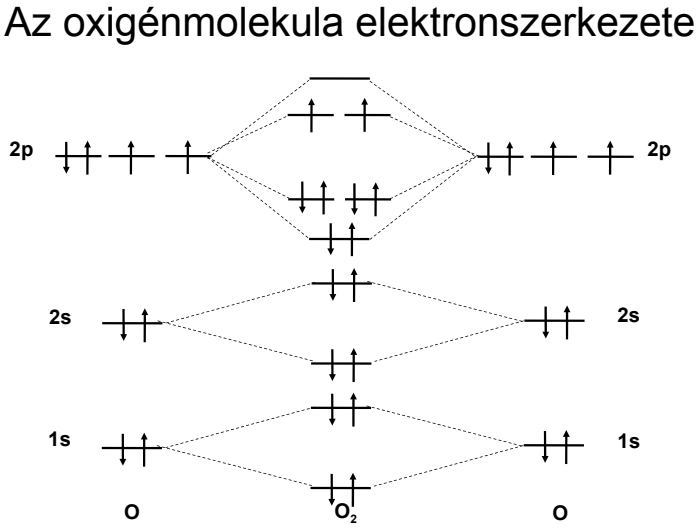
Configuration: $1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 3\sigma_g^2\ 1\pi_g^2$, i.e. open shell

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



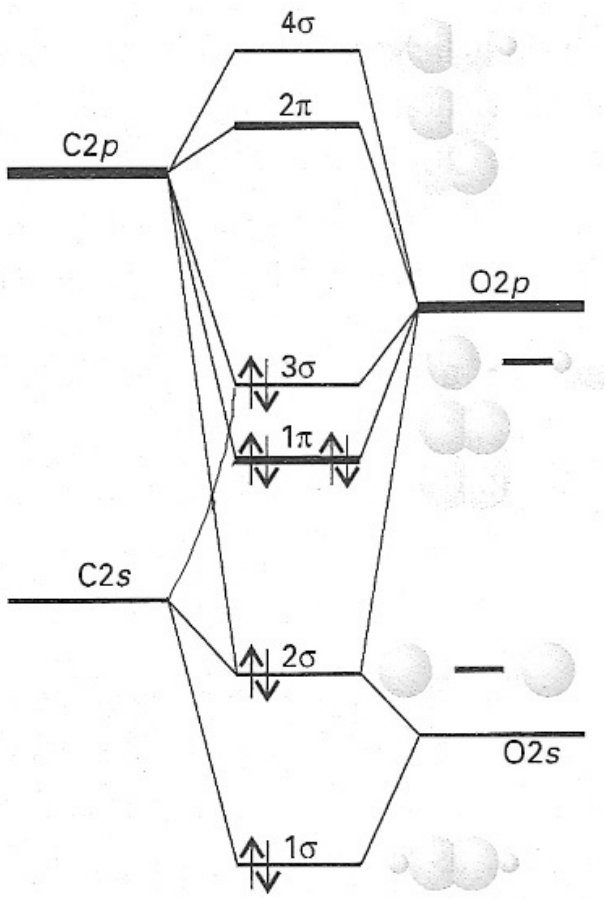
Configuration: $1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 3\sigma_g^2\ 1\pi_g^2$, i.e. open shell

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

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 χ_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] we show the results of Hartree-Fock-Roothan calculations

Consideration of symmetry for water molecule

Basis of the representation: H: $1s_A$, $1s_B$, O: 1s, 2s, $2p_x$, $2p_y$, $2p_z$

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

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1
Γ_{basis}	7	1	5	3

(The characters of the representation in the seven dimensional space (Γ_{basis}) will be evaluated on the blackboard.)

Consideration of symmetry for water molecule

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1
Γ_{basis}	7	1	5	3

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

$$\mathsf{n}_{\mathrm{A1}} = \frac{1}{4}(1\cdot1\cdot7 + 1\cdot1\cdot1 + 1\cdot1\cdot5 + 1\cdot1\cdot3) = 4$$

$$\mathsf{n}_{\mathrm{A2}} = \frac{1}{4}(1\cdot1\cdot7 + 1\cdot1\cdot1 + 1\cdot(-1)\cdot5 + 1\cdot(-1)\cdot3) = 0$$

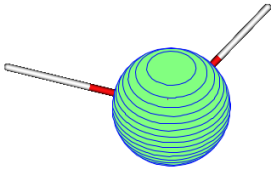
$$\mathsf{n}_{\mathrm{B1}} = \frac{1}{4}(1\cdot1\cdot7 + 1\cdot(-1)\cdot1 + 1\cdot1\cdot5 + 1\cdot(-1)\cdot3) = 2$$

$$\mathsf{n}_{\mathrm{B2}} = \frac{1}{4}(1\cdot1\cdot7 + 1\cdot(-1)\cdot1 + 1\cdot(-1)\cdot5 + 1\cdot1\cdot3) = 1$$

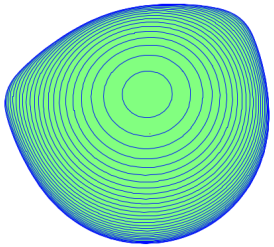
Thus: Γ_{basis}=4 $\mathsf{A}_1 \oplus 2\ \mathsf{B}_1 \oplus \mathsf{B}_2$

This means, there are four a_1, two b_1 and one b_2 orbitals.

