Advanced Physical Chemistry (fizkemhk17em)
Electronic Structure

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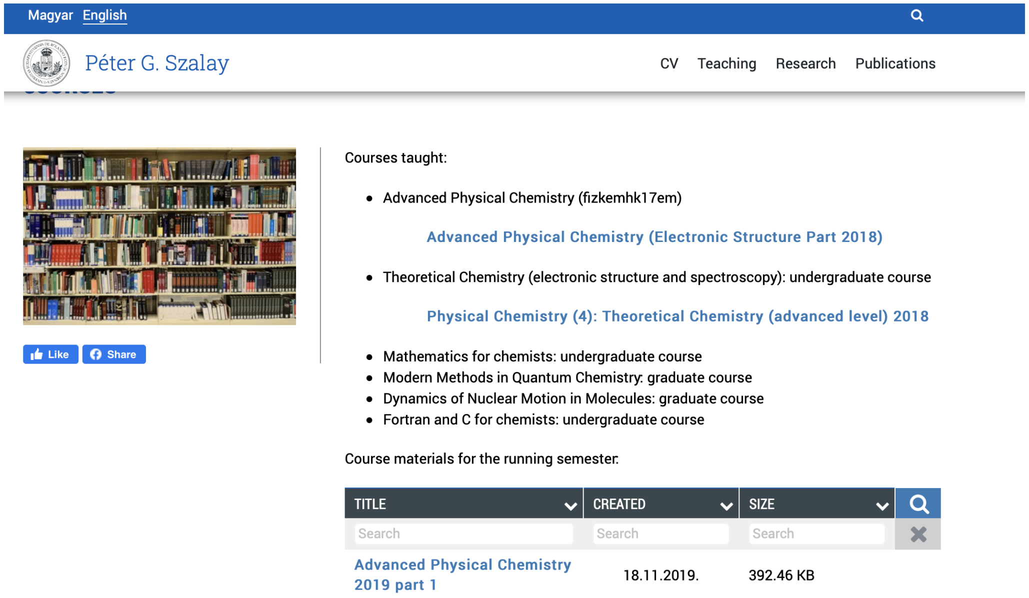
Goal of this part of the course

- **Learn the English terms used in quantum chemistry**
  - „*Reminder*" section
- **Talk about topics left out the BSc course**
  - „*Angular momentum*" and „*Group Theory*" sections
- **Repetion with this new knowledge**
  - „*Atomic structure*" and „*Molecular structure*" sections
- **Learn the basic knowledge to perform quantum chemical calculations**
  - „*Methods*" section

Syllabus

See at https://pgszalay.elte.hu/teaching

- Last years's document: Advanced Physical Chemistry (Electronic Structure Part 2018)
- This year's document: will apeare here in parts



Courses taught:

- Advanced Physical Chemistry (fizkemhk17em)

  Advanced Physical Chemistry (Electronic Structure Part 2018)

- Theoretical Chemistry (electronic structure and spectroscopy): undergraduate course

  Physical Chemistry (4): Theoretical Chemistry (advanced level) 2018

- Mathematics for chemists: undergraduate course
- Modern Methods in Quantum Chemistry: graduate course
- Dynamics of Nuclear Motion in Molecules: graduate course
- Fortran and C for chemists: undergraduate course

Course materials for the running semester:

TITLE	CREATED	SIZE
Advanced Physical Chemistry 2019 part 1	18.11.2019.	392.46 KB

Content of this part

- **Angular momentum**: operators, eigenvalues, eigenfunctions; magnetic moments; spin moments; application to the hydrogen atom.
- **Electronic structure of atoms**: orbitals, orbital energies, electronic configuration; angular momentum operators for many electron system; representation of atomic states and the corresponding notation; Hund's rule, spin-orbit interaction, atoms in magnetic field.
- **Molecular symmetry, group theory**: symmetry operations, point groups, representations and the character table, direct-product representation; application in electronic structure and spectroscopy.
- **Chemical bond**: quantum mechanical definition of chemical bond; approximations: IPA, MO theories, LCAO-MO, Valence Bond theory; diatomic molecules, electronic structure of transition-metal complexes; quantum chemistry of periodic systems.
- **Computational Chemistry**: determinant wave function, energy expression with determinant wave function, short derivation of the Hartree-Fock (HF) method, Hartree-Fock-Roothaan method, interpretation of the HF results (orbitals, density, population analysis, Koopmans theorem), basic elements of the Density Functional Theory (DFT), Hohenberg-Kohn theorems, Kohn-Sham DFT, functionals, hybrid methods; atomic basis sets.

Reminder

In quantum mechanics physical quantities are represented by operators.

Basic operators are the coordinate $\hat{x}$ and momentum $\hat{p}$:

$$\begin{aligned} \hat{x} &= x \\ \hat{p} &= -i\hbar\frac{\partial}{\partial x} \end{aligned}$$

All other operators can be derived by replacing coordinate and momentum in the classical formula by the operators.

Example: kinetic energy, Hamiltonian

Reminder

Measurement

According to quantum mechanics, the result of a measurement can only be the eigenvalue of the corresponding operator.

$$\hat{A}\phi_i(x) \quad = \quad a_i\phi_i$$

where a_i is the ith eigenvalue, ϕ_i is corresponding eigenfunction.

Reminder

Two operators commute, if

$$\begin{aligned}\hat{A}\cdot\hat{B}-\hat{B}\cdot\hat{A} &= 0\\ [\hat{A},\hat{B}] &= 0\end{aligned}$$

i.e. their commutator is vanishing. In this case the corresponding two physical quantities can be measured simultaneously.

Otherwise, the two physical quantities can be measured only with some uncertainty:

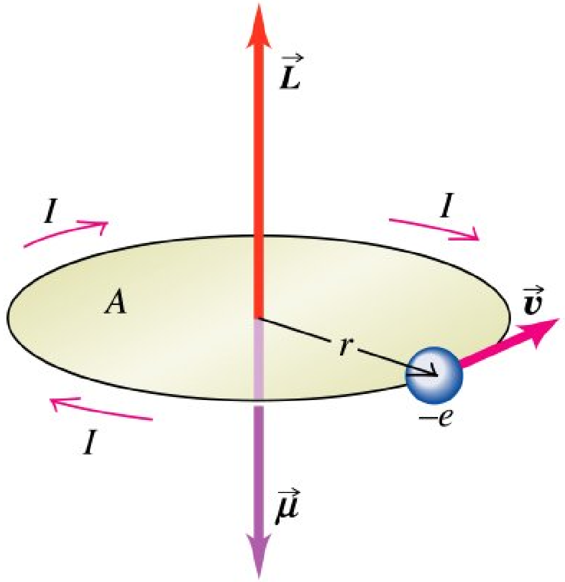
$$\begin{aligned}[\hat{x},\hat{p}_x] &= i\hbar \neq 0\\ &\downarrow\\ \Delta x\cdot\Delta p_x &\geq \frac{1}{2}\hbar\end{aligned}$$

This is the famous *Heisenberg uncertainty principle.*

Angular momentum operators

Classical angular momentum:

$$\begin{aligned} \underline{l} &= \underline{r} \times \underline{p} \\ l_x &= y p_z - z p_y \\ l_y &= z p_x - x p_z \\ l_z &= x p_y - y p_x . \end{aligned}$$



Angular momentum operators

Classical angular momentum:

$$\begin{aligned} \underline{l} &= \underline{r} \times \underline{p} \\ l_x &= yp_z - zp_y \\ l_y &= zp_x - xp_z \\ l_z &= xp_y - yp_x . \end{aligned}$$

Thus, with the definition of $\hat{x}$, and $\hat{p}$ one can obtain the corresponding operators for the angular momentum:

$$\begin{aligned} \hat{l}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ \hat{l}_y &= \dots \\ \hat{l}_z &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \\ \hat{\underline{l}}^2 &= \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 \end{aligned}$$

Angular momentum operators

It is easy to derive some important properties of the angular momentum operators:

$$
\begin{aligned}
\left[\hat{l}_x, \hat{l}_y\right] &= i\hbar\,\hat{l}_z \\
\left[\hat{l}_y, \hat{l}_z\right] &= i\hbar\,\hat{l}_x \\
\left[\hat{l}_z, \hat{l}_x\right] &= i\hbar\,\hat{l}_y \\
\left[\hat{l}^2, \hat{l}_i\right] &= 0, \quad i = x, y, z
\end{aligned}
$$

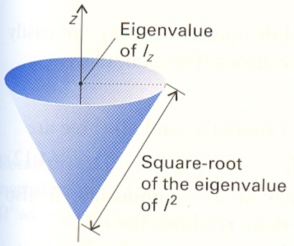


Fig. 4.2 The cone used to represent a state of angular momentum with specified magnitude and z-component.

This means that $\underline{\hat{l}}$ does not have any two components which can be measured at the same time. It is $\hat{l}^2$ (square length) and one component of $\underline{\hat{l}}$ which can be obtained simultaneously.

Angular momentum operators

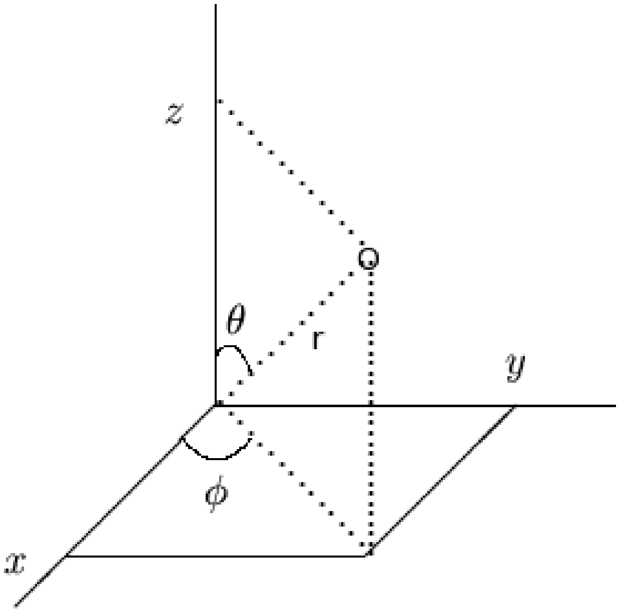
z component of the angular momentum:

$$\hat{l}_z = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right)$$

Let us use a spherical coordinate system!

$$\begin{aligned} x &= r\sin\vartheta\cos\varphi \\ y &= r\sin\vartheta\sin\varphi \\ z &= r\cos\vartheta \end{aligned}$$

$$\begin{aligned} \frac{\partial x}{\partial \varphi} &= -r\sin\vartheta\sin\varphi = -y \\ \frac{\partial y}{\partial \varphi} &= r\sin\vartheta\cos\varphi = x \\ \frac{\partial z}{\partial \varphi} &= 0 \end{aligned}$$



Angular momentum operators

$$
\begin{aligned}
\frac{\partial x}{\partial \varphi} &= -r \sin\vartheta \sin\varphi = -y \\
\frac{\partial y}{\partial \varphi} &= r \sin\vartheta \cos\varphi = x \\
\frac{\partial z}{\partial \varphi} &= 0
\end{aligned}
$$

First we recognize that

$$\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) = \frac{\partial}{\partial \varphi}$$

One can easily prove this using the „chain-rule":

$$
\begin{aligned}
\frac{\partial}{\partial \varphi} &= \frac{\partial}{\partial x}\frac{\partial x}{\partial \varphi} + \frac{\partial}{\partial y}\frac{\partial y}{\partial \varphi} + \frac{\partial}{\partial z}\frac{\partial z}{\partial \varphi} \\
&= -\frac{\partial}{\partial x}y + \frac{\partial}{\partial y}x + \frac{\partial}{\partial z}\cdot 0 = \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) \qquad QED
\end{aligned}
$$

Angular momentum operators

The z component of the angular momentum operator therefore reads:

$$\hat{l}_z \quad = \quad -i\hbar\frac{\partial}{\partial\varphi}$$

Eigenfunctions and eigenvalues of the z component of the angular momentum:

$$\boxed{\begin{aligned} l_z &= m\hbar, & m &= 0, \pm 1, ... \\ \Phi\left(\varphi\right) &= \frac{1}{\sqrt{2\pi}} \cdot e^{im\varphi}, & m &= 0, \pm 1, ... \end{aligned}}$$

Angular momentum operators

$\hat{l}^2$ in spherical coordinates:

$$\hat{l}^2 = -\hbar^2 \left[\underbrace{\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right)}_{\hat{A}(\vartheta)} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2} \right]$$

The eigensystem of the $\hat{l}^2$ operator

$$\lambda = l(l+1)\hbar^2 \qquad l \geq |m|$$

$$Y_l^m(\vartheta,\varphi) = \Theta_l^m(\cos(\vartheta)) \cdot e^{im\varphi}$$

$$l = 0, 1, 2, \ldots$$

$$m = -l, \ldots, 0, \ldots l$$

Magnetic moment

If a charged particle is moving on a circle (has angular momentum), it also has magnetic moment. The magnetic moment vector ($\underline{\mu}$) is therefore proportional to the angular momentum vector, for example the z component is:

$$\hat{\mu}_z \quad = \quad \frac{e}{2\,m_{el}} \hat{l}_z$$

The system having a magnetic moment will interact with the magnetic field, its energy will change due to this interaction:

$$\Delta\,E \quad = \quad B_z \cdot \frac{e}{2\,m_{el}} \cdot l_z$$

where B_z is the z component of the *magnetic induction*, which is quantity characterizing the strength of the magnetic field.

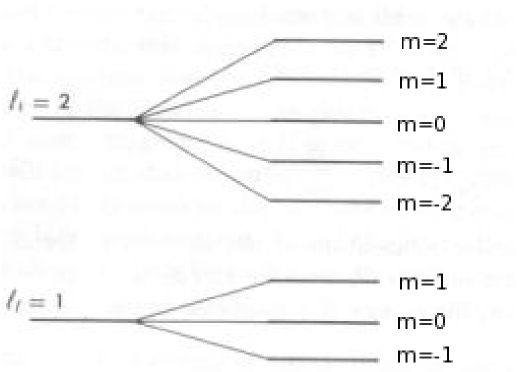
Magnetic moment

The possible values of $l_z = m \cdot \hbar$, where $m = 0, \pm 1, \ldots$ Therefore

$$\Delta\, E \quad = \quad B_z \cdot \mu_B \cdot m$$

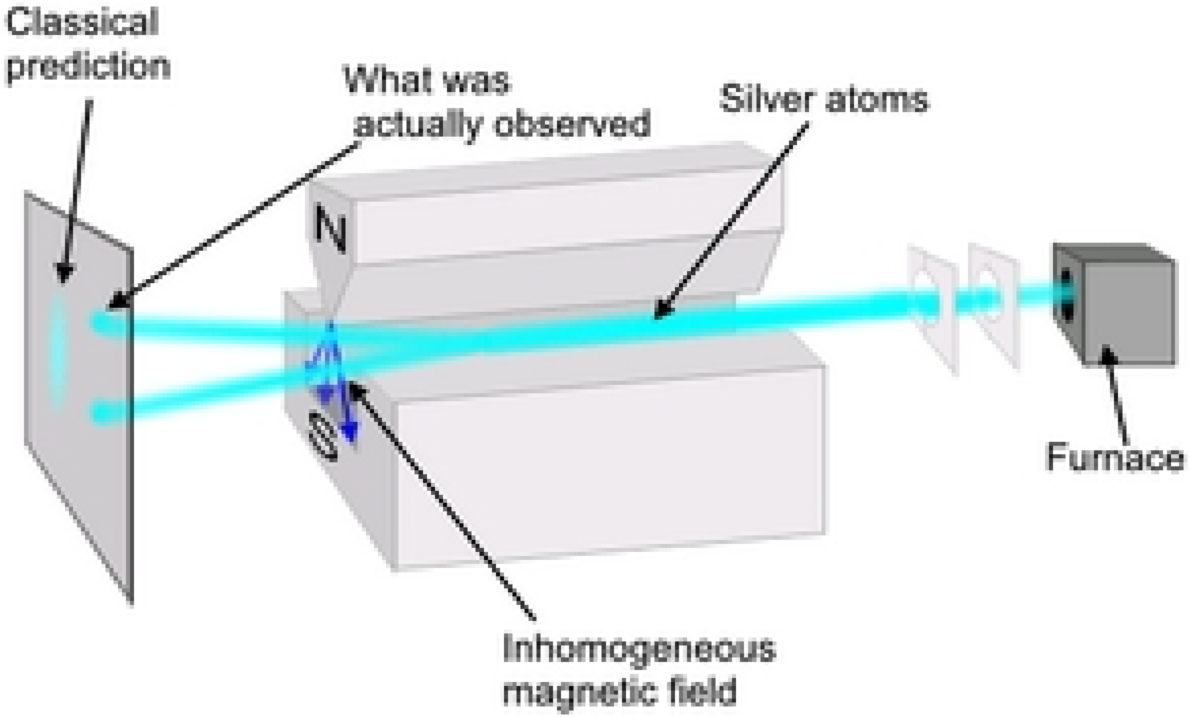
where $\mu_B = \frac{e\hbar}{2\, m_{el}}$ is a constant called *Bohr-magneton*.

What does this mean? According to the equations above, the energy of the particle with angular momentum in magnetic field depends on the quantum number m: if m is positive, it will grow; if m is negative, it will decrease; and it is not changing for $m = 0$. Since there are $2l + 1$ possible values of m, there will be $2l + 1$ different energy levels, the degeneracy of these levels will be lifted! This is the so called Zeeman-effect.



The spin of the electron

Stern-Gerlach experiment:



The beam splited in to 2 beams, and not 1, 3, 5, 7, etc., as expected form the properties of the angular momentum!!

The spin of the electron

To explain this experiment

- Pauli (1925): a „fourth quantum number" is needed;
- Goudsmit and Uhlenbeck suggested the concept of *spin*, as the „internal angular momentum"

In mathematical form:

$$\underline{\hat{s}} = (\hat{s}_x, \hat{s}_y, \hat{s}_z)$$

The spin of the electrons

The commutation properties of this new operator are the same as of the angular momentum, since it describes similar property:

$$[\hat{s}_x, \hat{s}_y] = i\hbar\hat{s}_z$$

$$[\hat{s}^2, \hat{s}_i] = 0 \qquad i = x, y, z$$

Eigenvalues have again similar properties than in case of the angular momentum:

$$\begin{array}{lll} \hat{s}^2 & \text{eigenvalues :} & s(s+1)\ [\hbar^2] \\ \hat{s}_z & \text{eigenvalues :} & m_s = -s, -s+1, \ldots, s\ [\hbar] \end{array}$$

The spin of the electrons

What are the possible values of the new quantum numbers s and m_s? This can be obtained from the Stern-Gerlach experiment: there were two beams, so that m_s can have only two values:

$$m_s = \frac{1}{2}, -\frac{1}{2}$$

Therefore

$$s = \frac{1}{2}$$

is the only proper choice!!!

Electron has a charge of -1, and a spin of $\frac{1}{2}$!!!!

The spin of the electron

There are two eigenvalues of s_z, therefore there are two eigenfunctions $\alpha(\sigma)$ and $\beta(\sigma)$ (σ is the spin coordinate):

$$\begin{aligned} \hat{s}_z\,\alpha(\sigma) &= \frac{1}{2}\,\alpha(\sigma) \\ \hat{s}_z\,\beta(\sigma) &= -\frac{1}{2}\,\beta(\sigma) \end{aligned}$$

Pauli matrices:

$$\begin{aligned} \hat{s}_z &= \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \\ \hat{s}_x &= \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \\ \hat{s}_x &= \begin{pmatrix} 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 \end{pmatrix} \end{aligned}$$

The spin of the electron

The total wave function of the electron must be supplemented by the spin, thus it depends on four variables:

$$\begin{aligned}\Psi(x,y,z,\sigma) &= u(x,y,z)\alpha(\sigma)\\ \text{or} &= u(x,y,z)\beta(\sigma)\end{aligned}$$

Spin-orbit interaction

There are two different types of angular momenta:

- angular momentum resulting from the motion of electrons ($\underline{\hat{l}}$), (*orbital angular momentum*);
- angular momentum originating from the spin ($\underline{\hat{s}}$) (*spin momentum*).

These magnetic moments can interact, causing an energy change:

$$\hat{H} \quad \rightarrow \quad \hat{H} + \zeta \cdot \underline{\hat{l}} \cdot \underline{\hat{s}}$$

where ζ is a constant.

Consequences:

- the Hamilton operator will not commute with $\hat{l}^2$, $\hat{l}_z$ and $\hat{s}_z$ operators;
- energy will depend on the quantum number l.

Quantum mechanical description of the hydrogen atom

The Hamiltonian of the hydrogen atom (in atomic units):

$$\hat{H} \quad = \quad -\frac{1}{2}\triangle - \frac{1}{r}$$

The Hamiltonian in spherical coordinates:

$$\hat{H} = -\frac{1}{2}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(-\hat{l^2}\right)\right] - \frac{1}{r}$$

Relation of the Hamiltonian with angular momentum:

$$\left[\hat{H}, \hat{l}_z\right] = 0 \quad \text{and} \quad \left[\hat{H}, \hat{l}^2\right] = 0$$

Since $\hat{l}_z$ and $\hat{l}^2$ depend only on the variables φ and ϑ, the wave function can be written as:

$$\Psi\left(r, \vartheta, \varphi\right) = R\left(r\right)\, Y_l^m\left(\vartheta, \varphi\right)$$

Quantum mechanical description of the hydrogen atom

Solution of the Schrödinger equation for the hydrogen atom

Eigenfunctions:

$$\Psi\left(r,\vartheta,\varphi\right) = R_{nl}\left(r\right)\,Y_l^m\left(\vartheta,\varphi\right) = R_{nl}\left(r\right)\,\Theta_l^m\left(\vartheta\right)e^{im\varphi}$$

Eigenvalues (hartree units):

$$E_n = -\frac{1}{2n^2}\left(E_h\right)$$

Quantum numbers:

$$\begin{aligned} n &= 1,2,3,... \\ l &= 0,1,2,...,n-1 \\ m &= -l,-l+1,...,0,l-1,l \end{aligned}$$

Quantum mechanical description of the hydrogen atom

Eigenfunctions of the hydrogen molecule (Ψ_{nlm})*:*

$1s$ $\Psi_{100} = \frac{1}{\sqrt{\pi}} e^{-r}$

$2s$ $\Psi_{200} = \frac{1}{4\sqrt{2\pi}} (2 - r) e^{-r/2}$

$2p_0$ $\Psi_{210} = \frac{1}{4\sqrt{2\pi}} r e^{-r/2} \cos(\vartheta)$

$2p_{\pm1}$ $\Psi_{21\pm1} = \frac{1}{8\sqrt{\pi}} r e^{-r/2} \sin(\vartheta) e^{\pm i\varphi}$

$3s$ $\Psi_{300} = \frac{2}{81\sqrt{3\pi}} (27 - 18r + 2r^2) e^{-r/3}$

$3p_0$ $\Psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} r(6 - r) e^{-r/3} \cos(\vartheta)$

$3p_{\pm1}$ $\Psi_{31\pm1} = \frac{1}{81\sqrt{\pi}} r(6 - r) e^{-r/3} \sin(\vartheta) e^{\pm i\varphi}$

$3d_0$ $\Psi_{320} = \frac{1}{81\sqrt{6\pi}} r^2 e^{-r/3} (3\cos^2(\vartheta) - 1)$

$3d_{\pm1}$ $\Psi_{32\pm1} = \frac{1}{81\sqrt{\pi}} r^2 e^{-r/3} \sin(\vartheta)\cos(\vartheta) e^{\pm i\varphi}$

$3d_{\pm2}$ $\Psi_{32\pm2} = \frac{1}{162\sqrt{\pi}} r^2 e^{-r/3} \sin^2(\vartheta) e^{\pm 2i\varphi}$

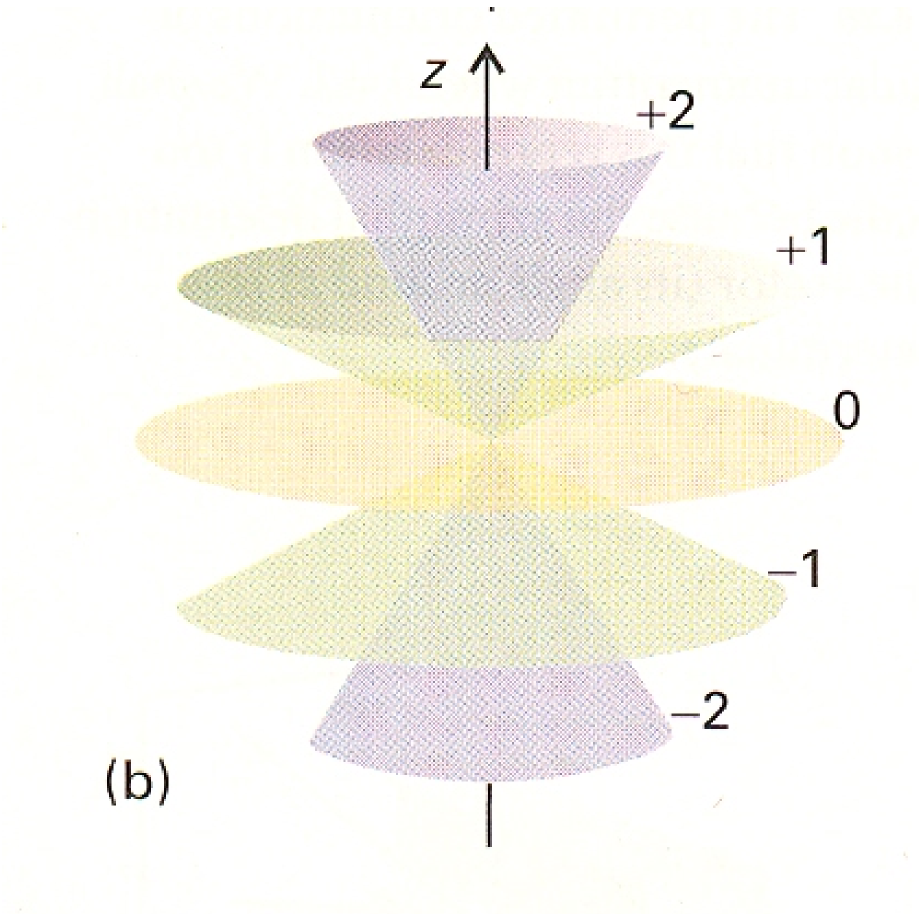
Angular momentum of the H atom

The angular momentum values belonging to the orbitals of the H atom:

orbital	n	l	m	$\lambda = l(l+1)[\hbar^2]$	$l_z = m[\hbar]$
1s	1	0	0	0	0
2s	2	0	0	0	0
$2p_0$	2	1	0	2	0
$2p_1$	2	1	1	2	1
$2p_{-1}$	2	1	-1	2	-1
3s	3	0	0	0	0
$3p_0$	3	1	0	2	0
$3p_1$	3	1	1	2	1
$3p_{-1}$	3	1	-1	2	-1
$3d_0$	3	2	0	6	0
$3d_1$	3	2	1	6	1
$3d_{-1}$	3	2	-1	6	-1
$3d_2$	3	2	2	6	2
$3d_{-2}$	3	2	-2	6	-2

Angular momentum of the H atom

Angular momentum vectors of the $3d$ orbitals:



The states of the hydrogen atom including spin

Wave function:

$$\Psi_{n,l,m,m_s}$$

Quantum numbers:

$$\begin{aligned} n &= 1, 2, \ldots \\ l &= 0, 1, \ldots, n-1 \\ m &= -l, -l+1, \ldots, l \\ m_s &= -\frac{1}{2}, \frac{1}{2} \end{aligned}$$

Energy depends still only on quantum number n ($2n^2$-fold degeneracy):

$$E_n = -\frac{1}{2\,n^2}\,[E_h]$$

Electronic structure of atoms

The Hamiltonian in atomic units:

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_{i}^{electrons} \Delta_i}_{\text{kinetic energy of electrons}} \underbrace{-\sum_{i}^{electrons} \frac{Z_A}{r_{iA}}}_{\text{electron-nuclei attraction}} \underbrace{+\sum_{i}^{electrons}\sum_{j<i}^{electrons} \frac{1}{r_{ij}}}_{\text{electron-electron repulsion}}$$

- Z_A being the charge of nucleus A;
- r_{ij} being the distance of electrons i and j;
- r_{iA} is the distance of electron i and nucleus A;

Electronic structure of atoms

The Hamiltonian in atomic units:

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_{i}^{electrons} \Delta_i}_{\text{kinetic energy of electrons}} \underbrace{-\sum_{i}^{electrons} \frac{Z_A}{r_{iA}}}_{\text{electron}-\text{nuclei attraction}} \underbrace{+\sum_{i}^{electrons}\sum_{j<i}^{electrons} \frac{1}{r_{ij}}}_{\text{electron}-\text{electron repulsion}}$$

Wave function of the many electron system

$$\begin{aligned} \Psi &= \Psi(x_1, y_1, z_1, \sigma_1, x_2, y_2, z_2, \sigma_2, ..., x_n, y_n, z_n, \sigma_n) \\ &\equiv \Psi(1, 2, ..., n) \end{aligned}$$

i.e. a function with $4n$ variables.

