Physical Chemistry (4): Theoretical Chemistry (advanced level) kv1c1lm1e/1 draft lecture notes

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2018. április 5.

Recommended literature

1. Draft of the lecture: www.chem.elte.hu/szalay_hu $\rightarrow$ Oktatás $\rightarrow$ Elméleti Kémia
   http://www.chem.elte.hu/departments/elmkem/szalay/szalay_files/elmkem/

2. Török Ferenc és Pulay Péter: Elméleti Kémia (egyetemi jegyzet)

3. P. W. Atkins: Fizikai Kémia II. Szerkezet, Nemzeti Tankönyvkiadó, 2002

4. Kapuy Ede és Török Ferenc: Atomok és Molekulák Kvantumelmélete (Akadémiai Kiadó)

5. P.W. Atkins and R.S. Friedman: Molecular Quantum Mechanics (Oxford University Press)

1. Basic concepts of Quantum Mechanics

Dalton's atomic theory allowed the development of modern chemistry, but lots of questions remained unanswered, and in particular the *WHY* is not being explained:

- What is the binding force between atoms?
  It is not the charge since atoms are neutral.
  How can even two atoms of the same kind (like H-H) form a bond?

- Why can atoms form molecules only with certain rates?

- What is the reason for the existence of the periodic table of Mendeleev?

At the turn of the 19th and 20th century new experiments appeared which could not be explained by the tools of the classical (Newtonian) mechanics. For the new theory new concepts were needed:

- quantization: energy can not have arbitrary value;

- particle-wave dualism.

All these led to the development of QUANTUM MECHANICS. Let us follow the route of this development and discuss the most important steps in some detail.

1.1. Introduction: same basic terms related to light

In the strict sense, „light" is a narrow range of the electromagnetic radiation, what we can sense with our eyes. In physics very often the term „light" is used for the entire spectrum.
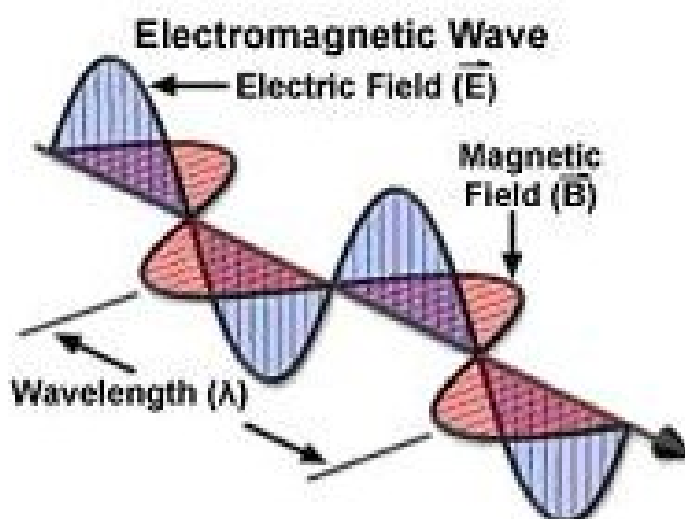
Electromagnetic radiation consists of oscillating magnetic and electric fields wich are perpendicular to each other, and to the direction of its propagation.
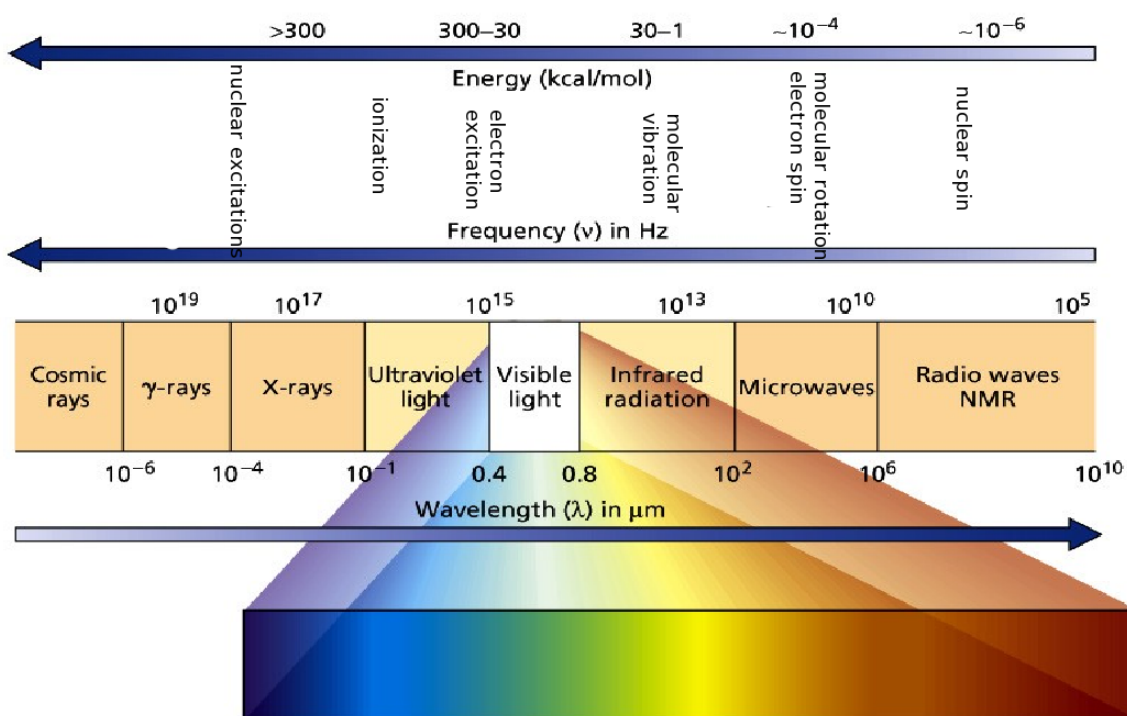
Basic terms:

- ν: frequency of the oscillation [1/s]

- ν^*: wavenumber [1/m]

- λ: wave length [m]

- c: speed of light

- polarized light: oscillations occur only in a plane

Important relations:

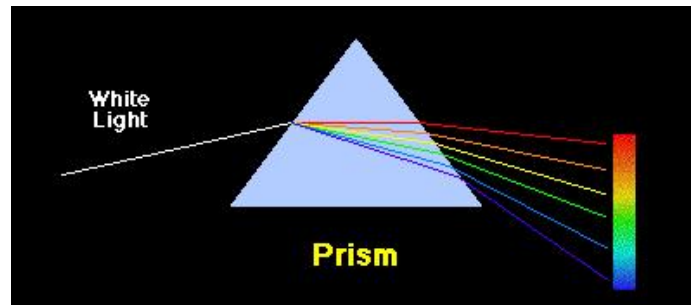$$\lambda = \frac{c}{\nu} \qquad \nu^* = \frac{1}{\lambda}$$

Ranges of the electromagnetic radiation:

What is spectroscopy?

Matter can *absorbe* or *emit* light. The absorbed/emitted light can be decomposed into its components, and the intensity of these will be characteristic for the matter light interacts with.

Light, thus, can be decomposed into its components, for example by a prism.

1.2. Observations leading to quantum mechanics

1.2.1. Black Body Radiation

A possible model of a „black body" consists of a closed pot which is isolated from its surrounding by a heated wall. Inside, depending on the temperature, specific electromagnetic radiation („light") appears which, after a while, will be in equilibrium (the amount of emitted and absorbed radiation is the same). We are interested in the „spectrum" of the radiation inside the pot. (To investigate the radiation, we make a small hole on the wall, such that the radiation exiting does not influence the equilibrium.) The radiation will be investigated by a prism which separates the components.
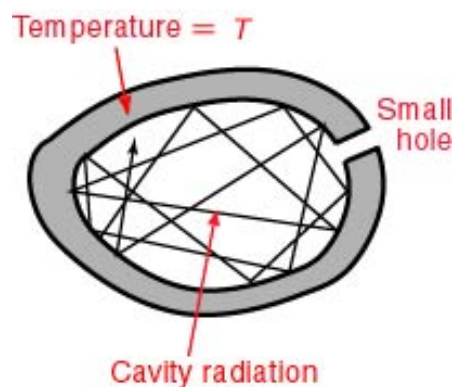
(The "black-body" spectrum of the cosmic space corresponds to a temperature of $T_B = 2.725$ K)

Let us plot the intensity as a function of the frequency and repeat this at different temperatures!

bbrc1b.gif

uvcatas.gif
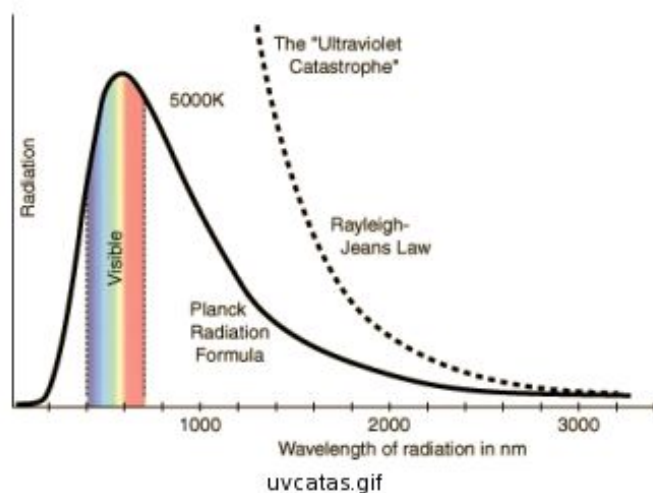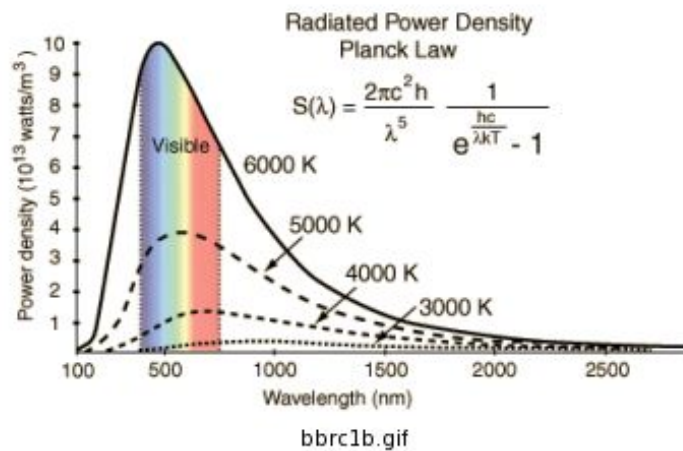
According to the classical theory, radiation is caused by elementary oscillators, with averaged energy of $\bar{\epsilon}$ which, according to the principle of equipartition, is proportional to the temperature. The amount of radiation emitted in a given frequency range should be proportional to the number of modes in that range. Classical physics suggested that all modes have an equal chance of being produced, and that the number of modes increases proportional by the square of the frequency.

The dotted curve in the second figure gives the dependence of energy density on the wavelength calculated according to the classical theory: the energy density corresponding to high frequency (low wave length) goes to infinity independent of the temperature. This is called the „ultraviolet catastrophe" which should not scare you since it simply means that theory can not describe the experiment.

In 1900 Planck came up with a new, unusual explanation: according to his theory, the energy of the individual oscillators can not be arbitrarily small, otherwise the energy could not be distributed among all the oscillators in infinite different ways (c.f. entropy).

Therefore, the observation can only be explained if the energy of the oscillators are *quantized* (not continuous), i.e. its value can only be $h\nu$, $2h\nu$, $3h\nu$ ... It follows, that at every temperature there is a maximum frequency, and oscillators with higher frequency are not vibrating, since the energy corresponding to each mode ($\bar{\epsilon}$) is smaller than $h\nu$. Here h is the so called Planck constant: $h = 6.626 \cdot 10^{-34} Js$

Planck himself did not like his own theory, since it required an assumption (postulate), i.e. the existence of the constant h; he aimed to derive this from the existing theory. He was not successful with this; now we know it is not possible to derive this, since it follows from a new theory. Thus, despite of his genius discovery, he could not participate in further development of quantum mechanics.

1.2.2. Heat capacity

According to the Dulong-Petit rule, heat capacity is given by $c_{v,m} \approx 3R$, i.e. it is independent of temperature. This is valid at temperatures which could be investigated until the end of the 19th century. Later, when measurements at lower temperatures could be performed the full curve of temperature dependence was obtained. It showed that at zero temperature heat capacity also goes to zero.
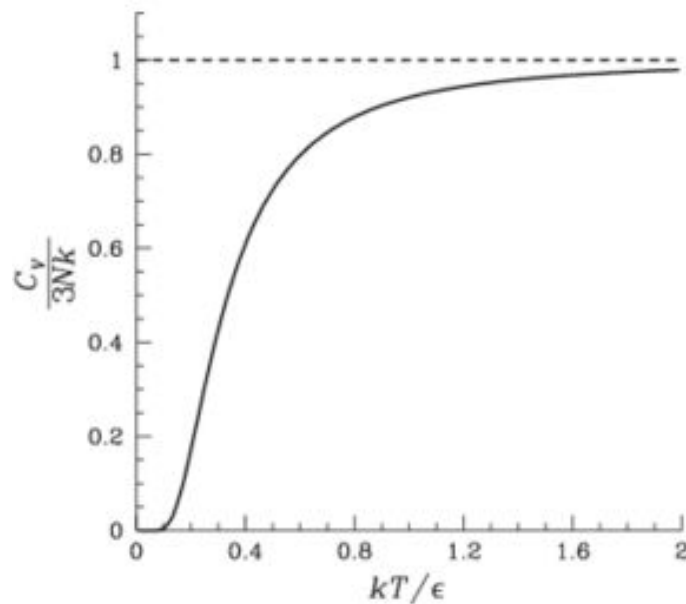
Einstein explained this using Planck's idea: matter is also quantized, the oscillators of the matter (vibrations) can not have arbitrary energy, like the oscillators causing the black body radiation. This means that by lowering the temperature certain oscillators do not have enough energy to show up. (The final form of the theory with several oscillators was derived by Debye.)

1.2.3. Photoelectric effect

photoel.gif
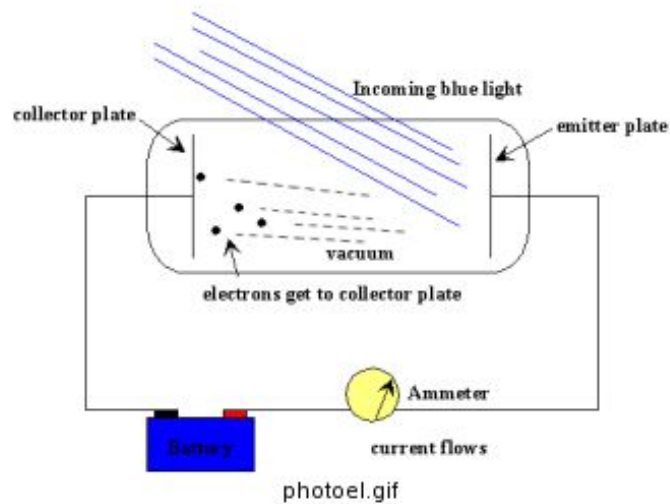
Shining light on a metal plate can result in electric current in the circuit. However, there is a threshold frequency, below this there is no current, irrespective of the intensity of the light, i.e.

- below the threshold frequency, no electron leaves the metal plate

- increasing the intensity of the light, the energy of the emitted electrons does not change, only their number grows.

According to the measurements, the following relation exists between the kinetic energy of the electron (T_e) and the frequency of the light (ν):

$$T_{el} = h\nu - A$$

where A depends on the nature of the metal plate (called „work function").

Explanation was given by Einstein again, using the quantization introduced by Planck: light consists of tiny „particles" (photons) which can have energy of $h\nu$ only. (Note that Planck opposed the use of his „uncompleted" theory to explain this (and other) phenomenon!!)

1.2.4. The Compton effect

compton.gif
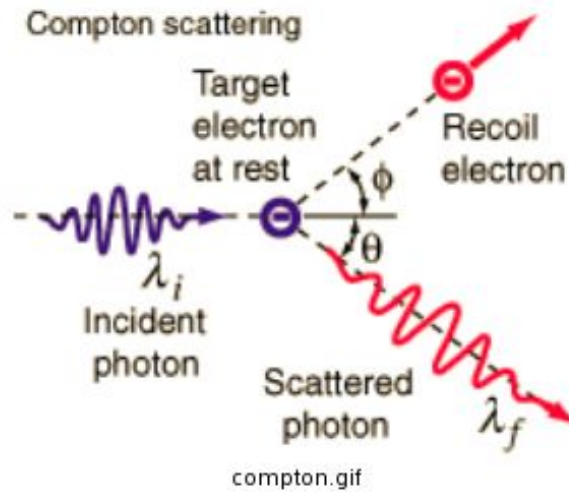
When photon collides with a resting electron, it looses energy. Therefore its frequency also changes. *The photon acts as a particle in this experiment!!* Note that a wave scattered on an object would not change its wave length or frequency!!!