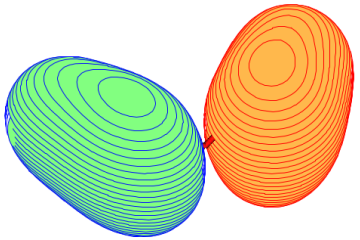
Bonding orbitals of water



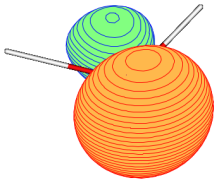
$1a_1 : 1s$



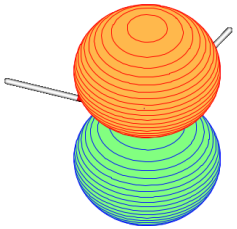
$2a_1 : 2s(-2p_z)+1s_A+1s_B$



$1b_1 : 2p_x+1s_A-1s_B$



$3a_1 : 2p_z(+2s)$

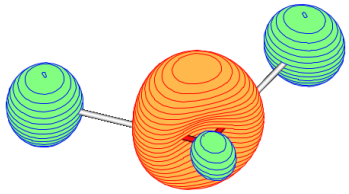


$1b_2 : 2p_y$

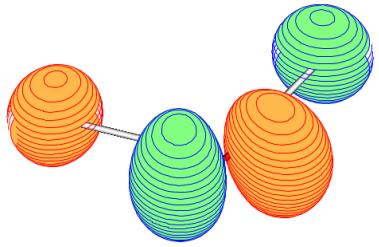
Configuration: $(1a_1)^2\ (2a_1)^2\ (1b_1)^2\ (3a_1)^2\ (1b_2)^2$

State: $^1A_1$ (orbitals are fully occupied $\Rightarrow$ total symmetric singlet state)

Anti-bonding orbitals of water



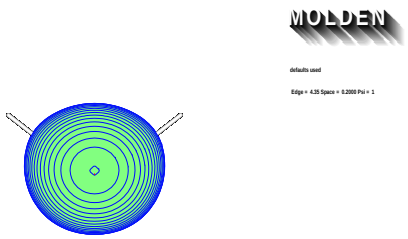
$4a_1 : 2s + 2p_z - 1s_A - 1s_B$

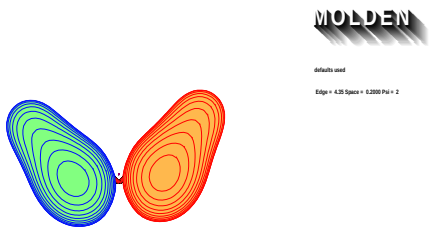


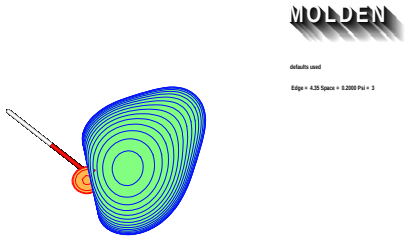
$2b_1 : 2p_x$

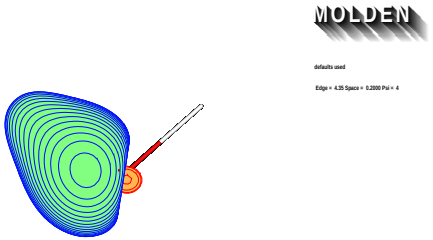
Localized orbitals of water

$2a_1$ $1b_1$







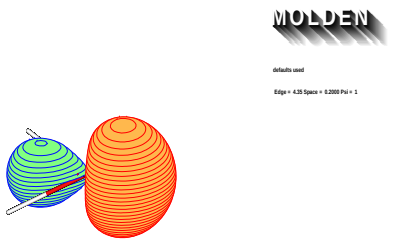


$2a_1 - 1b_1$ $2a_1+1b_1$

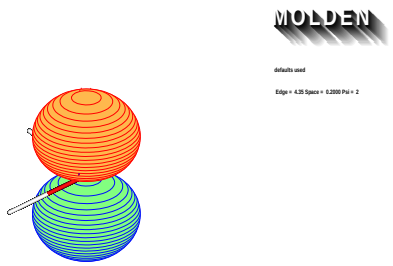
In this procedure we obtain two bonding orbitals corresponding to chemical intuition.