The Independent Particle Approximation

a) Hartree-method: Approximation of the wave function in a product form

$$\underbrace{\Psi(r_1, r_2, ..., r_n)}_{\text{wave function}} \approx \underbrace{\phi_1(r_1) \cdot \phi_2(r_2) ... \cdot \phi_n(r_n)}_{\text{product of spin orbitals}}$$

In this case the Schrödinger equation reduces to one-electron equations:

$$\begin{aligned} \hat{H}\Psi = E\Psi \quad \Rightarrow \quad & \hat{h}_1(r_1)\phi_1(r_1) = \varepsilon_1\phi_1(r_1) \\ & \hat{h}_2(r_2)\phi_2(r_2) = \varepsilon_2\phi_2(r_2) \\ & \ldots \\ & \hat{h}_n(r_n)\phi_n(r_n) = \varepsilon_n\phi_n(r_n) \end{aligned}$$

One n-electron equation ⇒ system of n one-electron equations

$$\hat{h}_i \quad \rightarrow \quad \hat{h}_i^{eff} = -\frac{1}{2}\Delta_i - \frac{Z_A}{r_{iA}} + V_i^{eff}$$

where V_i^{eff} is the interaction of electron i with all other electrons.

Pauli principle and the Slater determinant

b) Hartree-Fock-method:

To fulfill anti-symmetry of the wave function, use determinant (*Slater determinant*):

$$\Psi(r_1, r_2, ..., r_n) \quad = \quad \frac{1}{\sqrt{n}} \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \cdots & \phi_n(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \cdots & \phi_n(r_2) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_1(r_n) & \phi_2(r_n) & \cdots & \phi_n(r_n) \end{vmatrix}$$

To fulfill the indistinguishability, use the same operator (Fock operator) for all electrons:

$$\hat{h}_i^{eff} \quad \rightarrow \quad \hat{f}(r_i) = -\frac{1}{2}\Delta_i - \frac{Z_A}{r_{iA}} + U^{HF}$$

with U^{HF} being an averaged (Hartree-Fock) potential.

The Hartree-Fock equation:

$$\hat{f}(r_i)\varphi_i(r_i) \quad = \quad \varepsilon_i\varphi_i(r_i) \qquad i = 1, \cdots, n$$

Electronic structure of atoms

In the Independent Particle Approximation the equations to solve:

$$\begin{aligned}\hat{h}(i)\phi_i &= \varepsilon_i\phi_i \\ \hat{h}(i) &= -\frac{1}{2}\Delta_i - \frac{1}{r_{iA}} + V\end{aligned}$$

Since $\hat{h}$ is similar to the Hamiltonian of the hydrogen atom, the solutions will also be similar:

The *angular part* of the wave functions will be the SAME. Therefore we can again classify the orbitals as $1s$, $2s$, $2p_0$, $2p_1$, $2p_{-1}$, etc.

The *radial part*: $R(r)$ will differ, since the potential is different here than for the H atom: since it is not a simple Coulomb-potencial, the degeneracy according to l quantum number will be lifted, i.e. the orbital energies will depend not only on n but also on l ($\varepsilon = \varepsilon_{nl}$).

Electronic structure of atoms: angular momentum

one particle:	$\hat{l}^2$	$\hat{l}_z$	$\hat{s}^2$	$\hat{s}_z$
many particle:	$\hat{L}^2$	$\hat{L}_z$	$\hat{S}^2$	$\hat{S}_z$

The angular momentum of the system is given by the sum of the individual angular momentum of the particles (so called vector model or Sommerfeld model):

$$\underline{\hat{L}} = \sum_i \underline{\hat{l}}(i)$$

$$\underline{\hat{S}} = \sum_i \underline{\hat{s}}(i)$$

It follows that the z component of $\underline{\hat{L}}$ and $\underline{\hat{S}}$ is simply the sum of the z component of the individual vectors:

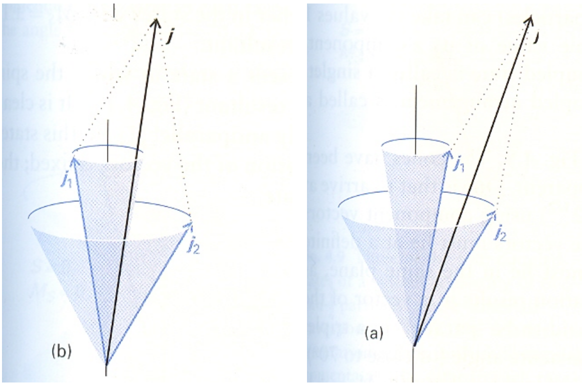
$$M_L = \sum_i m(i) \qquad M_S = \sum_i m_s(i)$$

Electronic structure of atoms: angular momentum

$$\underline{\hat{L}} = \sum_i \underline{\hat{l}}(i) \qquad \underline{\hat{S}} = \sum_i \underline{\hat{s}}(i)$$

The length of the vector is much more complicated: due to the quantizations and uncertainty principle, we can get different results: For exemple for two particles:

$$\begin{aligned} L &= (l(1)+l(2)), (l(1)+l(2)-1), \cdots, |l(1)-l(2)| \\ S &= (s(1)+s(1)), (s(1)-s(2)) \end{aligned}$$



Classification and notation of the atomic states

The Hamiltonian commutes with $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$ and $\hat{S}_z$ operators ⇒ we can classify the atomic states by the corresponding quantum numbers of the angular momentum operators:

$$\Psi_{L,M_L,S,M_s} \quad = \quad |L, M_L, S, M_s\rangle$$

The latter notation is more popular.

In analogy to the hydrogen atom, the *states* can be classified according to the quantum numbers:

Angular momentum:							
L=	0	1	2	3	4	5	···
notation:	S	P	D	F	G	H	···
degeneracy (2L+1)	1	3	5	7	9	11	···

Spin momentum:						
S=	0	$\frac{1}{2}$	1	$\frac{3}{2}$	2	···
multiplicity (2S+1):	1	2	3	4	···	
denomination:	singlet	doublet	triplet	quartet	···	

Classification and notation of the atomic states

In the full notation one takes the notation of the above table for the given L and writes the multiplicity as superscript before it:

Examples:

$L = 0, S = 0$: ^{1}S read: singlet S

$L = 2, S = 1$: ^{3}D read: triplet D

Total degeneracy is (2S+1)(2L+1)-fold!!

Construction of the atomic states

Since there is a high-level degeneracy, degenerate orbitals are often not fully occupied → configuration is not sufficient to represent the states.

Example: carbon atom

$1s^2\ 2s^2\ 2p^2$

$2p$ is open subshell, since only two electrons are there for six possible places on the $2p$ subshell.

What are the possibilities to put the two electrons onto these orbitals?

spatial part: $2p_0$, $2p_1$, $2p_{-1}$

spin part: α, β

These gives altogether six spin orbitals which allow to construct $\begin{pmatrix} 6 \\ 2 \end{pmatrix} = 15$ determinants, i.e. we have 15 different states.

Construction of the atomic states

Let us construct the states by summing the angular momenta:

$$l(1) = 1, l(2) = 1 \quad \rightarrow \quad L = (l(1) + l(2)), (l(1) + l(2) - 1), ..., |l(1) - l(2)| = 2, 1, 0$$

$$s(1) = \frac{1}{2}, s(2) = \frac{1}{2} \quad \rightarrow \quad S = (s(1) + s(2)), (s(1) - s(2)) = 1, 0$$

Possible states:

$$\begin{array}{ccc} {}^1S & {}^1P & {}^1D \\ {}^3S & {}^3P & {}^3D \end{array}$$

Considering the degeneracy there are 36 states. But we can have only 15, as was shown above!

Construction of the atomic states

We also have to consider *Pauli principle*, which says that two electrons can not be in the same state.

If we consider this, too, the following states will be allowed:

$$^1S \quad ^3P \quad ^1D$$

These give exactly 15 states, so that everything is round now!

Construction of the atomic states

Summarized: carbon atom in the $2p^2$ configuration has three energy levels.

What is the order of these states?

Hund's rule (from experiment; „Nun, einfach durch Anstieren der Spektren"):

- the state with the maximum multiplicity is the most stable (there is an interaction called „exchange" which exists only between same spins);
- if multiplicities are the same, the state with larger L value is lower in energy;

In case of the carbon atom:

$$E_{^3P} < E_{^1D} < E_{^1S}$$

Spin-orbit interaction, total angular momentum

As in case of the hydrogen atom, orbital and spin angular momenta interact. The Hamiltonian changes according to these interaction as:

$$\hat{H} \quad \rightarrow \quad \hat{H} + \sum_i \zeta \, \hat{l}(i) \cdot \hat{s}(i)$$

Consequence: $\hat{L}^2$ and $\hat{S}^2$ do not commute with $\hat{H}$ anymore, thus L and S will not be suitable to label the states („not good quantum numbers”). One can, however, define the *total angular momentum* operator as:

$$\underline{\hat{J}} \quad = \quad \underline{\hat{L}} + \underline{\hat{S}}$$

which

$$[\hat{H}, \hat{J}^2] = 0 \qquad [\hat{H}, \hat{J}_z] = 0$$

i.e. the eigenvalues of $\hat{J}^2$ and $\hat{J}_z$ are good quantum numbers.

Spin-orbit interaction, total angular momentum

These eigenvalues again follow the same pattern than in case of other angular momentum-type operators we have already observed:

$$\begin{aligned} \hat{J}^2 &\rightarrow J(J+1)\ [\hbar^2] \\ \hat{J}_z &\rightarrow M_J\ [\hbar] \end{aligned}$$

The quantum numbers J and M_J of the total angular momentum operators follow the same summation rule which was discussed above, i.e.

$$J = L+S, L+S-1, \cdots, |L-S|$$

Energy depends on J only, therefore degenerate energy level might split!!

Spin-orbit interaction, total angular momentum

Notation: even though L and S are not good quantum numbers, we keep the notation but we extend it with a subscript giving the value of J.

Example I: carbon atom, ${}^3P$ state:

$$\begin{aligned} L=1,\quad S=1 \quad &\rightarrow \quad J=2,1,0 \\ {}^3P \quad &\rightarrow \quad {}^3P_2,\ {}^3P_1,\ {}^3P_0 \end{aligned}$$

Energy splits into three levels!

Example II: carbon atom ${}^1D$ state:

$$\begin{aligned} L=2,\quad S=0 \quad &\rightarrow \quad J=2 \\ {}^1D \quad &\rightarrow \quad {}^1D_2 \end{aligned}$$

There is no splitting of energy here, J can have only one value. This should not be a surprise since $S=0$ means zero spin momentum, therefore no spin-orbit inetarction!!!

Electronic structure of atom: magnetic field

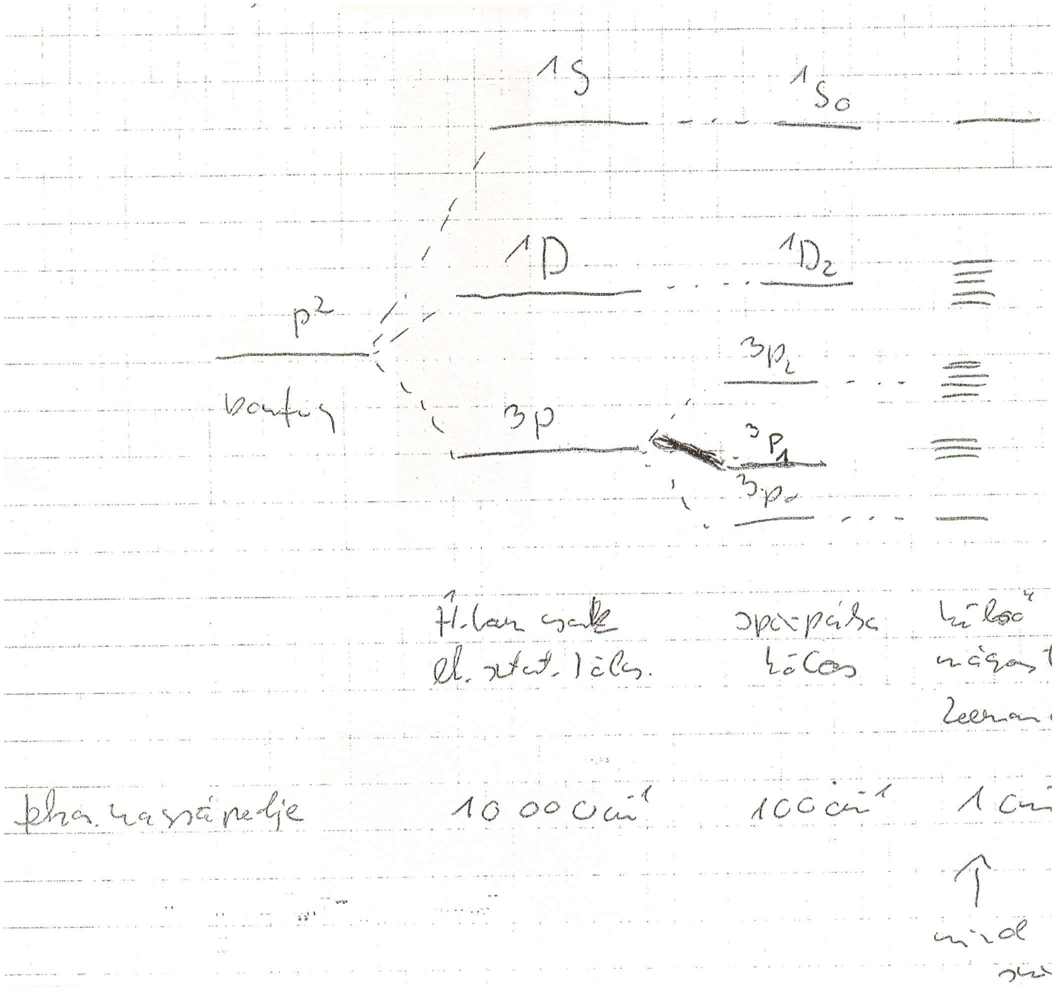
Considering the total angular momentum, the change of energy in magnetic field reads:

$$\begin{aligned} \Delta E &= M_J \cdot \mu_B \cdot B_z \\ M_J &= -J, -J+1, \ldots, J \end{aligned}$$

This means, levels will split into $2J+1$ sublevels!

Electronic states of atoms: summary

Carbon atom in $2p^2$ configuration:



Electronic states of atoms: summary

Other configuration for p shell:

p^1	and	p^5	^2P	B, F
p^2	and	p^4	$^3P,\ ^1D,\ ^1S$	C, O
p^3			$^4S,\ ^2D,\ ^2P$	N
p^6	(closed shell)		^1S	Ne

.

Basic Terms of Group Theory

Basic Terms of Group Theory

A *group* ($\mathcal{G}$) is a collection of *elements* which are interrelated by an *operation*:

$$A \cdot B \quad = \quad C$$

for which the following rules must be obeyed:

- set $\mathcal{G}$ is *closed* under the operation:
  if $A, B \in \mathcal{G}$ then $C \in \mathcal{G}$
- there must be a *unit element* (E, identity) such that:
  $E \cdot A = A \cdot E = A$
- multiplication is *associative*:
  $A \cdot (B \cdot C) = (A \cdot B) \cdot C$
- all elements must have its *reciprocal* (A^{-1}) in the group:
  $A \cdot S = S \cdot A = E \qquad\qquad S \equiv A^{-1}$

Basic Terms of Group Theory

Note that the multiplication is not necessarily commutative:

$$A \cdot B \quad \neq \quad B \cdot A$$

Abelian group: the multiplication for any pair of elements *is* commutative.

Basic Terms of Group Theory

Note that the multiplication is not necessarily commutative:

$$A \cdot B \quad \neq \quad B \cdot A$$

Abelian group: the multiplication for any pair of elements *is* commutative.

Dimension of the group (h):

- *finite group*: $h < \infty$
- *infinite group*: $h = \infty$

Basic Terms of Group Theory

Group multiplication table: shows the results of multiplication for any pair of group elements

	A	B	C	D
A	A	B	C	D
B	B	A	D	C
C	C	D	A	B
D	D	C	B	A

Properties:

- each element appears only once in each row and column
- multiplication is single valued

Basic Terms of Group Theory

Group multiplication table: shows the results of multiplication for any pair of group elements

	A	B	C	D
A	A	B	C	D
B	B	A	D	C
C	C	D	A	B
D	D	C	B	A

Properties:

- each element appears only once in each row and column
- multiplication is single valued

Subgroup: is a subset of elements which obey the definition of a group, i.e. multiplication does not lead out of the group.

It must always include E, and of course the invers of all elements.

Basic Terms of Group Theory

Conjugate elements: A and B are conjugate to each other, if

- $A, B, X \in \mathcal{G}$ and
- $B = X^{-1} \cdot A \cdot X$

Properties:

- If A is conjugate to B than B must be conjugate to A, i.e. the group must have an element Y such that:
  $A = Y^{-1} \cdot B \cdot Y$
- If A is conjugate to B and C then B and C are also conjugate to A.

Class: the complete set of elements which are conjugate to each other.

Basic Terms of Group Theory

Representation of a group

Remember the definitions: the group is defined by the multiplication table (relation of the elements) and not by any individual property of the elements.

The same group can also be *represented* for example by:

- operators (e.g. symmetry operation → symmetry groups)
- permutations (permutational groups)
- ...
- matrices (*matrix representation*)

Basic Terms of Group Theory

Assume a group with the following multiplication table:

	E	B	C	D
E	E	B	C	D
B	B	E	D	C
C	C	D	E	B
D	D	C	B	E

The following matrices obey the same multiplication table:

$$\mathbf{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{B} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\mathbf{C} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{D} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Basic Terms of Group Theory

Assume a group with the following multiplication table:

C_{2v}	E	C_2	σ_v	σ'_v
E	E	C_2	σ_v	σ'_v
C_2	C_2	E	σ'_v	σ_v
σ_v	σ_v	σ'_v	E	C_2
σ'_v	σ'_v	σ_v	C_2	E

The following matrices obey the same multiplication table:

$$\mathbf{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{C}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_v = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \sigma'_v = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Basic Terms of Group Theory

Representation of a group I

How many matrix representations can a group have?
. – As many as you just generate!!!

For example, by similarity transformation we get new set of matrices which also form a representation:

$$A' = L^{-1}AL \qquad B' = L^{-1}BL$$

$$A' \cdot B' = L^{-1}AL \cdot L^{-1}BL = L^{-1}A \cdot BL = L^{-1}CL = C'$$

By similarity transformation the character of a matrix[1] does not change

→ **the characters of the representing matrices will be characteristic to the representation** of the given dimensionality.

---

[1] Sum of the diagonal elements; also called „spur" or „trace".

Basic Terms of Group Theory

Representation of a group II

How many matrix representations can a group have?

. – As many as you just generate!!!

Also, you can create representation by forming direct sum of matices:

Basic Terms of Group Theory

Consider a group of two elements:

	A	B
A	A	B
B	B	A

Representation (1) (one dimensional):

$$\mathbf{A}^{(1)} = (1)$$

$$\mathbf{B}^{(1)} = (-1)$$

Representation (2) (two dimensional):

$$\mathbf{A}^{(2)} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\mathbf{B}^{(2)} = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$$

Direct sum representation:

$$\mathbf{A} = \mathbf{A}^{(1)} \oplus \mathbf{A}^{(2)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{B} = \mathbf{B}^{(1)} \oplus \mathbf{B}^{(2)} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix}$$

Basic Terms of Group Theory

Now the other way around: reducing the representation:

$$\mathbf{A} = \left(\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & 1 & 0 \\ 0 & 0 & 1 \end{array}\right) \qquad \mathbf{B} = \left(\begin{array}{c|cc} -1 & 0 & 0 \\ \hline 0 & 0 & i \\ 0 & -i & 0 \end{array}\right)$$

In case of matrices showing block structure, the representation can be split up. Here:

$$\begin{aligned} \mathbf{A} &= \mathbf{A}^{(1)} \oplus \mathbf{A}^{(2)} \\ \mathbf{B} &= \mathbf{B}^{(1)} \oplus \mathbf{B}^{(2)} \end{aligned}$$

There are two subrepresentations in this case, matrices $\mathbf{A}^{(1)}, \mathbf{B}^{(1)}$ form representation $\Gamma^{(1)}$, and matrices $\mathbf{A}^{(2)}, \mathbf{B}^{(2)}$ form representation $\Gamma^{(2)}$.

In notation:

$$\Gamma = \Gamma^{(1)} \oplus \Gamma^{(2)}$$

Basic Terms of Group Theory

Representation of a group III

Are there special ones among the representations?

. – Yes, these are the so called *irreducible representations*.

Irreducible representations: is a nonzero representation that has no proper subrepresentation.

- basic building blocks of representations
- any representation can be build up from these basic elements

Basic Terms of Group Theory

Representation of a group III

General procedure of reducing the representation:

– assume we have a group represented by matrices $\mathbf{E}, \mathbf{B}, \mathbf{C}, \mathbf{D}, ...$

– we perform the same similarity transformation on all of them:

$$\begin{aligned} \mathbf{E}' &= \mathbf{L}^{-1}\,\mathbf{E}\,\mathbf{L} \\ \mathbf{B}' &= \mathbf{L}^{-1}\,\mathbf{B}\,\mathbf{L} \\ \mathbf{C}' &= \mathbf{L}^{-1}\,\mathbf{C}\,\mathbf{L} \end{aligned}$$

– similarity transformation does not change the multiplication rules
. → transformed matrices still give a representation (same character).

Basic Terms of Group Theory

– Special transformation can lead to block diagonal matrices, e.g.:

$$\mathbf{B}' = \mathbf{L}^{-1}\mathbf{B}\mathbf{L} \quad = \quad \begin{pmatrix} \mathbf{B}'_1 & 0 & 0 & 0 & \cdots \\ 0 & \mathbf{B}'_2 & 0 & 0 & \cdots \\ 0 & 0 & \mathbf{B}'_3 & 0 & \cdots \\ 0 & 0 & 0 & \mathbf{B}'_4 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \end{pmatrix}$$

– Block diagonal matrices can be multiplied block-wise:

$$\begin{aligned} \mathbf{B}'_1 \cdot \mathbf{C}'_1 &= \mathbf{D}'_1 \\ \mathbf{B}'_2 \cdot \mathbf{C}'_2 &= \mathbf{D}'_2 \\ &\vdots \end{aligned}$$

obeying the same multiplication rules

→ each block is a new representation.

Basic Terms of Group Theory

Therefore:

If there exists a transformation which brings all matrices of a group to the same block structure, the representation can be split into „smaller” representations → i.e. the original representation *reducible*.

Note:

- the character of the representation is changed when it is splited into smaller pieces
- the sum of the character of new representations equals the character of the original representations

Notation: $\Gamma = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \cdots$

Therefore, a representation is *Irreducible* if:

- no transformation leading simultaneously to block structure of the matrices exists

Basic Terms of Group Theory

How many *irreducible representations* of a group are there?

– One can show that the number of all irreducible representations equals to the number of the classes of the group.

Basic Terms of Group Theory

How many *irreducible representations* of a group are there?

– One can show that the number of all irreducible representations equals to the number of the classes of the group.

Character table:

Example: Character table of the C_{2v} point group

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

Columns correspond to the classes (in this case elements)

Rows correspond to the irreps and show the character of the elements

Basic Terms of Group Theory

Basis of a representation

We know the relation between operators and matrices:

Consider a set of (linearly independent) functions $\{\phi_i\}$ such that the space spanned is an invariant space with respect to all operators of the group. E.g.:

$$\begin{aligned}
\hat{A}\phi_i &= \sum_j A_{ij}\phi_j \\
\hat{B}\phi_i &= \sum_j B_{ij}\phi_j \\
\hat{C}\phi_i &= \sum_j C_{ij}\phi_j \\
&\ldots
\end{aligned}$$

Basic Terms of Group Theory

Basis of a representation

The matrix representation of an operator in this basis can be given as:

$$\begin{aligned} A_{ij} &= \langle \phi_i | \hat{A} | \phi_j \rangle \\ (&= \int \phi_i(x)^* \hat{A} \phi_j(x) dx \ ) \end{aligned}$$

The matrices defined this way from operators belonging to a group, form also a group with the same multiplication table:

- the matrices $\mathbf{A}, \mathbf{B}, \ldots$ are the *matrix representation of operators* $\hat{A}$, $\hat{B}$, ... on the basis $\{\phi_i\}$.

Notes:

- when transforming the matrices, in fact we transform the basis
- when finding the block diagonal form of the matrices and splitting up the representation accordingly, we divide up the space into smaller subspaces. Now the elements of subspaces will be used as basis of the representations.

Basic Terms of Group Theory

Reducing reducible representations

To split up reducible representations into irreducible ones, one can use the following formula:

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

with:

h: order of the group

N_k: order of the class

$\chi^i(k)$: character of kth class corresponding to irrep i

$\chi(k)$: character of kth class corresponding to the reducible representation

Basic Terms of Group Theory

To find the subspace spanning the irreducible representations, the following operator can be used, which projects into the space of the ith irrep:

$$\hat{P}_i \;=\; \sum_{\hat{R}} \chi^i(\hat{R})\,\hat{R}$$

with $\hat{R}$ being the element of the group, $\chi^i(\hat{R})$ being its character corresponding to the ith irrep.