1.2.5. Scattering of electron beam

davgermer.gif

thomson.gif
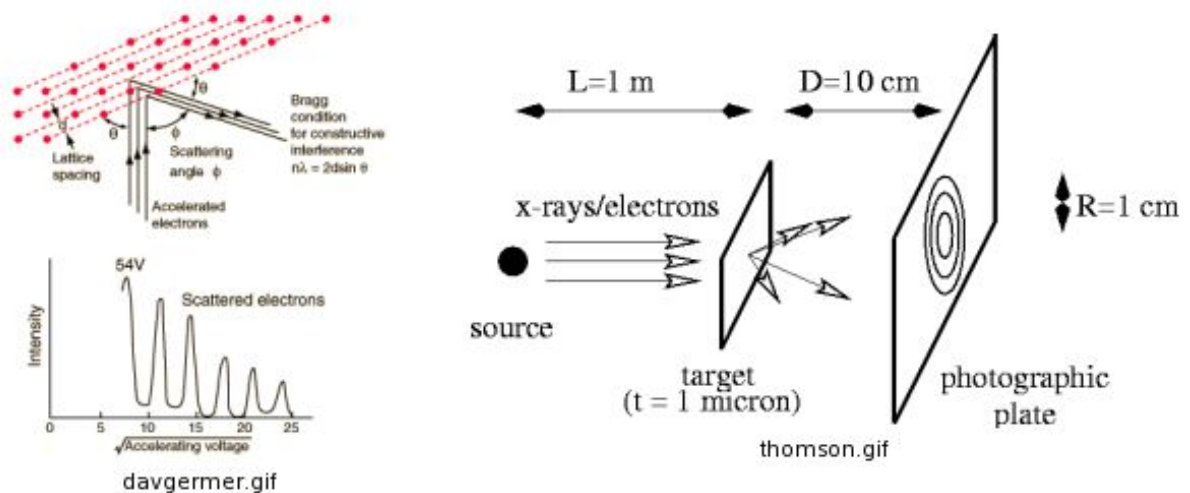
The figure above shows the experiment by Davisson and Germer (1927), as well as by George Paget Thomson (1928). Using an electron beam, interference circles can be observed on the photographic plate, just like in case of X-ray radiation → in this experiment the electron beam acted as a wave.

1.2.6. The hydrogen atom
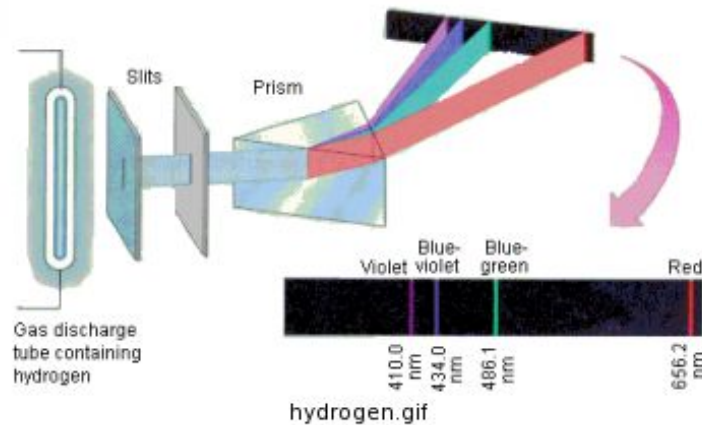
The hydrogen atom has four lines in the visible range of its emission spectrum (experiment first performed by Ångsröm in 1871):

hydrogen.gif

It was Balmer who gave a formula to describe the position of these lines (so called Balmer formula):

$$\frac{1}{\lambda} \;=\; R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3, 4, 5, 6$$

where R is the so called Rydberg constant, λ is the wave length.

After the discovery that light brings energy of $h\nu$ (see e.g. photoelectric effect), one could conclude that the energy of the hydrogen atom must also be quantized!!

How is this possible? According to the Rutherford model, in the hydrogen atom an electron „orbits" around the nucleus (proton). However,

a) why can its energy not be arbitrary?

b) why does it not crash into the nucleus? An orbiting charge dissipate energy (electromagnetic field, think about the electric current in a spiral wire), thus after a while it looses its entire energy and could not orbit anymore.

Explanation by Bohr: in his atomic model, the electron must fullfil some „quantum" conditions:

bohr.gif
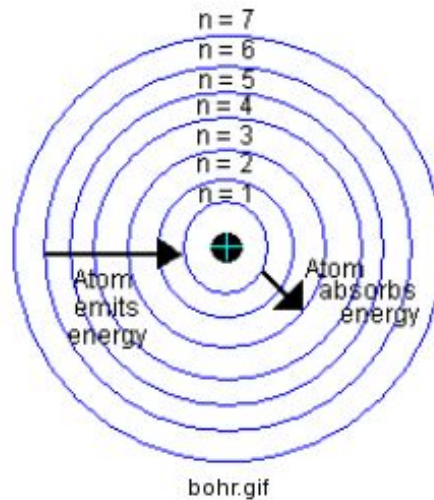
- in case of orbits having certain radius the electron does not dissipate energy; these are the so called *stationary states*;

- if the electron jumps from one orbit to the other, it emits (or absorbs) energy in form of electromagnetic field („light").

- the possible values for the energy are given by the following formula:

$$E = -\frac{1}{2n^2}\frac{e^2}{a_0} \qquad \text{with n is an integer number}$$

(e is the charge of the electron, a_0 the unit length (1 bohr)).

This energy expression gives back the Balmer formula. However, this theory can not be applied for helium or any other atom!!!

Homework: Show that Bohr's energy formula gives the Balmer formula for the wave length corresponding to the transition between energy levels.

1.2.7. Summary

Event	New concept	Discoverer
black body radiation	energy quantized ($h\nu$)	Planck (1900)
photoelectric effect	energy of light is quantized (photon)	Einstein (1905)
heat capacity at low temperature goes to zero	matter is quantized	Einstein (1905), Debye
Compton effect	electromagnetic radiation acts like a particle	Compton (1923)
scattering of the electron beam	electron acts like a wave	Davisson (1927), G.P. Thomson (1928)

Important consequence of all these: particle-wave dualism (dual nature of matter)

Luis de Broglie[1] in 1924(!!!) came up with the formula relating momentum (p) to wave length (λ), properties of particles and waves, respectively:

$$\lambda \;=\; \frac{h}{p}$$

To consider all these, existing theories need to be revised completely! Although Bohr could „fix" the old theory with quantum conditions to describe the hydrogen atom, this technique does not work in general.

The new theory was presented by:

- Heisenberg (1925) as „matrix mechanics"

- Schrödinger (1926) as „wave mechanics"

It turned out later that the two theories are equivalent, they use only slightly different mathematics. Now we call this theory as (non-relativistic) quantum mechanics.

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[1]Louis-Victor-Pierre-Raymond, 7th duc de Broglie

1.3. Basic concepts of quantum mechanics

1.3.1. Postulates

Postulates or axioms: basic assumptions, directly not observable in experiments, but the theory based on them explains all observations.

Postulate I

A *hermitian* operator is ASSIGNED to each physical quantity. The following relation must be satisfied by the operators of *position* ($\hat{x}$) and *momentum* ($\hat{p}_x$):

$$[\hat{x}, \hat{p}_x] = i\hbar$$

The operators of all other physical quantities are derived by replacing x and p_x in the classical formulae by the operators $\hat{x}$ and $\hat{p}_x$ („quantization", principle of correspondence).

Postulate II

The outcome of the measurement of a physical quantity must yield one of the eigenvalues of the corresponding operator. After the measurement the system ends up in the eigenstate corresponding to that eigenvalue:

$$\hat{A}\Phi_i = a_i\Phi_i$$

with a_i and Φ_i being the eigenvalue and the corresponding eigenstate, respectively.

Postulate III

The state of the system is represented by its *wave function (state function, state vector)*. The wave function completely determines the outcome of the measurements. The wave function (Ψ) is continuous, single-valued and square-integrable.

Postulate IV

If the system is in state Ψ, the expectation value of a measurement performed on a quantity represented by the operator $\hat{A}$ is given by:

$$\bar{A} = \int \Psi(x)\hat{A}\Psi(x)dx \equiv \langle\Psi|\hat{A}|\Psi\rangle$$

Postulate V

The time dependence of the *state function* is given by the so called (time dependent) Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\Psi(x,t)$$

In this equation $\hat{H}$ is the *hamiltonian* of the system, t is the time.

Postulate V+1

Φ_i state functions form a basis of an *irreducible* representation corresponding to the point group of the system.

Postulate V+2

The wave function of electrons is antisymmetric with respect to the interchange of the particles. (In general: antisymmetric for fermions and symmetric for bosons.)

1.3.2. Some remarks on the postulates

ad I

One possible choice: $\hat{x}$ is the multiplication by x ($\hat{x}f(x) = xf(x)$)

In this case the momentum is: $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$

For the kinetic energy we get: $T = \frac{p_x^2}{2m} \quad \Rightarrow \quad \hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

In three dimensions: $\hat{T} = -\frac{\hbar^2}{2m}\left(\frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}\right) = -\frac{\hbar^2}{2m}\Delta = -\frac{\hbar^2}{2m}\nabla^2$.

Potential energy: $\hat{V} = V(x,y,z)$

Hamiltonian becomes: $\hat{H} = \hat{T} + \hat{V}$

z component of *angular momentum*: $\hat{l}_z = -i\hbar\frac{\partial}{\partial \phi}$ (ϕ is the angle to axis z).

ad II

According to postulate II, the measurement of a physical quantity can only result the eigenvalues of the corresponding operator:

$$\hat{A}\phi_i^A = a_i\phi_i^A \qquad i = 1, ... \tag{1}$$

The eigenvalues of some physical quantities are discrete (cannot have arbitrary values), therefore physical quantities are *quantized*. For example, the eigenfunction of the z component of the angular momentum ($\hat{l}_z$) are given by $\frac{1}{\sqrt{2\pi}}e^{im\phi}$, while the eigenvalues are $m\hbar$, with $m = 0, \pm 1, \pm 2, ...$ The energy of the system is in most cases quantized, as well.

Other quantities, like the position of a particle ($\hat{x}f(x) = xf(x)$) and momentum ($\hat{p}_x e^{ipx} = \hbar\, p\, e^{ipx}$), are not quantized and these quantities can have arbitrary values (in an interval). It is said that these operators possess *continuous spectrum*.

What do we get if we measure quantity A corresponding to operator $\hat{A}$ on a system which is in a state represented by the wave function Ψ?

a) If Ψ coincides with one of the eigenfunctions of $\hat{A}$, we will measure the corresponding eigenvalue: $\Psi = \phi_i^A \rightarrow A = a_i$

b) If Ψ does not coincide with any of the eigenfunctions of operator $\hat{A}$ then the result of the measurement can not be predicted: $\Psi \neq \phi_i^A \rightarrow A = ?$. However, according to postulate II we certainly will get one of the eigenvalues, though one can not predict which one. One can, however predict the *expectation value* of the measurement: $\bar{A} = \langle\Psi|\hat{A}|\Psi\rangle$. The results of the measurement will be scattered around this value with uncertainty of ΔA. After the measurement the system will be in the state corresponding to the measured eigenvalue!!

Consequently: measurement is not an „*inspection*" rather an „*interaction*" with the system.

ad III

In quantum mechanics the state of a system is represented by the wave function (or state function) which depends on the coordinates of the particles:

$$\Psi = \Psi(x,y,z) = \Psi(\underline{r})$$

or in case of n particles:

$$\Psi \;=\; \Psi(x_1, y_1, z_1, x_2, y_2, z_2, ..., x_n, y_n, z_n) = \Psi(\underline{r}_1, \underline{r}_2, ..., \underline{r}_n)$$

The wave function is an abstraction, has no physical meaning, but its square, the so called *probability density* can be used for interpretation:

$$\Psi^*(x^0, y^0, z^0) \cdot \Psi(x^0, y^0, z^0) dx \; dy \; dz$$

is the probability of finding a particle at point (x^0, y^0, z^0) (more precisely in its infinitesimal proximity).

Shorter notation: $\Psi^*\Psi dv$ or $|\Psi|^2 dv$

We have to use a normalized wave function, otherwise the probability of finding the particle in the entire space would not be one:

$$\int \int \int \Psi^* \cdot \Psi \; dx \; dy \; dz = 1$$

ad IV

Expectation value: average value of the outcome of several measurements. According to *postulate IV*, expectation value can be calculated as: $\langle \Psi | \hat{A} | \Psi \rangle$. On the other hand, according to *postulate II*, these measurements need to be performed on distinct identical systems, since after a measurement the system will be in the state corresponding to the measured eigenvalue.

Consider the eigenfunctions of an operator which satisfy: $\hat{A}\phi_i = a_i\phi_i$. The wave function can be expanded on the basis of these eigenfunctions: $\Psi = \sum_i c_i\phi_i$.

Inserting this form of the wave function into the expression of the expectation value, we get:

$$
\begin{aligned}
\hat{A} \;&=\; \sum_i \sum_j c_i c_j \langle \phi_i | \hat{A} | \phi_j \rangle \\
&=\; \sum_i \sum_j c_i c_j a_j \langle \phi_i | \phi_j \rangle \\
&=\; \sum_i c_i^2 a_i
\end{aligned}
$$

Therefore the probability of obtaining the eigenvalue a_i is $p_i = |c_i|^2$.

If $\Psi = \phi_i$, then $\bar{A} = a_i$, i.e. the outcome of the measurement is assured without any uncertainty.

Two physical quantities can be measured at the same time (without uncertainty) if their operators commute:

$$[\hat{A}, \hat{B}] \;=\; 0$$

If this is not fulfilled, the two quantities can not be measured with arbitrary precision:

$$[\hat{A}, \hat{B}] \;=\; i\hat{C}$$
$$\downarrow$$
$$\Delta A \cdot \Delta B \;\geq\; \frac{1}{2}|\bar{C}|$$

with ΔA and ΔB are the uncertainty of the quantities A and B.

Specifically, for position (coordinate) and momentum:

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

This is the famous *Heisenberg uncertainty principle* which is now a consequence of the postulates. (Note that the system of postulates can be formulated differently with, for example, the uncertainty principle as one of the postulates.)

ad V

Stationary state: in this state, the expectation value of the time independent operators is constant in time.

Look for a particular solution of the (time dependent) Schrödinger equation:

$$\Psi(x,t) \;=\; \Phi(x)\varphi(t)$$

Inserting this into the time dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t}\Psi(x,t) \;=\; \hat{H}(x)\Psi(x,t)$$
$$i\hbar\ \Phi(x)\frac{\partial \varphi(t)}{\partial t} \;=\; \varphi(t)\hat{H}(x)\Phi(x)$$
$$i\hbar\ \varphi^{-1}(t)\frac{\partial \varphi(t)}{\partial t} \;=\; \Phi(x)^{-1}\hat{H}(x)\Phi(x)$$

The right hand side of the equation depends only on x, while the left one only on t, therefore they both have to possess a constant value (say E). Therefore, we get

$$\hat{H}\Phi(x) \;=\; E\Phi(x)$$

and

$$i\hbar\ \frac{\partial \varphi(t)}{\partial t} \;=\; E\ \varphi(t)$$

The solution of the latter equation is:

$$\varphi(t) \;=\; \exp\left(-\frac{iE}{\hbar}t\right)$$

therefore the complete wavefunction is:

$$\Psi(x, t) = \Phi(x) \exp\left(-\frac{iE}{\hbar}t\right)$$

Now let us calculate the expectation value of a time independent operator $\hat{A}$ with this wave function:

$$\begin{aligned}
\bar{A} &= \langle \Phi(x) \exp\left(-\frac{iE}{\hbar}t\right) |\hat{A}| \Phi(x) \exp\left(-\frac{iE}{\hbar}t\right) \rangle \\
&= \int \Phi(x) \exp\left(\frac{iE}{\hbar}t\right) \hat{A}\Phi(x) \exp\left(-\frac{iE}{\hbar}t\right) dx \\
&= \exp\left(\frac{iE}{\hbar}t\right) \exp\left(-\frac{iE}{\hbar}t\right) \int \Phi(x)\hat{A}\Phi(x) dx \\
&= \langle \Phi(x)|\hat{A}|\Phi(x) \rangle
\end{aligned}$$

It is independent of time, therefore the state is „*stationary*".

ad V+2

Degeneracy is caused by symmetry (see later).

1.4. Ways to solve the (time independent) Schrödinger equation

General form of the Schrödinger equation:

$$\hat{H}(\mathbf{r})\ \Psi(\mathbf{r})\ =\ E\ \Psi(\mathbf{r})$$

One particle in one dimension:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\ \Psi(x)\ +\ \hat{V}(x)\Psi(x) =\ E\ \Psi(x)$$

This is a differential equation which is

- of second order,

- variable coefficient („függvényegyütthatós”),

- linear,

- homogeneous.

In case of one particle: 3 dimensions.
In case of n particles: 3n dimensions.

How can one solve it?

- Analytically – only in a few simple cases

- Variationally – set up the energy functional and make it stationary with respect to the wave function (or its parameters). Very often, the solution is written as a linear combination of basis functions $\Longrightarrow$ method of linear variations by Ritz.

- Perturbationally – $\hat{H} = \hat{H}_0 + \hat{H}'$, where the complete eigensystem (value and function) of $\hat{H}_0$ is known.

1.4.1. Variational solution

see Kémiai Matematika!!!

1.4.2. Basics of perturbation theory

Split the operator into two components („*partitioning*"):

$$\hat{H} \;=\; \hat{H}^0 + \hat{H}'$$

such that all eigenvalues and eigenfunctions of $\hat{H}^0$ are known:

$$\hat{H}^0\Psi^0 \;=\; E^0\Psi^0$$

with Ψ^0 being normalized. Expand the energy and wave function:

$$
\begin{aligned}
E &= E^0 + E^1 + E^2 + E^3 + ... \\
\Psi &= \Psi^0 + \Psi^1 + \Psi^2 + \Psi^3 + ...
\end{aligned}
$$

with $\langle\Psi^0|\Psi^i\rangle = 0$, i.e. all corrections are orthogonal to the zeroth order wave function. Inserting this into the Schrödinger equation we get:

$$(\hat{H}^0 + \hat{H}')(\Psi^0 + \Psi^1 + \Psi^2 + \Psi^3 + ...) \;=\; (E^0 + E^1 + E^2 + E^3 + ...)(\Psi^0 + \Psi^1 + \Psi^2 + \Psi^3 + ...)$$

which should be satisfied for each order, i.e. we collect the terms of the same order:

Zeroth order:

$$\hat{H}^0\Psi^0 \;=\; E^0\Psi^0,$$

i.e. we obtained the zeroth order equation.