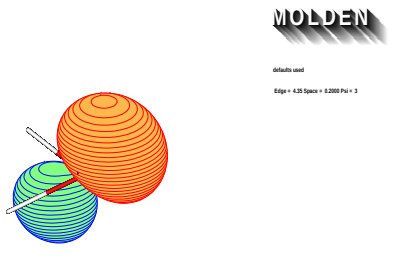
Localized orbitals of water

$3a_1$

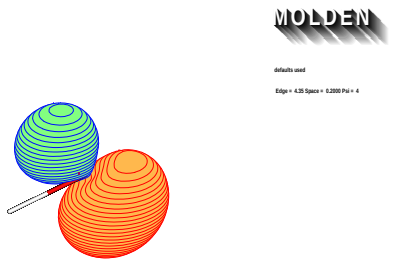


$1b_2$





$3a_1 + 1b_2$



$3a_1 - 1b_2$

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
  $\rightarrow$ open shell, can take additional electrons

- „ligands”: negative ion, or strong dipole, usually closed shell
  $\rightarrow$ donate electrons (non-bonding pair, π-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:

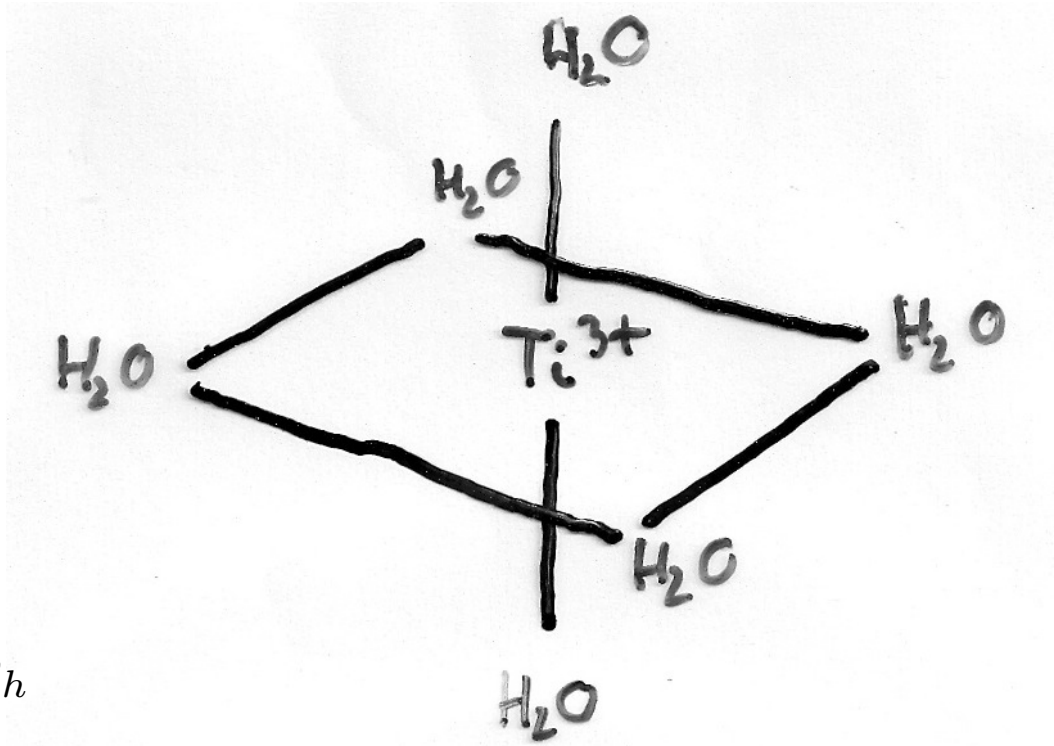
- the ligands (bound by electrostatic interaction) perturb the electronic structure of the central atom (ion)
- electrons of the ligands are absolutely not considered

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

	atom	complex
pointgroup	O_3^+	lower symmetry
orbitals	degenerate d	(partial) break off of the degeneracy

The theory is purely based on symmetry!!