Basic Terms of Group Theory

Reducing reducible representations

Example: Two matrices $\mathbf{A}$ and $\mathbf{B}$ considered above:

$$\mathbf{A} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbf{B} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix}$$

Character table for this group[2]

C_s	$\hat{A}$	$\hat{B}$
A'	1	1
A”	1	-1
$\Gamma_{3\ dim}$	3	-1

The characters of the $\Gamma_{3\ dim}$ representation are given as the spur (trace) of the corresponding matrices.

---

[2] Note that this is the C_s point group, introduced later.

Basic Terms of Group Theory

C_s	$\hat{A}$	$\hat{B}$
A'	1	1
A"	1	-1
$\Gamma_{3\ dim}$	3	-1

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

$$\mathrm{n}_{\mathrm{A}'} = \tfrac{1}{2}(1{\cdot}1{\cdot}3+1{\cdot}1{\cdot}(-1)) = 1$$

$$\mathrm{n}_{\mathrm{A}''} = \tfrac{1}{2}(1{\cdot}1{\cdot}3+1{\cdot}(-1){\cdot}(-1)) = 2$$

Thus: $\Gamma_{3\ dim}$=A' $\oplus$ 2 A"

$$\mathbf{A} = \left(\begin{array}{c|c|c} 1 & 0 & 0 \\ \hline 0 & 1 & 0 \\ \hline 0 & 0 & 1 \end{array}\right) \qquad \mathbf{B} = \left(\begin{array}{c|c|c} 1 & 0 & 0 \\ \hline 0 & -1 & 0 \\ \hline 0 & 0 & -1 \end{array}\right)$$

Basic Terms of Group Theory

Direct product representations

Consider two representations on the two bases $\{\phi_i(x)\}$ and $\{\psi_i(y)\}$:

$$\hat{A}\phi_i(x) = \sum_j A^{\phi}_{ij}\phi_j(x) \qquad \hat{A}\psi_i(y) = \sum_j A^{\psi}_{ij}\psi_j(y)$$

Then:

$$\hat{A}\phi_i(x)\psi_j(y) \quad = \quad \sum_k \sum_l A^{\phi}_{ik} A^{\psi}_{jl} \psi_k(x)\phi_l(y)$$

i.e. the set $\{f_{ij}(x,y)\} = \{\phi_i(x) \cdot \psi_j(y)\}$ also form a basis for the representation, that of the outer product of the two matrices:

$$\mathbf{A}^{\phi\otimes\psi} \quad = \quad \mathbf{A}^{\phi} \otimes \mathbf{A}^{\psi}$$

with $\mathbf{A}^{\phi\otimes\psi}$ having a dimension as product of the dimensions of the two representations.

Basic Terms of Group Theory

Direct product representations

Outer product of two matrices:

$$\mathbf{A} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \qquad \mathbf{B} = \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix}$$

$$\begin{aligned} \mathbf{A} \otimes \mathbf{B} &= \begin{pmatrix} \mathbf{A}B_{11} & \mathbf{A}B_{12} \\ \mathbf{A}B_{21} & \mathbf{A}B_{22} \end{pmatrix} \\ &= \begin{pmatrix} A_{11}B_{11} & A_{12}B_{11} & A_{11}B_{12} & A_{12}B_{12} \\ A_{21}B_{11} & A_{22}B_{11} & A_{21}B_{12} & A_{22}B_{12} \\ A_{11}B_{21} & A_{12}B_{21} & A_{11}B_{22} & A_{12}B_{22} \\ A_{21}B_{21} & A_{22}B_{21} & A_{21}B_{22} & A_{22}B_{22} \end{pmatrix} \end{aligned}$$

Character of $\mathbf{A} \otimes \mathbf{B}$?

Basic Terms of Group Theory

Direct product representations

Outer product of two matrices:

$$\mathbf{A} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \qquad \mathbf{B} = \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix}$$

$$\begin{aligned} \mathbf{A} \otimes \mathbf{B} &= \begin{pmatrix} \mathbf{A}B_{11} & \mathbf{A}B_{12} \\ \mathbf{A}B_{21} & \mathbf{A}B_{22} \end{pmatrix} \\ &= \begin{pmatrix} A_{11}B_{11} & A_{12}B_{11} & A_{11}B_{12} & A_{12}B_{12} \\ A_{21}B_{11} & A_{22}B_{11} & A_{21}B_{12} & A_{22}B_{12} \\ A_{11}B_{21} & A_{12}B_{21} & A_{11}B_{22} & A_{12}B_{22} \\ A_{21}B_{21} & A_{22}B_{21} & A_{21}B_{22} & A_{22}B_{22} \end{pmatrix} \end{aligned}$$

$$\chi_{\mathbf{A}\otimes\mathbf{B}} = (A_{11} + A_{22}) \cdot (B_{11} + B_{22}) = \chi_A \cdot \chi_B$$

Basic Terms of Group Theory

Direct product representations

Notation:

$$\Gamma^{\phi\otimes\psi} \quad = \quad \Gamma^{\phi} \otimes \Gamma^{\psi}$$

Character of the direct product representation:

The characters of the direct product representation are the products of the character of the representations forming the original representations.

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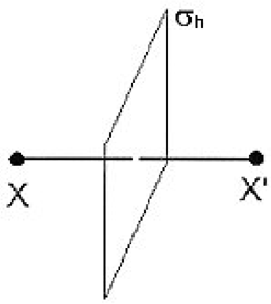
Spatial Symmetry of Molecules

Symmetry operations

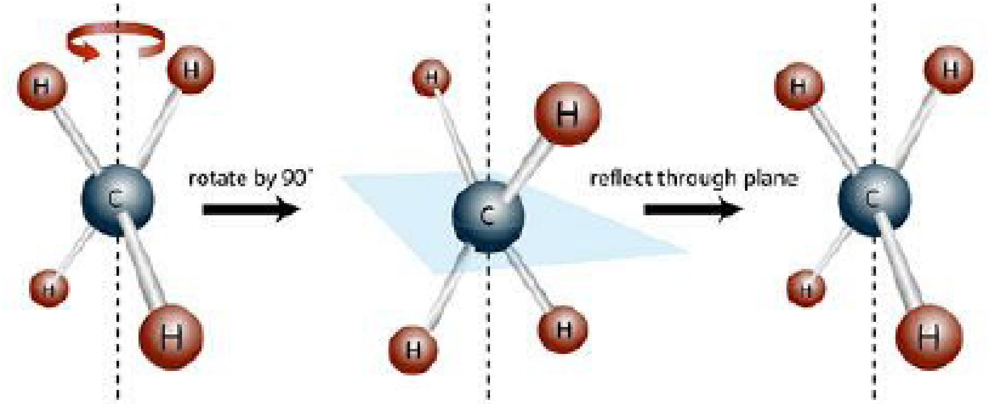
- $\hat{C}_n$ – proper rotation (around the proper axis) by $2\pi/n$

- $\hat{\sigma}$ – reflection (special cases: $\hat{\sigma}_v$, $\hat{\sigma}_h$, $\hat{\sigma}_d$)



Symmetry operations

- $\hat{S}_n$ – improper rotation: rotation ($\hat{C}_n$) followed by reflection in a plane perpendicular to the rotation axis (σ_h)



- $\hat{i}$ – inversion ($\hat{i} = \hat{S}_2$)

- $\hat{E}$ – unity: maps the object on itself (required only for mathematical purposes)

Point groups

Symmetry operations leaving an object (molecule) unchanged, form a group.

E.g. water (see next page):

Operators: $\hat{C}_2$, $\hat{\sigma}_v$, $\hat{\sigma}'_v$, $\hat{E}$

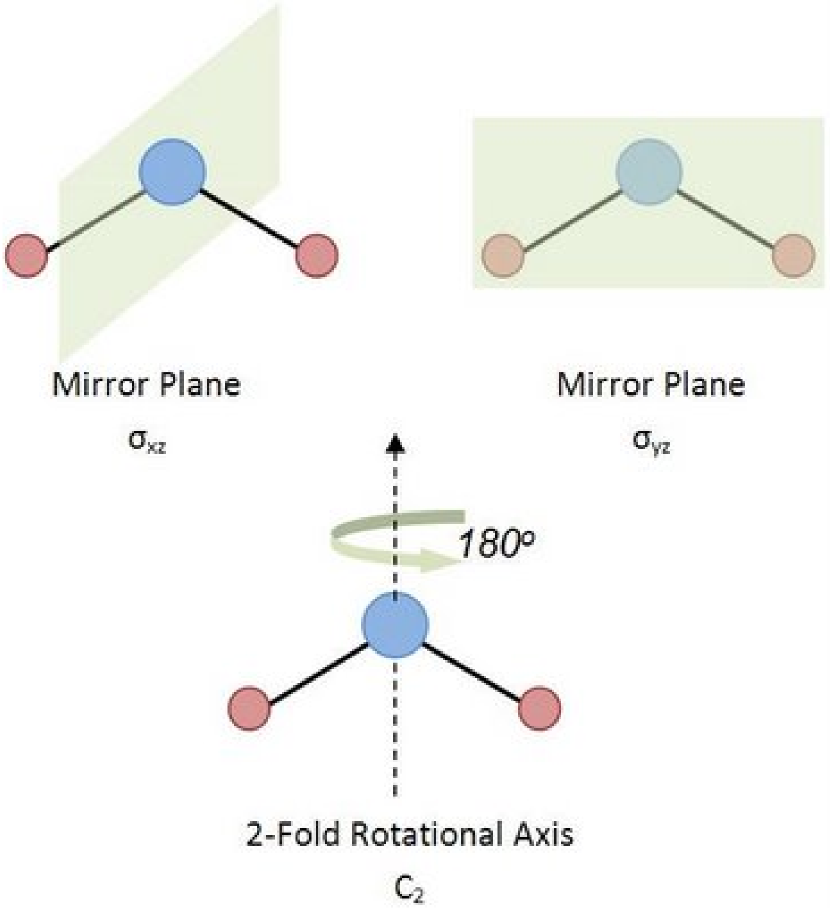
Multiplication table:

$\hat{C}_{2v}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{E}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{C}_2$	$\hat{C}_2$	$\hat{E}$	$\hat{\sigma}'_v$	σ_v
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$	$\hat{E}$	$\hat{C}_2$
$\hat{\sigma}'_v$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$	$\hat{C}_2$	$\hat{E}$

The group formed by the symmetry operations is called the *point group*.

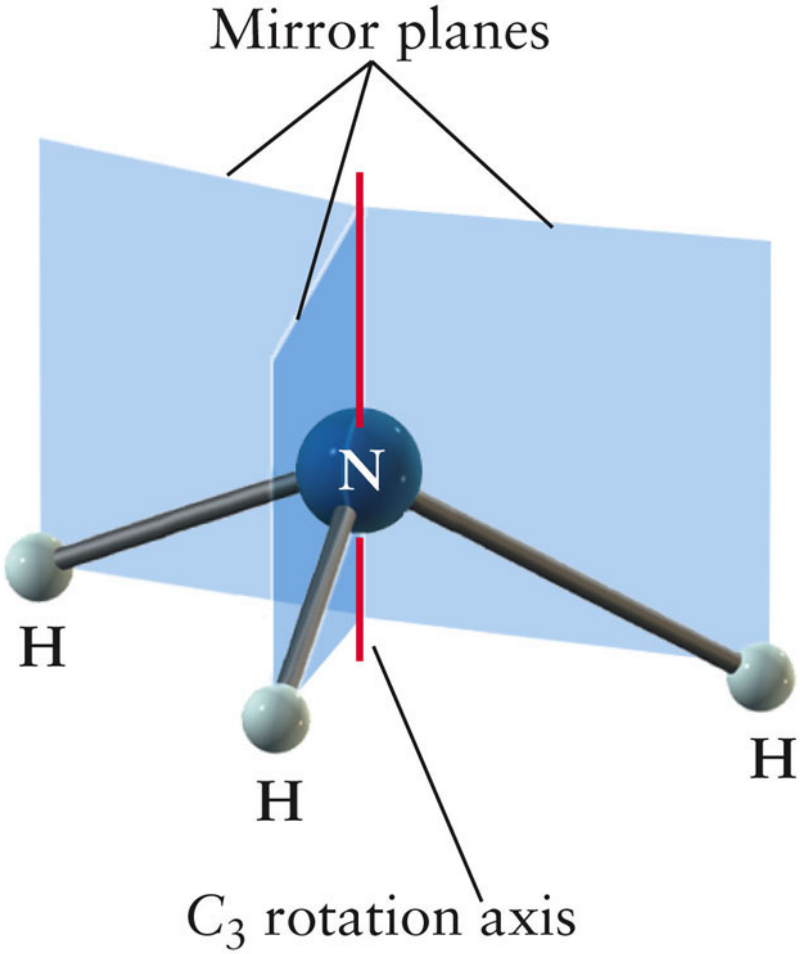
Point groups

Water: $\hat{C}_2$, $\hat{\sigma}_v$, $\hat{\sigma}'_v$, $\hat{E}$



Point groups

Ammonia: $\hat{C}_3$, 3 times $\hat{\sigma}_v$, $\hat{E}$



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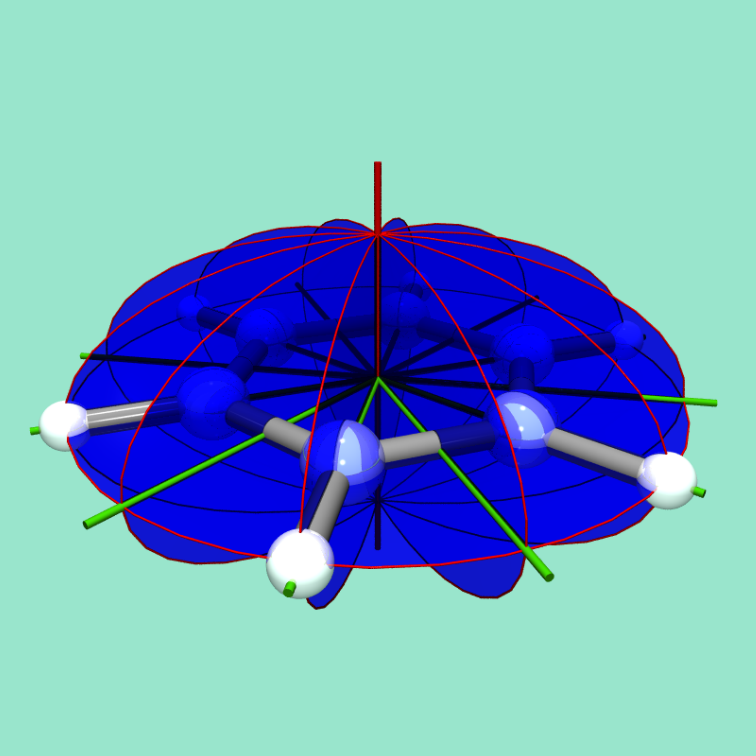
Point groups

Benzene: $\hat{C}_6$, 6 times $\hat{C}_2$, $\hat{\sigma}_h$ (horizontal, perpendicular to the main axis), 6 times $\hat{\sigma}_v$ (including the main axis), $\hat{i}$, etc.



Generators of a group

Set of elements ($\mathcal{S}$) of the group $\mathcal{G}$ are called *generators* if all elements of $\mathcal{G}$ can be generated by multiplication of the elements of $\mathcal{S}$.

Example: benzene

Elements of the point group $\mathrm{D_{6h}}$:

$$\hat{E},\ 2\hat{C}_6,\ 2\hat{C}_3,\ \hat{C}_2,\ 3\hat{C}_2',\ 3\hat{C}_2",\ \hat{i},\ 2\hat{S}_6,\ 2\hat{S}_3,\ \hat{\sigma}_h,\ 3\hat{\sigma}_v,\ 3\hat{\sigma}_d$$

Three generators are able to produce these elements.

Set 1: $\hat{C}_6, \hat{C}_2'$ and $\hat{i}$.

$$\hat{C}_3 = \hat{C}_6 \cdot \hat{C}_6, \quad \hat{C}_2 = \hat{C}_6 \cdot \hat{C}_6 \cdot \hat{C}_6, \quad \hat{C}_2" = \hat{C}_6 \cdot \hat{C}_2', \quad \hat{\sigma}_v = \hat{C}_2' \cdot \hat{i} \text{ etc.}$$

Set 2: $\hat{C}_6$, $\hat{\sigma}_v$, $\hat{\sigma}_v$

Set 3:..... several others

The set of the generators is not unique!

Point groups

Symmetry of molecules are represented by the collection of symmetry operations leaving it unchanged, i.e. by the *point group*.

Point groups are represented by the so called *Schoenflies-symboles*:

- C_n: groups including proper rotation $\hat{C}_n$ only
- C_{nv}: groups including proper rotation $\hat{C}_n$ and reflection to a plain including the axis $\hat{\sigma}_v$
- C_{nh}: groups including proper rotation $\hat{C}_n$ and reflection to a plain perpendicular to the axis $\hat{\sigma}_h$
- D_n: groups including proper rotation $\hat{C}_n$ and n additional proper rotation $\hat{C}_2$ perpendicular to the main axis
- D_{nh}: same as D_n with and additional reflection to a plane perpendicular to the main axis.

Point groups

- D_{nd}: same as D_n with and additional reflection to a plane including the main axis.
- S_n: includes improper rotation $\hat{S}_n$
- T_d: tetrahedral point group
- ...
- $C_{\infty v}$: proper rotation with arbitrary angle ($\hat{C}_\infty$) and reflection to a plane including this axis ($\hat{\sigma}_v$)
- $D_{\infty h}$: proper rotation with arbitrary angle ($\hat{C}_\infty$) and reflection to a plane perpendicular to this axis ($\hat{\sigma}_h$)
- O_3^+: spherical symmetry

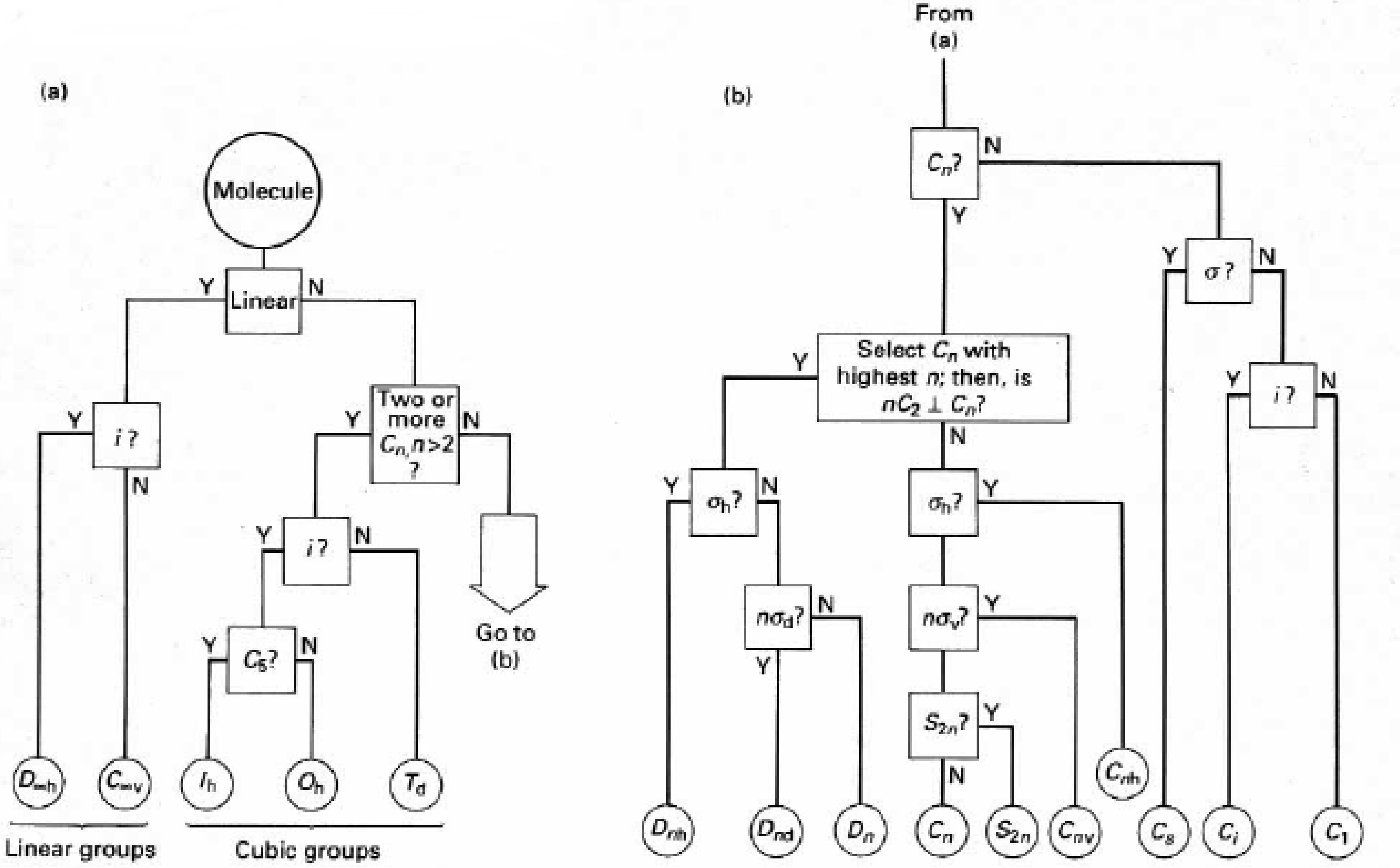
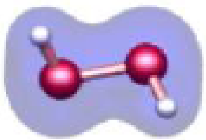


Figure 3.15
Shriver, Atkins, and Langford: *INORGANIC CHEMISTRY*, second edition
©1990, 1994 D. F. Shriver, P. W. Atkins, and C. H. Langford
W. H. Freeman and Company

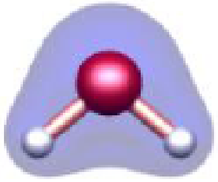
Point groups

Molecular examples:

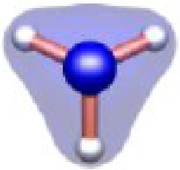
molecule	symmetry operations	point group
water	$\hat{C}_2$, $\hat{\sigma}_v$, $\hat{\sigma}'_v$, $\hat{E}$	C_{2v}
ammonia	$\hat{C}_3(z)$, 3 x $\hat{\sigma}_v$, $\hat{E}$	C_{3v}
benzene	$\hat{C}_6$, 6 x $\hat{C}_2$, $\hat{\sigma}_h$, 6 x $\hat{\sigma}_v$, $\hat{i}$, etc.	D_{6h}
formaldehyde	$\hat{C}_2(z)$, $\hat{\sigma}_v$, $\hat{\sigma}'_v$, $\hat{E}$	C_{2v}
ethene		D_{2h}
acetylene		$D_{\infty h}$
carbon monoxide		$C_{\infty v}$



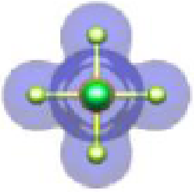
H_2O_2:
C_2



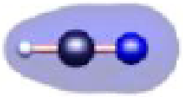
H_2O:
C_{2v}



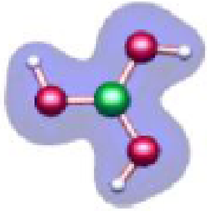
NH_3:
C_{3v}



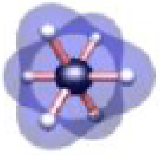
SF_5Cl:
C_{4v}



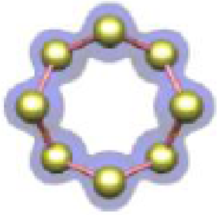
HCN:
$C_{\infty v}$



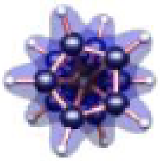
$B(OH)_3$:
C_{3h}



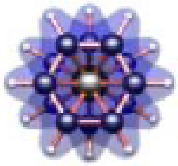
C_2H_6:
D_{3d}



S_8:
D_{4d}

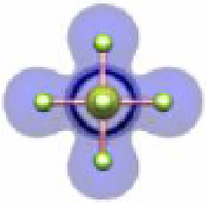


$Fe(C_5H_5)_2$:
D_{5d}

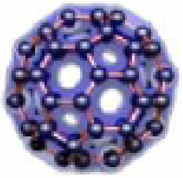


$Cr(C_6H_6)_2$:
D_{6d}

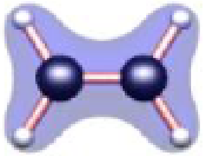
CH_4:
T_d



SF_6:
O_h

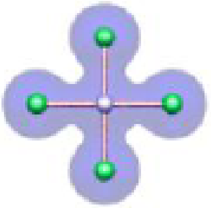


C_{60}:
I_h



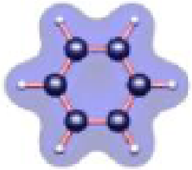
C_2H_4:
D_{2h}

C_2H_6:
D_{3h}

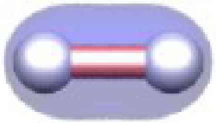


$[PdCl_4]^{2-}$:
D_{4h}

$Fe(C_5H_5)_2$:
D_{5h}



C_6H_6:
D_{6h}



H_2:
$D_{\infty h}$

http://newton.ex.ac.uk/research/qsystems/people/goss/symmetry/Molecules.html

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Symmetry and quantum mechanics

Symmetry and quantum mechanics

Symmetry operations are represented by operators ($\hat{R}$).

What does it mean mathematically: „The operations leave the molecule unchanged"?

It does not change the properties → The symmetry operators commute with the corresponding operators (e.g. Hamiltonian):

$$\hat{R}\hat{H} = \hat{H}\hat{R}$$

Symmetry and quantum mechanics

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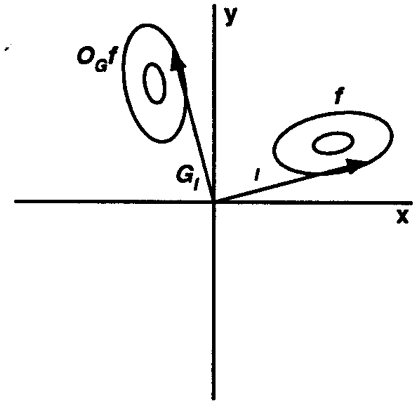
Figure 10.2: Transformation of functions



Action of a symmetry operator on a function:

$$\hat{R}f(\mathbf{x}) = f(\hat{R}^{-1}\mathbf{x})$$

Symmetry and quantum mechanics

$$\hat{R}\hat{H} = \hat{H}\hat{R}$$

Commuting operators have a common set of eigenfunctions[3]

$$\Downarrow$$

The eigenfunction of the Hamiltonian must also be eigenfunction of the symmetry operators.

$$\hat{R}\Psi = r\Psi$$

---

[3] For easier understanding we disregard degeneracy for the time being.

Symmetry and quantum mechanics

$$\hat{R}\Psi \quad = \quad r\Psi$$

What are the eigenvalues?

- Like the object (molecule), the wave function is unchanged under the symmetry operation: $r = 1$
- The wave function can also change sign under the symmetry operation, since in this case the density $|\Psi|^2$ is still unchanged: $r = -1$

This eigenvalue will be representative for the wave function („good quantum numbers”):

- $r = 1$: symmetric
- $r = -1$: antisymmetric

Symmetry and quantum mechanics

$$\hat{R}\Psi = r\Psi$$

What about the eigenfunctions?

- They form a basis for a representation of the symmetry operations.

Symmetry axiom: the eigenfunctions of the Hamiltonian form an *irreducible representation* of the symmetry operations.