First order:

$$\hat{H}^0\Psi^1 + \hat{H}'\Psi^0 \;=\; E^0\Psi^1 + E^1\Psi^0$$

Multiplying the equation from the left by Ψ^0 and integrating over the coordinates:

$$\underbrace{\langle\Psi^0|\hat{H}^0|\Psi^1\rangle}_{E^0\langle\Psi^0|\Psi^1\rangle=0} + \langle\Psi^0|\hat{H}'|\Psi^0\rangle \;=\; E^0\underbrace{\langle\Psi^0|\Psi^1\rangle}_{=0} + E^1\underbrace{\langle\Psi^0|\Psi^0\rangle}_{=1}$$

Therefore

$$E^1 \;=\; \langle\Psi^0|\hat{H}'|\Psi^0\rangle$$

i.e. the first order correction of the energy is calculated as the expectation value of the *perturbation*. Physical meaning: the perturbation is small and the change in energy is calculated with the *unchanged* wavefunction.

Higher orders can be obtained similarly, but in this case also the perturbed wave function up to Ψ^{i-1} is needed.

1.4.3. Example of the analytic solution: particle in the box

The following simple systems can be solved analytically:

- Harmonic oscillator, Morse-oscillator (see later with Prof. Császár)

- Particle in the box

- Potential barrier

- ...

- H atom

- H_2^+ „molecule"

The *particle in the box* is a very instructive model system which shows nicely the new properties of quantum objects:
Hamiltonian:

pbox0.gif
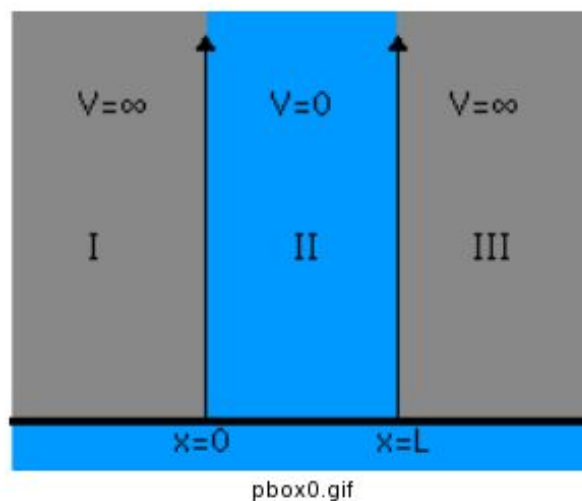
$$V(x) = 0, \ 0 < x < L$$
$$V(x) = \infty, \ \text{otherwise}$$

Within the box of length L the Hamiltonian is equal to the kinetic energy:

$$\hat{H} = \hat{T} \underbrace{+V(x)}_{0},$$

The particle can not leave the box, the probability of finding it outside the box is zero, therefore the wave function must also vanish there. To keep the wave function continuos, it has to vanish already at the walls (*boundary condition*):

$$\Psi(0) = \Psi(L) = 0$$

Therefore the Schrödinger equation to solve reads:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi(x) = E\Psi(x)$$
$$\Psi'' = \overline{E}\Psi$$

with $\overline{E} = -\frac{2m}{\hbar^2}E$

The general solution to this equation is a function, the second derivative of which is proportional to itself:

$$\Psi(x) = A \cdot \cos(lx) + B \cdot \sin(kx)$$

As the consequence of the boundary condition:

$$A = 0 \quad \text{since} \quad \cos(0) \neq 0 \tag{2}$$
$$kL = n\pi, \ n\epsilon N \quad \text{since then} \quad \sin(kL) = 0 \tag{3}$$
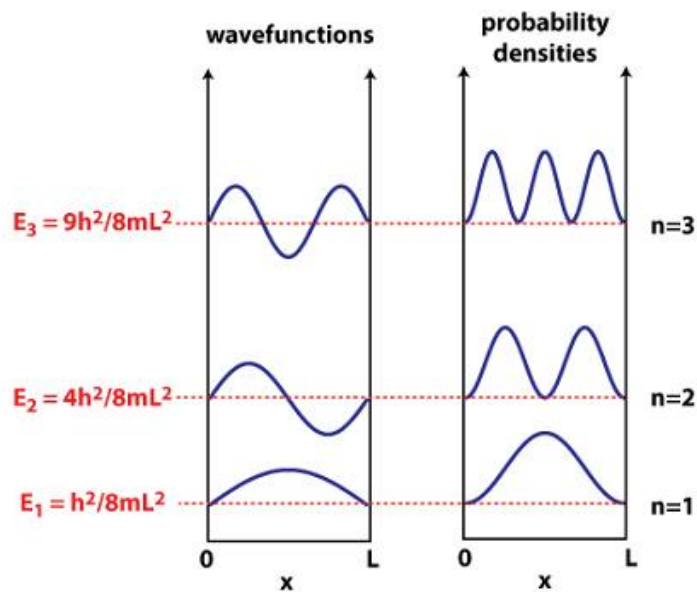
This means that not any sine functions are acceptable: *QUANTIZATION* appears *due to the boundary conditions.*

Put this back to the equation, the following solution can be obtained:

$$E = n^2 \cdot \frac{h^2}{8mL^2}; \quad n = 1, 2, ...$$
$$\Psi(x) = \sqrt{\frac{2}{L}}\sin\left(n\frac{\pi}{L}x\right)$$

The form of the wave function:

Notes:

- Energy is quantized, it grows quadratically with the quantum number n, it is invers proportional to L^2 and m.

  If $L \to \infty$, $E_2 - E_1 \sim \frac{2^2 - 1^2}{L^2} \to 0$. This means that quantization disappears with $L = \infty$.

  The same is true for growing mass $m \to \infty$.

- There is a *zero point energy (ZPE)*!

  Energy is not 0 for the lowest level (*ground state*).

  If, however, $L \to \infty$, $E_0 \to 0$.

  Why is ZPE there? This is an unknown term for classical mechanics!

  It can be explained by the uncertainty principle: $\Delta x \cdot \Delta p \geq \frac{1}{2}\hbar$.

  Since here we have $\hat{V} = 0$, $E \sim p^2$, i.e. the energy of the particle stems exclusively from its momentum.

  Assume that $E = 0$, than $p = 0$, therefore $\Delta x = \infty$, which is a contradiction since $\Delta x \leq L$, the particle must be in the box. Therefore we conclude that the energy can never become zero, since in this case its uncertainty would also be zero which is possible only for a very large box where the uncertainty of the coordinate is large.

  Or alternatively, one can also say: if $L \to 0 \implies \Delta x \to 0 \implies \Delta p \to \infty \implies \Delta E \to \infty$. This means that the energy of all levels MUST BE larger and larger if the size of the box gets smaller.

- Wave function: the larger n is, the more nodes the wave function possesses: ground state has none, first excited state has one, etc. (*Node*: where the wave function changes sign).

- Investigate also the probabilities: $\Psi^*\Psi$! (See the right hand side of the figure above.)

  In the ground state the particle can be found everywhere in the box, the largest probability corresponds to the middle of the box.

  In the first excited state, finding the particle in the middle of the box is zero. How can the particle pass from the left to the right? Bad question, since a particle is neither on the left or the right, but on both sides.

- How does the solution look like in 3D?

$$E = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_a^2}{a^2} + \frac{n_b^2}{b^2} + \frac{n_c^2}{c^2} \right),$$
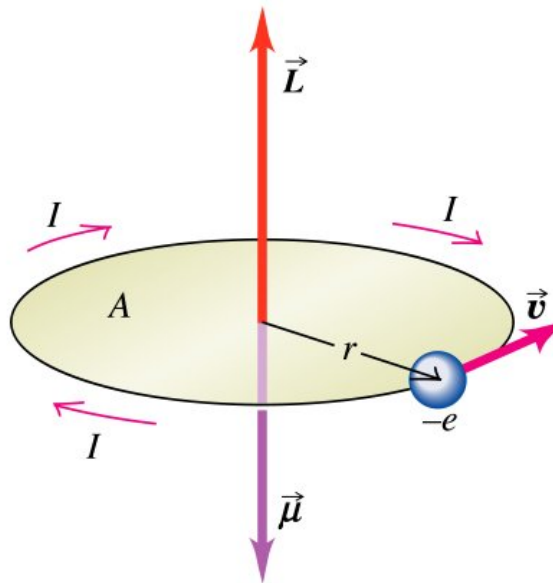
  where a, b, c are the three measures of the box and $n_a, n_b, n_c = 1, 2, ...$ are the quantum numbers.

  If $a = b = L$, then

n_a	n_b	$E\left(\frac{h^2}{8mL^2}\right)$
1	1	2
2	1	5
1	2	5

We have found *degeneracy* which is caused by *the symmetry* of the system (two measures are the same).

1.5. Angular momentum operators

Classical angular momentum

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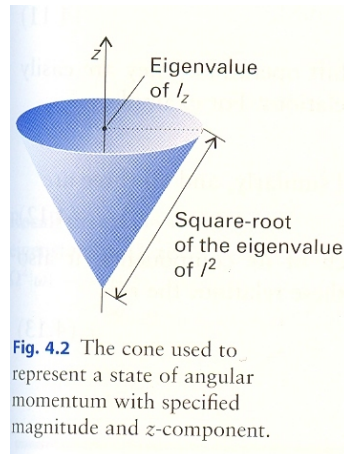l_y &= zp_x - xp_z \\
l_z &= xp_y - yp_x.
\end{aligned}
$$

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

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

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

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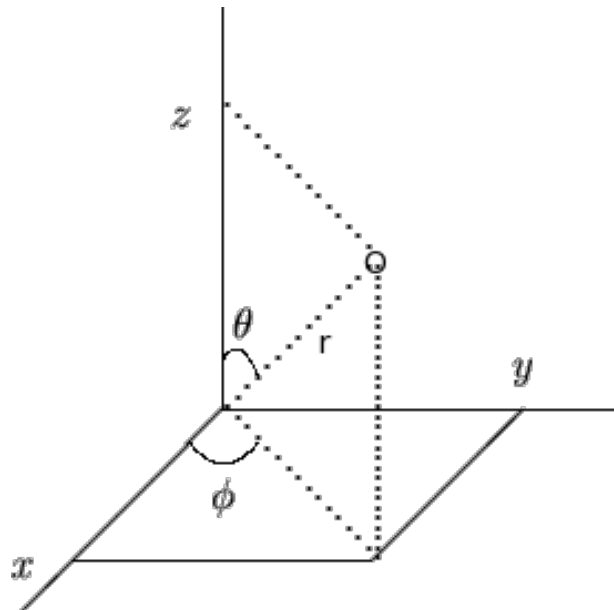\end{aligned}
$$

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

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

1.5.1. 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 since the hydrogen atom and all other atoms have spherical symmetry.

$$x = r\sin\vartheta\cos\varphi \quad y = r\sin\vartheta\sin\varphi \quad z = r\cos\vartheta$$

$$\frac{\partial x}{\partial \varphi} = -r\sin\vartheta\sin\varphi = -y$$

$$\frac{\partial y}{\partial \varphi} = r\sin\vartheta\cos\varphi = x$$

$$\frac{\partial z}{\partial \varphi} = 0$$

Let us prove that

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

This is easily done using the chain rule:

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

Therefore, in spherical coordinates the z component of the angular momentum is given by:

$$\hat{l}_z = -i\hbar \frac{\partial}{\partial \varphi}, \quad 0 \le \varphi \le 2\pi$$

Thus, choosing the appropriate coordinate system, the form of this operator becomes quite simple and even its eigenvalue equation can be solved easily:

$$
\begin{aligned}
-i\hbar \frac{\partial}{\partial \varphi}\Phi(\varphi) &= l_z \Phi(\varphi) \\
\Phi(\varphi) &= A \cdot e^{im\varphi}
\end{aligned}
$$

Here, too, we have a boundary condition, due to the periodicity in φ:

$$
\begin{aligned}
\Phi(0) &= \Phi(2\pi) \\
e^{im0} &= e^{im2\pi} = 1
\end{aligned}
$$

$$
\begin{aligned}
&\cos(m2\pi) \quad +i\sin(m2\pi) = 1 \\
\cos(m2\pi) = 1 \text{ and } &\sin(m2\pi) = 0 \qquad \text{if} \qquad m = 0, \pm 1, \pm 2, ...
\end{aligned}
$$

Quantization comes again from the boundary condition!!!
Now we insert the eigenfunction into the differential equation in order to calculate the eigenvalues:

$$
\begin{aligned}
-i\hbar(im) A \cdot e^{im\varphi} &= l_z A \cdot e^{im\varphi}, \quad m = 0, \pm 1, ... \\
l_z &= m\hbar, \qquad m = 0, \pm 1, ...
\end{aligned}
$$

The normalized eigenfunction reads:

$$\Phi(\varphi) = \frac{1}{\sqrt{2\pi}} \cdot e^{im\varphi}, \quad m = 0, \pm 1, ...$$

Eigenfunctions and eigenvalues of the z component of the angular momentum

$$
l_z = m\hbar, \qquad m = 0, \pm 1, ...
$$
$$
\Phi(\varphi) = \frac{1}{\sqrt{2\pi}} \cdot e^{im\varphi}, \quad m = 0, \pm 1, ...
$$

It is seen that the z component can not take arbitrary values, its magnitude is determined by the quantum number m.

1.5.2. The $\hat{l}^2$ operator

Let us first write this operator 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 eigenvalue equation reads:

$$
\hat{l}^2 Y(\vartheta, \varphi) = \lambda Y(\vartheta, \varphi)
$$

Since $\left[\hat{l}^2, \hat{l}_z\right] = 0$, the two operators have common eigenfunctions. Therefore $Y(\vartheta, \varphi)$ must be the eigenfunction of $\hat{l}_z$, as well. Since the eigenfunctions of $\hat{l}_z$ depend only on the variable φ, one can write:

$$
Y^m(\vartheta, \varphi) = \Theta(\vartheta) \Phi_m(\varphi), \quad \text{with } \Phi_m = \frac{1}{\sqrt{2\pi}} e^{im\varphi}
$$

Inserting this into the eigenvalue equation:

$$
\hat{l}^2 \Theta(\vartheta) \Phi_m(\varphi) = -\hbar^2 \Phi_m(\varphi) \hat{A}\Theta(\vartheta) - \hbar^2 \frac{1}{\sin^2\vartheta} \Theta(\vartheta) \frac{\partial^2 \Phi_m(\varphi)}{\partial\varphi^2} = \lambda\Theta(\vartheta) \Phi_m(\varphi)
$$

Above it was shown that: $-i\hbar \frac{\partial\Phi_m}{\partial\varphi} = m\hbar\Phi_m(\varphi)$, therefore

$$
-\hbar^2 \frac{\partial^2 \Phi_m(\varphi)}{\partial\varphi^2} = m^2\hbar^2\Phi_m(\varphi).
$$

Inserting this into the above equation, then by „simplifying" with $\Phi_m(\varphi)$ [2] we arrive to an equation which only depends on ϑ:

$$
-\hbar^2 \left(\hat{A}\Theta(\vartheta) - m^2 \frac{1}{\sin^2\vartheta} \Theta(\vartheta) \right) = \lambda\Theta(\vartheta)
$$

---

[2]Precisely: multiplying from the left by $\Phi_m(\varphi)$, then integrating according to φ.

Therefore, one has to solve the following equation:

$$-\hbar^2 \left[\frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta} \left(\sin\vartheta \frac{\partial}{\partial\vartheta} \right) - m^2 \frac{1}{\sin^2\vartheta} \right] \Theta(\vartheta) = \lambda\Theta(\vartheta)$$

This is a differential equation already discussed during the „kém.mat." course: its solutions are the *associated Legendre polynomials*:

$$\Theta(\vartheta) = P_l^m(\cos\vartheta)$$
$$P_l^m(x) = \left(1 - x^2\right)^{\frac{|m|}{2}} \frac{d^{|m|}}{dx^{|m|}} P_l(x)$$

with $P_l(x)$ being the *Legendre polynomial* of grade l. After applying the differential operator of rank m on this polynomial, we obtain another polynomial of grade $(l - |m|)$. With other words, the following relation must hold between the known quantum number m and the new quantum number l:

$$l - |m| \geq 0$$
$$l \geq |m|.$$

To remember, the first couple of Legendre and associated Legendre polynomials read:

Legendre	associated Legendre
$P_0(x) = 1$	$P_1^1(x) = \sqrt{(1 - x^2)}$
$P_1(x) = x$	$P_2^1(x) = 3x\sqrt{(1 - x^2)}$
$P_2(x) = \frac{1}{2}(3x^2 - 1)$	$P_2^2(x) = 3(1 - x^2)$

Summerized, the eigensystem of operator $\hat{l}^2$ reads:

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

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

$$l = 0, 1, 2, ...$$
$$m = -l, ..., 0, ...l$$

$Y_l^m(\vartheta, \varphi)$ is the so called *spherical function*, Θ_l^m is a polynomial in the variable $\cos(\vartheta)$.

The square of the angular momentum – and thus its length – can not have arbitrary values, its magnitude is determined by the quantum number l. The following relation needs to be fulfilled by the quantum numbers: $l \geq |m|$, because the length of a vector can not be smaller than any of its components ($|\underline{l}| \geq l_z$).