$Ti^{3+}(H_2O)_6$



Pointgroup: O_h

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

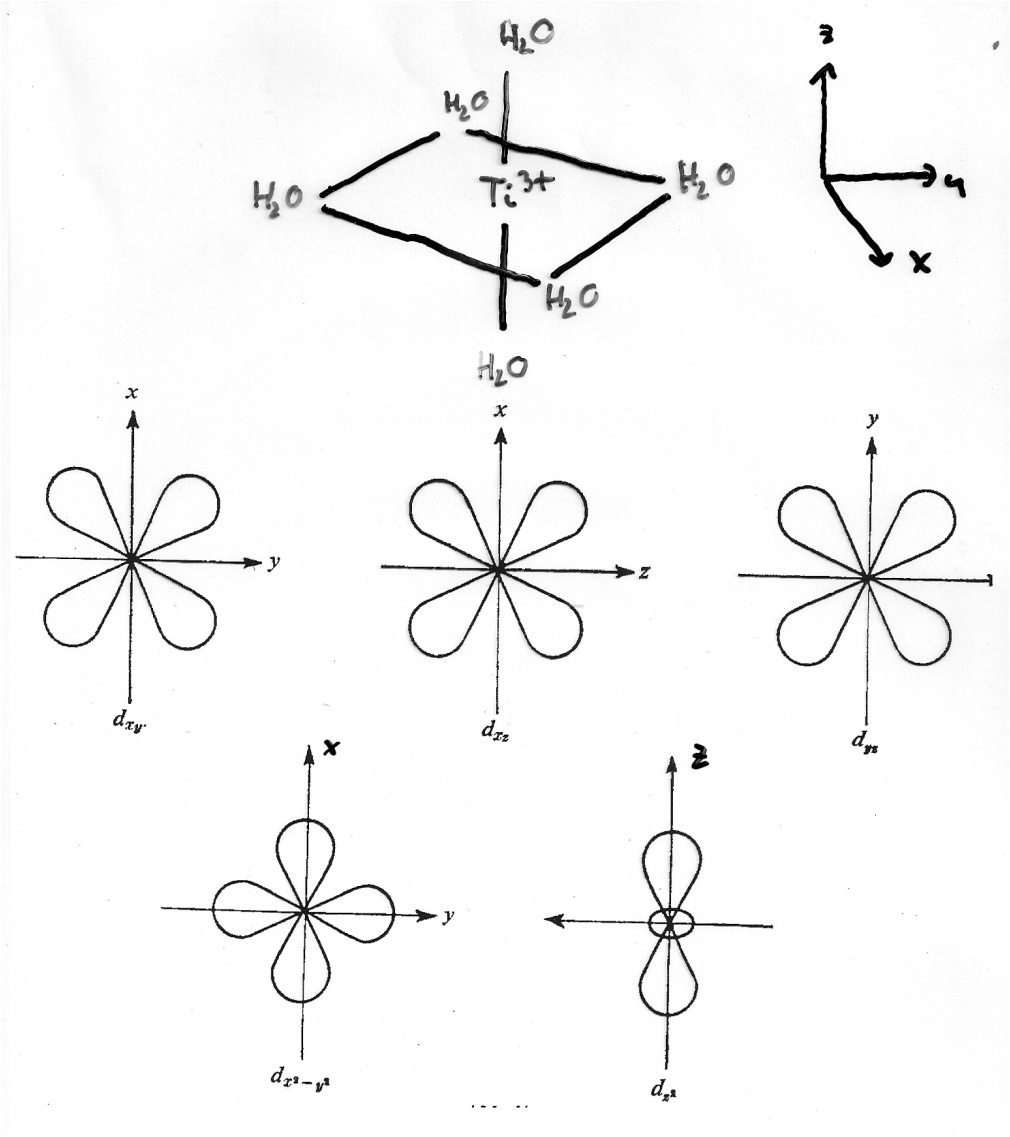
$$\Gamma(5\ functions) = T_{2g} + E_g$$

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

Character table of pointgroup O_h

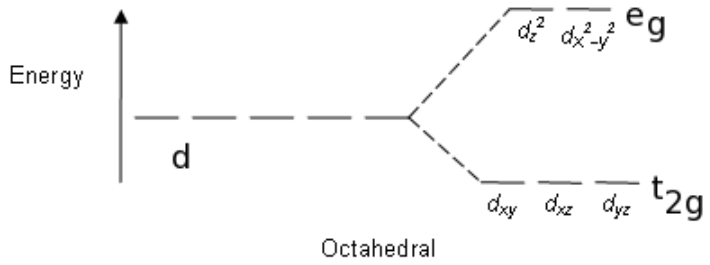
O_h	I	$8C_3$	$6C_2$	$6C_4$	$3C_2=(C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2,\ x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

$Ti^{3+}(H_2O)_6$



$\mathbf{Ti^{3+}(H_2O)_6}$

Energy levels:



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 $\rightarrow$ 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 π orbitals)

Symmetrized basis:

according to the pointgroup of the complex, we split it into irreducible representations.