Symmetry and quantum mechanics

We have several symmetry operations, all can have two eigenvalues.

For water, this means 2^3 possibilities ($\hat{E}$ has only one eigenvalue).

Are all of these possible?? No, only four combinations are possible:

C_{2v}	E	C_2	σ_{zx}	σ_{zy}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

The four possibilities are the *irreducible representation*.

The *character table* shows the eigenvalue of the individual operators corresponding to the irreps.

Thus, wave functions can be classified according to the rows of the character table, i.e. according to the irreps.

Symmetry and quantum mechanics

We have several symmetry operations, all can have two eigenvalues.

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A_1	1	1	1	1
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B_1	1	-1	1	-1
B_2	1	-1	-1	1

The four possibilities are the *irreducible representation*.

The *character table* shows the eigenvalue of the individual operators corresponding to the irreps.

Thus, the wave function of water can be classified as A_1, A_2, B_1 or B_2.

Symmetry and quantum mechanics

Other example: ammonia

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Here there is also two-dimensional irrep. This means:

- there are two eigenfunctions of the Hamiltonian which have the same symmetry property
- any combination of these two functions still define a representation of the group (with the same character)

Symmetry and quantum mechanics

Other example: ammonia

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Here there is also two-dimensional irrep. This means:

- there are two eigenfunctions of the Hamiltonian which have the same symmetry property
- any combination of these two functions still define a representation of the group (with the same character)

$\Rightarrow$ it follows that these functions belong to the same eigenvalue of the Hamiltonian, i.e. *degenerate*!

Symmetry and quantum mechanics

In summary:

It is worth to use symmetry:

- to classify states
- to speed up calculations
- predict degeneracy

Hamiltonian of molecules

$$\hat{H} \quad = \quad \underbrace{\hat{T}_{el}(\mathbf{r}) + \hat{V}_{el-nucl}(\mathbf{r},\mathbf{R}) + \hat{V}_{el-el}(\mathbf{r}) + \hat{V}_{nucl-nucl}(\mathbf{R})}_{\hat{H}_e(\mathbf{r},\mathbf{R})} + \underbrace{\hat{T}_{nucl}(\mathbf{R})}_{\hat{T}_n(\mathbf{R})}$$

$$\hat{H}(\mathbf{r},\mathbf{R}) \quad = \quad \hat{H}_e(\mathbf{r},\mathbf{R}) + \hat{T}_n(\mathbf{R})$$

with

- $\mathbf{r}$ denoting the coordinates of the electrons;
- $\mathbf{R}$ denoting the coordinates of the nuclei;
- $\hat{T}_{nucl}$ kinetic energy operator of the nuclei;
- see also earlier notations.

Wave function of molecules

$$\Psi \quad = \quad \Psi(\mathbf{r},\mathbf{R})$$

It depends on the coordinates of the electrons and nuclei, but these are not separable due to coupling present in the Hamiltonian:

$$\Psi(\mathbf{r},\mathbf{R}) \quad \neq \quad \Phi(\mathbf{r})\chi(\mathbf{R})$$

Schrödinger equation

$$\hat{H}(\mathbf{r},\mathbf{R})\Psi(\mathbf{r},\mathbf{R}) \quad = \quad E_{TOT}\Psi(\mathbf{r},\mathbf{R})$$

The equation depends on both the electronic and nuclear coordinates, fully coupled!

The Born-Oppenheimer approximation

electrons are much lighter than electrons ($\frac{M}{m_{el}} \approx 1836$)

$\Downarrow$ equipartition

electrons are much faster

$\Downarrow$

electrons folow nuclei instantaneously (adiabatic approximation)

$\Downarrow$

<u>from the point of view of electrons</u> the nuclei are steady

$\Downarrow$

Equation for the electronic problem: $\hat{H}_e(\mathbf{r};\mathbf{R})\Phi(\mathbf{r};\mathbf{R}) = E(\mathbf{R})\Phi(\mathbf{r};\mathbf{R})$

for nuclei: $(\hat{T}_n\,(\mathbf{R}) + E(\mathbf{R}))\,\chi(\mathbf{R}) = E_{TOT}\chi(\mathbf{R})$

Born-Oppenheimer approximation

Notice that:

- in *Born-Oppenheimer (BO)* approximation we have separate uncoupled equation for electrons and nuclei;
- nuclei *are not* motionless;
- the potential $E(\mathbf{R})$ acting on the nuclei is the coordinate dependent energy from the electronic Schrödinger equation;
- potential $E(\mathbf{R})$ is thus the result of the *Born-Oppenheimer* approximation, without this the notion of potential (potential curve, potential surface, PES) does not exist;
- generally, BO is a good approximation, but it fails if the energy of different electronic states are close (e.g. in photochemistry).

The H_2^+ molecular ion

This is a three-body problem and can not be solved analytically.

However, using the BO approximation, it can be reduced to a single-electron problem:

The Hamiltonian:

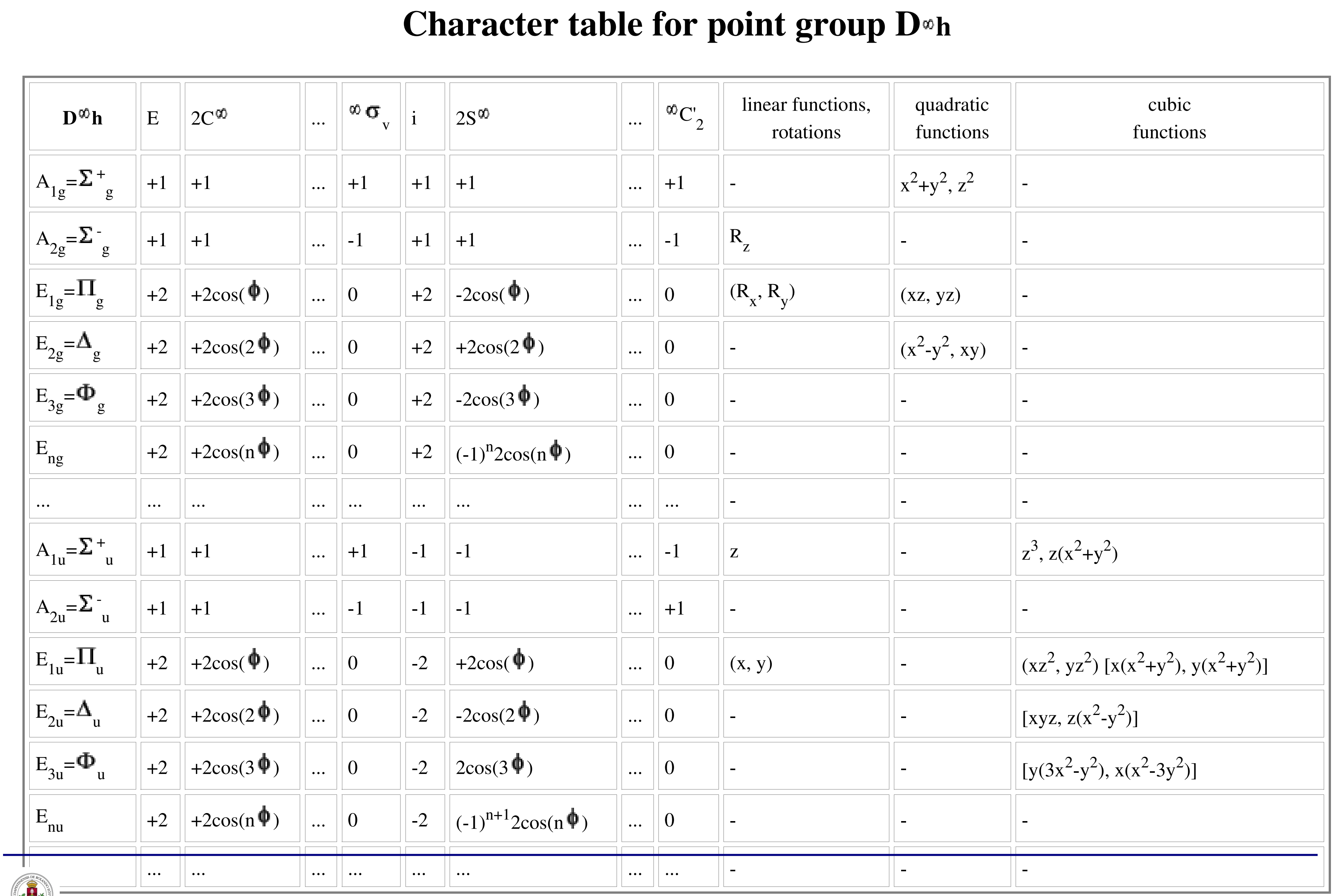
$$\hat{H} = -\frac{1}{2}\Delta_1 - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} + \frac{1}{R}$$

with r_{1A} and r_{1B} are the distances of the electron from nuclei A and B, R is the distance of the two nuclei.

The Schrödinger equation:

$$\hat{H}\Phi_i(1;R) = E_i(R)\Phi_i(1;R)$$

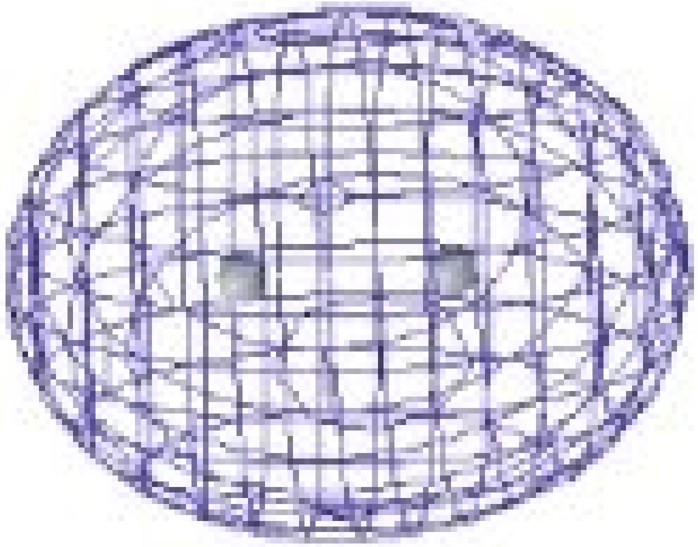
Analytic solution is possible in elliptic coordinates.



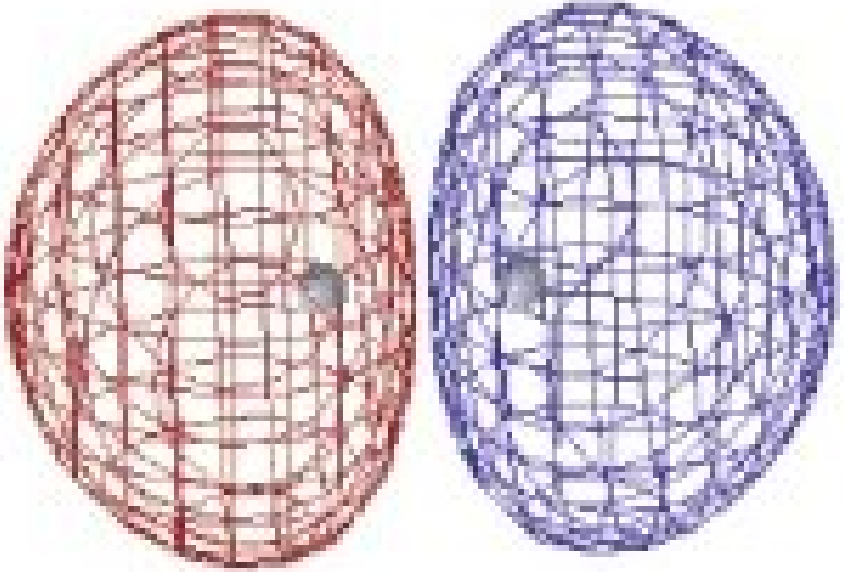
Character table for point group D∞h

D∞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 ion: solutions

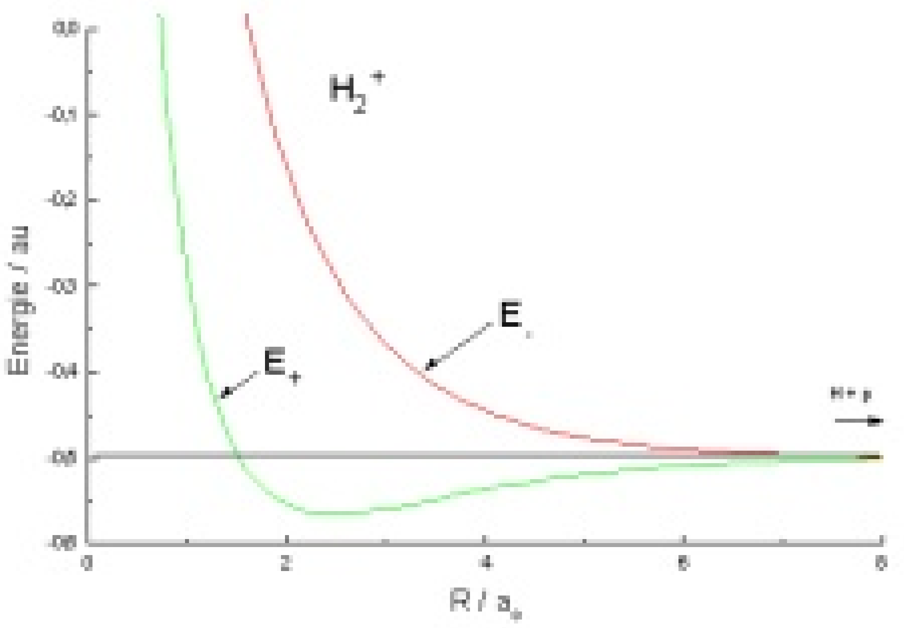


Φ_1, symmetry: Σ_g^+



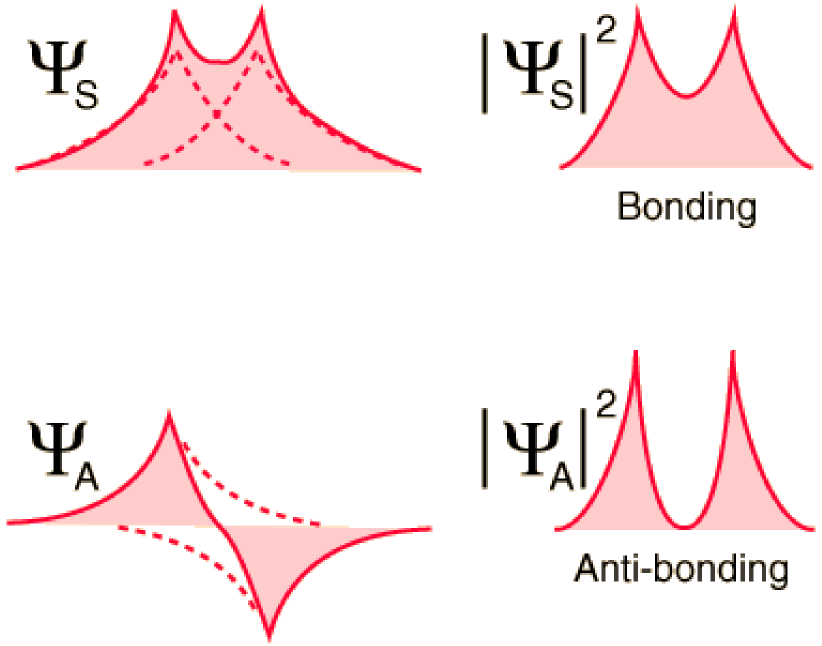
Φ_2, symmetry Σ_u^+

H_2^+ molecule ion: solutions



H2_Ion_Energien.gif

H_2^+ molecule ion: what is the chemical bond



- decrease of energy when atoms approach each other
- increase of electron density between the atoms

H_2^+ molecule ion: minimal basis

Basis: $\chi_1 = 1s_A \qquad \chi_2 = 1s_B$

Overlap of the basis functions: $S_{11} = S_{22} = 1 \qquad S_{21} = \langle \chi_1 | \chi_2 \rangle \equiv S$

Matrix elements of $\hat{H}$:

$$H_{11} = \langle \chi_1 | \hat{H} | \chi_1 \rangle = \langle 1s_A | \hat{H} | 1s_A \rangle \equiv \alpha$$

$$H_{22} = \langle \chi_2 | \hat{H} | \chi_2 \rangle = \langle 1s_B | \hat{H} | 1s_B \rangle \equiv \alpha$$

$$H_{12} = \langle \chi_1 | \hat{H} | \chi_2 \rangle = \langle 1s_A | \hat{H} | 1s_B \rangle \equiv \beta$$

The $\mathbf{H}$ matrix and the $\mathbf{S}$ matrix:

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

$$\mathbf{S} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}$$

H_2^+ molecule ion: minimal basis

Eigenvalue equation $\mathbf{Hc} = E\mathbf{Sc}$:

$$\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

Secular determinant:

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0$$

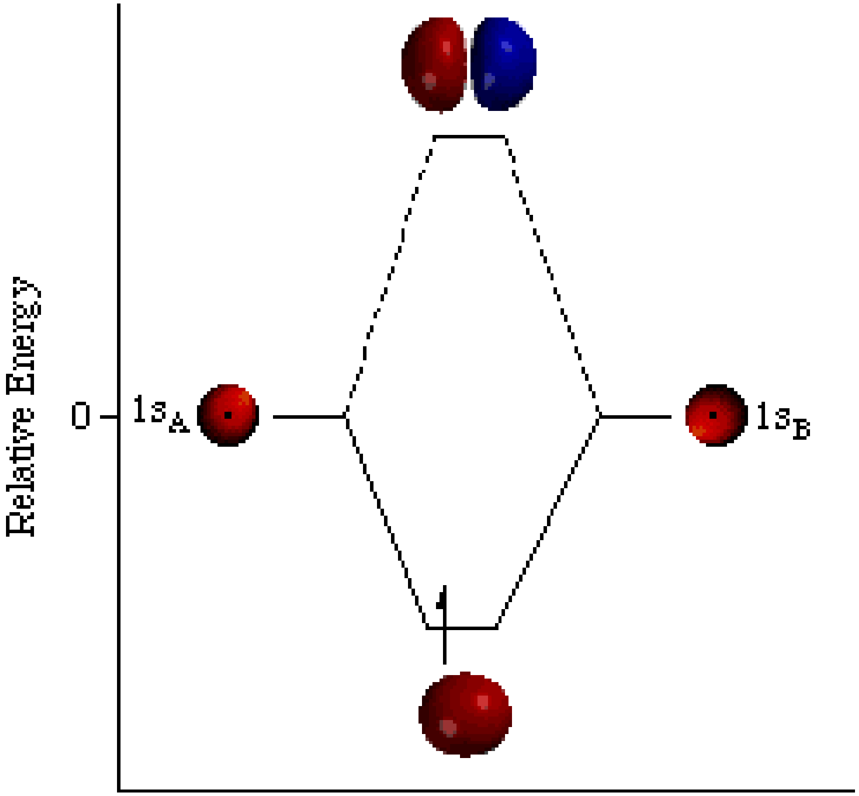
$$\Downarrow$$

$$E_1 = \frac{\alpha + \beta}{1 + S} \qquad C_1 = C_2 = \frac{1}{\sqrt{2(1+S)}}$$

$$E_2 = \frac{\alpha - \beta}{1 - S} \qquad C_1 = -C_2 = \frac{1}{\sqrt{2(1-S)}}$$

H_2^+ molecule ion: minimal basis

Orbital diagram:



From this calculation: $R_e \approx 2.5\,\mathrm{bohr}$. How good is this?

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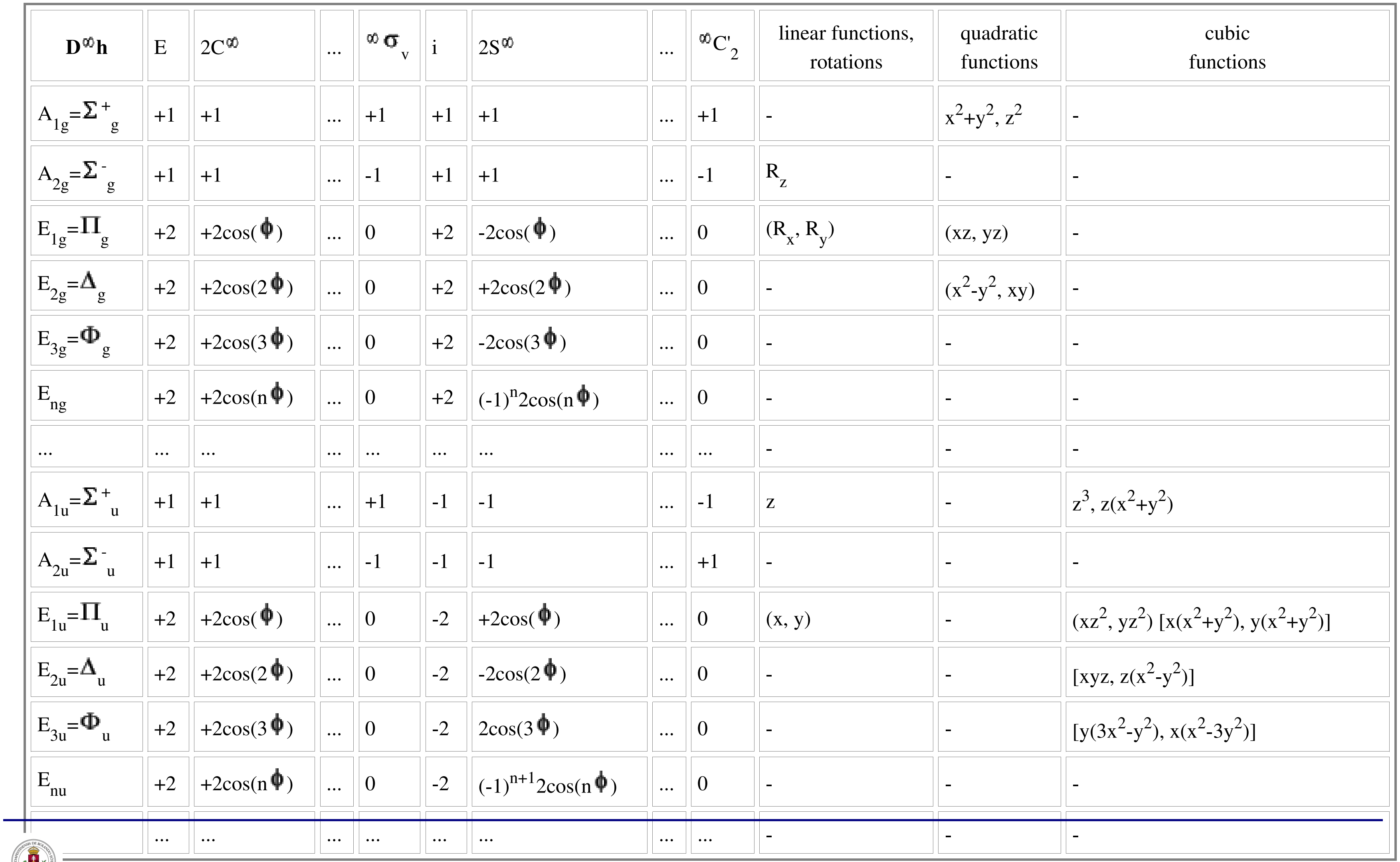
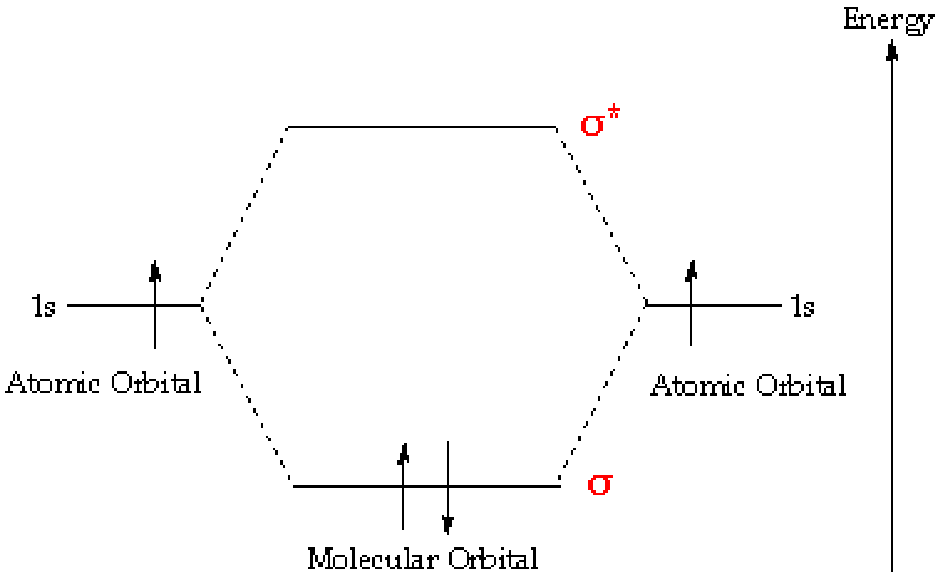
Electronic structure of diatomic molecules

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



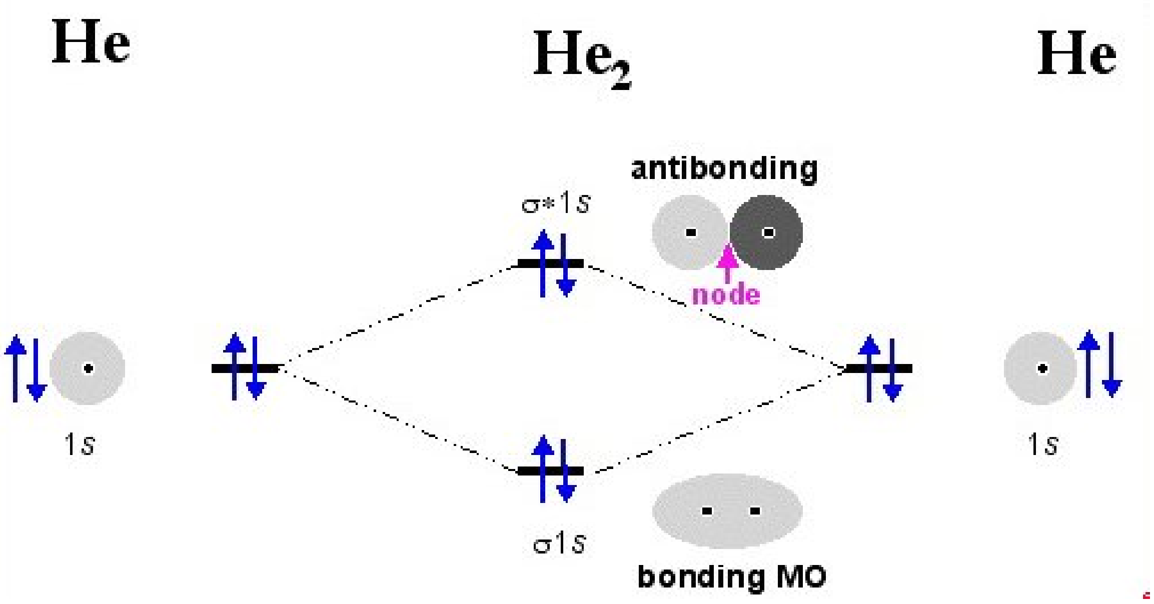
Configuration: $1\sigma_g^2$

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



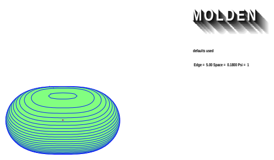
Configuration: $1\sigma_g^2 1\sigma_u^2$