1.6. Quantum mechanical description of the hydrogen atom

1.6.1. Hamiltonian for the hydrogen atom

Atomic units

To avoid dealing with very small numbers, let us introduce the so called „atomic units":

Quantity	Atomic unit	SI	Conversion
Ang. mom.	$\hbar$	$[J\,s]$	$\hbar = 1,05459 \cdot 10^{-34} Js$
Mass	m_e	$[kg]$	$m_e = 9,1094 \cdot 10^{-31} kg$
Charge	e	$[C]$	$e = 1,6022 \cdot 10^{-19} C$
Permittivity	$4\pi\varepsilon_0$	$\left[\frac{C^2}{Jm}\right]$	$4\pi\varepsilon_0 = 1,11265 \cdot 10^{-10} \frac{C^2}{Jm}$
derived quantities:			
Length	a_0 (*bohr*)	$[m]$	$1\,bohr = \frac{4\pi\varepsilon_0 \hbar^2}{m_e\, e^2} = 0,529177 \cdot 10^{-10} m$
Energy	E_h (*hartree*)	$[J]$	$1\,hartree = \frac{e^2}{4\pi\varepsilon_0 a_0} = 4,359814 \cdot 10^{-18} J$
			$1\;E_h \approx 27,21\,eV$
			$E_h \approx 627\,kcal/mol$

The Hamiltonian in (SI units):

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m_e}\triangle - \frac{e^2}{4\pi\varepsilon_0\, r}$$

i.e. the potential consists of the Coulomb interactions of electron and nucleus.

The Hamiltonian in atomic units reads:

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

Clearly, the problem can dealt with in spherical coordinates[3]:

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

1.6.2. Solution of the Schrödinger equation for the hydrogen atom

To solve the Schrödinger equation, one first can use the following relations:

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

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

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

---

[3]see the full form of $\triangle$ and $\hat{l}^2$ using spherical coordinates in course kém.mat.!

We insert this into the Schrödinger equation and, similarly to the procedure used in case of $\hat{l}^2$, we can get rid of the part depending on ϑ, φ. One gets:

$$\left[\underbrace{-\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{r}\frac{\partial}{\partial r}}_{\text{kinetic energy}} \underbrace{-\frac{1}{r} + \frac{l(l+1)}{2r^2}}_{V_{eff}} \right] R(r) = E\,R(r).$$

which is an equation in variable r only. One can observe that this last step introduced the eigenvalues of $\hat{l}^2$ into the equation. V_{eff} is an effective potential: for $l = 0$ it is a simple Coulomb interaction, for $l \neq 0$ beside the Coulomb interaction, also centrifugal force is considered.
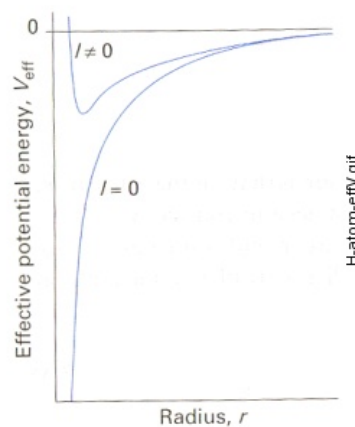
The solutions of this equation can be given in the following form:

$$R_{nl}(r) = e^{-\frac{r}{n}}\, r^l\, L_{nl}(r), \qquad n \geq l + 1 \qquad (\Longrightarrow l = 0, 1, 2, ..., n - 1)$$

with L_{nl} being the *associated Laguerre polynomial*.

Here again, a new quantum number has appeared: $n = 1, 2, ...$, and there is a constraint between n and l.

Summarized, the solutions of the Schrödinger equation of H-atom:
Eigenfunctions:

$$\Psi(r, \vartheta, \varphi) = R_{nl}(r)\, Y_l^m(\vartheta, \varphi)$$

Eigenvalues (hartree units):

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

Quantum numbers:

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

1.6.3. Discussion of the solution

Discussion of the solution: energy

- energy increases with n and the density of the levels also increases;

- energy depends only on the quantum number n, while eigenfunctions also depend on l and $m \to$ high degree of degeneracy!! (See also below.)

- the formula corresponds to the Bohr formula, thus it correctly describes Balmer ($n_1 = 2$,VIS) and Lyman ($n_1 = 1$,UV) series.
  To remind you, the Balmer-formula reads:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Discussion of the solution: degeneracy

Energy is n^2-fold degenerate, since:

$$\sum_{l=0}^{n-1} (2l + 1) = n^2$$

For example:

n	deg.	
1	1	one s
2	4	one s, three p
3	9	oen s, three p, five d

What is the reason for degeneracy?

- according to m: spherical symmetry – maintained also in many-electron atoms

- according to l: $\frac{1}{r}$ potential (symmetry of the Coulomb-field) – only in hydrogen atom

Discussion of the solution: eigenfunction

The total wave function reads:

$$\Psi (r, \vartheta, \varphi) = N \, R_{nl} (r) \, Y_l^m (\vartheta, \varphi) = N \, r^l \, L_{nl} (r) \, e^{-\frac{r}{n}} P_l^{|m|} (\cos \vartheta) \, e^{im\varphi}$$

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

What can we tell about the radial part?

$$
\begin{aligned}
e^{-\frac{r}{n}} &\rightarrow & \text{orbitals with higher quantum number } n \text{ fall off slower} \\
L_{nl}(r) &\rightarrow & \text{this is a polynomial of grad } n - l - 1, \text{ which has } n - l - 1 \text{ nodes} \\
r^l &\rightarrow & \text{in case of } l \neq 0 \text{ the wave function is 0 at the nucleus.}
\end{aligned}
$$

Angular part:

- responsible for the direction in space

- its form is a consequence of the spherical symmetry (this form is maintained also for many-electron atoms).

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

$1s$	$\Psi_{100} = \frac{1}{\sqrt{\pi}} e^{-r}$
$2s$	$\Psi_{200} = \frac{1}{4\sqrt{2\pi}} (2 - r) e^{-r/2}$
$2p_0$	$\Psi_{210} = \frac{1}{4\sqrt{2\pi}} r e^{-r/2} \cos(\vartheta)$
$2p_{\pm 1}$	$\Psi_{21\pm 1} = \frac{1}{8\sqrt{\pi}} r e^{-r/2} \sin(\vartheta) e^{\pm i\varphi}$
$3s$	$\Psi_{300} = \frac{2}{81\sqrt{3\pi}} (27 - 18r + 2r^2) e^{-r/3}$
$3p_0$	$\Psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} r(6 - r) e^{-r/3} \cos(\vartheta)$
$3p_{\pm 1}$	$\Psi_{31\pm 1} = \frac{1}{81\sqrt{\pi}} r(6 - r) e^{-r/3} \sin(\vartheta) e^{\pm i\varphi}$
$3d_0$	$\Psi_{320} = \frac{1}{81\sqrt{6\pi}} r^2 e^{-r/3} (3\cos^2(\vartheta) - 1)$
$3d_{\pm 1}$	$\Psi_{32\pm 1} = \frac{1}{81\sqrt{\pi}} r^2 e^{-r/3} \sin(\vartheta) \cos(\vartheta) e^{\pm i\varphi}$
$3d_{\pm 2}$	$\Psi_{32\pm 2} = \frac{1}{162\sqrt{\pi}} r^2 e^{-r/3} \sin^2(\vartheta) e^{\pm 2i\varphi}$

Discussion of the solution: representation of orbitals
Radial part:
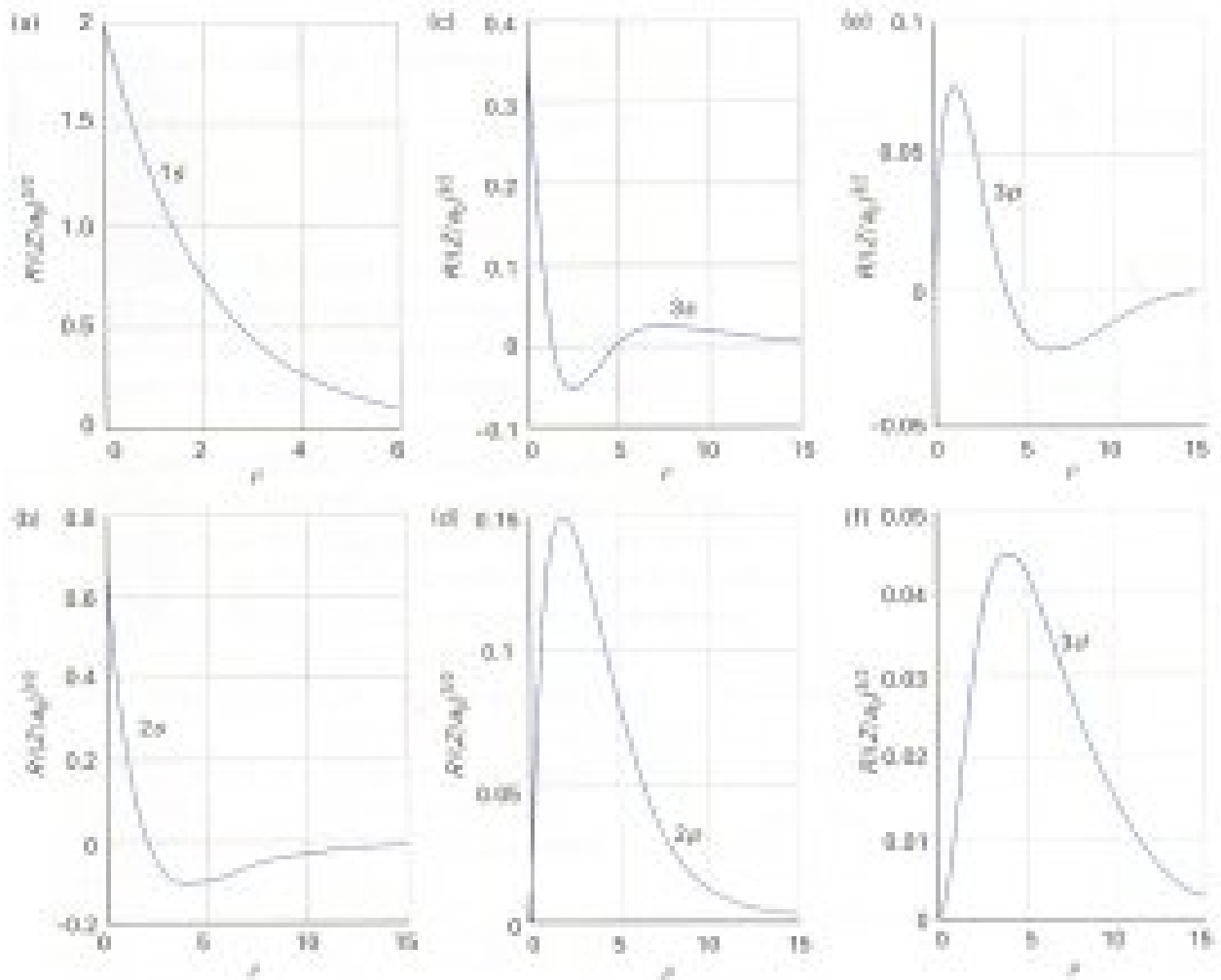
Angular part: directional diagram
    Rules to draw the directional diagrams:

- ϑ and φ define a direction in space;

- we draw a vector of length $|Y(\vartheta, \varphi)|$ into this direction;

- connect the tip of the vectors;

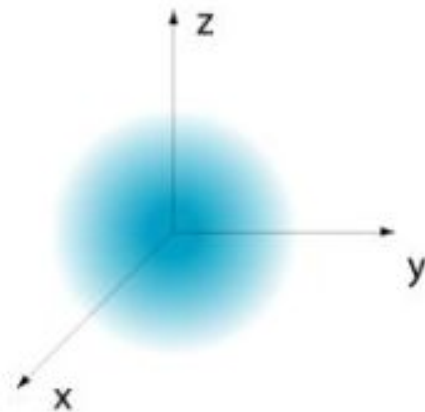- denote the sign of $Y(\vartheta, \varphi)$.

Example: draw orbitals $2p_0$, $1s$, and $3d_0$

Discussion of the solution: representation of orbitals
  Angular part: directional diagram

1s orbital
$n = 1, \ell = 0, m_\ell = 0$

The 1s standing wave function (orbital) is all positive (i.e., no negative lobes) and has no nodal surfaces. It is spherically symmetric.
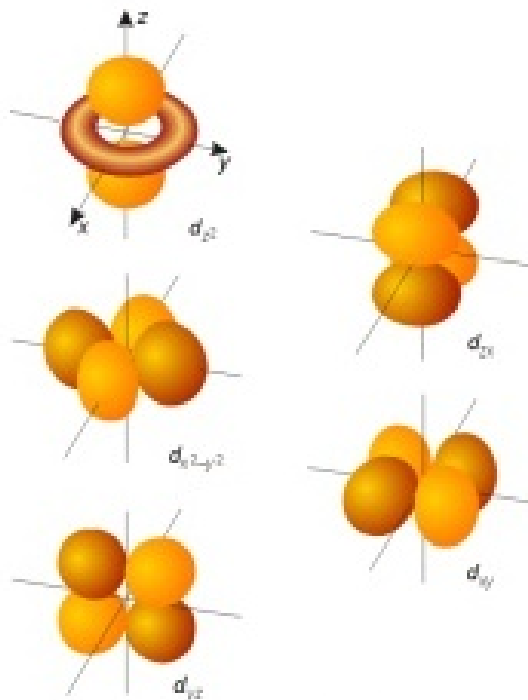
Directional diaram: 1s orbital

2p orbitals
$n = 2, \ell = 1, m_\ell = -1, 0, +1$

This region has positive amplitude

p_y

Angular nodal surface between its positive and negative lobe in x-y plane.
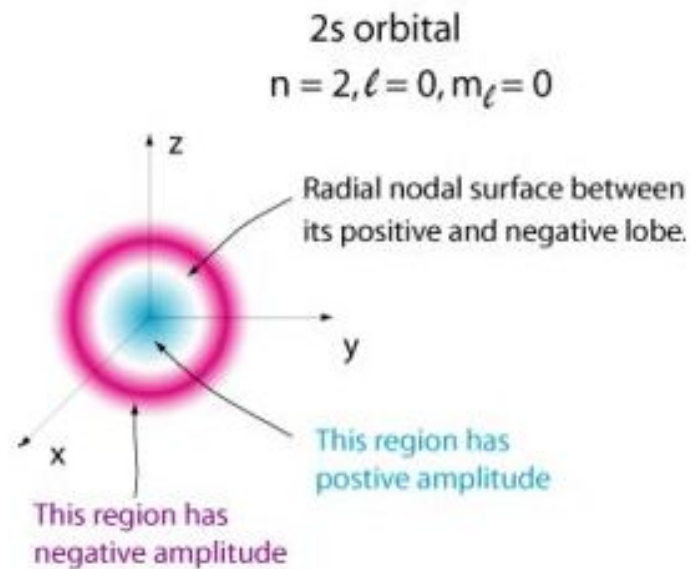
This region has negative amplitude
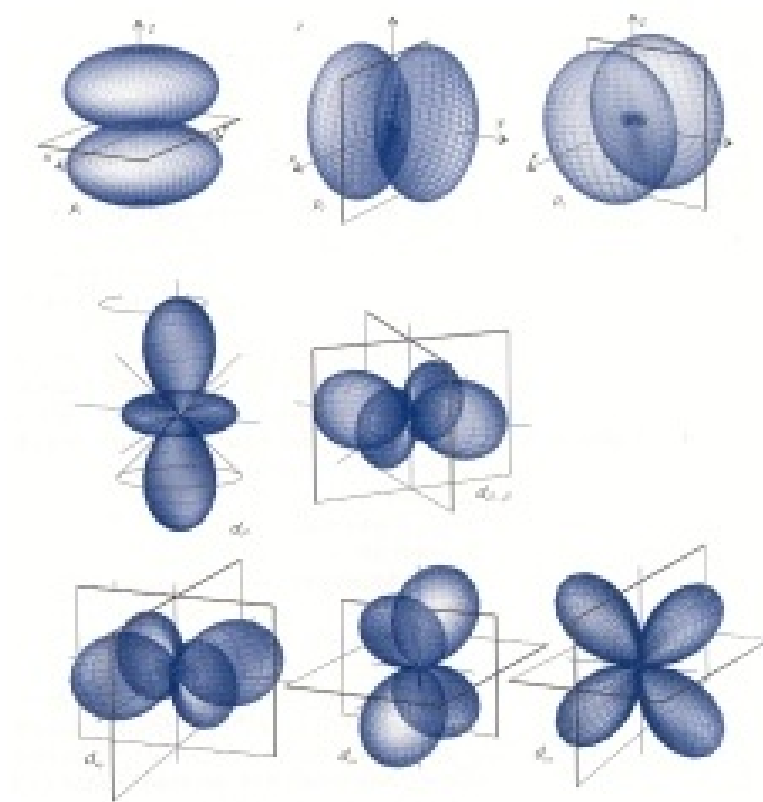
p_y

p_x
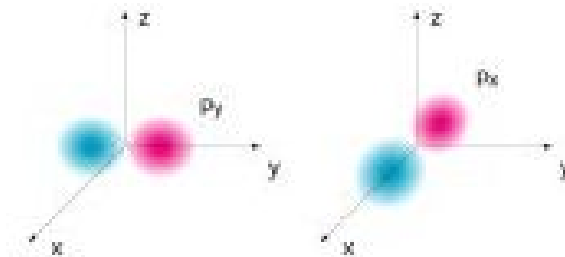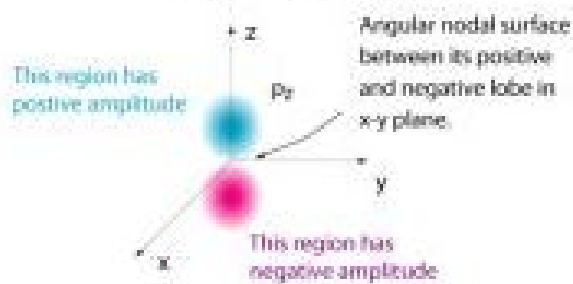
Directional diaram: 2p orbitals

Directional diaram: 3d orbitals

What directional diagrams does not show: nodes originating from radial part. These can be seen if we look „into" the orbitals. For example, in case of 2s:
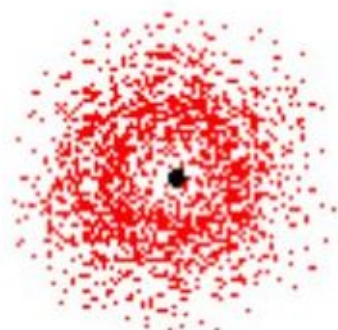
Discussion of the solution: representation of orbitals
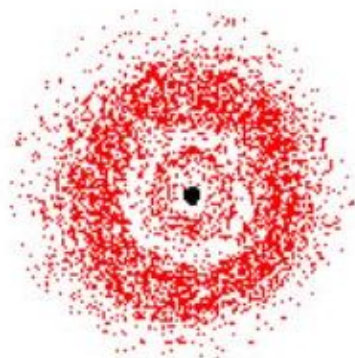   Some other pictures of the p and d orbitals:

Discussion of the solution: representation of orbitals

    Representation of the orbitals: „dotting" – the frequency of the dots represents the value: denser points represent larger value of the wave function.

a 1s orbital

a 2s orbital

a p orbital

Discussion of the solution: changing to real functions

$2p_0$ function points to z direction, since

$$2p_0 = \frac{1}{4\sqrt{2\pi}} e^{-r/2} \underbrace{r\cos(\vartheta)}_{z} = 2p_z$$

We can not draw p_1 and p_{-1} functions, since these are complex. We can, however, take a real combination of these, since they are degenerate with respect to energy (i.e. the results will represent a function with the same energy):

$$
\begin{aligned}
\frac{1}{\sqrt{2}}\left(2p_1 + 2p_{-1}\right) &= \frac{1}{\sqrt{2}}\frac{1}{8\sqrt{\pi}}\left(re^{-r/2}\sin(\vartheta)e^{i\varphi} + re^{-r/2}\sin(\vartheta)e^{-i\varphi}\right)\\
&= \frac{1}{8\sqrt{2\pi}}e^{-r/2}r\sin(\vartheta)\underbrace{\left(e^{i\varphi} + e^{-i\varphi}\right)}_{2\cos(\varphi)}\\
&= \frac{1}{4\sqrt{2\pi}}e^{-r/2}\underbrace{r\sin(\vartheta)\cos(\varphi)}_{x} = 2p_x
\end{aligned}
$$

$$\frac{1}{i\sqrt{2}}\left(2p_1 - 2p_{-1}\right) = 2p_y$$

Now we can draw the directional diagram of $2p_y$ and $2p_x$ functions (see the figure above).