Character table of pointgroup O_h

O_h	I	$8C_3$	$6C_2$	$6C_4$	$3C_2=(C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2,\ x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

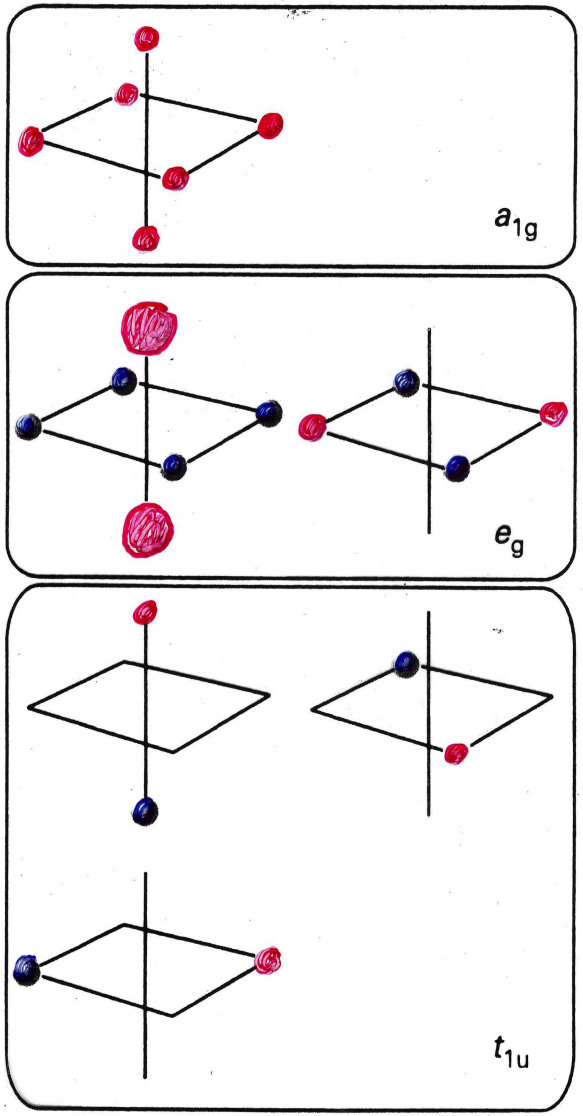
Octahedral complex (O_h)

Basis:

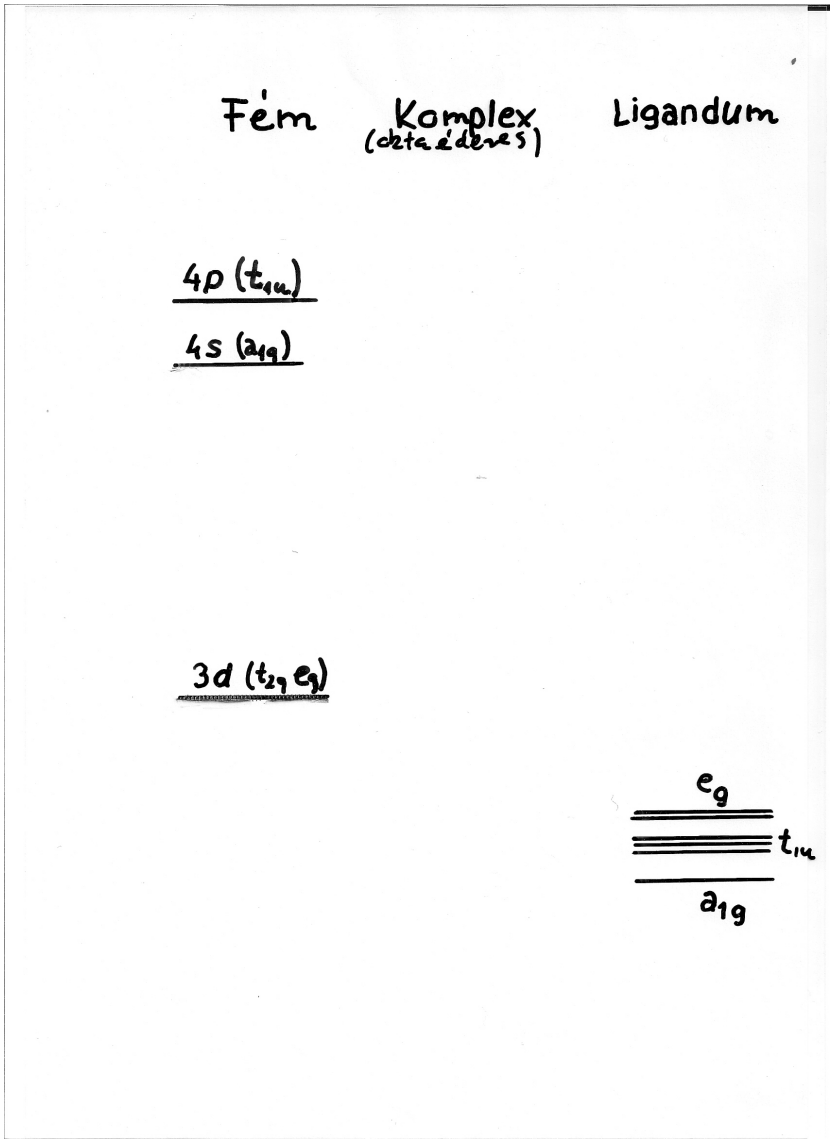
- atom (ion): 3d, 4s, 4p orbitals $\rightarrow$
  $\Gamma(3d) = T_{2g} + E_g$
  $\Gamma(4s) = A_{1g}$
  $\Gamma(4p) = T_{1u}$