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

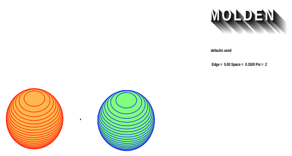
Notation for the state: ${}^1\Sigma_g^+$

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

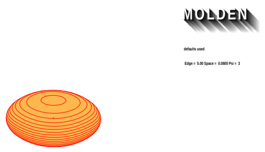
Diatomic molecules: molecular orbitals



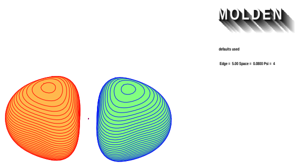
$1\sigma_g$



$1\sigma_u$



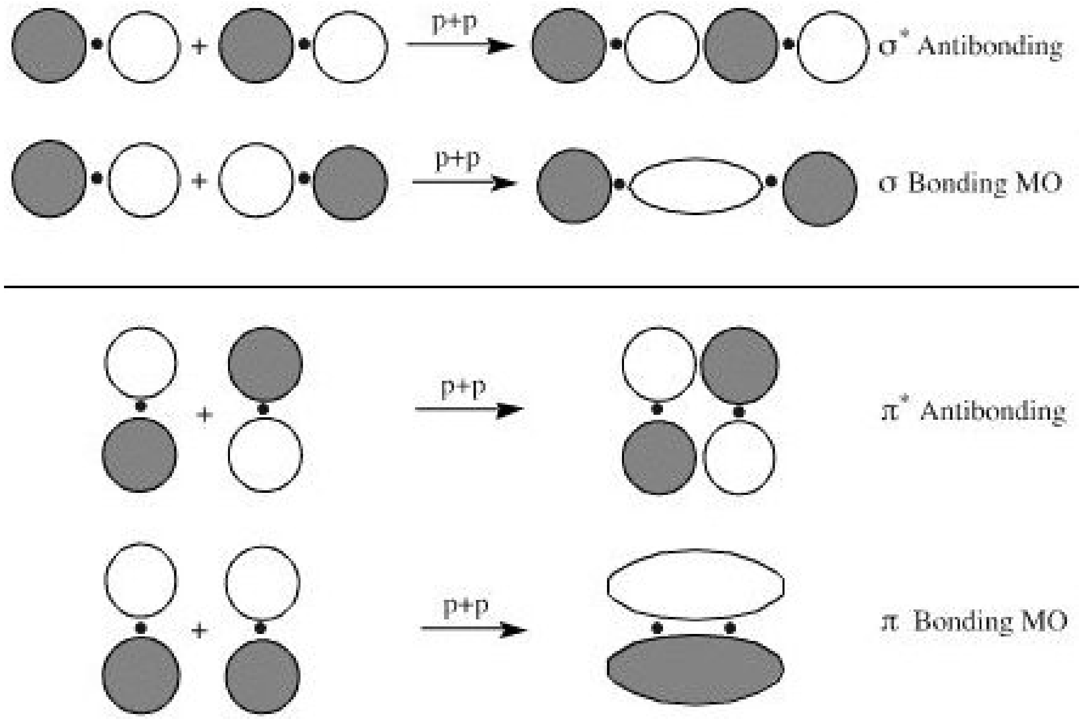
$2\sigma_g$



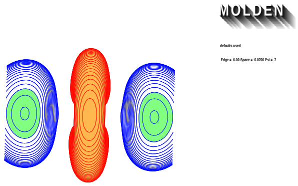
$2\sigma_u$

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):

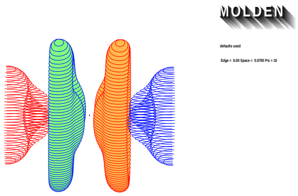


Diatomic molecules: molecular orbitals



$1\pi_u$

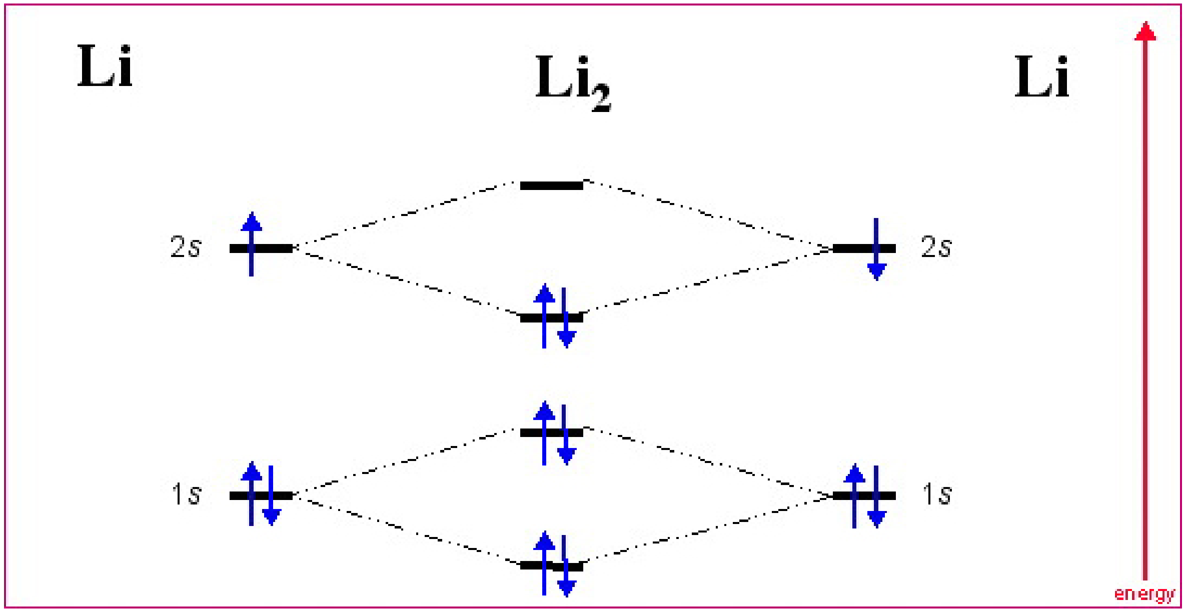
$3\sigma_g$



$1\pi_g$

$3\sigma_u$

Li_2 molecule



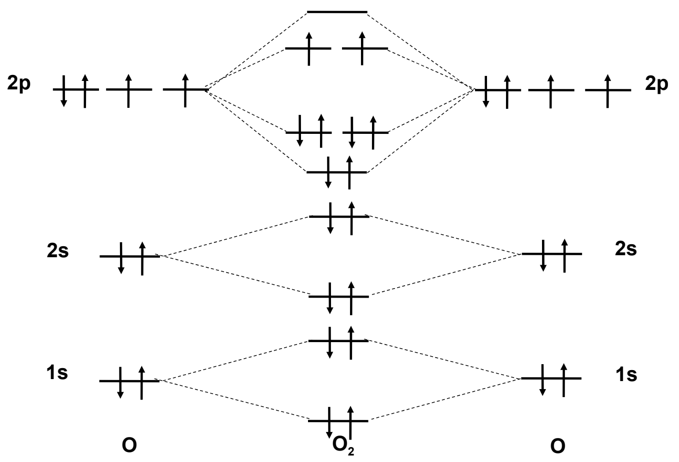
Configuration: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2$

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



Az oxigénmolekula elektronszerkezete

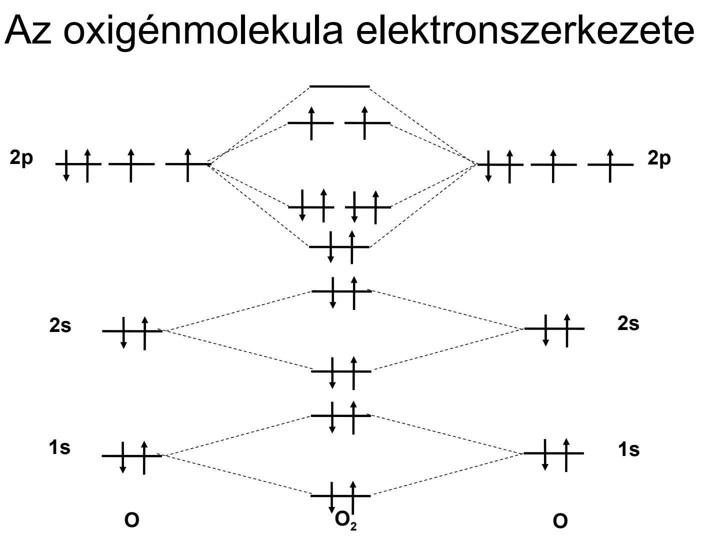
Configuration: $1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 3\sigma_g^2\ 1\pi_g^2$, i.e. open shell

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



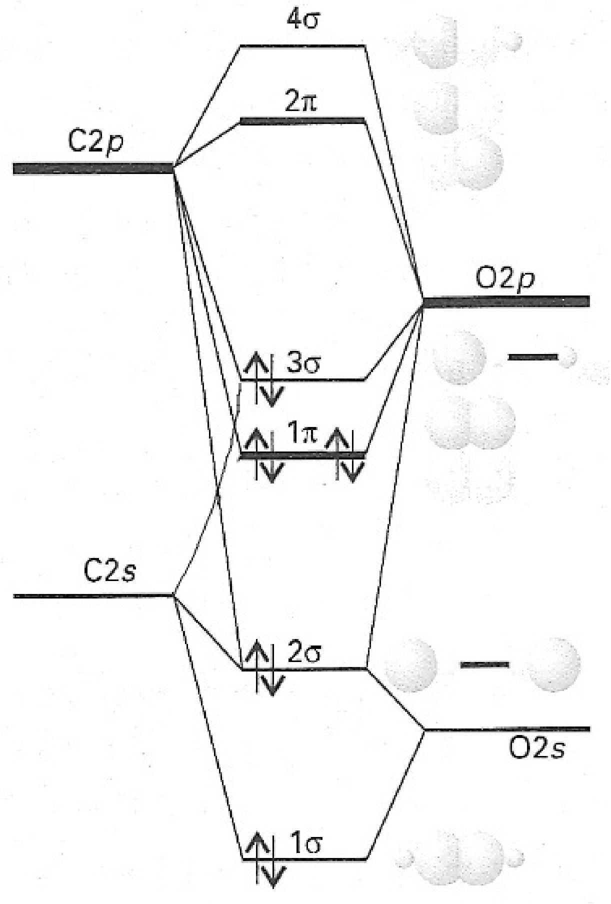
Configuration: $1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 3\sigma_g^2\ 1\pi_g^2$, i.e. open shell

Bond-order: ≈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:



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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[4]

$$\phi_i = \sum_a C_{ai}\chi_a$$

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: $1s_{\mathrm{A}}$, $1s_{\mathrm{B}}$

O: 1s, 2s, $2p_{\mathrm{x}}$, $2p_{\mathrm{y}}$, $2p_{\mathrm{z}}$

---

[4] we show the results of Hartree-Fock-Roothan calculations

Consideration of symmetry for water molecule

Basis of the representation: H: $1s_{\mathrm{A}}$, $1s_{\mathrm{B}}$, O: 1s, 2s, $2p_{\mathrm{x}}$, $2p_{\mathrm{y}}$, $2p_{\mathrm{z}}$

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

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

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

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

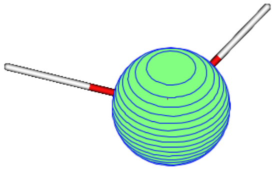
$$n_{\mathrm{B1}} = \frac{1}{4}(1{\cdot}1{\cdot}7 + 1{\cdot}(-1){\cdot}1 + 1{\cdot}1{\cdot}5 + 1{\cdot}(-1){\cdot}3) = 2$$

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

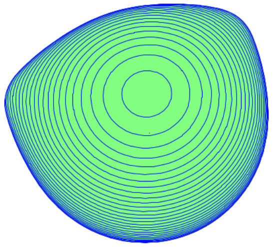
Thus: Γ_{basis}=4 $A_1 \oplus 2\ B_1 \oplus B_2$

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

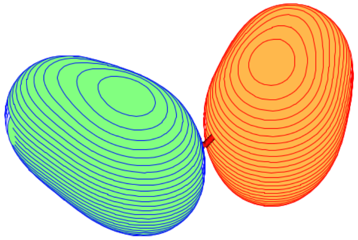
Bonding orbitals of water



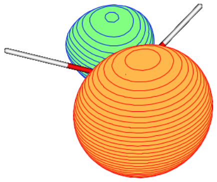
$1a_1 : 1s$



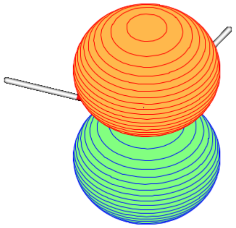
$2a_1 : 2s(-2p_z)+1s_A+1s_B$



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



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

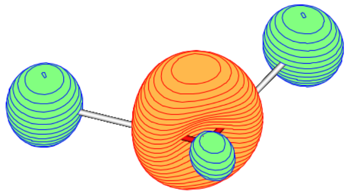


$1b_2 : 2p_y$

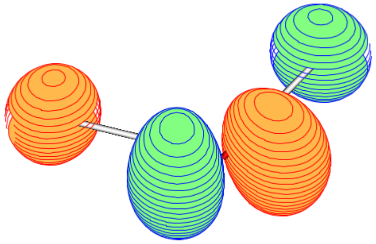
Configuration: $(1\mathrm{a}_1)^2$ $(2\mathrm{a}_1)^2$ $(1\mathrm{b}_1)^2$ $(3\mathrm{a}_1)^2$ $(1\mathrm{b}_2)^2$

State: $^1\mathrm{A}_1$ (orbitals are fully occupied ⇒ total symmetric singlet state)

Anti-bonding orbitals of water



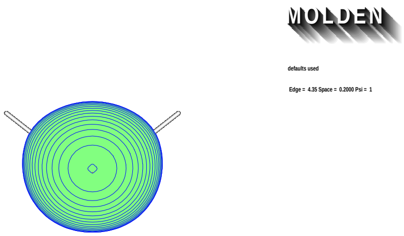
$4a_1 : 2s + 2p_z - 1s_A - 1s_B$

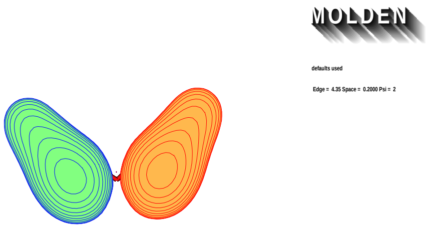


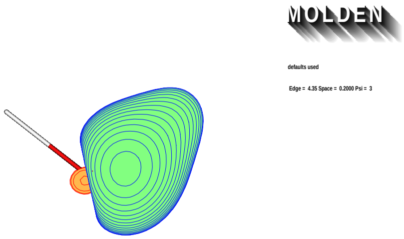
$2b_1 : 2p_x$

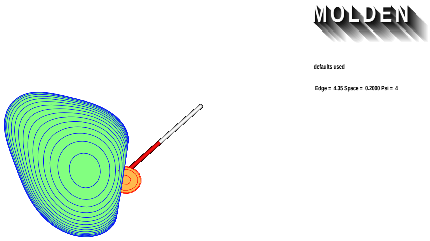
Localized orbitals of water

$2a_1$ $1b_1$







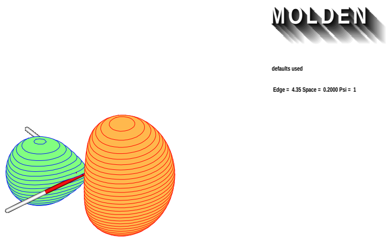


$2a_1 - 1b_1$ $2a_1 + 1b_1$

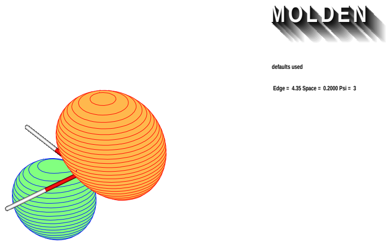
In this procedure we obtain two bonding orbitals corresponding to chemical intuition.

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.

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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, 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:

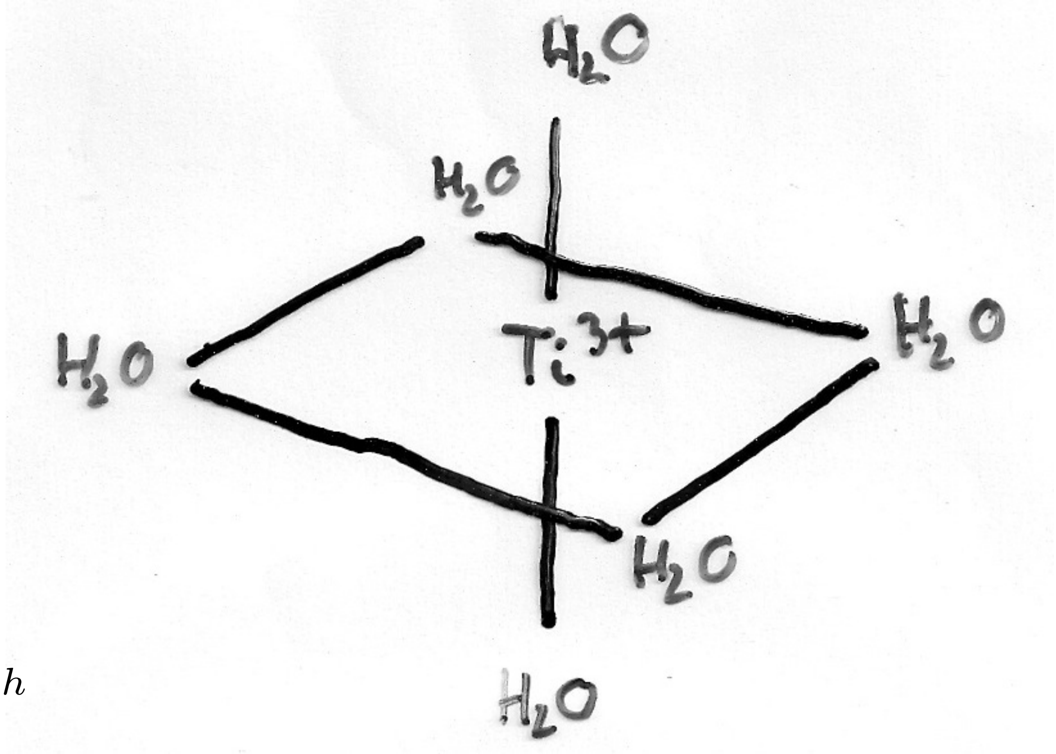
- the ligands (bound by electrostatic interaction) perturb the electronic structure of the central atom (ion)
- electrons of the ligands are absolutely not considered

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!!

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



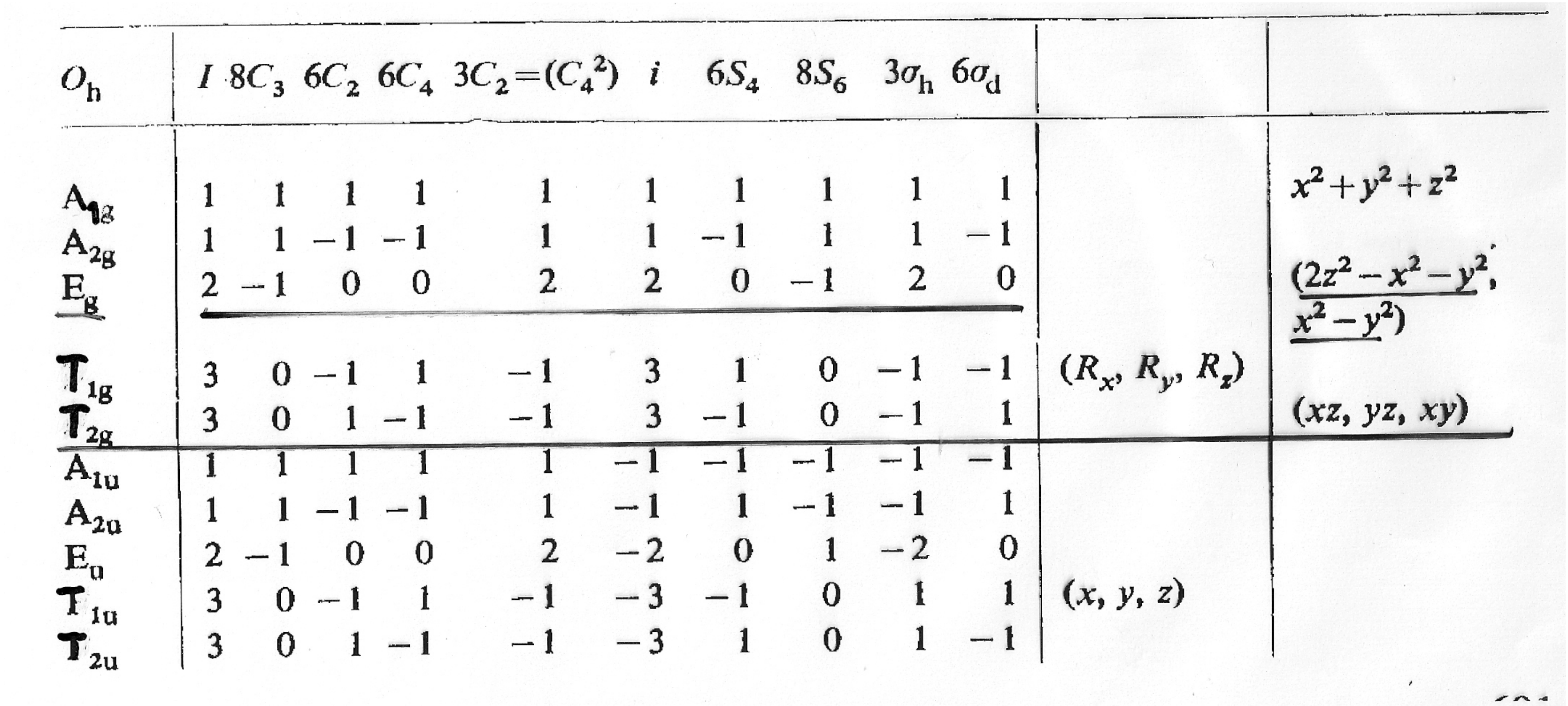
Pointgroup: O_h

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

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

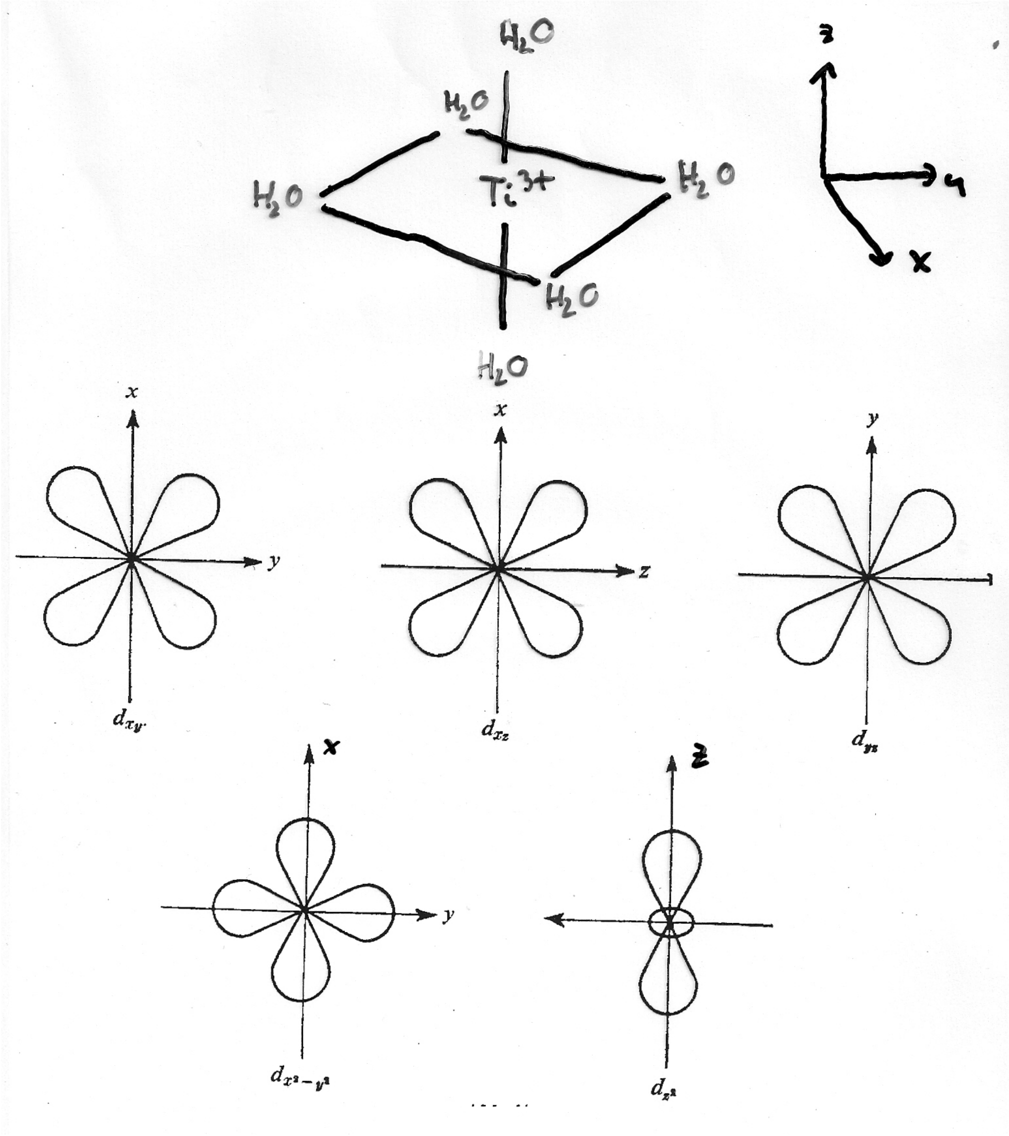
$$T_{2g} : d_{z^2}, d_{x^2-y^2} \qquad E_g : d_{xy}, d_{xz}, d_{yz}$$

Character table of pointgroup O_h



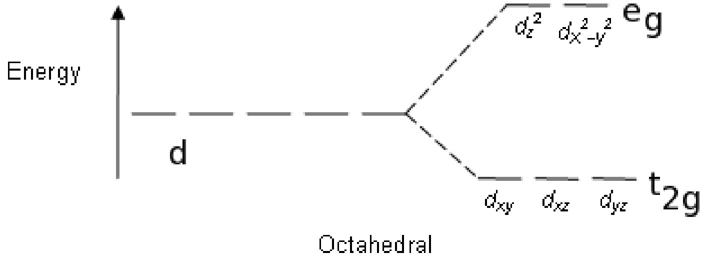
O_h	I	$8C_3$	$6C_2$	$6C_4$	$3C_2=(C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz,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

$\mathbf{Ti}^{3+}(\mathbf{H}_2\mathbf{O})_6$



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

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 → bonding and anti-bonding orbitals are formed
- symmetry is again important: which orbitals do mix?