The same way we can treat the d functions. $3d_0$ is real and points in z direction.

$$3d_0 = \frac{1}{81\sqrt{6\pi}}e^{-r/3}\underbrace{r^2(3\cos^2(\vartheta)}_{3z^2} - 1) = \frac{1}{81\sqrt{6\pi}}e^{-r/3}(3z^2 - r^2) = 3d_{z^2}$$

We can form the combination of $3d_1$ and $3d_{-1}$ functions:

$$\frac{1}{\sqrt{2}}\left(3d_1 + 3d_{-1}\right) = 3d_{xz}$$

$$\frac{1}{i\sqrt{2}}\left(3d_1 - 3d_{-1}\right) = 3d_{yz}$$

Similarly in case of $3d_2$ and $3d_{-2}$ functions:

$$\frac{1}{\sqrt{2}}\left(3d_2 + 3d_{-2}\right) = 3d_{x^2-y^2}$$

$$\frac{1}{i\sqrt{2}}\left(3d_2 - 3d_{-2}\right) = 3d_{xy}$$

Discussion of the solution: electron density

Remember: the wave function has no physical meaning, but its square, the density $(\Psi(r)^* \cdot \Psi(r)dr = |\Psi|^2 dr)$ has and it gives the probability of finding the particle at a given point.

What is the probability of finding the electron at distance r from the nucleus? In case of 1s orbital this seems to be easy, since the wave function depends only on r:

$$|\Psi|^2 dr = \Psi^*(r) \cdot \Psi(r)dr = \frac{1}{\pi}e^{-2r}dr$$

Ábra!!!!!!!

Inspecting this function, it seems that the most probable position of the electron is at the nucleus. What did we really obtain? The function shows the probability of finding the electron *along the radius.*

More appropriate question: what is the probability finding the electron at a given distance r from the nucleus? This is not a point but a shell of the sphere!!! The further away we go from the nucleus, the larger the volume of the shell becomes.
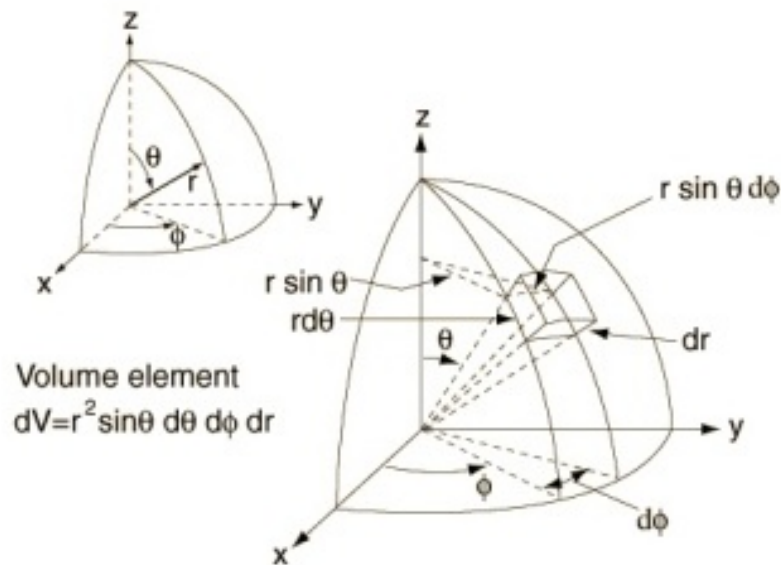
First, when calculating the volume element, the proper transformation to spherical coordinates reads:

$$dx\ dy\ dz \ \to r^2 \sin(\vartheta)\ dr\ d\vartheta\ d\varphi$$

To get the density as the function of r only, we need to sum (integrate) over all possible values of ϑ and φ:

$$\int_\vartheta \int_\varphi \Psi(r,\vartheta,\varphi)^* \cdot \Psi(r,\vartheta,\varphi)r^2 \sin(\vartheta)dr\ d\vartheta\ d\varphi$$
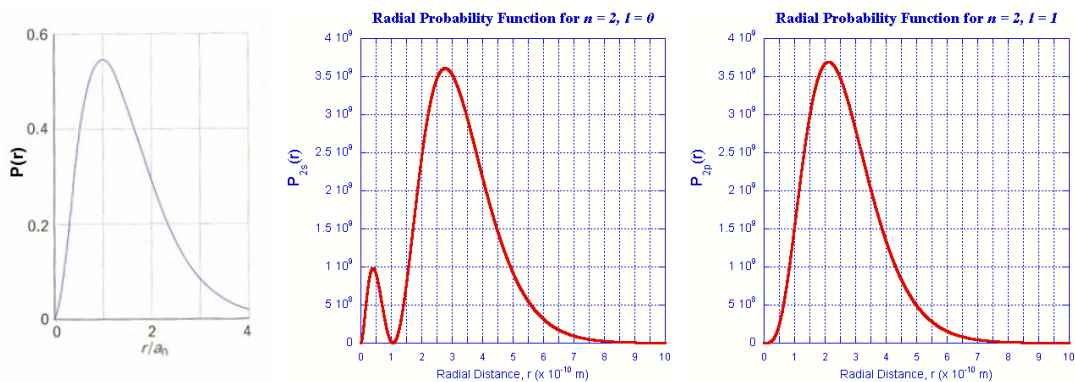
In case of 1s orbital:

$$\int_\vartheta \int_\varphi \Psi(r,\vartheta,\varphi)^* \cdot \Psi(r,\vartheta,\varphi)r^2 dr \; \sin(\vartheta)d\vartheta \; d\varphi \; = \; \underbrace{\int_{\vartheta=0}^{\pi} \int_{\varphi=0}^{2\pi} \sin(\vartheta)d\vartheta \; d\varphi}_{4\pi} \Psi(r)^* \cdot \Psi(r)r^2 dr$$
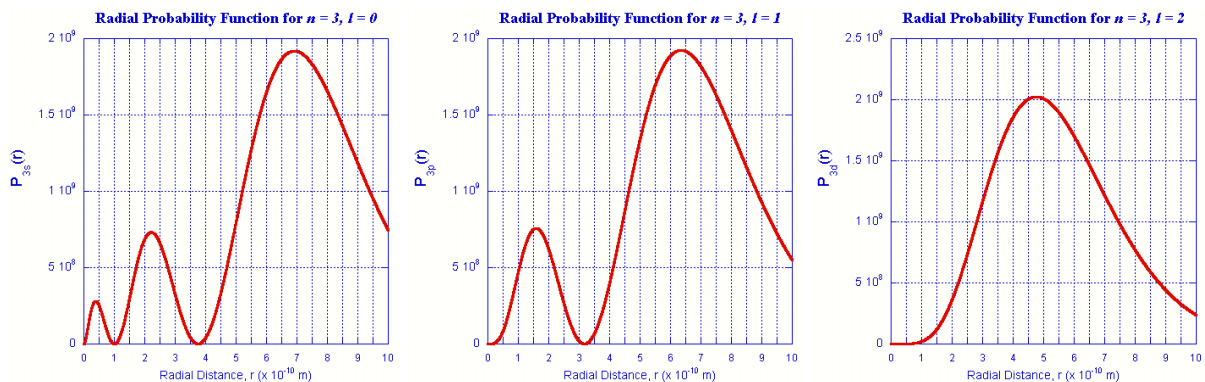
$$= \; 4\pi r^2 \Psi(r)^* \cdot \Psi(r)dr$$

This quantity is called *radial density*.

Radial density of the 1s, 2s and 2p orbitals:

Radial density of the 3s, 3p and 3d orbitals:

Discussion of the solution: radius of the atom

In Bohr's atomic theory the radius of the H-atom is a trivial concept: the atom ends at the orbit where the electron is situated. In case of the 1s orbital the radius is 1 bohr. But how can this concept be defined in case of quantum mechanics? The problem is that density does not „end", the function decays exponentially.

Proper questions in the language of quantum mechanics:

- Where is the maximum of the electron density?

- What is the average distance of the electron from the nucleus?

- What is the probability of finding an electron within a given distance r_0?

Where is the maximum of the (radial) electron density?

$$\frac{\partial}{\partial r}(4\pi r^2 \Psi^* \cdot \Psi) = 0$$

In case of 1s orbital:

$$\frac{\partial}{\partial r}(4\, e^{-2r}r^2) = 4\left(-2e^{-2r}r^2 + 2re^{-2r}\right) = 0$$
$$2e^{-2r}r(1-r) = 0$$

$e^{-2r} = 0$ asymptotic behaviour: not a real extremum.

$r = 0$ minimum

$(1 - r) = 0$ maximum

Thus the maximum of the radial electron density is exactly at 1 bohr!!

What is the average distance from the nucleus?

$$\bar{r} = \langle\Psi|\hat{r}|\Psi\rangle = \int \Psi^*\hat{r}\Psi \; dv$$

In case of 1s function [4]:

---

[4]The following definite integral has been used:

$$\int_0^\infty x^n e^{-ax} \; dx = \frac{n!}{a^{n+1}}$$

$$\begin{aligned}
\bar{r} &= \frac{1}{\pi}\int_{r=0}^{\infty}\int_{\vartheta=0}^{\pi}\int_{\varphi=0}^{2\pi} e^{-r}re^{-r}r^2\sin(\vartheta)dr\ d\vartheta d\varphi \\
&= \frac{1}{\pi}4\pi\int_{r=0}^{\infty} re^{-2r}r^2 dr \\
&= 4\int_{r=0}^{\infty} r^3 e^{-2r}dr = \frac{4\cdot 3\cdot 2}{4\cdot 4} = \frac{3}{2}
\end{aligned}$$

This means that the expectation value of the distance of the electron from the nucleus is 1.5 bohr in case of 1s orbital.

The general formula valid for all orbitals can be given in an analytic form, one only needs to insert the quantum numbers:

$$\bar{r} = \frac{a_0}{2}[3n^2 - l(l+1)]$$

What is the probability of finding an electron within a given distance r_0?

We have to sum the probabilities from 0 to r_0, this is an integration:

$$\int_{r=0}^{r_0}\int_{\vartheta=0}^{\pi}\int_{\varphi=0}^{2\pi} \Psi^* \cdot \Psi\ r^2\sin(\vartheta)dr\ d\vartheta d\varphi$$

Example: 1s orbital, $r_0 = 1$bohr

$$\begin{aligned}
\frac{4\pi}{\pi}\int_0^1 r^2\ e^{-2r}dr &= 4\left[e^{-2r}\left(\frac{r^2}{-2} - \frac{2r}{4} + \frac{2}{-8}\right)\right]_0^1 \\
&= 4\left(e^{-2}\left(-\frac{1}{2} - \frac{1}{2} - \frac{1}{4}\right) + \frac{1}{4}\right) = 0.324..
\end{aligned}$$

(The following indefinite integral was used: $\int x^2 e^{ax}\ dx = e^{ax}\left(\frac{x^2}{a} - \frac{2x}{a^2} + \frac{2}{a^3}\right)$)
The table below demonstrates the result:

r_0(bohr)	0.1	0.2	1.	1.5	2.	5
%	0.12	4.8	32.4	57.6	76	99.6

We can clearly see that the probability decays vers slowly, the electron can be found with a probability of only 76% within 2 bohr.

Let us compare the results of the Bohr model and quantum mechanics (in case of the 1s ground state):

	Bohr model	Quantum mechanics
Maximum of the probability	1 bohr	1 bohr
Average distance	1 bohr	1.5 bohr
Probability within 1 bohr	100%	32.4%

Discussion of the results: angular momentum

The eigenfunctions for the hydrogen atom has been selected so that they are also eigenfunctions of $\hat{l}^2$ and $\hat{l}_z$ operators:

$\hat{l}^2$ operator: $\lambda = l(l+1)\hbar^2$ $\qquad\qquad$ $\hat{l}_z$ operator: $l_z = m\hbar$

where l and m are the quantum numbers.

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

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

Note:

For all s type orbitals the length of angular momentum vector ($\sqrt{\lambda}$) is $0 \rightarrow$ the electron does not „orbit" around the nucleus!!
What is it doing then? Why it is not in the nucleus?
The answer again can be given using the Heisenberg relation: if the electron is at the nucleus, than $\Delta x = 0 \rightarrow \Delta p$ and thus the kinetic energy is infinitely large. This is a contradiction!

Electrons in s state do not have angular momentum!!!

Angular momentum vectors of the $3d$ orbitals:

(b)
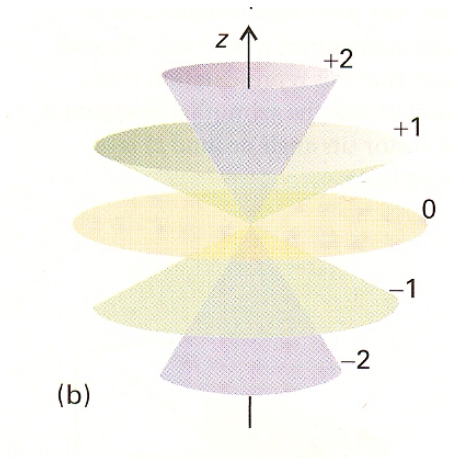
1.6.4. Magnetic moments

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

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

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

If two operators differ only by a constant factor, also the eigenvalues will differ by this factor only. Thus, we can easily calculate the eigenvalues of the magnetic monets:

$$\text{eigenvalues of} \quad \hat{\mu}_z : \quad \frac{e}{2\,m_{el}}\hbar \cdot m$$

with m being the quantum number introduced in connection to the $\hat{l}_z$ operator. (This relation gives an explanation why it is often called *magnetic quantum number*).

The interaction of a system possessing a magnetic moment and the magnetic field is given by the product of the *magnetic induction* ($\hat{\underline{B}}$) characterizing the magnetic field and magnetic moment of the system:

$$\hat{\underline{B}} \cdot \hat{\underline{\mu}}$$

If this interaction exists, it needs to be included in the Hamiltonian of the system:

$$\hat{H} \quad \rightarrow \quad \hat{H} + \underbrace{\hat{\underline{B}} \cdot \hat{\underline{\mu}}}_{\hat{H}'}$$

Considering $\hat{H}'$ as *perturbation*, the first order correction (see perturbation theory above) to the energy of the H-atom is given by:

$$E^{(1)} = \langle \Psi_{nlm} | \hat{\underline{B}} \cdot \hat{\underline{\mu}} | \Psi_{nlm} \rangle$$

Assume that the magnetic field is along the z axis:

$$E^{(1)} = \langle \Psi_{nlm}|B_z \cdot \hat{\mu}_z|\Psi_{nlm}\rangle = \langle \Psi_{nlm}|B_z \cdot \frac{e}{2m_{el}} \underbrace{\hat{l}_z|\Psi_{nlm}}_{\hbar\, m|\Psi_{nlm}\rangle}\rangle = B_z \cdot \underbrace{\frac{e}{2m_{el}}\hbar}_{\mu_B}\, m$$

$$= B_z \cdot \mu_B \cdot m$$

with μ_B being the so called *Bohr magneton*, a constant.