- ligand:
  $\Gamma(\lambda_1, ...\lambda_6) = A_{1g} + E_g + T_{1u}$

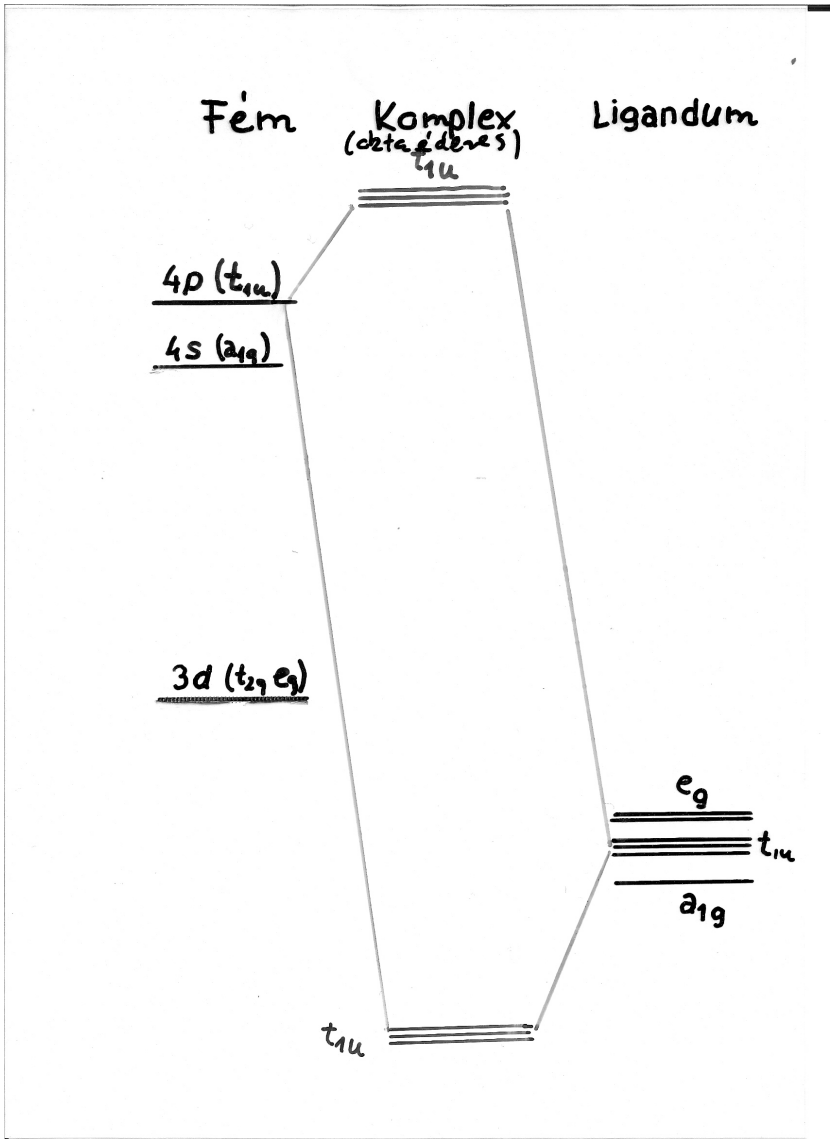
$Ti^{3+}(H_2O)_6$ – orbitals of the waters