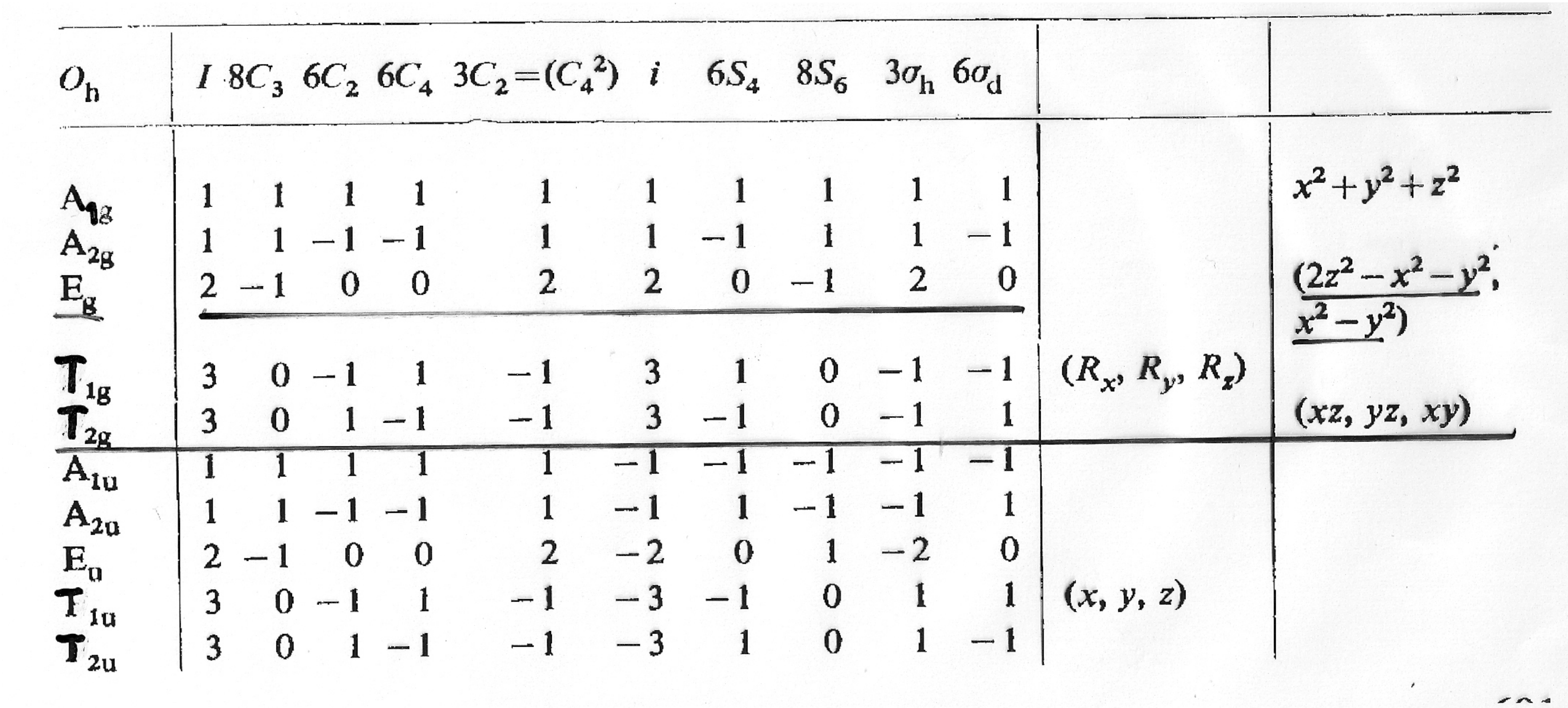
Basis:

- 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



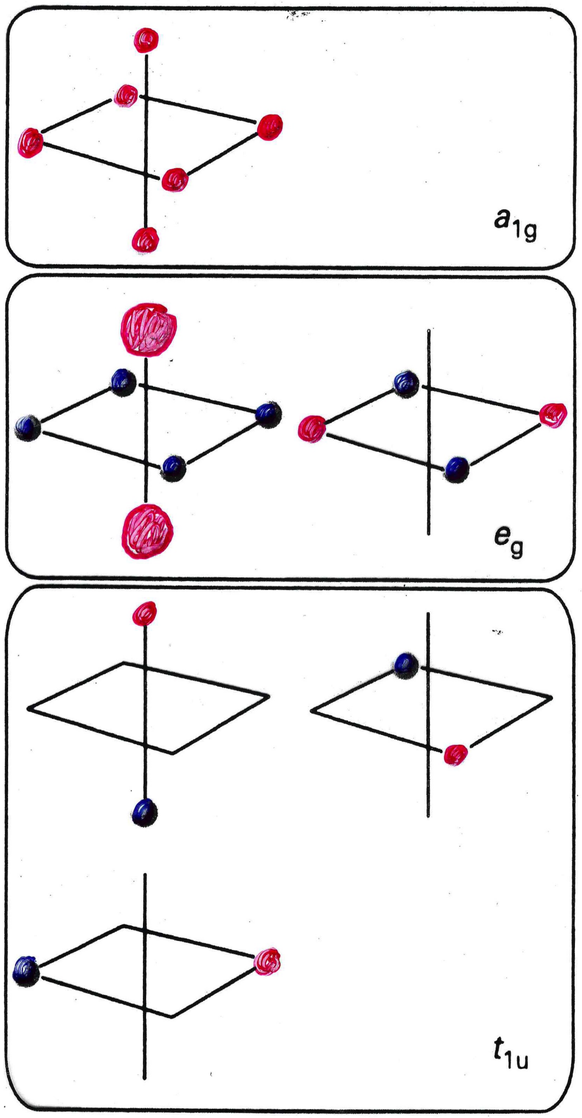
O_h	I	$8C_3$	$6C_2$	$6C_4$	$3C_2=(C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz,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

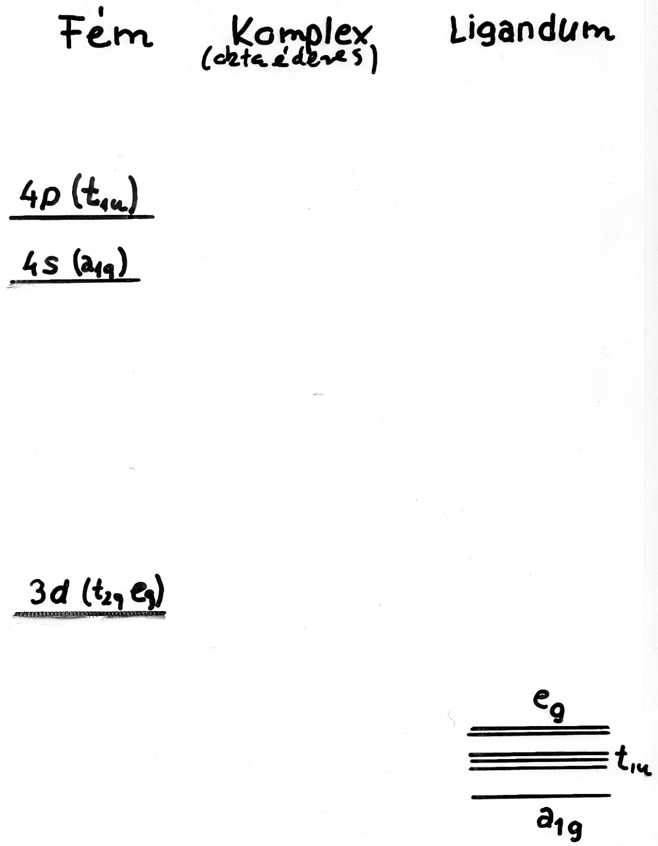
Basis:

- atom (ion): 3d, 4s, 4p orbitals $\rightarrow$
  $\Gamma(3d) = T_{2g} \oplus E_g$
  $\Gamma(4s) = A_{1g}$
  $\Gamma(4p) = T_{1u}$
- ligand:
  $\Gamma(\lambda_1, ...\lambda_6) = A_{1g} \oplus E_g \oplus T_{1u}$

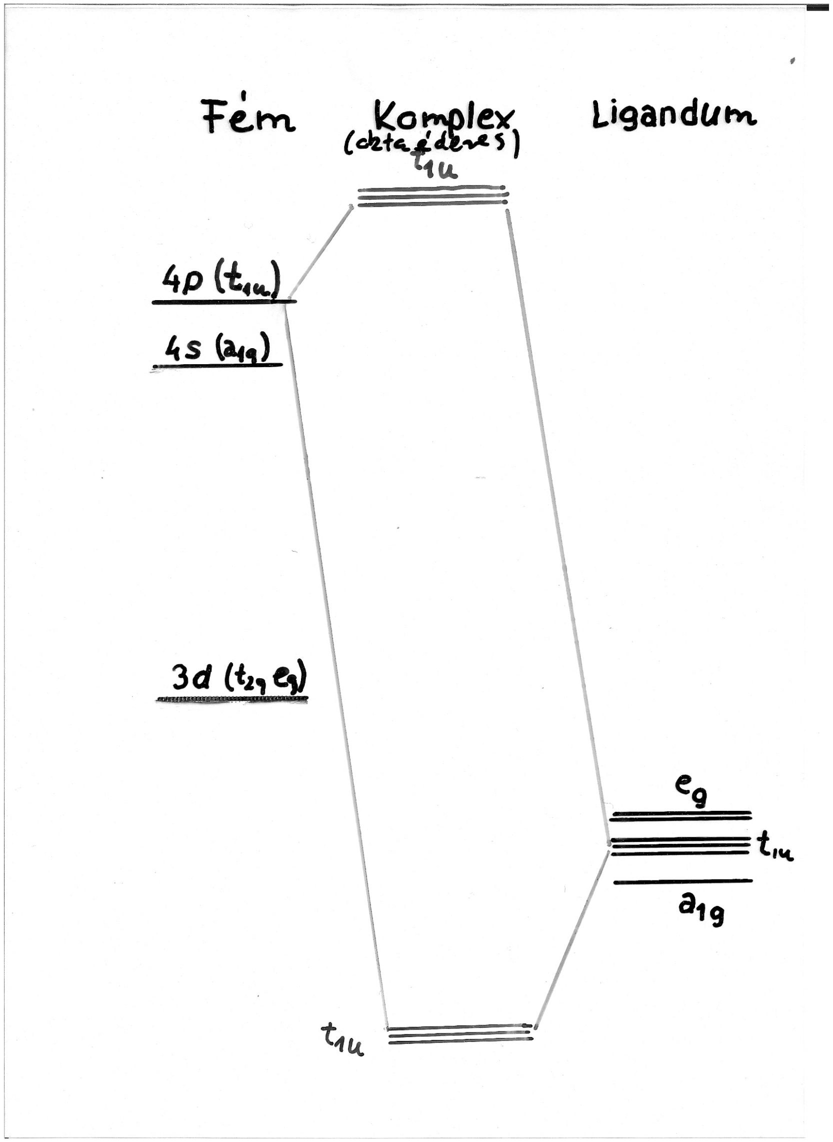
$Ti^{3+}(H_2O)_6$ – orbitals of the waters



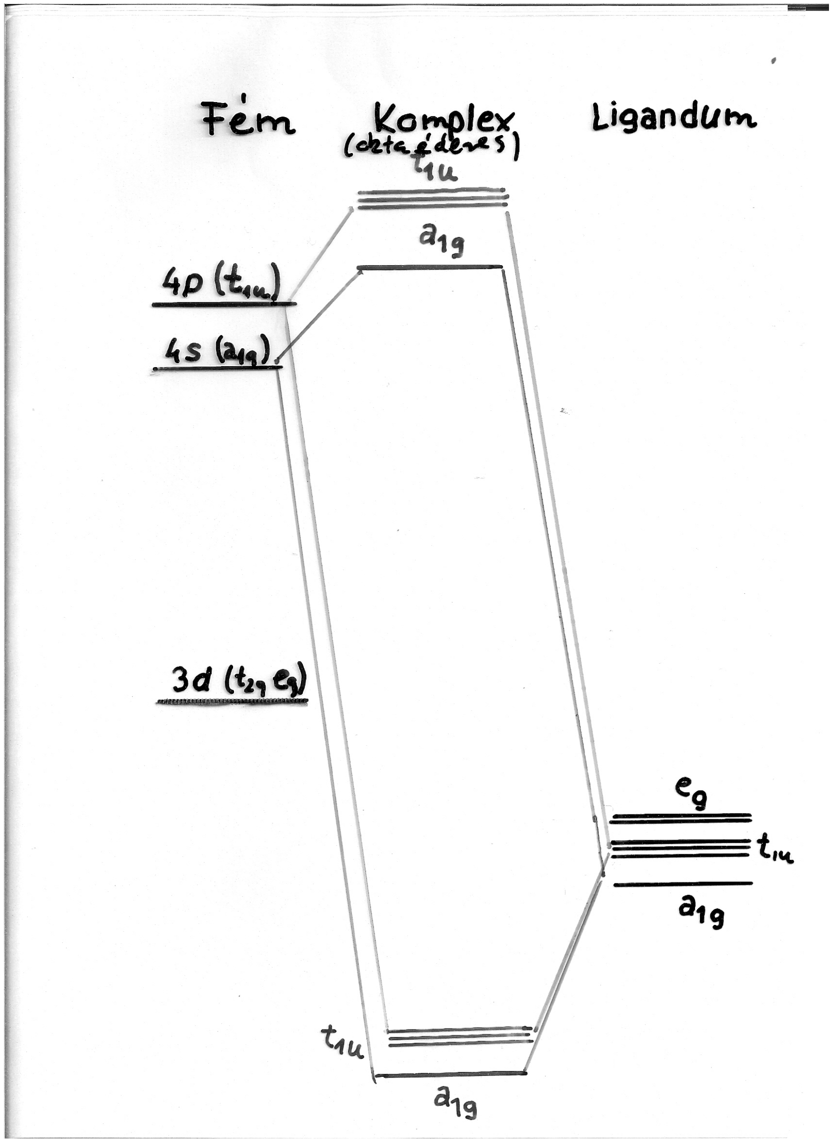
$Ti^{3+}(H_2O)_6$ – MO theory



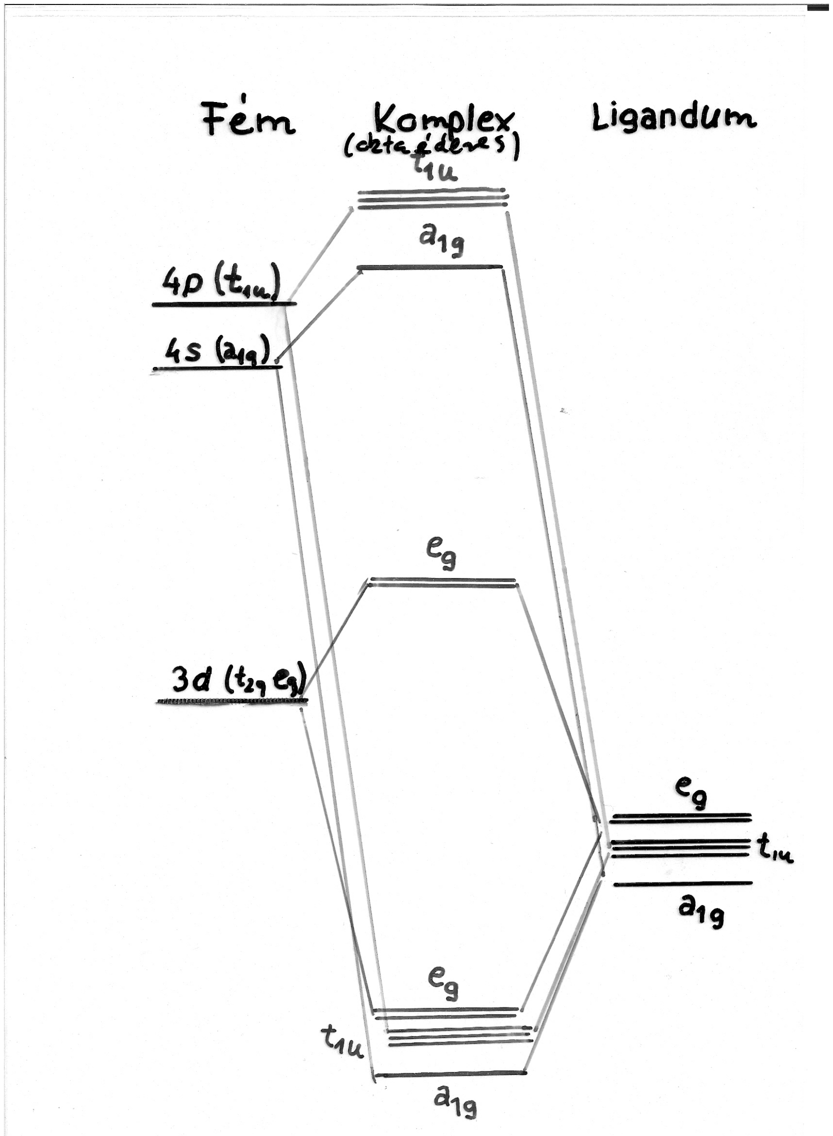
$Ti^{3+}(H_2O)_6$ – MO theory



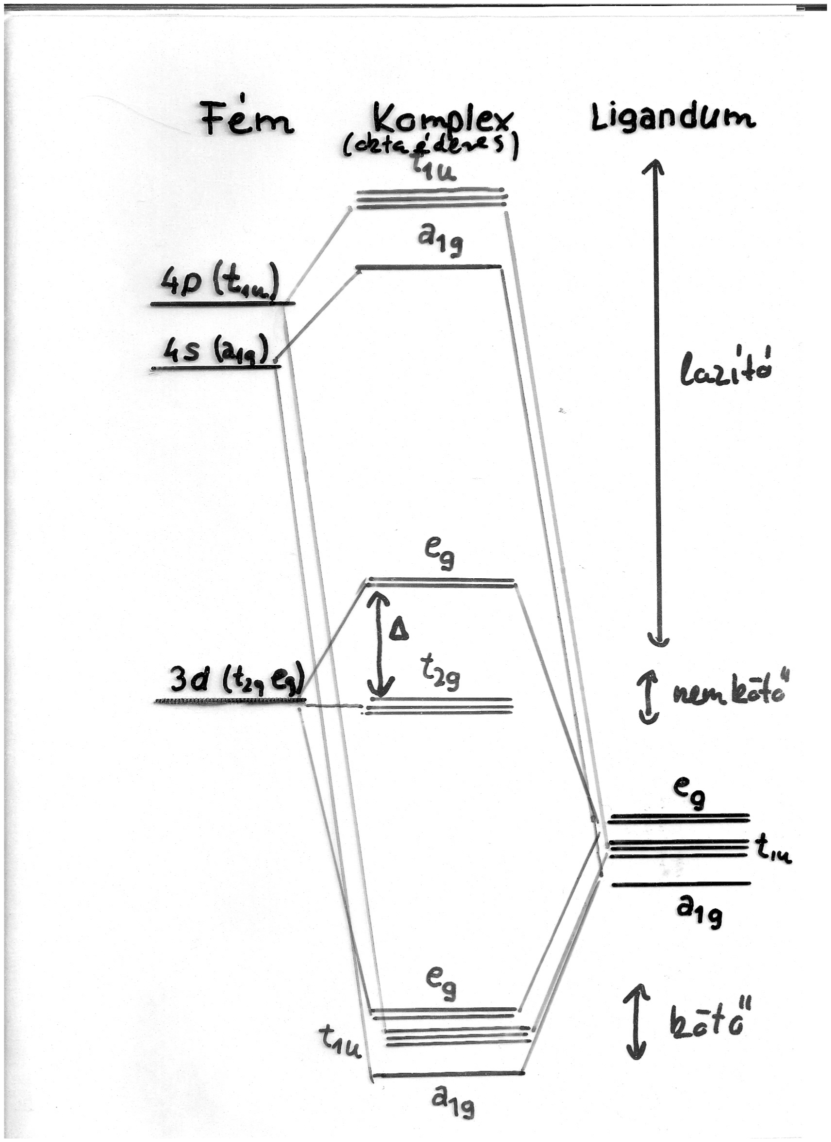
$Ti^{3+}(H_2O)_6$ – MO theory



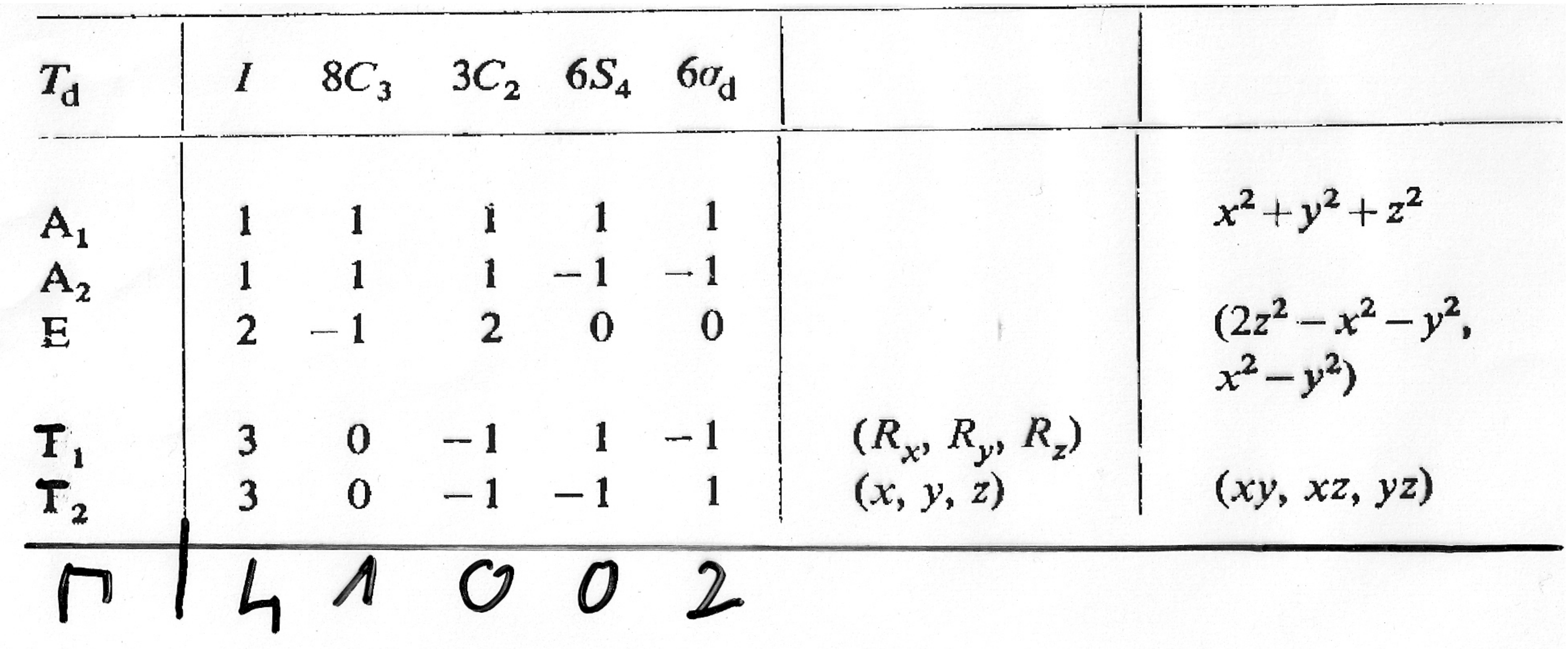
$Ti^{3+}(H_2O)_6$ – MO theory



$Ti^{3+}(H_2O)_6$ – MO theory

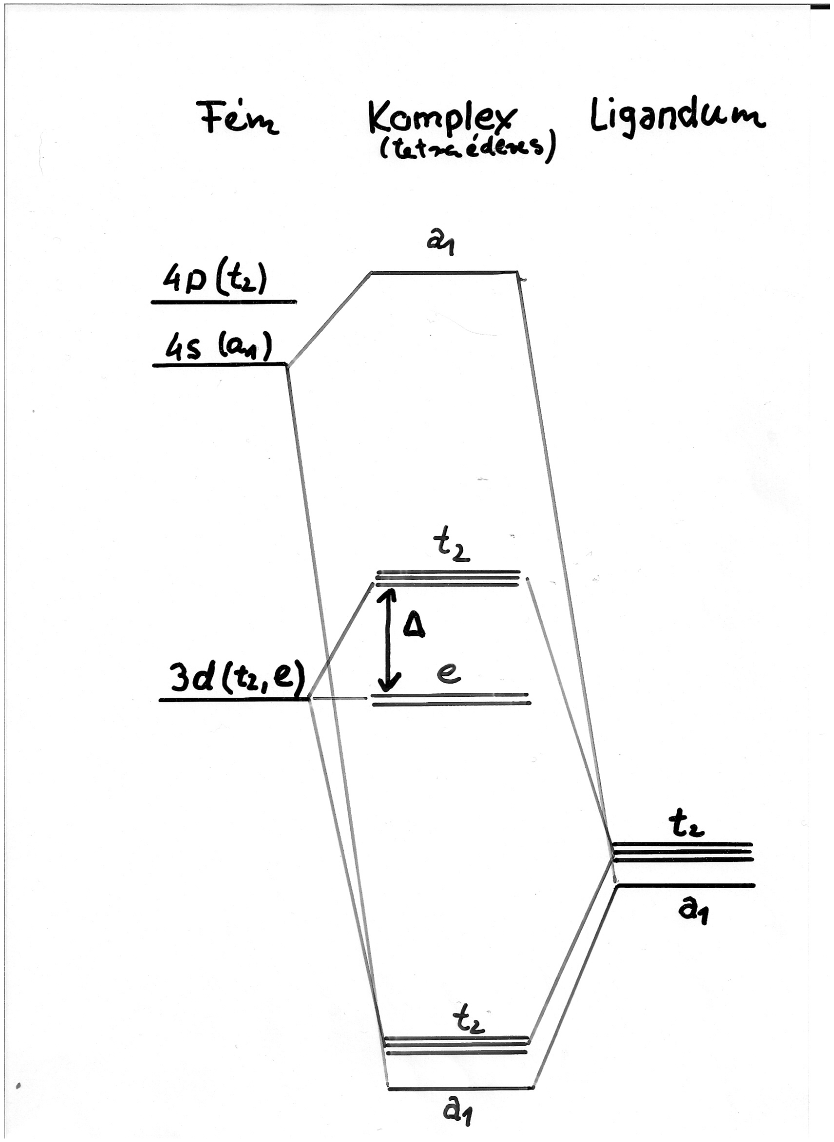


Character table of pointgroup $\mathrm{T_d}$



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



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Methods

The Independent Particle Approximation (IPA)

Hartree-method: Approximation of the wave function in a product form

$$\underbrace{\Psi(r_1, r_2, \ldots, r_n)}_{\text{wave function}} = \underbrace{\phi_1(r_1) \cdot \phi_2(r_2) \ldots \cdot \phi_n(r_n)}_{\text{product of spin orbitals}}$$

spinorbital:

$$\begin{aligned} \varphi_i(i) = \varphi_i(x_i, y_i, z_i, \sigma_i) &= u(x_i, y_i, z_i)\alpha(\sigma_i) \\ \text{or} &= \underbrace{u(x_i, y_i, z_i)}_{\text{spatial orbital}}\beta(\sigma_i) \end{aligned}$$

The Independent Particle Approximation (IPA)

Hartree-method: Approximation of the wave function in a product form

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In this case the Schrödinger equation reduces to one-electron equations:

$$\begin{aligned} \hat{H}\Psi = E\Psi \quad \Rightarrow \quad & \hat{h}_1(1)\varphi_1(1) = \varepsilon_1\varphi_1(1) \\ & \hat{h}_2(2)\varphi_2(2) = \varepsilon_2\varphi_2(2) \\ & \ldots \\ & \hat{h}_n(n)\varphi_n(n) = \varepsilon_n\varphi_n(n) \end{aligned}$$

One n-electron equation ⇒ system of n one-electron equations

$$\hat{h}_i \quad \rightarrow \quad \hat{h}_1^{eff} = -\frac{1}{2}\Delta_i - \frac{Z_A}{r_{iA}} + V_i^{eff}$$

where V_i^{eff} is the interaction of electron i with all other electrons.