What does this mean? According to the equation above, the energy of the hydrogen atom in magnetic field will depend 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*.
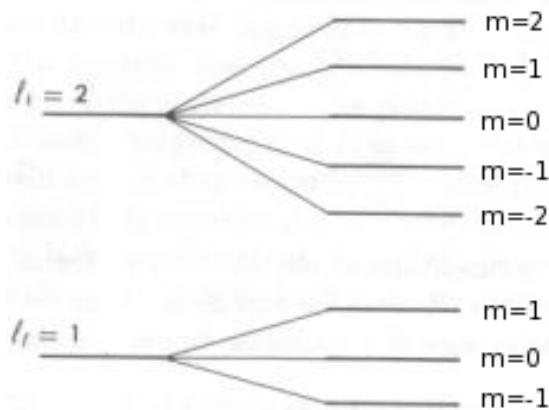
1.6.5. The spin of the electron

The Zeeman effect can be demonstrated if a beam of H atoms is injected into a inhomogeneous magnetic field, since the beam must split into $2l+1$ beams according to the values of m. This means 1, 3, 5, 7, etc. beams are expected depending on the initial quantum number l of the H-atom.

Stern and Gerlach observed, however, that the beam splited into *two (2)* beams:
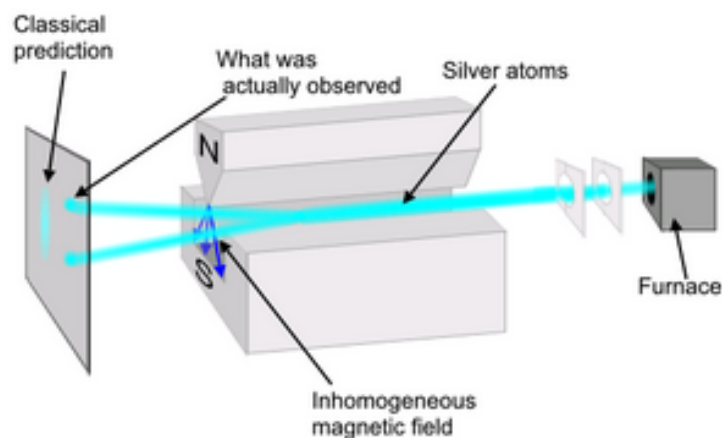
(Note that Stern and Gerlach conducted the experiment with silver atoms, but it also has only one electron on its outermost s orbital.)

These experiments *can not be explained* by the theory we have presented so far!!!!

Conclusion:

- Pauli (1925): a „fourth quantum number" is needed;

- Goudsmit and Uhlenbeck suggested the concept of *spin* as the „internal angular momentum".

Classically: if the electron is not a point-like particle, it can rotate around its axis, either to the right or to the left.

In quantum mechanics: the electron as a particle has „intrinsic" angular momentum, which is its own property, like its charge.

In the *non-relativistic quantum mechanics* we are doing here, spin does not appear, i.e. we have an experiment which *contradicts the postulates*! Either we need a new theory (this would be relativistic quantum mechanics), or we try to fix the theory by *introducing spin phenomenologically.*

To do this, one needs to introduce an operator to describe spin:

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

What do we need to know about an operator in order to work with it?

- what is it acting on?

- what is its effect?

- commutation relations.

The commutation properties of this new operator are the same as of the angular momentum, since it describes similar phenomena (magnetic moment):

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

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

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

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

What are the possible values of the new quantum numbers s and m_s? These 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, as a particle has, beside its charge, another intrinsic property, spin. Electron has a charge of -1, and a spin of $\frac{1}{2}$!!!!

What do the spin operators act on? $\hat{s}_z$ has only two eigenvalues and associated eigenfunctions:

$$\hat{s}_z\,\alpha(\sigma) = \frac{1}{2}\,\alpha(\sigma)$$

$$\hat{s}_z\,\beta(\sigma) = -\frac{1}{2}\,\beta(\sigma)$$

with σ being the spin variable (spin coordinate). On this basis, considering the commutation relations, the matrices of the spin operators can be derived (Pauli matrices, see Kémiai Matematika):

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

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

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

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

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

Notes:

- in what follows we will only deal with pure spin states;

- the usual Hamiltonian does not depend on spin, the product form given in the previous equation is not an approximation!

1.6.6. The states of the hydrogen atom, revisited

Wave function:

$$\Psi_{n,l,m,m_s} = \Psi_{n,l,m,m_s}(r, \vartheta, \varphi, \sigma)$$

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 the quantum number n:

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

therefore the degeneracy is $2n^2$-fold!!!

H-atom in magnetic field, revisited

Spin is alike angular momentum and a magnetic moment is associated with it. According to the experiments, the associated magnetic moment is twice as large as in case of the angular momentum associated with the orbital:

$$
\hat{\mu}_z = \frac{e}{m_{el}}\hat{s}_z
$$

$$
E^{(1)} = \langle \Psi_{nlmm_s} | B_z \frac{e}{m_{el}}\hat{s}_z | \Psi_{nlmm_s} \rangle = B_z \frac{e}{m_{el}} m_s
$$

(c.f. the factor of two in the denominator).

Considering both $\hat{l}_z$ and $\hat{s}_z$:

$$
E^{(1)} = B_z \mu_B (m + 2\,m_s)
$$

Thus, energy levels are split up into $2(2l+1)$ levels!

1.6.7. Spin-orbit interaction

We have seen above that there are two different types of angular momenta:

- angular momentum resulting from the motion of electrons ($\hat{\underline{l}}$), will be called as *orbital angular momentum*;

- angular momentum originating from the spin ($\hat{\underline{s}}$) (*spin momentum*).

Since both angular momenta create magnetic moments, these can interact. The magnitude of the interaction depends on the two momenta:

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

where ζ is a constant.

Consequences:

- the Hamilton operator will not commute with either $\hat{l}^2$, $\hat{l}_z$ and $\hat{s}_z$ operators;

- energy will depend on the quantum number l.

This effect is very small, it is of the order $10^{-4} - 10^{-5}$ hartree, but can be observed with very accurate spectroscopic methods. For heavier atoms it can be larger and for atoms with large atomic number it must be considered.

2. Many-electron systems

2.1. The Hamiltonian

$$
\hat{H} = -\frac{\hbar^2}{2m_{el}} \sum_i^{electrons} \left(\frac{\partial^2}{\partial x_i{}^2} + \frac{\partial^2}{\partial y_i{}^2} + \frac{\partial^2}{\partial z_i{}^2} \right) - \sum_i^{electrons} \sum_A^{nuclei} \frac{Z_A \cdot e^2}{r_{iA} 4\pi\epsilon_0}
$$
$$
+ \sum_i^{electrons} \sum_{j<i}^{electrons} \frac{e^2}{r_{ij} 4\pi\epsilon_0} + \sum_A^{nuclei} \sum_{B<A}^{nuclei} \frac{Z_A Z_B e^2}{r_{AB} 4\pi\epsilon_0}
$$

with

- $\{x_i, y_i, z_i\}$ being the coordinates of electron i;

- Z_A being the charge of nucleus A;

- r_{ij} being the distance of electrons i and j;

- r_{AB} being the distance of nuclei A and B;

- r_{iA} is the distance of electron i and nucleus A;

- for constants see earlier.

The Hamiltonian in atomic units

$$
\hat{H} = \underbrace{-\frac{1}{2} \sum_i^{electrons} \left(\frac{\partial^2}{\partial x_i{}^2} + \frac{\partial^2}{\partial y_i{}^2} + \frac{\partial^2}{\partial z_i{}^2} \right)}_{\text{kinetic energy of electrons}} \underbrace{- \sum_i^{electrons} \sum_A^{nuclei} \frac{Z_A}{r_{iA}}}_{\text{electron−nuclei attraction}}
$$
$$
\underbrace{+ \sum_i^{electrons} \sum_{j<i}^{electrons} \frac{1}{r_{ij}}}_{\text{electron−electron repulsion}} \underbrace{+ \sum_A^{nuclei} \sum_{B<A}^{nuclei} \frac{Z_A Z_B}{r_{AB}}}_{\text{repulsion of the nuclei}}
$$

Note: The kinetic energy of the nuclei have been separated using the Born-Oppenheimer approximation (see later).

2.2. 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.

2.3. The Schrödinger equation

$$\hat{H}\,\Psi(1,2,...,n) \;\; = \;\; E\;\Psi(1,2,...,n)$$

Problem: the Hamiltonian can not be written as a sum of terms corresponding to individual electrons ($\sum_i$), therefore the wave function is not a product:

- Schrödinger equation can not be solved exactly

- *the solution is not intuitive*

2.4. Approximation of the wave function in a product form

Physical meaning:

- Independent Particle Approximation (IPA), or

- Independent Electron Model (IEM)

a) assume, there is no interaction between electrons
This unphysical situation helps us to find a suitable approximation:

$$\hat{H} = \sum_i h_i(i) \;\; \Rightarrow \;\; \underbrace{\Psi(1,2,...,n)}_{\text{wave function}} = \underbrace{\phi_1(1)\cdot\phi_2(2)...\cdot\phi_n(n)}_{\text{product of spin orbitals}}$$

Spin orbitals

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

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

$$\begin{aligned}
\hat{H}\Psi = E\Psi \;\; \Rightarrow \;\; & \hat{h}_1(1)\phi_1(1) = \varepsilon_1\phi_1(1)\\
& \hat{h}_2(2)\phi_2(2) = \varepsilon_2\phi_2(2)\\
& ...\\
& \hat{h}_n(n)\phi_n(n) = \varepsilon_n\phi_n(n)
\end{aligned}$$

One n-electron equation $\Rightarrow$ system of n one-electron equations

Total energy in this case is a simple sum: $E = \sum_i \varepsilon_i$
What is $\hat{h}_i$?

$$\hat{h}_i \;\; = \;\; -\frac{1}{2}\Delta_i - \frac{Z_A}{r_{iA}}$$

which resembles the Hamiltonian of the H-atom $\Rightarrow$ eigenfunctions will be hydrogen-like!
Problem: electron-electron interaction is missing!!!

b) Hartree method:

Consider the one-electron problem of the first electron, but let us complete $\hat{h}_1$ with the interaction with the other electrons:

$$\hat{h}_1 \quad \rightarrow \quad \hat{h}_1^{eff} = -\frac{1}{2}\Delta_i - \frac{Z_A}{r_{iA}} + V_1^{eff}$$

where V_1^{eff} is the interaction of electron 1 with all other electrons.

How to obtain V_1^{eff}?

- Interaction of two charges: $\frac{Q_1 Q_2}{r_{12}}$

- If Q_2 is a distributed charge corresponding to the electron on orbital φ_2: $Q_2 = -|\varphi_2(r_2)|^2$

- Thus: $\frac{Q_1 Q_2}{r_{12}} = -Q_1 \int \frac{|\varphi_2|^2}{r_{12}} dv_2$

- The charge of electron 1: $Q_1 = -1$

- Thus: $V_1^{eff} = \sum_{j=2} \int \frac{|\varphi_j(j)|^2}{r_{1j}} dv_j$

The energy (ε_1) and orbital (φ_1) of electron 1 can be obtained by solving the eigenvalue equation of $\hat{h}_1^{eff}$:

$$\hat{h}_1^{eff}\varphi_1(1) \quad = \quad \varepsilon_1\varphi_1(1)$$

Similarly, for electron 2

$$V_2^{eff} \quad = \quad \sum_{j\neq 2} \int \frac{|\varphi_j(j)|^2}{r_{2j}} dv_j$$

$$\hat{h}_2^{eff}\varphi_2(2) \quad = \quad \varepsilon_2\varphi_2(2)$$

Finally for electron n:

$$V_n^{eff} \quad = \quad \sum_{j\neq n} \int \frac{|\varphi_j(j)|^2}{r_{nj}} dv_j$$

$$\hat{h}_n^{eff}\varphi_n(n) \quad = \quad \varepsilon_n\varphi_n(n)$$

These equations are not independent since the orbitals of all other electrons are needed to obtain V_i^{eff}. Therefore, these equations have to be solved iteratively:

1. starting orbitals (e.g. system neglecting the electron-electron interaction):

2. obtain V_i^{eff}

3. solve the equations $\rightarrow$ new orbitals

4. go to step 2

We call this procedure Self-Consistent Field (SCF), since at convergence the field (electron-electron interaction) generated by the actual set of orbitals results in the same set of orbitals.

Total energy: $E \neq \sum_i \varepsilon_i$, i.e. not a sum of the orbital energies since in this case we would count electron-electron interaction twice. Therefore, energy has to be calculated as an expectation value:

$$E = \langle \Psi | \hat{H} | \Psi \rangle$$

c) Hartree-Fock method: see later

2.5. Pauli principle and the Slater determinant

An important principle of quantum mechanics: identical particles can not be distinguished. Therefore the operator permuting two electrons ($\hat{P}_{12}$) can not change the wave function, or at the most it can change its sign:

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

Change of the sign is eligible since only the square of the wave function has physical meaning which does not change with the sign.

According to *postulate V+2-es* (so called Pauli principle) the wave function of the electrons must be anti-symmetric with respect to the interchange of two particles. In case of two electrons:

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

The product wave function used in the Hartree method does not fulfill this requirement, it isn't anti-symmetric. Therefore, instead of a product, we have to use a determinantal wave function.

$$\Psi(1, 2, ..., n) = \frac{1}{\sqrt{n}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_n(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_n(2) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_1(n) & \phi_2(n) & \cdots & \phi_n(n) \end{vmatrix}$$

This type of wave function is called the *Slater determinant*.
Remember the properties of determinants:

a) Interchanging two rows of a determinant, the sign of the determinant will change.
   $\rightarrow$ interchanging two orbitals, the wave function will change sign;

b) If two columns of a determinant are equal, the value of the determinant is 0
   $\rightarrow$ if two electrons are on the same orbital, the wave function vanishes;

c) Adding a row of a determinant to another row, the value of the determinant is unchanged
   $\rightarrow$ any combination of the orbitals will give the same wave function.

Conclusions:

a) and b) Pauli principle is fulfilled automatically

c) **orbitals do not have physical meaning, only the space spaned by them!!!**

Hartree-Fock method
    In the Hartree method, equations as well as $\hat{h}_i^{eff}$ corresponding to different electrons differ:

$$
\begin{aligned}
\hat{h}_1^{eff}\varphi_1(1) &= \varepsilon_1\varphi_1(1) \\
\hat{h}_2^{eff}\varphi_2(2) &= \varepsilon_2\varphi_2(2) \\
&\cdots \\
\hat{h}_n^{eff}\varphi_n(n) &= \varepsilon_n\varphi_n(n)
\end{aligned}
$$

This contradicts the principle of indistinguishability of identical particles.
    Therefore in the Hartee-Fock method the same operator (Fock operator) is used for all electrons:

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

with U^{HF} being an averaged (Hartree-Fock) potential (see later).
    The Hartree-Fock equation:

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

The wave function Ψ is a determinant constructed from the orbitals φ_i, while energy can be calculated as an expectation value: $\langle\Psi|\hat{H}|\Psi\rangle$.

3. Electronic structure of atoms

Underlying physical principle: Independent Particle Approximation

3.1. Energy, orbitals, wave function

According to the discussion above, we should solve the Hartree, or the Hartree-Fock equations first. In both cases we get orbital energies (ε_i) and orbitals (ϕ_i), therefore for a quantitative discussion it does not matter which one we use. The form of the equation reads:

$$\hat{h}(i)\phi_i = \varepsilon_i\phi_i$$
$$\hat{h}(i) = -\frac{1}{2}\Delta_i - \frac{1}{r} + V$$

where V denotes the electron-electron repulsion and is given for both the Hartree and the Hartree-Fock methods above.

As a solution we get:

- ϕ_i orbitals

- ε_i orbital energies

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, i.e. $Y(\vartheta, \varphi)$. 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 from that of the H atom: since it is not a simple Coulomb potential, the degeneracy according to l quantum number will be lifted, i.e. orbital energies will depend not only on n but also on l ($\varepsilon = \varepsilon_{nl}$).

Wave function: constructed from the occupied orbitals as a product (Hartree) or as a determinant (Hartree-Fock); occupied orbitals are selected according to the increasing value of the orbital energy (so called *Aufbau principle*).
Some important terms:

- *Shell*: collection of the orbitals with the same quantum number n;

- *Subshell*: collection of orbitals with common n and l quantum numbers, which are degenerate according to the discussion above. Orbital $1s$ as well as $2s$ form subshells alone, while $2p_0$, $2p_1$ és $2p_{-1}$ (or $2p_x$, $2p_y$, $2p_z$) orbitals form the subshell $2p$. Subshell $3d$ has five components, $4f$ seven, etc.

- *Configuration*: defines the occupation of the subshells. Examples:
  He: $1s^2$
  C: $1s^2\ 2s^2\ 2p^2$

3.2. Angular momentum of atoms

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

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

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

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

Since $\underline{L}$ and $\underline{S}$ are again angular momentum operators, the eigenvalues are given by similar rules:

$$\hat{L}^2 \rightarrow L(L+1)\,[\hbar^2] \quad L = 0, 1, 2, \ldots$$
$$\hat{L}_Z \rightarrow M_L\,[\hbar] \quad M_L = -L, -L+1, \ldots, L$$
$$\hat{S}^2 \rightarrow S(S+1)\,[\hbar^2] \quad S = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$$
$$\hat{S}_Z \rightarrow M_S\,[\hbar] \quad M_S = -S, -S+1, \ldots, S$$

Let us try to obtain the eigenvalues of these operators. From the definition it follows:

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

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

and therefore

$$M_L = \sum_i m(i)$$

$$M_s = \sum_i m_s(i)$$

To obtain the length of the many particle angular momentum vectors is more complicated, in particular, since – due to the uncertainty principle – the direction of the one-particle vectors is unknown. The following figure demonstrates this uncertainty of the summation:

(b)

(a)
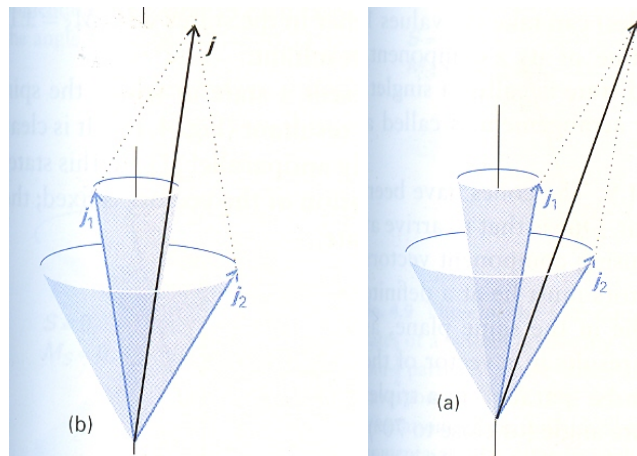
since the angular momentum vectors are not known, only the cone it is situated on, therefore the summation can lead to different results. For example, in case of two particles the possible values of the L and S quantum numbers are given by:

$$L = (l_1 + l_2), (l_1 + l_2 - 1), \cdots, |l_1 - l_2|$$
$$S = (s_1 + s_2), (s_1 - s_2)$$

For more particles the values can be obtained recursively, adding the components one by one.