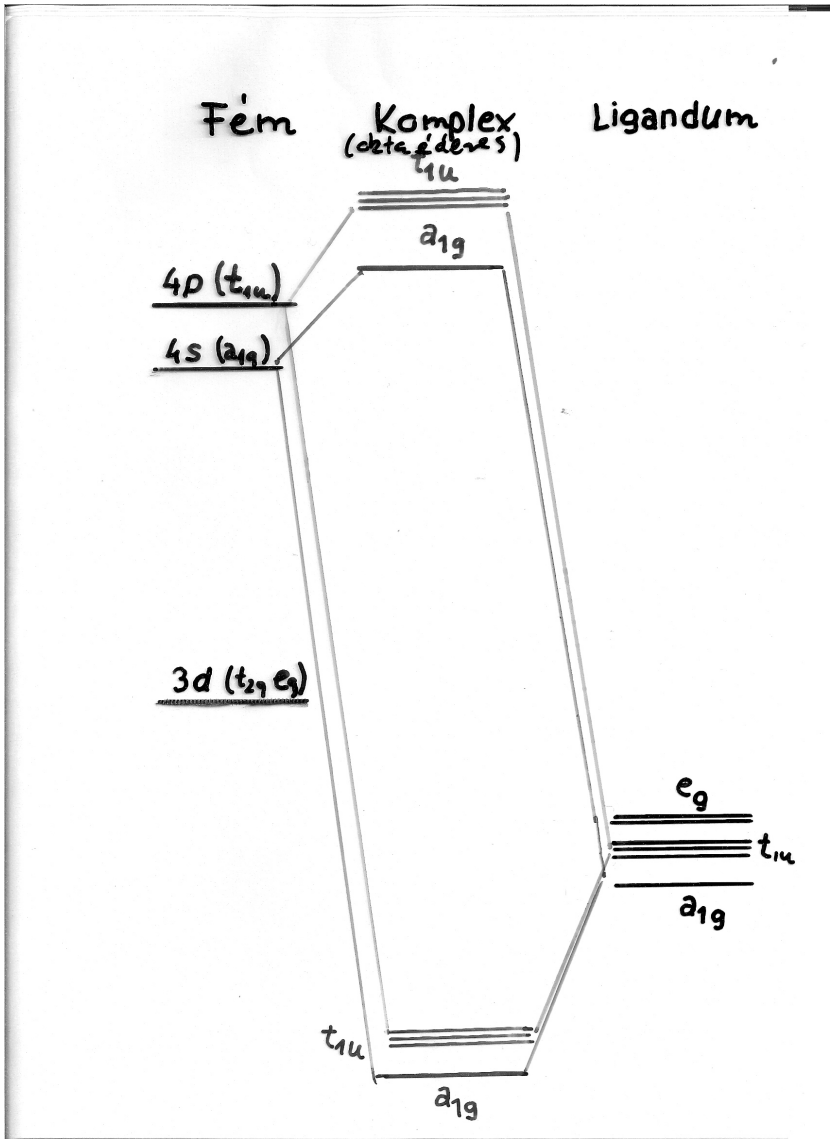
$Ti^{3+}(H_2O)_6$ – MO theory



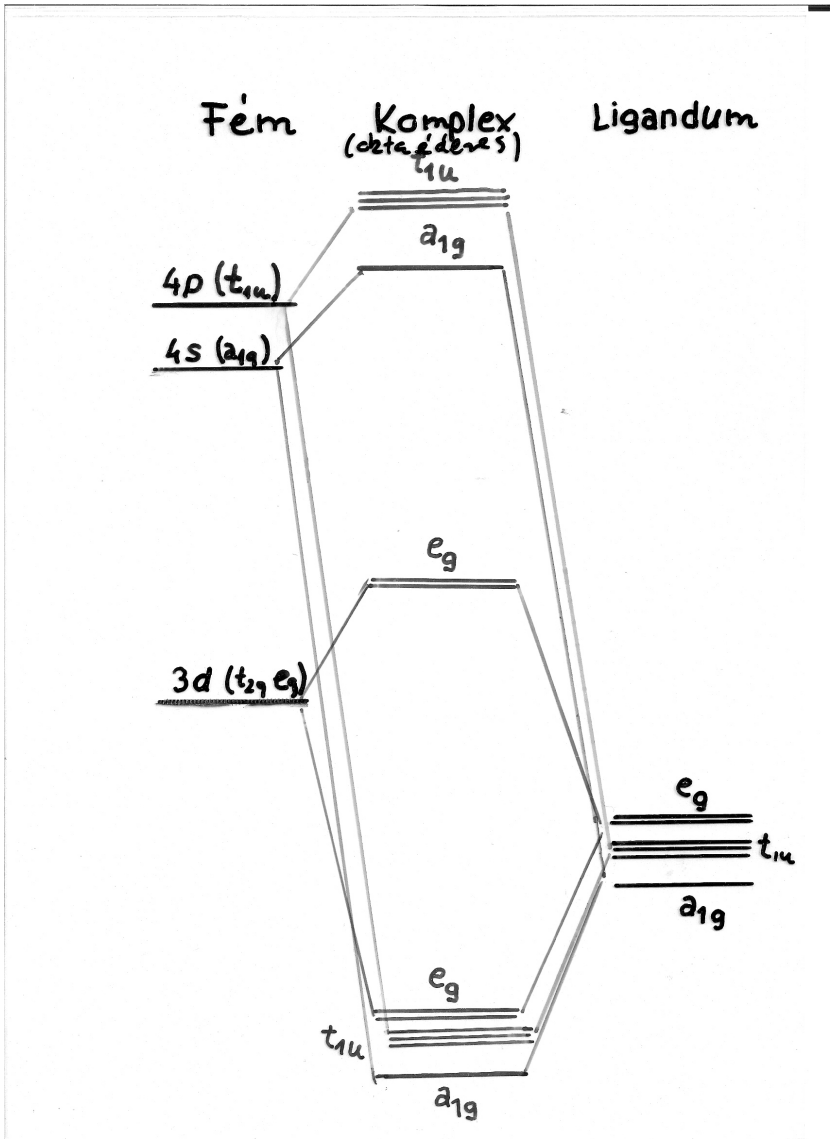
$Ti^{3+}(H_2O)_6$ – MO theory



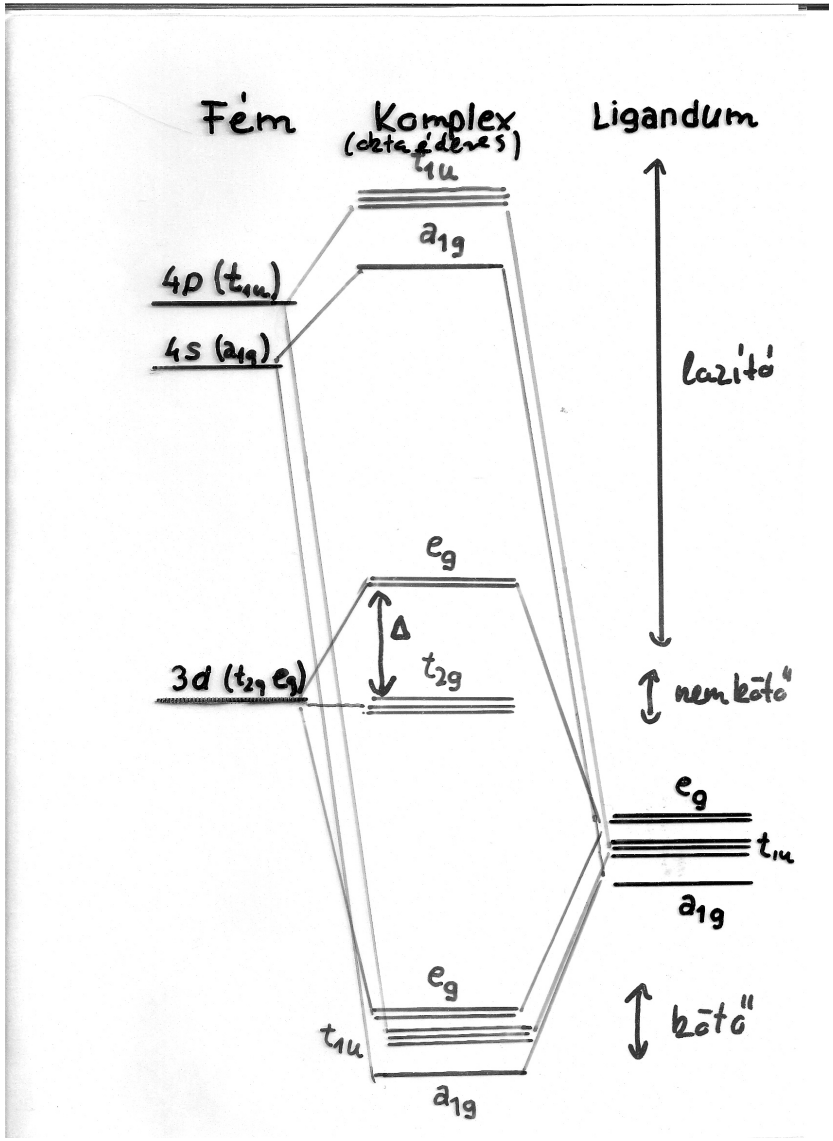
$Ti^{3+}(H_2O)_6$ – MO theory



$Ti^{3+}(H_2O)_6$ – MO theory



$Ti^{3+}(H_2O)_6$ – MO theory



Character table of pointgroup T_d

T_d	I	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2,\ x^2-y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)
Γ	4	1	0	0	2		

Tetrahedral complex – MO theory