Slater-determinant

According to the *Pauli principle*, the wave function of the electrons is anti-symmetric with respect to the interchange of two electrons:

$$\hat{P}_{12}\Psi(1,2,...,n) = -\Psi(1,2,...,n)$$

To fullfil anti-symmetry, instead of product wave function we have to use determinant (*Slater determinant*):

$$\Psi(1,2,...,n) = \frac{1}{\sqrt{n}}\begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \cdots & \varphi_n(1) \\ \varphi_1(2) & \varphi_2(2) & \cdots & \varphi_n(2) \\ \vdots & \vdots & \vdots & \vdots \\ \varphi_1(n) & \varphi_2(n) & \cdots & \varphi_n(n) \end{vmatrix}$$

$$= \frac{1}{\sqrt{n!}}\left(\varphi_1(1)\cdot\varphi_2(2)\cdot ... \cdot\varphi_n(n) - \varphi_1(2)\cdot\varphi_2(1)\cdot ... \cdot\varphi_n(n) + ...\right)$$

Expectation value of the energy with determinant wave function

Split up the Hamiltonian into zero-, one- and two-electron parts:

$$\hat{H} = \underbrace{-\sum_i \frac{1}{2}\Delta_i - \sum_i \sum_A \frac{Z_A}{r_{iA}}}_{\hat{H}_1 =: \sum_i \hat{h}(i)} + \underbrace{\sum_{i>j} \frac{1}{r_{ij}}}_{\hat{H}_2} + \underbrace{\sum_{A<B} \frac{Z_A Z_B}{r_{AB}}}_{\hat{H}_0}$$

The expression for the energy (Ψ stands for a determinant):

$$E = \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle = \left\langle \Psi \middle| \sum_i \hat{h}_i \middle| \Psi \right\rangle + \left\langle \Psi \middle| \sum_{i>j} \frac{1}{r_{ij}} \middle| \Psi \right\rangle + H_0$$

Expectation value of the energy with determinant wave function

$$E = \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle = \left\langle \Psi \middle| \sum_i \hat{h}_i \middle| \Psi \right\rangle + \left\langle \Psi \middle| \sum_{i<j} \frac{1}{r_{ij}} \middle| \Psi \right\rangle + H_0$$

One can derive that

$$E \quad = \quad \sum_i H_{ii} + \sum_{i>j} (J_{ij} - K_{ij}) + H_0$$

- $H_{ii} = \int \phi_i | \hat{h} | \phi_i \; dv_1$
  – one-electron contribution of electron i including the kinetic energy and the attraction to the nuclei;

- $J_{ij} = \int\int \phi_i(1)\phi_j(2) \frac{1}{r_{12}} \phi_i(1)\phi_j(2) \; dv_1 \; dv_2$
  – Coulomb integral representing the electron-electron interaction;

- $K_{ij} = \int\int \phi_i(1)\phi_j(2) | \frac{1}{r_{12}} | \phi_j(1)\phi_i(2) \; dv_1 \; dv_2$
  – exchange integral, consequence of the anti-symmetry.

The Hartree-Fock method

Wave function: determinant:

$$\Psi(1,2,...,n) \quad = \quad \frac{1}{\sqrt{n!}}\begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \cdots & \varphi_n(1) \\ \varphi_1(2) & \varphi_2(2) & \cdots & \varphi_n(2) \\ \vdots & \vdots & \vdots & \vdots \\ \varphi_1(n) & \varphi_2(n) & \cdots & \varphi_n(n) \end{vmatrix}$$

We look for the „*the best*" determinant!

- Since the determinant consist of orbitals, we have to obtain those orbitals which result in „*the best*" determinant.

What is „*the best*" ?

- According to the variation principle, the best determinant gives the lowest energy.

The Hartree-Fock method

Expression of the energy:

$$E = \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle = \sum_i H_{ii} + \sum_{i>j} \left(J_{ij} - K_{ij} \right),$$

which is the *functional* of the orbitals ($\{\phi_i, i = 1, ..., n\}$). Therefore we have to look for the minimum of this functional.

Required condition: orbitals are orthonormal:

$$\left\langle \phi_i \middle| \phi_j \right\rangle = S_{ij} = \delta_{ij} \quad \forall\, i, j \quad \rightarrow \quad \left\langle \Psi \middle| \Psi \right\rangle = 1$$

Therefore the functional to be varied is (ε's are Lagrange-multiplicators):

$$\begin{aligned} G &= E - \sum_i \sum_j \varepsilon_{ij} \left(S_{ij} - \delta_{ij} \right) \\ \delta G &= \sum_i \delta H_{ii} + \frac{1}{2} \sum_{ij} \left(\delta J_{ij} - \delta K_{ij} \right) - \sum_{ij} \varepsilon_{ij}\, \delta S_{ij} = 0 \end{aligned}$$

The Hartree-Fock method

G functional has extremum for those orbitals which fulfill:

$$\left[\hat{h} + \sum_j \left(\hat{J}_j - \hat{K}_j\right)\right] \Big|\phi_i\Big\rangle = \sum_j \varepsilon_{ij} \Big|\phi_j\Big\rangle \qquad i = 1, ..., n$$

By defining the operator:

$$\hat{f} := \hat{h} + \sum_j \left(\hat{J}_j - \hat{K}_j\right) = \hat{h} + \hat{U}^{HF}$$

we arrive at the following equation:

$$\hat{f}\phi_i = \varepsilon_i \, \phi_i \qquad i = 1, ..., n$$

This is the so called *Hartree-Fock equation*.
The orbitals satisfying the *Hartree-Fock-equation* are called *canonical orbitals*.

The Hartree-Fock-Roothaan method

Above we have derived the HF equations which, as solution to them, result in orbitals (one-electron wave functions):

$$\hat{f}\phi_i = \varepsilon_i \, \phi_i \qquad\qquad i = 1, ..., n$$

Further approximation: look for the orbitals as the linear combination of atomic basis function (*LCAO-MO* approximation):

$$\phi_i = \sum_a C_{ai} \chi_a$$

with χ_a standing for the atomic orbitals. Inserting this into the HF equations:

$$\hat{f} \sum_a C_{ai} \chi_a \quad = \quad \varepsilon_i \sum_a C_{ai} \chi_a$$

The Hartree-Fock-Roothaan method

$$\hat{f}\sum_a C_{ai}\chi_a = \varepsilon_i \sum_a C_{ai}\chi_a \qquad /\langle\chi_b|$$

$$\sum_a C_{ai}\underbrace{\left\langle \chi_b \middle| \hat{f} \middle| \chi_a \right\rangle}_{F_{ba}} = \varepsilon_i \sum_a C_{ai}\underbrace{\left\langle \chi_b \middle| \chi_a \right\rangle}_{S_{ba}}$$

$$\underline{\underline{F}}\,\underline{C}_i = \varepsilon_i\,\underline{\underline{S}}\,\underline{C}_i$$

or by gathering all vectors $\underline{C}_i$ into a matrix:

$$\underline{\underline{F}}\,\underline{\underline{C}} = \underline{\underline{\varepsilon}}\,\underline{\underline{S}}\,\underline{\underline{C}}$$

This is a matrix eigenvalue equation (Hartree-Fock-Roothaan equation).

Interpretation of the results of the Hartree-Fock method

The orbitals (ϕ_i) are obtained from the Hartree-Fock equations:

$$\hat{f}\phi_i = \varepsilon_i \, \phi_i$$

In praxis, the orbitals are linear combination of atomic orbitals:

$$\phi_i = \sum_a C_{ai}\chi_a$$

The wave function of the system should be built from the orbitals:

$$\Psi = \frac{1}{\sqrt{n!}} \det(\phi_1, \cdots, \phi_n)$$

Interpretation of the results of the Hartree-Fock method

The density matrix

According to the quantum mechanics, instead of the wave function, it is the probability density, which bears physical meaning

$$\Psi^*(\underline{r}_1, \underline{r}_2, \cdots, \underline{r}_n)\Psi(\underline{r}_1, \underline{r}_2, \cdots, \underline{r}_n)dv_1 dv_2 \cdots dv_n$$

The probability of finding an electron at point $\underline{r}$ (*electron density*):

$$\rho(\underline{r}) \quad = \quad n\int\int\cdots\int \Psi^*(\underline{r}_1, \underline{r}_2, \cdots, \underline{r}_n)\Psi(\underline{r}_1, \underline{r}_2, \cdots, \underline{r}_n)dv_2 dv_3 \cdots dv_n$$

In front of the integral the multiplier n is used to add up the contribution of all undistinguishable electrons.

Interpretation of the Hartree-Fock results

In case of determinant wave function, the electron density can be given as the sum of the density of the individual electrons (c.f. Independent Particle Approximation):

$$\begin{aligned}
\rho(\underline{r}) &= \sum_i^n \phi_i(\underline{r})\phi_i(\underline{r}) \\
&= \sum_i^n \sum_a C_{ai}\chi_a(\underline{r}) \sum_b C_{bi}\chi_b(\underline{r}) \\
&= \sum_a \sum_b \underbrace{\sum_i^n C_{ai}C_{bi}}_{P_{ab}} \chi_a(\underline{r})\chi_b(\underline{r})
\end{aligned}$$

In the second row of the above equation, the orbitals have been expanded on the atomic orbitals, in the last, the *density matrix* $\underline{\underline{P}}$ has been introduced.

Interpretation of the Hartree-Fock results

Population analysis according to Mulliken

From the above formula it is clear that by integrating the electron density over the whole space, we obtain the number of electrons:

$$n = \int \rho(\underline{r})dv = \sum_a \sum_b P_{ab} \int \chi_a(\underline{r})\chi_b(\underline{r})dv$$
$$= \sum_a \sum_b P_{ab} S_{ab}$$

According to the last equation, the electron density can be distributed according to contribution by the individual basis functions:

- $P_{aa}S_{aa} = P_{aa}$ gives the charge associated with the basis function χ_a
- $P_{ab}S_{ab}$ gives the charge associated with the overlap $\chi_a\chi_b$

Interpretation of the Hartree-Fock results

From this contributions one can obtain:

- $\sum_{a\in A} P_{aa}S_{aa} = \sum_{a\in A} P_{aa}$, which is the charge on atom A
- $\sum_{a\in A}\sum_{b\in B} P_{ab}S_{ab}$, which gives the charge associated with the overlap of atoms A and B (NOT bond-order!!)

Finally, the total (Mulliken) charge on atom A can be obtained if we add all contributions associated with atom A:

$$\sum_{a\in A}\sum_{b} P_{ab}S_{ab} = \sum_{a\in A} (\underline{\underline{P}}\ \underline{\underline{S}})_{aa}$$

Interpretation of the Hartree-Fock results

Orbital energy, total energy

The eigenvalue of the *Fock-operator* appearing in the Hartree-Fock equation (ε_i) is the orbital energy:

$$\varepsilon_i = \left\langle \phi_i \middle| \hat{f} \middle| \phi_i \right\rangle = \left\langle \phi_i \middle| \hat{h} + \sum_j (\hat{J}_j - \hat{K}_j) \middle| \phi_i \right\rangle = H_{ii} + \sum_j (J_{ij} - K_{ij})$$

The sum of the orbital energies of all occupied orbitals *is not equal* to the total energy:

$$\begin{aligned} E &\neq \sum_i \varepsilon_i = \sum_i H_{ii} + \sum_i \sum_j (J_{ij} - K_{ij}) \\ E &= \sum_i H_{ii} + \frac{1}{2} \sum_i \sum_j (J_{ij} - K_{ij}) = \sum_i \varepsilon_i - \frac{1}{2} \sum_i \sum_j (J_{ij} - K_{ij}) \end{aligned}$$

Thus one has to subtract the electron-electron interaction since it appears twice in the sum of the orbital energies.

Interpretation of Hartree-Fock results

Ionization energy, Koopmans' theorem

Consider a closed shell system (M), and remove an electron from it (M^+). We assume that the orbitals do not change in this process:

$$\begin{aligned} E_M &= 2H_{11} + 2H_{22} + 4J_{12} - 2K_{12} + J_{11} + J_{22} \\ E_{M^+} &= 2H_{11} + H_{22} + 2J_{12} - K_{12} + J_{11} \\ \Delta E &= E_{M^+} - E_M = -H_{22} - 2J_{12} + K_{12} - J_{22} = -\varepsilon_2 \end{aligned}$$

Interpretation of Hartree-Fock results

The ionization energy is therefore equals the negative of the energy of the orbitals from where the electron has been removed (*Koopmans' theorem*):

$$IP = -\varepsilon_i$$

This approximation works since the errors of the two approximations cancel each other:

- we use determinental wave function (the so called electron correlation is not considered);

- orbitals of the ions are not optimized (no orbital relaxation).

Interpretation of Hartree-Fock results

The ionization energy is therefore equals the negative of the energy of the orbitals from where the electron has been removed (*Koopmans' theorem*):

$$IP \quad = \quad -\varepsilon_i$$

This approximation works since the errors of the two approximations cancel each other:

- we use determinental wave function (the so called electron correlation is not considered);

- orbitals of the ions are not optimized (no orbital relaxation).

Similarly, one could calculate electron affinity:

$$EA = E_{M^-} - E_M = \varepsilon_a$$

this is, however, a much worse approximation.

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Density Functional Theory (DFT)

Wave function vs. density

The wave function is a 4N dimensional function which determines all properties of the system:

$$\Psi \quad = \quad \Psi\left(\tau_1, \tau_2, \ldots, \tau_N\right) \qquad \tau_i = (\mathbf{r}_i, \sigma_i)$$

$$E = \langle \Psi | \hat{H} | \Psi \rangle \quad \text{i.e.} \quad E = E[\Psi]$$

On the other hand, the density is a three dimensional function:

$$\rho(\mathbf{r}_1) = N \cdot \int\int \ldots \int \Psi\left(\tau_1, \tau_2, \ldots, \tau_N\right)^* \; \Psi\left(\tau_1, \tau_2, \ldots, \tau_N\right) d\sigma_1 d\tau_2 \cdots d\tau_N,$$

which gives the probability of finding a single electron at a given point.

The density can be calculated from the wave function:

$$\Psi \quad \rightarrow \quad \rho(\mathbf{r})$$

Intuitively, one would assume that it also gives all properties of the systems:

$$\rho \overset{?}{\rightarrow} E \quad \text{i.e.} \quad E \overset{?}{=} E[\rho]$$

Splitting up of the Hamiltonian

$$\hat{H} = \underbrace{-\sum_i \frac{1}{2}\Delta_i}_{\hat{T}} + \underbrace{\sum_{i<j} \frac{1}{r_{ij}}}_{V_{ee}} \underbrace{- \sum_i \sum_A \frac{Z_A}{r_{iA}}}_{V(\mathbf{r})}$$

- $\hat{T}$ kinetic energy, not system specific;
- V_{ee} electron-electron repulsion, defined by N, not system specific;
- $V(\mathrm{r})$ depends only on the nuclei, called the „external potential”.

The first two terms is the same for all system, while the „external potential” defines which molecule we consider (where are the nuclei, what is their charge).

First theorem of Hohenberg-Kohn (HK1)

$$\begin{array}{ccl} V(\mathbf{r}), N & \rightarrow & \hat{H} \\ & & \downarrow Schrodinger\ equation \\ \rho(\mathbf{r}) & \leftarrow & E, \Psi \end{array}$$

The energy of the system, its wave function and therefore also the density is determined by the „external potential”, i.e. by the molecule.

HK1:

A $V(\mathbf{r})$ *„external potential” (disregarding a trivial constant term) is defined completely by the electron density.*

Therefore, considering also the relations in the above figure:

$$V(\mathbf{r}) \quad \leftrightarrow \quad \rho(\mathbf{r})$$

Energy as functional of the density

Molecule → position of the nuclei → $V(\mathbf{r}) \rightarrow \rho(\mathbf{r}) \rightarrow$ energy

Therefore the energy is a functional of the density:

$$E[\rho] \quad = \quad T[\rho] + E_{ee}[\rho] + E_{ne}[\rho]$$

- $T[\rho]$ is the kinetic energy, its form is unknown
- $E_{ee}[\rho] = J[\rho] + E_x[\rho]$: electron-electron interaction, summ of the Coulomb (J) and the exchange (E_x) contributions. The functional form is known for (J) but not for (E_x).
- $E_{ne}[\rho]$ interaction between electron and nuclei, form is know, can be calculated from V ($\int \rho \; V \; dr$)

$T[\rho]$ and $E_{ee}[\rho]$ are universal, $E_{ne}[\rho]$ system dependent.
$J[\rho], E_{ne}[\rho]$ are known, $T[\rho], E_x[\rho]$ are unknown!

Second theorem of Hohenberg-Kohn (HK2)

HK2:

The variational principle is also valid for the energy functional, i.e. the energy is minimal with the exact electron density

This means, the best density can be obtain by minimization, provided the form of the functional is known.

But the form of the functional is not known!

What we know is that the relations can be rationalized through the Schrödinger equation, but we do not know whether an analytical form exists at all (most probably it does not exists!!)

$$\begin{tikzcd}
V(\mathbf{r}), N \arrow[r] \arrow[d, leftrightarrow] & \hat{H} \arrow[d, "Schrodinger\ egyenlet"] \\
\rho(\mathbf{r}) & E, \Psi \arrow[l]
\end{tikzcd}$$

Kohn-Sham (KS) DFT

Construct the functional of the kinetic energy for a system with non-interacting particles, assuming the same density as of the investigated system:

$$T_S = \sum_i^{occ} \langle \varphi_i | -\frac{1}{2}\Delta | \varphi_i \rangle$$

and

$$\rho(\mathbf{r}) = \sum_i^{occ} \varphi_i^*(\mathbf{r})\varphi_i(\mathbf{r})$$

Note the we have introduced orbitals, from now on we not just directly use the density!

T_S is not the same as $T[\rho]$ it is just an approximation:

$$T[\rho] = T_S[\rho] + E_c[\rho]$$

with correction E_c being the „correlation contribution" which is *not known*!!

$$E_{xc}[\rho] = T[\rho] - T_S[\rho] + E_x[\rho] = E_c[\rho] + E_x[\rho]$$

is the so called *exchange-correlation* functional, which collects all the the unknown contributions. **We have no idea how it looks like!!!**

Kohn-Sham (KS) DFT

Thus, the so called *Kohn-Sham energy functional* has the form:

$$E_{KS}[\rho] \quad = \quad T_S[\rho] + J[\rho] + E_{ne}[\rho] + E_{xc}[\rho]$$

Applying the variational principle (look for the „best" density which gives the lowest energy), we arrive at one-particle equations which are similar to that of the Hartree-Fock method and called the Kohn-Sham equation:

$$\begin{aligned} \hat{h}_{KS}\, \varphi_i &= \varepsilon_i\, \varphi_i \\ \hat{h}_{KS} &= -\frac{1}{2}\Delta + \hat{V}_{ne} + \hat{J} + \hat{V}_{xc} \end{aligned}$$

Comparing to the Fock operator

$$\hat{f} \quad = \quad -\frac{1}{2}\Delta + \hat{V}_{ne} + \hat{J} - \hat{K}$$

the only difference is that the exchange $(\hat{K})$ is replaced by „exchange-correlation" potential (V_{xc}) .

Kohn-Sham (KS) DFT

$$\begin{aligned} \hat{h}_{KS}\,\varphi_i &= \varepsilon_i\,\varphi_i \\ \hat{h}_{KS} &= -\frac{1}{2}\Delta + \hat{V}_{ne} + \hat{J} + \hat{V}_{xc} \end{aligned}$$

From the Kohn-Sham equation we get orbitals and orbital energies and we can calculate the density from the orbitals. Using the density, all the properties can be calculated.

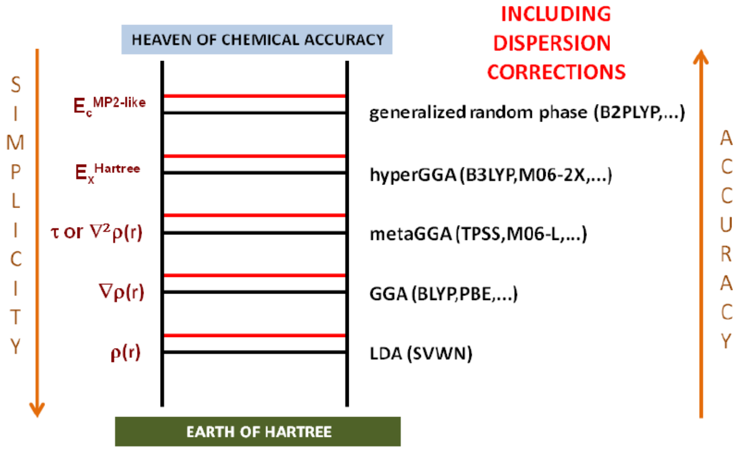
Problem: if we don't know E_{xc}, we do not know V_{xc}, either!!!!

The different DFT methods differ in the choice of the functional V_{xc}.

DFT functionals

There are several levels of the approximation (Jacob's ladder of DFT):

1. Assuming homogeneous electron gas – V_{xc} can be calculated from the density;
2. Gradient-corrected (GGA - General Gradient Approximation) functionals:
   - functional V_{xc} depends not only on the density but also on its gradients
   - expansion according to these quantities
   - empirical parameters ← fitted on chemical systems
3. Hybrid methods
   - exchange part of the potential from Hartree-Fock („exact exchange")
   - new parameters ← fitted on chemical properties
4. Correction for long distance interactions
   - empirical
   - from wave function methods



HEAVEN OF CHEMICAL ACCURACY

INCLUDING DISPERSION CORRECTIONS

SIMPLICITY

ACCURACY

$E_c^{MP2\text{-like}}$ generalized random phase (B2PLYP,...)

$E_x^{Hartree}$ hyperGGA (B3LYP,M06-2X,...)

τ or $\nabla^2\rho(r)$ metaGGA (TPSS,M06-L,...)

$\nabla\rho(r)$ GGA (BLYP,PBE,...)

$\rho(r)$ LDA (SVWN)

EARTH OF HARTREE

DFT functionals

Approximation	exchange V_x	correlation V_c
1) homogeneous electron gas	LDA	VWN
2) Gradient-corrected (GGA)	PW86	LYP
	B88	PW91
	PBE	PBE
3) Hybrid methods	B3	B3
	PBE0	
4) Correction for long distance interactions	DFT-D	
	Double-hybrid DFT	
	M06	
	M06-2X	
	M06-L	
	M06-HF	

The name of the functional is the combination of the names of the exchange and correlation part (e.g. B3-LYP). Abbreviations on the following page

DFT functionals

Abbreviations:

LDA – Local Density Approximation (used mostly in solid state physics)

VWN – Vosko, Wilk, Nusair correlation functional

PW86 – Perdew an Wang functional from 1986

LYP – Lee, Young and Parr correlation functional

B88 – Becke's exchange functional from 1988

PW90 – Perdew and Wang functional from 1991

PBE – Perdew, Burke and Erzenhof functional

B3 - Becke's hybrid functional

PBE – Perdew, Burke and Erzenhof hybrid exchange functional

DFT-D – dispersion-corrected functional (Grimme)

M06-yy – Truhlar's (Minnesota) series of functionals

Performance of the DFT methods (kcal/mol)*

Method	Mean abs. dev.	Maximum error
G2**	1.6	8.2
SVWN (LDA-VWN)	90.9	228.7
BLYP	7.1	28.4
BPW91	7.9	32.2
B3LYP	3.1	20.1
B3PW91	3.5	21.8

* Using atomization and ionization energy as well as electron affinity of 126 molecules.

** combination of wave function methods (best one can do, very expensive).

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Basis sets used in computational chemistry

The LCAO-MO approximation

Above we have discussed the approximation: molecular orbitals are expanded on atomic bases:

$$\varphi_i = \sum_a c_{ai}\,\chi_a$$

This is the so called LCAO-MO (Linear Combination of Atomic Orbitals for Molecular Orbitals) approximation, which is almost always used in computational chemistry, both in Hartree-Fock and DFT calculations.

The quality of the basis largely determines the quality of the results.

Form of the basis functions

According to the chemical intuition, MO's can be obtained from AO's. Best choice would be to use atomic orbitals obtained for the atoms within the IPA calculation.

STO: Slater-type orbitals

$$\chi_{n,l,m}(r,\theta,\varphi) \quad \sim r^{n-1}e^{-\zeta r}\,Y_l^m(\theta,\varphi)$$

ζ is the parameter of the function. A few Slater functions give already a quite good qualitative description.

Problem: calculation of the electron-electron interaction is complicated with these functions.

Form of the basis functions

GTO: Gauss-type orbitals

$$g_b = \chi_{ijk} = x^i\, y^j\, z^k\, e^{-\zeta r^2}$$

This form is based on Cartesian coordinates, and instead of quantum number l, the exponent of x, y, z coordinates are used to form the necessary functions:

- s function $i = j = k = 0$;
- p function, e.g. $i = 1,\ j = k = 0$;
- d function, e.g. $i = 1,\ j = 1,\ k = 0$.

Here also ζ is the only parameter.

Advantage: product of two Gaussian functions placed in different points of space is also a Gaussian function, therefore the electron-electron interaction can be calculated easily!

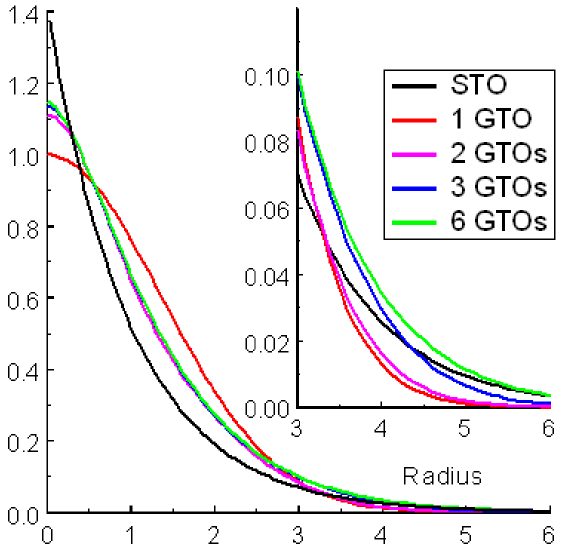
Disadvantage: falloff is too fast, and there is no *cusp* $\rightarrow$ for the same quality more Gaussian functions are needed than Slater functions.

Form of the basis functions

CGTO: Contracted Gauss-type orbitals

$$\chi_a = \sum_b d_{ab}\, g_b$$

i.e. the basis functions are fixed combination of so called primitive Gaussian functions (described on the previous slide). Coefficients d_{ab} are additional parameters of the basis set, they are obtained from a previous calculation. One possibility: expansion of Slater function on the Gaussian ones ($STO - nG$).