3.3. 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 $\Rightarrow$ we can chose the eigenfunction of the Hamiltonian such that these are eigenfunctions of the angular momentum operators at the same time. This means we can classify the atomic states by the corresponding quantum numbers of the angular momentum operators:

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

The latter notation is more popular.
Thus, in analogy to the hydrogen atom, the *states* can be classified according to the quantum numbers. For this, L and S suffices, since energy depends only on these two.

L=	0	1	2	3	4	5	$\cdots$
notation:	S	P	D	F	G	H	$\cdots$
degeneracy	1	3	5	7	9	11	$\cdots$
S=	0	$\frac{1}{2}$	1	$\frac{3}{2}$	2	$\cdots$	
multiplicity (2S+1):	1	2	3	4	$\cdots$		
denomination:	singlet	doublet	triplet	quartet	$\cdots$		

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!!

3.4. Construction of atomic states

Since there is a high-level degeneracy among the orbitals, most of the time we face open shell systems, where degenerate orbitals are not fully occupied. In this case one can construct several states for the same configuration, i.e. configuration is not sufficient to represent the atomic 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 give altogether six spinorbitals, wich can be occupied by the available two electrons. The number of the possibilities are given by $\begin{pmatrix} 6 \\ 2 \end{pmatrix}$ which results in 15 different determinants. This means there will be 15 states in this case. Do the determinants form the states? With other words: are these determinants eigenfunctions of $\hat{L}^2$ and $\hat{S}^2$?

To see this, let us construct the states by summing the angular momenta: Since we do not know angular momentum vectors completely (remember the uncertainty principle applying for the components!), the summation of two angular momentum vectors will not be unique either, we get different possibilities:

$$l(1) = 1 \qquad l(2) = 1$$
$$s(1) = \frac{1}{2} \qquad s(2) = \frac{1}{2}$$
$$\Downarrow$$

$$L = l(1) + l(2), l(1) + l(2) - 1, \ldots, |l(1) - l(2)| = 2, 1, 0$$
$$S = s(1) + s(2), s(1) + s(2) - 1, \ldots, |s(1) - s(2)| = 1, 0$$

The possible states therefore are:

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

Considering the degeneracy: ^1S gives one state, ^1P gives three states, ^1D gives five, ^3S gives three states, ^3P gives nine states (three times three), ^3D gives fifteen states (three times five), which are altogether 36 states. But we can have only 15, as was shown above!

What is the problem? 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!

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 (see later);

- if multiplicities are the same, the state with larger L value is lower in energy;

In case of the carbon atom:

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

3.5. Spin-orbit interaction, total angular momentum

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

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

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:

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

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

$$\hat{J}^2 \;\rightarrow\; J(J+1) \, [\hbar^2]$$
$$\hat{J}_z \;\rightarrow\; M_J \, [\hbar]$$

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!!

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:

$$L = 1, \;\; S = 1 \;\rightarrow\; J = 2, 1, 0$$
$$^3P \;\rightarrow\; {}^3P_2, \, {}^3P_1, \, {}^3P_0$$

Energy splits into three levels!

Example II: carbon atom ^1D state:

$$L = 2, \;\; S = 0 \;\rightarrow\; J = 2$$
$$^1D \;\rightarrow\; {}^1D_2$$

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!!!

3.6. Atom in external magnetic field

Considering the total angular momentum, the change of energy in magnetic field reads:
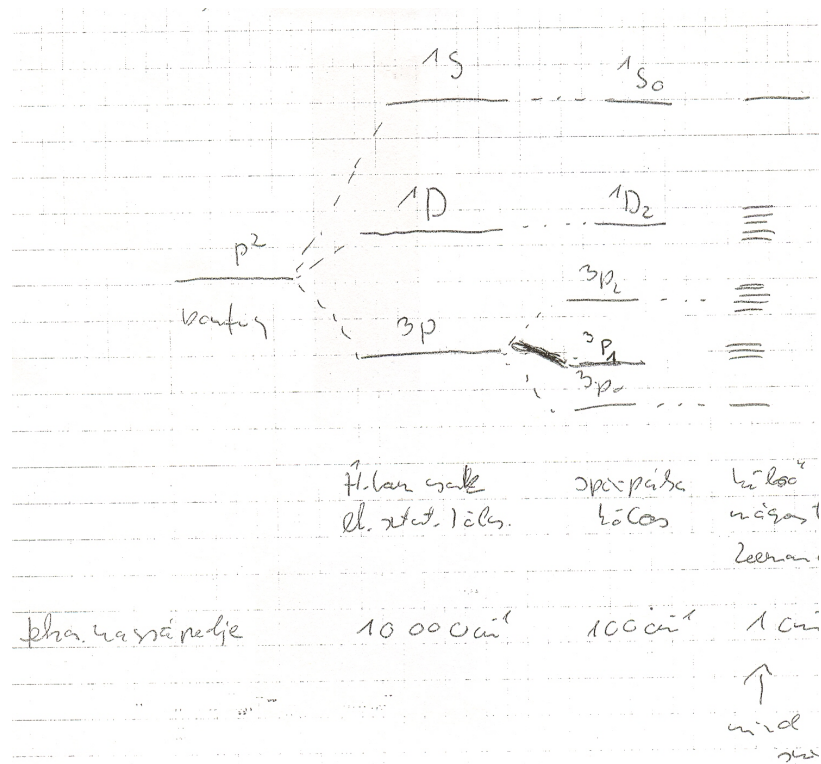
$$\Delta E = M_J \cdot \mu_B \cdot B_z$$
$$M_J = -J, -J+1, \dots, J$$

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

3.7. Summarized

Carbon atom in $2p^2$ configuration:

Other configuration for p shell:

$$
\begin{array}{ll}
p^1 \text{ and } p^5 & {}^2P \\
p^2 \text{ and } p^4 & {}^3P, \ {}^1D, \ {}^1S \\
p^3 & {}^4S, \ {}^2D, \ {}^2P \\
p^6 \text{ (closed shell)} & {}^1S
\end{array}
$$

4. Electronic structure of molecules

4.1. Separation of the motion of electrons and nuclei

Hamiltonian

New compared to atoms: electrons are moving in the field of several nuclei. One important consequence is that the symmetry of the system is lower than in case of atoms.

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_i^{electrons}\Delta_i - \sum_i^{electrons}\sum_A^{nuclei}\frac{Z_A}{r_{iA}} + \sum_{j<i}^{electrons}\frac{1}{r_{ij}} + \sum_{B<A}^{nuclei}\frac{Z_A Z_B}{r_{AB}}}_{\hat{H}_e(\mathbf{r},\mathbf{R})} \underbrace{-\frac{1}{2}\sum_A\frac{1}{m_A}\Delta_A}_{\hat{T}_n(\mathbf{R})}$$

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

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

with

- $\mathbf{r}$ denoting the coordinates of the electrons;

- $\mathbf{R}$ denoting the coordinates of the nuclei;

- see also earlier notations.

The coordinates of the electrons and the nuclei do not separate, interaction between electrons and nuclei couples them.

The Born-Oppenheimer approximation:

$$\text{electrons are much lighter than nuclei } (\tfrac{M}{m_{el}} \approx 1836)$$
$$\Downarrow \text{ equipartition}$$
$$\text{electrons are much faster}$$
$$\Downarrow$$
$$\text{electrons follow immediately nuclei (adiabatic approximation)}$$
$$\Downarrow$$
$$\underline{\text{from the point of view of the electrons}} \text{ nuclei are steady}$$
$$\Downarrow$$
Equation for electrons: $\hat{H}_e(\mathbf{r};\mathbf{R})\Phi(\mathbf{r};\mathbf{R}) = E(\mathbf{R})\Phi(\mathbf{r};\mathbf{R})$
for nuclei: $(\hat{T}_n(\mathbf{R}) + E(\mathbf{R}))\chi(\mathbf{R}) = E_{TOT}\chi(\mathbf{R})$

Notes:

- within the *Born-Oppenheimer (BO)* approximation the equation for electrons and nuclei have been separated;

- nuclei are *not* steady;

- the potential acting on the nuclei is $E(\mathbf{R})$, i.e. electronic energy (eigenvalue of the electronic Schrödinger equation) at different nuclear distances;

- the potential energy surface $E(\mathbf{R})$ is thus the consequence of the *Born-Oppenheimer* approximation, without this approximation the potential (potential curve, potential energy surface – PES) can not be defined;

- usually a very good approximation, it breaks down if the energies of two electronic states are close (e.g. photochemistry).

From now on, we will deal with the first (electronic) equation, that of the nuclei will be considered in the second part of the semester; we will omit the index e, $\hat{H}$ will refer to the electronic Hamiltonian.

4.2. 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, respectively, while R is the distance of the two nuclei.

The Schrödinger equation:

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

Analytic solution is possible in elliptic coordinates; we do not solve it, only analyze the solutions.

Symmetry of the system: $D_{\infty h}$.

Character table for point group D∞h

$D_{\infty h}$	E	$2C_\infty$	...	$\infty\sigma_v$	i	$2S_\infty$	...	∞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	-	-	-
...	...	...	...	...	...	...	...	...	-	-	-

The solutions $(\Phi_i(1; R))$, the wave function of the system, now *orbital*, since it refers to one electron):
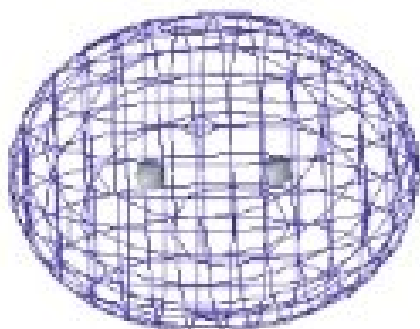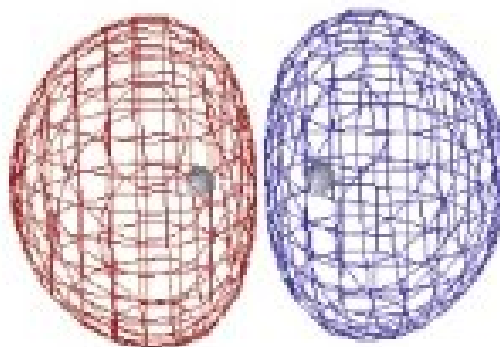
Φ_1, symmetry is Σ_g^+

Φ_2, symmetry is Σ_u^+
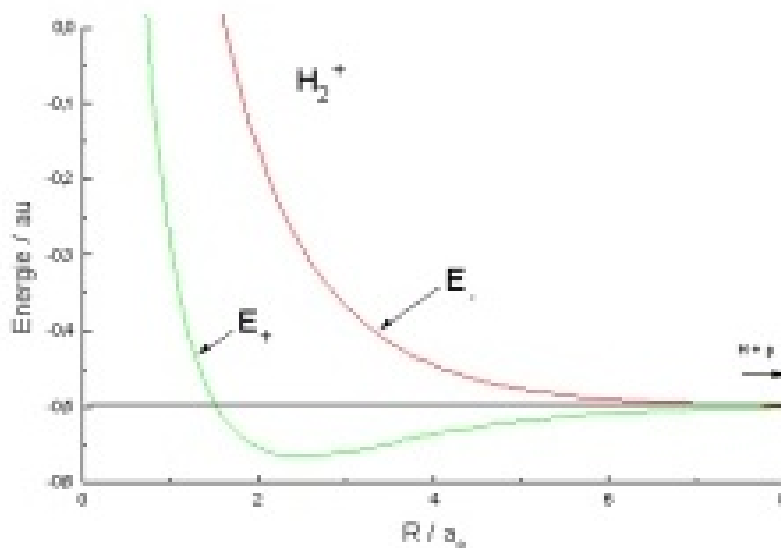
Equilibrium bond distance: 2.00 bohr, dissociation energy: 2.8 eV

Basic question: what is the chemical bond?
  Answer according to the figures:

- according to the form of the lower PES: energy decreases when the two nuclei get closer to each other;

- form of the corresponding orbital: electron density between the two nuclei increases.
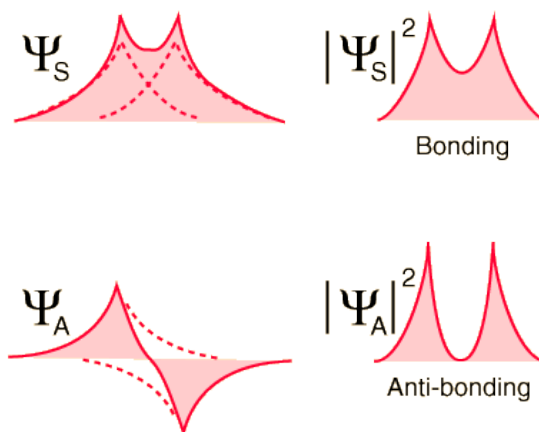
Quantum mechanics can not tell more, but this is mathematically a perfect explanation. For chemists there are of course other explanations based on *approximate models*, see later.

4.3. The LCAO-MO approximation

σ_g and σ_u orbitals are complicated functions. Can we use something simpler?

If we consider the formation of molecules as atoms approaching each other, molecular orbitals can be viewed as two hydrogenic ground state orbitals ($1s$) approaching. Therefore:

$$\sigma_g = N_1 \cdot (1s_A + 1s_B)$$
$$\sigma_u = N_2 \cdot (1s_A - 1s_B)$$

where $1s_A$ and $1s_B$ are the $1s$ orbitals of the two atoms.

The validity of this approximation is clearly seen from the form of the molecular orbitals. Is there a mathematical explanation?

$$\hat{H} = \underbrace{-\frac{1}{2}\Delta - \frac{1}{r_{1A}}}_{\text{H atom at position } A} - \underbrace{\frac{1}{r_{1B}}}_{=0 \text{ at position } A} + \underbrace{\frac{1}{R}}_{constant}$$

This means the Hamiltonian at nucleus A can be approximated by the Hamiltonian of an H atom, and similarly also at position B. Therefore the wave function can be approximated by the combination of $1s_A$ and $1s_B$ functions.

In general: within the *Linear Combination of Atomic Orbitals for Molecular Orbitals* (LCAO-MO) theory, molecular orbitals are approximated by the linear combination of atomic orbitals:

$$\phi_i = \sum_r c_{ir}\chi_r$$

with χ_r denoting atomic orbitals. Mathematically: molecular orbitals are expanded in the basis of atomic orbitals (basis functions) with coefficients c_{ir}.

How many function do we need?

- for an exact expansion infinitely many functions are required;

- according to the above discussion, AO-s form a very good basis, a few of them suffice;

- we need at least as many basis function as many occupied orbitals we have in the atoms (so called minimal basis).

How can one obtain the coefficients: *variational principle*, i.e. minimize the energy ($E = \langle\phi_i|\hat{H}|\phi_i\rangle \to min$), which leads to a matrix eigenvalue problem (see Kémiai Matematika):

$$\mathbf{H}c = E\mathbf{S}c$$

with

- $\mathbf{H}$ is the matrix of the Hamiltonian: $H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle$;

- $\mathbf{c}$ is the vector of the coefficients;

- **S** is the overlap matrix $S_{ij} = \langle \phi_i | \phi_j \rangle$, which needs to be considered since atomic orbitals are not orthogonal. Their overlap is important to get bonding!!!

Example: H_2^+ molecule ion, minimal basis
Basis: $\chi_1 = 1s_A$ $\qquad \chi_2 = 1s_B$
Overlap of the basis functions: $S_{11} = S_{22} = 1$ $\qquad S_{12} = \langle \chi_1 | \chi_2 \rangle \equiv S$
We look for the wave functions in the following form:

$$
\begin{aligned}
\chi_1 &= c_{11}\, 1s_A + c_{12}\, 1s_B \\
\chi_2 &= c_{21}\, 1s_A + c_{22}\, 1s_B
\end{aligned}
$$

Matrix elements of the Hamiltonian:

$$
\begin{aligned}
H_{11} &= \langle \chi_1 | \hat{H} | \chi_1 \rangle = \langle 1s_A | \hat{H} | 1s_A \rangle \equiv \alpha \\
H_{22} &= \langle \chi_2 | \hat{H} | \chi_2 \rangle = \langle 1s_B | \hat{H} | 1s_B \rangle \equiv \alpha \\
H_{12} &= \langle \chi_1 | \hat{H} | \chi_2 \rangle = \langle 1s_A | \hat{H} | 1s_B \rangle \equiv \beta
\end{aligned}
$$

H and **S** matrices:

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

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

The $\mathbf{Hc} = E\mathbf{Sc}$ eigenvalue equation:

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

The secular determinant:

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

$$\Downarrow$$

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

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

Results:
Energy: orbital energy diagram:
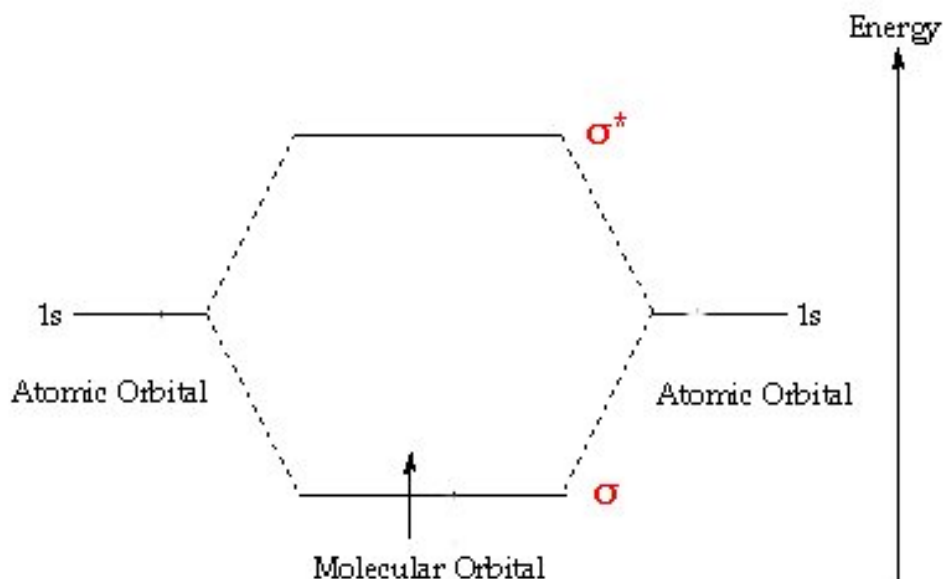
From this calculation: $R_e \approx 2.5$ bohr. How good is this?