Gaussian basis functions used in practice

- **Minimal basis**: one function for all occupied sub-shell. For example:
  H one s-type function
  C two s, one set of p (all together five functions)

- **Double zeta (DZ) basis**: two functions for all occupied sub-shell. For example:
  H two s-type functions
  C four s, two sets of p (all together ten functions)
  O four s, two sets of p (all together ten functions)

- **Triple zeta (TZ) basis**: three functions for all occupied sub-shell.

- **Polarization functions:** include also functions with larger l than that of the occupied shells. For example, in case of DZP:
  H two s-type functions and one set of p
  C four s, two sets of p one set of d
  O four s, two sets of p one set of d

For the description of electron correlation, polarization functions are necessary!

- **Diffuse functions:** include additional functions with smaller *zeta* exponents. These decay slower and required to describe extended wave function (e.g. anions).

Gaussian basis functions used in practice

- Split-valence basis

Chemistry takes place in the valence shell, therefore it is not necessary to use too many functions for the inner shells. Leave out the functions describing the core from the optimization procedure, use them with a fixed coefficient. For example, use contraction like:

$$\underbrace{4}_{\substack{\text{inner shell}\\ \text{four GTO}\\ \text{one CGTO}}} \quad - \quad \underbrace{2\;1}_{\substack{\text{valence shell}\\ \text{2+1 GTO}\\ \text{2 db CGTO}}} \quad \underbrace{G}_{\text{Gaussian}}$$

For example, the 3-21G basis:

	subshell	primitive Gaussians		contracted Gaussians
H	1 s	3 Gaussians	→	two functions
	1 s	3 Gaussians	→	one function
C	2 s	3 Gaussians	→	two functions
	2 p	3x3 Gaussians	→	2x3 functions

Gaussian basis functions used in practice

- Split-valence basis (cont.)

Polarization functions

$6-31G^{*}$ ← polarization function on second row atoms
$6-31G^{**}$ ← polarization function als on H atom

Diffuse functions (small exponents, slow falloff)

$6-31G+$ ← diffuse function on second row atoms
$6-31G++$ ← diffuse function also on H atom

These are important for long range interactions, diffuse electron distributions (e.g. anions).

Gaussian basis functions used in practice

- „Correlation Consistent” basis: cc-pVXZ

cc: correlation consistent – for higher level (correlation) calculations

p: polarized – includes polarization function

V: valence – „split valence” type

XZ: DZ (double zeta), TZ (triple zeta), QZ, quadruple zeta, etc.

For example, cc-pVTZ is „triple zeta” type basis (polarization functions in red):

H	three s type functions, two stes of p, one set of d
C	one + three s type functions, three sets of p, two stes of d, one set of f
O	one + three s type functions, three sets of p, two stes of d, one set of f

Further variants:

aug-cc-pVXZ: includes also diffuse functions

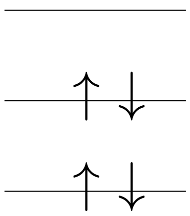
cc-pCVXZ: includes also „core” functions

.

Wave function methods: inclusion of electron correlation

Reminder: The Hartree–Fock method

Wave function: a Slater-determinant corresponding to a configuration:

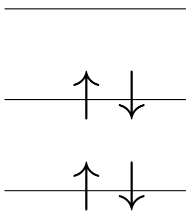


$$\Psi_{HF} = \hat{A}(\varphi_1(1)\,\varphi_2(2)\,\varphi_3(3)...\varphi_n(n))$$

antisymmetrizer - Pauli principle

Reminder: The Hartree–Fock method

Wave function: a Slater-determinant corresponding to a configuration:



$$\Psi_{HF} = \hat{A}(\varphi_1(1)\,\varphi_2(2)\,\varphi_3(3)...\varphi_n(n))$$

antisymmetrizer - Pauli principle

Molecular orbitals (φ_i) obtained from:

$$\begin{aligned} \hat{f}\,\varphi_i &= \varepsilon_i\,\varphi_i \\ \varphi_i &= \sum_\alpha c_{i\alpha}\chi_\alpha \qquad\qquad \chi_\alpha: \text{ basis functions} \end{aligned}$$

Reiminder: The Hartree–Fock method

Advantages:

- Independent particle approximation → concept of orbitals
- not very expensive

Problems:

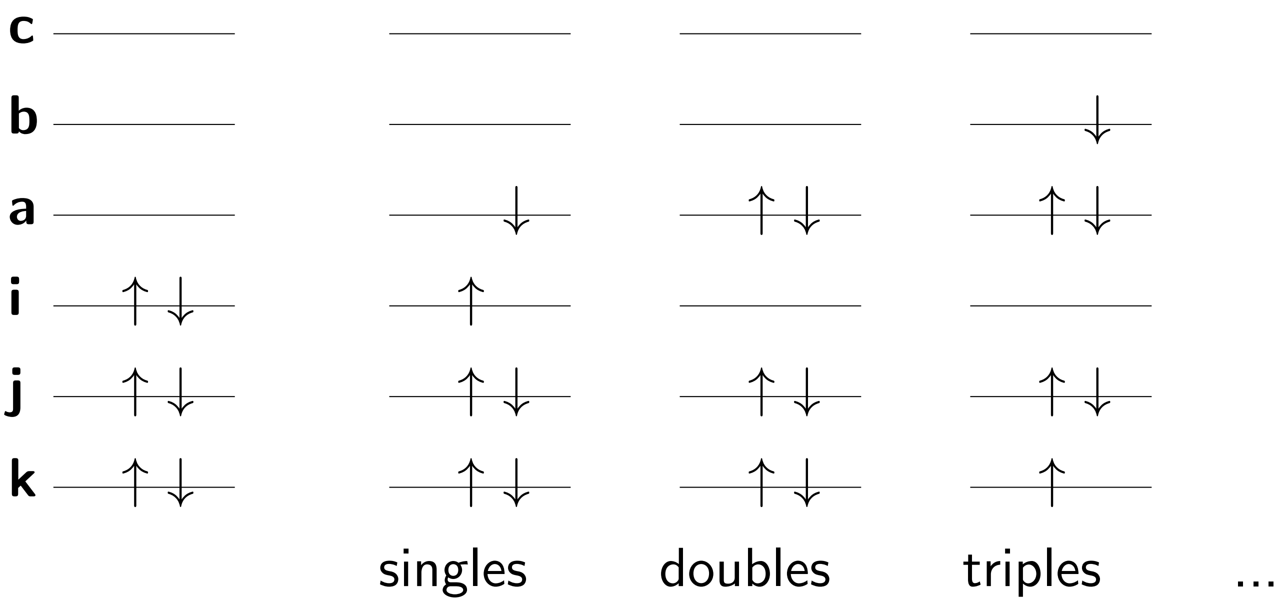
- do not describe the proper interaction of electrons
  → lack of „**electron correlation**"
- accuracy is limited

Going beyond Hartree-Fock

- Density Functional Theory - DFT
- Configuration Interaction (CI) - expand the wave function on several determinants
- Perturbation Theory (PT) - use HF as start
- Coupled Cluster (CC) - exponential expansion of the wave function

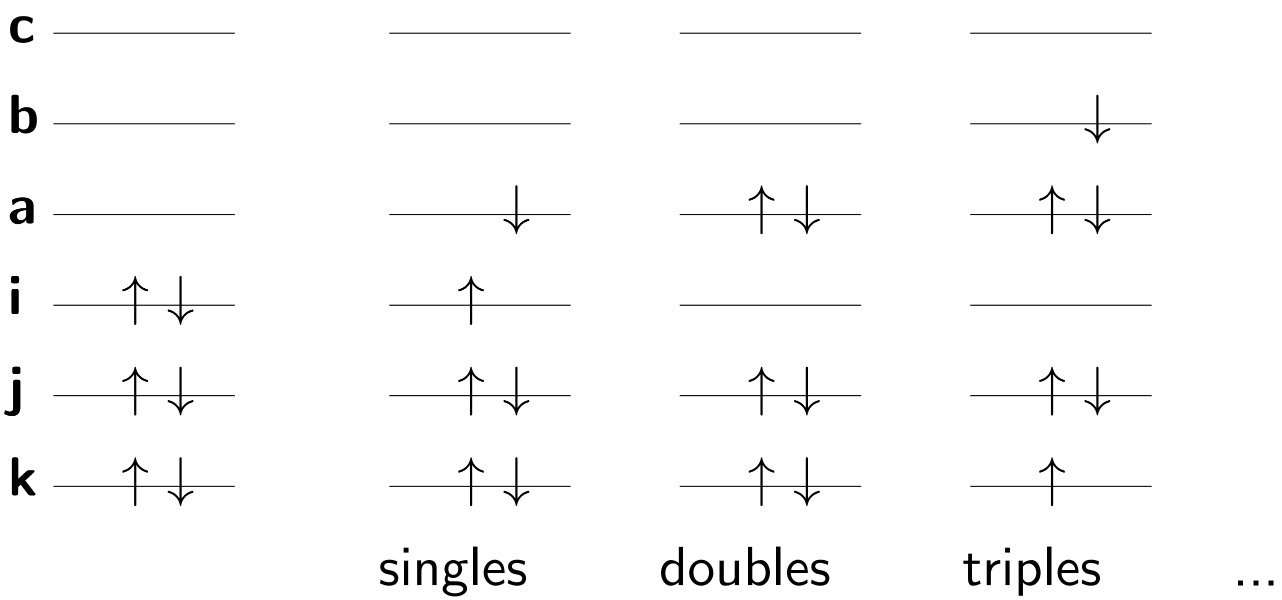
The Configuration Interaction (CI) method

Wave function: linear combination of Slater-determinants



The Configuration Interaction (CI) method

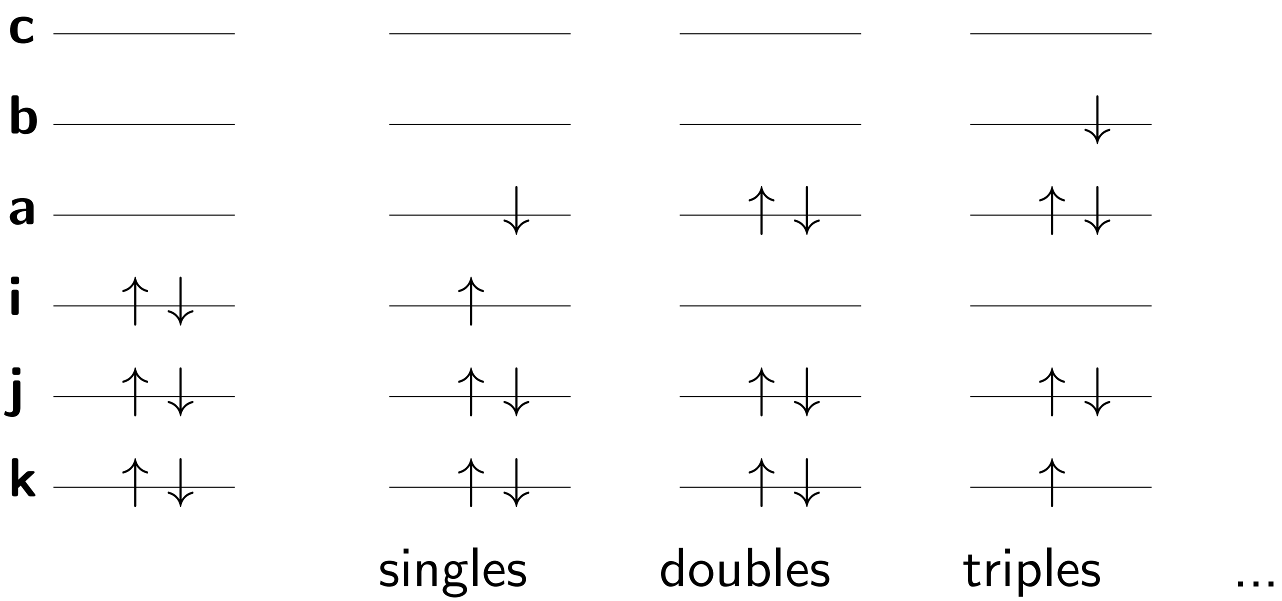
Wave function: linear combination of Slater-determinants



$$\Psi_{CI} = c_0\Psi_{HF} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j\ \ a>b} c_{ij}^{ab}\Phi_{ij}^{ab} + \sum_{i>j>k\ \ a>b>c} c_{ijk}^{abc}\Phi_{ijk}^{abc} + \ldots$$

The Configuration Interaction (CI) method

Wave function: linear combination of Slater-determinants

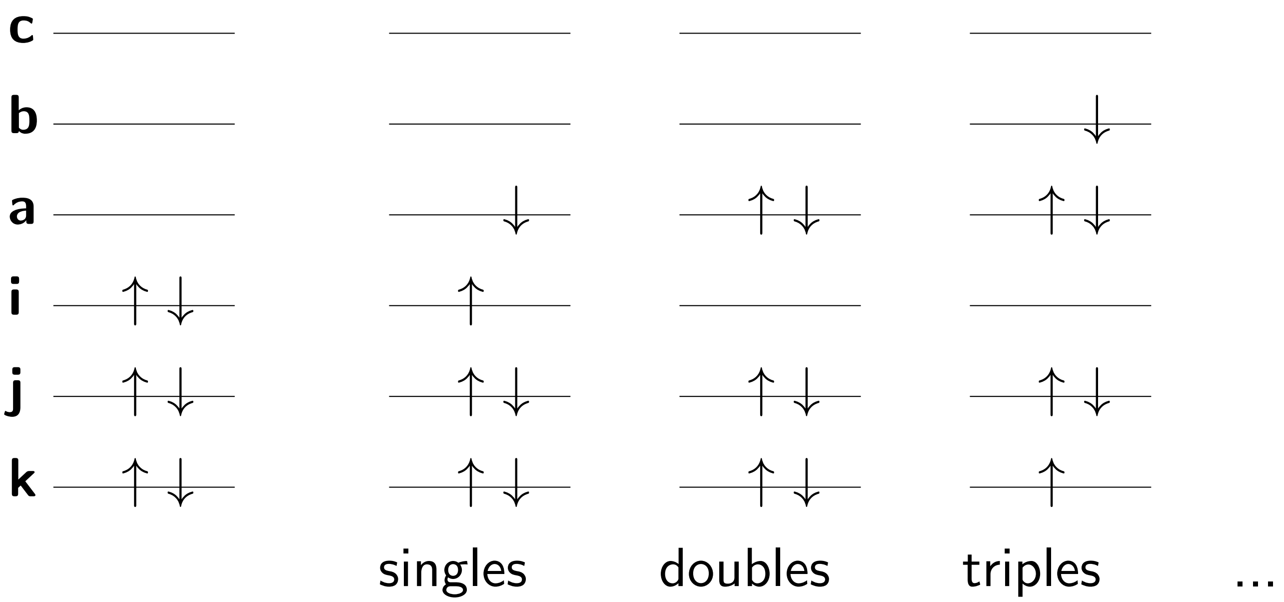


$$\Psi_{CI} = c_0 \Psi_{HF} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j \ \ a>b} c_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{i>j>k \ \ a>b>c} c_{ijk}^{abc} \Phi_{ijk}^{abc} + \ldots$$

↑ CIS

The Configuration Interaction (CI) method

Wave function: linear combination of Slater-determinants

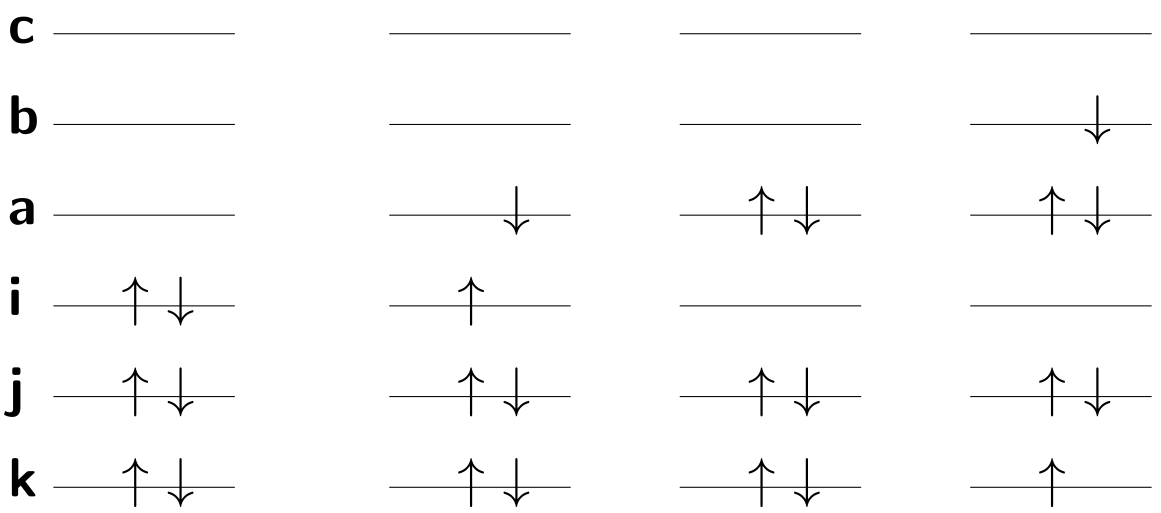


$$\Psi_{CI} = c_0 \Psi_{HF} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j \ a>b} c_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{i>j>k \ a>b>c} c_{ijk}^{abc} \Phi_{ijk}^{abc} + \ldots$$

↑ CISD

The Configuration Interaction (CI) method

Wave function: linear combination of Slater-determinants



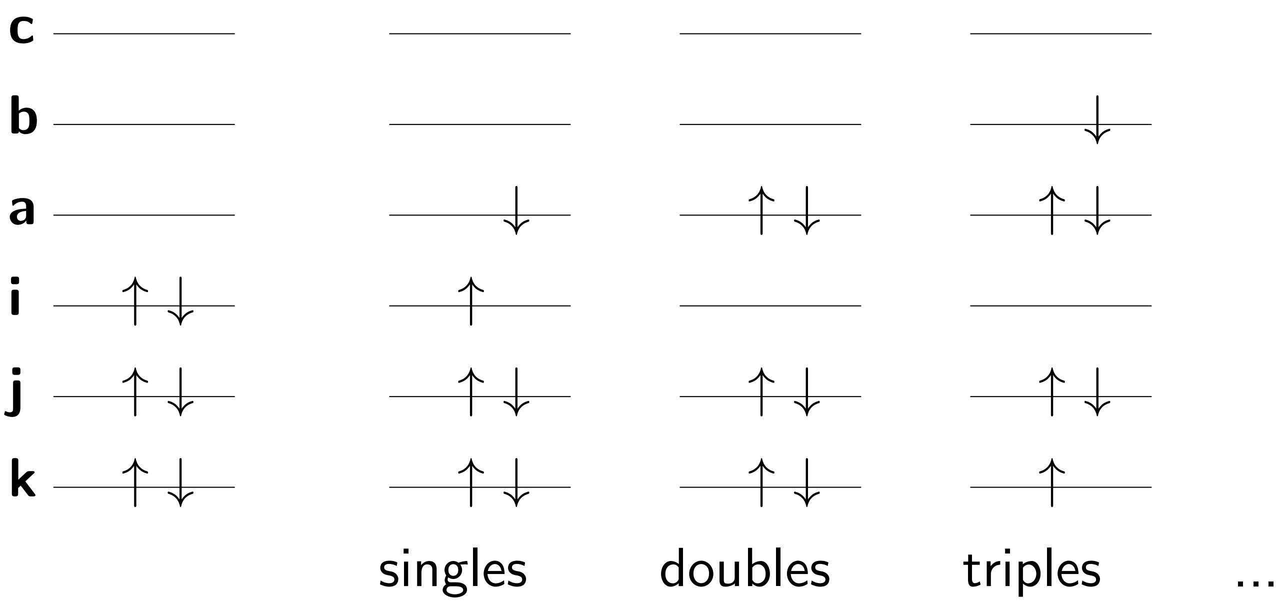
singles doubles triples ...

$$\Psi_{CI} = c_0 \Psi_{HF} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j \;\; a>b} c_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{i>j>k \;\; a>b>c} c_{ijk}^{abc} \Phi_{ijk}^{abc} + \ldots$$

↑ CISDT

The Configuration Interaction (CI) method

Wave function: linear combination of Slater-determinants



$$\Psi_{CI} = c_0 \Psi_{HF} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j \ a>b} c_{ij}^{ab} \Phi_{ij}^{ab} + \sum_{i>j>k \ a>b>c} c_{ijk}^{abc} \Phi_{ijk}^{abc} + \ldots$$

Full CI

The CI equations

A general way of writing the CI wave function as linear combination of determinants:

$$\Psi_{CI} = \sum_p c_p \Phi_p$$

How can we obtain the coefficients? **Variationally**

This leads to a matrix eigenvalue equation:

$$\underline{\underline{H}}\,\underline{c} = E\underline{c}$$

where the matrix elements are:

$$H_{rp} = \langle \Phi_r | \hat{H} | \Phi_p \rangle$$

The elements of the eigenvector $\underline{c}$ define the expansion in the first equation.

CI expansion space: Truncated CI

In practice: CISD - only single and double excitations

$$\Phi_{\mathrm{CISD}} = c_0\Phi_{\mathrm{HF}} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j\ a>b} c_{ij}^{ab}\Phi_{ij}^{ab}$$

- doubles, because these give the largest contribution to energy
- singles also, because needed for one electron properties (not expensive anyway)

CI expansion space: Truncated CI

In practice: CISD - only single and double excitations

$$\Phi_{\text{CISD}} = c_0 \Phi_{\text{HF}} + \sum_{ia} c_i^a \Phi_i^a + \sum_{i>j\ a>b} c_{ij}^{ab} \Phi_{ij}^{ab}$$

- doubles, because these give the largest contribution to energy
- singles also, because needed for one electron properties (not expensive anyway)

This approximation is valid if: $c_0 \sim 1$,

i.e. the wave function is dominated by the reference (HF) determinant

CI expansion space: Truncated CI

$$c_0 \sim 1$$

This is usually *satisfied*:

- ground electronic states at equilibrium geometry

Very often this is *not satisfied*:

- low lying virtual orbital
- dissociation, long bonds
- excited states
- etc.

Main problem with CI

Energy does not scale properly with the size of the system:

- not size-consistent
- not size-extensive

Size-consistency

Consider two subsystems at infinite separation. We have two choices:

- treat the two systems separately;
- consider only a super-system.

Provided that there is no interaction between the two systems, the two treatments should give the **same result, a basic physical requirement.**

Size-consistency

Let us use the CID wave function to describe this system!

$$\text{For the super} - \text{system we have}: \qquad \Psi_{CID} = \Phi_{HF} + \Phi_D$$

Φ_D is the sum of all double excitations out of Φ_{HF} (including coefficients).

For the subsystems we can write:

$$\begin{aligned} {}^A\Psi_{CID} &= {}^A\Phi_{HF} + {}^A\Phi_D \\ {}^B\Psi_{CID} &= {}^B\Phi_{HF} + {}^B\Phi_D \end{aligned}$$

The product of these two wave functions gives the other choice for the wave function of the super-system:

$$\begin{aligned} {}^{A+B}\Psi_{CID} &= {}^A\Psi_{CID}\,{}^B\Psi_{CID} \\ &= {}^A\Phi_{HF}\,{}^B\Phi_{HF} + {}^A\Phi_{HF}\,{}^B\Phi_D + {}^B\Phi_{HF}\,{}^A\Phi_D + {}^A\Phi_D\,{}^B\Phi_D \\ &= \Phi_{HF} + \Phi_D + {}^A\Phi_D\,{}^B\Phi_D \end{aligned}$$

Size-consistency

This simple model enables us to identify the origin of the size-consistency error:

The difference of the two super-system wave functions:

$$ {}^{A}\Psi_{CID}\, {}^{B}\Psi_{CID} - \Psi_{CID} \quad = \quad {}^{A}\Phi_{D}\, {}^{B}\Phi_{D} $$

i.e. simultaneous double excitations on the subsystems are missing from the CI wave function.

This error is present also if there is an interaction between A and B, but we cannot quantify it by two calculations

$\Downarrow$

lack of size-extensivity

The Coupled-Cluster method

Wave function:

$$\Psi_{CC} \quad = \quad e^{\hat{T}}\Phi_{HF}$$

where $\hat{T}_n$ is an excitation operator:

$$\hat{T} \quad = \quad \hat{T}_1 + \hat{T}_2 + \ldots$$

$\hat{T}$ produces excited determinants, as in CI:

$$\hat{T}_n\Phi_0 \quad = \quad \frac{1}{n!}\sum_{abc\ldots ijk\ldots} t_{ijk..}^{abc..}\Phi_{ijk..}^{abc..}$$

The Coupled-Cluster method

Expanding the exponential

$$\Psi_{CC} \quad = \quad e^{\hat{T}}\Phi_{HF} = (1 + \hat{T} + \frac{1}{2}\hat{T}^2 + ...)\Phi_{HF}$$

which includes higher excitations, i.e. in case of Coupled-Cluster wave function higher excitations are included without increasing the number of parameters.

For example, restricting $\hat{T}$ to singles and doubles ($\hat{T} = \hat{T}_1 + \hat{T}_2$, CCSD method):

$$\Psi_{CCSD} \quad = \quad e^{\hat{T}_1+\hat{T}_2}\Phi_{HF} = (1 + \hat{T}_1 + \hat{T}_2 + ... + \frac{1}{2}\hat{T}_2^2 + ...)\Phi_{HF}$$

i.e. the quadruply excited term $\frac{1}{2}\hat{T}_2^2$ appears in the expansion, which plays an important role for accuracy (**simultaneous double excitation**).

The Coupled-Cluster method

Truncated versions:

- **CCSD** ($\hat{T} = \hat{T}_1 + \hat{T}_2$)
- **CCSD(T)** ($\hat{T} = \hat{T}_1 + \hat{T}_2 +$ approximate $\hat{T}_3$)
- **CCSDT** ($\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$)
- **CCSDTQ** ($\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4$)

Widely used and very accurate for **ground** states!

CCSD(T) is considered as the golden standard of quantum chemistry

PERTURBATION THEORY

The starting point of Rayleigh-Schrödinger Perturbation Theory is the partitioning of the Hamiltonian:

$$\hat{H} \quad = \quad \hat{H}_0 + \hat{V}$$

with $\hat{H}_0$ being the zeroth order part of the Hamiltonian, $\hat{V}$ is the perturbation. We need to know the solution for $\hat{H}_0$, i.e.

$$\hat{H}_0 \Psi_0 \quad = \quad E_0 \Psi_0$$

with Ψ_0 and E_0 being the zeroth order wave function and energy, respectively.

PERTURBATION THEORY

In quantum chemistry we often use the so called Møller-Plesset (MP) partitioning:

$$\hat{H}_0 = \sum_i \hat{f}(i)$$

i.e. sum of the one-electron Fock-operators, since in this case:

$$\begin{aligned} \Psi_0 &= \mathrm{Determinant\ from\ the\ Hartree-Fock\ calculation} \\ E_0 &= \sum_i \varepsilon_i \end{aligned}$$

1st order: Hartree-Fock method

2nd order: MP2 or MBPT(2) method

3rd order: MP3 of MBPT(3) method

etc.

PERTURBATION THEORY

MP2: cheap way to include electron correlation

MP3: usually not any better than MP2

MP4: often very good but expensive

Main problems:

- **series may not converge**
- **gets very expensive**