For qualitative purposes quite acceptable (we could describe the bonding), but also for quantitative purposes it is encouraging that with such a small basis we obtain good result.

We can also use symmetry. First set up the so called symmetry adapted basis, i.e. we form such combinations of the basis functions which transform according to the *irreducible representations* of the point group of the molecule:

$$\Sigma_g^+ \text{ symmetry} \qquad s_1 = \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B)$$

$$\Sigma_u^+ \text{ symmetry} \qquad s_2 = \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B)$$

The $\hat{H}$ matrix in this basis:

$$\left\langle s_1 \middle| \hat{H} \middle| s_1 \right\rangle = \left\langle \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B) \middle| \hat{H} \middle| \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B) \right\rangle = \frac{2\alpha + 2\beta}{2(1+S)} = \frac{\alpha + \beta}{(1+S)}$$

$$\left\langle s_2 \middle| \hat{H} \middle| s_2 \right\rangle = \left\langle \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B) \middle| \hat{H} \middle| \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B) \right\rangle = \frac{2\alpha - 2\beta}{2(1-S)} = \frac{\alpha - \beta}{(1-S)}$$

$$\left\langle s_1 \middle| \hat{H} \middle| s_2 \right\rangle = \left\langle \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B) \middle| \hat{H} \middle| \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B) \right\rangle = \frac{\alpha - \alpha + \beta - \beta}{2\sqrt{(1+S)(1-S)}} = 0$$

$$\mathbf{H} = \begin{pmatrix} \frac{\alpha+\beta}{(1+S)} & 0 \\ 0 & \frac{\alpha-\beta}{(1-S)} \end{pmatrix}$$

This matrix is diagonal, its eigenvalues are the diagonal elements:

$$E_1 = \frac{\alpha + \beta}{(1 + S)} \quad \text{and} \quad E_2 = \frac{\alpha - \beta}{(1 - S)}$$

i.e. we obtained the results without diagonalization.

Note: in general, the use of symmetry reduces the size of the matrix to be diagonalized, since it breaks up into smaller blocks belonging to different irreps.

4.4. Expectation value of energy in case of determinant wave function

Let us decompose the Hamiltonian according to zero-, one- and two-electron terms:

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

Expression for the energy:

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

with Ψ being the determinant wave function. It can be shown that

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

where:

- $H_{ii} = \left\langle \phi_i | \hat{h} | \phi_i \right\rangle$ – is the one-electron term containing kinetic energy and interaction with the nuclei;

- $J_{ij} = \left\langle \phi_i(1)\phi_j(2) | \frac{1}{r_{12}} | \phi_i(1)\phi_j(2) \right\rangle$ – so called Coulomb integral, representing electron-electron interaction;

- $K_{ij} = \left\langle \phi_i(1)\phi_j(2) | \frac{1}{r_{12}} | \phi_j(1)\phi_i(2) \right\rangle$ – so called exchange integral.

This means that in case of determinant wave function, in addition to the Coulomb interaction, there is also an *exchange interaction* among electrons. One can show that the exchange interaction can be non-zero only in case of electrons of the same spin. This is the explanation for the Hund's rule, since, due to this interaction, it is more favourable to put electrons to degenerate orbitals with same spin than with opposite spin.

4.5. Electronic structure of the hydrogen molecule

The Hamiltonian:

$$\hat{H} = \underbrace{-\sum_i^2 \frac{1}{2}\Delta_i - \sum_i^2 \frac{1}{r_{iA}} - \sum_i^2 \frac{1}{r_{iB}}}_{\hat{H}_1 =: \sum_i \hat{h}(i)} + \underbrace{\frac{1}{r_{12}}}_{\hat{H}_2} + \underbrace{\frac{1}{R}}_{\hat{H}_0}$$

Another partitioning:

$$\hat{H} = \underbrace{-\frac{1}{2}\Delta_1 - \frac{1}{r_{1A}}}_{\hat{H}_A} \underbrace{-\frac{1}{2}\Delta_2 - \frac{1}{r_{2B}}}_{\hat{H}_B} \underbrace{-\frac{1}{r_{2A}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + H_0}_{\hat{H}'}$$

These two forms offer two approximations:

- MO theory – according to the first form;

- VB theory – according to the second one.

4.5.1. MO theory for the hydrogen molecule

Similarly to atoms, we use independent electron approximation.
The wave function is a determinant:

$$\Psi_{MO} = \begin{vmatrix} \phi_1(1) & \phi_2(1) \\ \phi_1(2) & \phi_2(2) \end{vmatrix}$$

Where to obtain the MOs from? In case of atoms, the AOs were taken from the hydrogen atom, here we can use the corresponding one-electron system, the $H_2{}^+$:

$$\phi_1 = \sigma_g \alpha \qquad \phi_2 = \sigma_g \beta$$

with σ_g being the bonding orbital of $H_2{}^+$ ($\sigma_g = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B)$).

Configuration: σ_g^2
State: $^1\Sigma_g^+$ $\qquad\qquad\qquad\qquad \Sigma_g^+ \otimes \Sigma_g^+ = \Sigma_g^+$
Let us expand the determinant wave function:

$$\begin{aligned} \Psi_{MO} &= \frac{1}{\sqrt{2}}(\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)) \\ &= \frac{1}{\sqrt{2}}(\sigma_g\alpha(1)\sigma_g\beta(2) - \sigma_g\alpha(2)\sigma_g\beta(1)) \\ &= \underbrace{\sigma_g(1)\sigma_g(2)}_{\text{spatial part}} \underbrace{\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1))}_{\text{determinant of the singlet spinfunction}} \end{aligned}$$

Inserting the expansion form of the orbital into the spatial part:

$$
\begin{aligned}
\Psi_{MO}^{spatial} &= \sigma_g(1)\sigma_g(2) \\
&= \frac{1}{2(1+S)}(1s_A(1) + 1s_B(1))(1s_A(2) + 1s_B(2)) \\
&= \frac{1}{2(1+S)}(\underbrace{1s_A(1)1s_A(2)}_{\text{ionic}} + \underbrace{1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)}_{\text{covalent}} + \underbrace{1s_B(1)1s_B(2)}_{\text{ionic}})
\end{aligned}
$$

Energy:

$$
\begin{aligned}
E &= \langle \Psi_{MO}|\hat{H}|\Psi_{MO}\rangle \\
&= H_{11} + H_{22} + J_{12} - K_{12}
\end{aligned}
$$

with

$$
\begin{aligned}
H_{11} &= \langle \sigma_g\alpha(1)|\hat{h}|\sigma_g\alpha(1)\rangle = \langle \sigma_g|\hat{h}|\sigma_g\rangle \\
H_{22} &= \langle \sigma_g\beta(2)|\hat{h}|\sigma_g\beta(2)\rangle = \langle \sigma_g|\hat{h}|\sigma_g\rangle \\
J_{12} &= \langle \sigma_g\alpha(1)\sigma_g\beta(2)|\frac{1}{r_{12}}|\sigma_g\alpha(1)\sigma_g\beta(2)\rangle = \langle \sigma_g(1)\sigma_g(2)|\frac{1}{r_{12}}|\sigma_g(1)\sigma_g(2)\rangle \underbrace{\langle \alpha(1)\beta(2)|\alpha(1)\beta(2)\rangle}_{=1} \\
K_{12} &= \langle \sigma_g\alpha(1)\sigma_g\beta(2)|\frac{1}{r_{12}}|\sigma_g\alpha(2)\sigma_g\beta(1)\rangle = \langle \sigma_g(1)\sigma_g(2)|\frac{1}{r_{12}}|\sigma_g(2)\sigma_g(1)\rangle \underbrace{\langle \alpha(1)\beta(2)|\alpha(2)\beta(1)\rangle}_{=0}
\end{aligned}
$$

There is no exchange interaction between electrons of opposite spin!

Excited state:
   Configuration: $\sigma_g\alpha \; \sigma_u\alpha$
   State: $^3\Sigma_u^+$ $\Sigma_g^+ \otimes \Sigma_u^+ = \Sigma_u^+$
   Here the exchange interaction does not vanish:

$$
K_{12} = \langle \sigma_g\alpha(1)\sigma_u\alpha(2)|\frac{1}{r_{12}}|\sigma_g\alpha(2)\sigma_u\alpha(1)\rangle = \langle \sigma_g(1)\sigma_u(2)|\frac{1}{r_{12}}|\sigma_g(2)\sigma_u(1)\rangle \underbrace{\langle \alpha(1)\alpha(2)|\alpha(2)\alpha(1)\rangle}_{=1}
$$

The exchange interaction is negative, therefore the energy of the state with higher multiplicity is lower (Hund's rule).

4.5.2. Valence Bond (VB) description of the hydrogen molecule

$$
\hat{H}(1,2) = \hat{H}_A(1) + \hat{H}_B(2) + \hat{H}'(1,2)
$$

This form suggests the use of perturbation theory, since the Hamiltonian is built from the Hamiltonians of the non-interactive atoms ($\hat{H}_A$ and $\hat{H}_B$), as well as the interaction ($\hat{H}'$) between them as perturbation.

The wave function in case of non-interacting atoms:

$$
f_1(1,2) = 1s_A(1)1s_B(2) \quad \text{or} \quad f_2(1,2) = 1s_A(2)1s_B(1)
$$

Heitler-London (spatial) wave function:

$$\Phi_{HL}^{\text{spatial}}(1,2) \;=\; c_1 f_1(1,2) + c_2 f_2(1,2)$$

(one has to choose antisymmetric spin function for the symmetric spatial function).

Coefficients can again be obtained by variational principle:

$$\mathbf{Hc} = E\mathbf{Sc} \quad \rightarrow \quad E_{1,2} = \frac{H_{11} \pm H_{12}}{1 \pm S_{12}}$$

(we have used that $H_{11} = H_{22}$).

The matrix elements:

$$H_{11} = \langle f_1|\hat{H}|f_1\rangle = \langle f_1|\hat{H}_A|f_1\rangle + \langle f_1|\hat{H}_B|f_1\rangle + \langle f_1|\hat{H}'|f_1\rangle = -1 + Q$$

since

$$\langle f_1|\hat{H}_A|f_1\rangle = \langle 1s_A(1)1s_B(2)|\hat{H}_A(1)|1s_A(1)1s_B(2)\rangle = \underbrace{\langle 1s_A(1)|\hat{H}_A(1)|1s_A(1)\rangle}_{-\frac{1}{2}}\underbrace{\langle 1s_B(2)|1s_B(2)\rangle}_{1} = -\frac{1}{2}$$

$$\langle f_1|\hat{H}_B|f_1\rangle = \langle 1s_A(1)1s_B(2)|\hat{H}_B(2)|1s_A(1)1s_B(2)\rangle = \underbrace{\langle 1s_B(2)|\hat{H}_B(2)|1s_B(2)\rangle}_{-\frac{1}{2}}\underbrace{\langle 1s_A(1)|1s_A(1)\rangle}_{1} = -\frac{1}{2}$$

Observe: this is the ground state energy of the hydrogen atom!

$$\langle f_1|\hat{H}'|f_1\rangle \cdot = Q$$

This is a kind of Coulomb interaction.

Similarly:

$$H_{22} = -1 + Q$$

Finally:

$$H_{12} = \langle f_1|\hat{H}|f_2\rangle = \langle f_1|\hat{H}_A|f_2\rangle + \langle f_1|\hat{H}_B|f_2\rangle + \langle f_1|\hat{H}'|f_2\rangle = -S_{AB}^2 + A$$

since

$$\begin{aligned}
\langle f_1|\hat{H}_A|f_2\rangle &= \langle 1s_A(1)1s_B(2)|\hat{H}_A(1)|1s_A(2)1s_B(1)\rangle \\
&= \underbrace{\underbrace{\langle 1s_A(1)|\hat{H}_A(1)|}_{-\frac{1}{2}\langle 1s_A(1)|}1s_B(1)\rangle}_{-\frac{1}{2}S_{AB}}\underbrace{\langle 1s_B(2)|1s_A(2)\rangle}_{S_{AB}} = -\frac{1}{2}S_{AB}^2 \\
\langle f_1|\hat{H}_B|f_2\rangle &= \langle 1s_A(1)1s_B(2)|\hat{H}_B(2)|1s_A(2)1s_B(1)\rangle \\
&= \underbrace{\underbrace{\langle 1s_B(2)|\hat{H}_B(2)|}_{-\frac{1}{2}\langle 1s_B(2)|}1s_A(2)\rangle}_{-\frac{1}{2}S_{AB}}\underbrace{\langle 1s_A(1)|1s_B(1)\rangle}_{S_{AB}} = -\frac{1}{2}S_{AB}^2 \\
\langle f_1|\hat{H}'|f_2\rangle \cdot &= A
\end{aligned}$$

The last one is an exchange-like interaction.

The overlap is:

$$S_{12} = \langle f_1 | f_2 \rangle = \langle 1s_A(1)1s_B(2) | 1s_A(2)1s_B(1) \rangle = \langle 1s_A(1) | 1s_B(1) \rangle \langle 1s_B(2) | 1s_A(2) \rangle = S_{AB}^2$$

Thus energies and the corresponding coefficients read:

$$E_1 = \frac{H_{11} + H_{12}}{1 + S_{12}} = \frac{Q + A}{1 + S_{AB}^2} - 1 \qquad c_1 = c_2 = \frac{1}{\sqrt{2(1 + S_{AB}^2)}}$$

$$E_2 = \frac{H_{11} - H_{12}}{1 - S_{12}} = \frac{Q - A}{1 - S_{AB}^2} - 1 \qquad c_1 = -c_2 = \frac{1}{\sqrt{2(1 + S_{AB}^2)}}$$

-1: energy of two hydrogen atoms in ground state, $Q + A$: their interaction.

The ground state wave function therefore reads:

$$\Psi_{HL}^{\text{spatial}} = (1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)) \cdot \frac{1}{\sqrt{2(1 + S_{AB}^2)}}$$

Comparing this to the wave function obtained in the MO theory: this is the covalent part, the ionic part is missing!

Add some ionic functions:

$$f_3(1,2) = 1s_A(1)1s_A(2)$$
$$f_4(1,2) = 1s_B(1)1s_B(2)$$

Thus the complete VB wave function reads:

$$\Psi_{VB}^{\text{spatial}} = c_{HL}\Psi_{HL}^{\text{spatial}} + c_{ion}(f_3 + f_4)$$

Coefficients can again be obtained using variational principle. Observe that this is better than MO wave function since the weight of the covalent and ionic parts are not fixed.

The results of the calculations:

- at equilibrium distance: $c_{HL} \approx c_{ion}$, therefore MO is a good approximation here;

- at big R: $c_{HL} \to 1$, $c_{ion} \to 0$.

4.6. Electronic structure of A_2-type diatomic molecules

Symmetry: $D_{\infty h}$

The symmetry of the orbitals according to the irreps of the $D_{\infty h}$ pointgroup:

symbol of the irrep	dimension	symbol of the orbital
Σ_g^+	1	σ_g
Σ_u^+	1	σ_u
Π_g	2	π_g
Π_u	2	π_u
Δ_g	2	δ_g
Δ_u	2	δ_u
Σ_g^-	1	$-$
etc.		

Thus there are non-degenerate (σ_g, σ_u) and double degenerate (π_u, π_g, etc.) orbitals.

We take the orbitals (at least their qualitative form) from H_2^+ system:

$1\sigma_g$ orbital (-1.10 hartree)
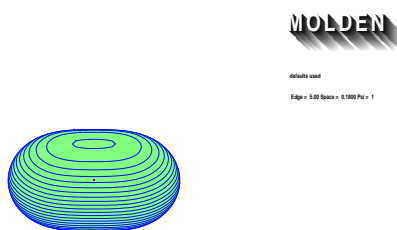
$1\sigma_u$ orbital (-0.23 hartree)
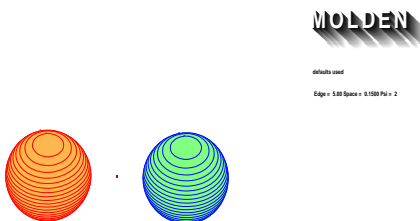
$2\sigma_g$ orbital (-0.04 hartree)
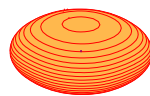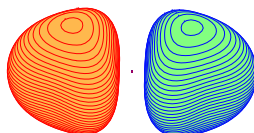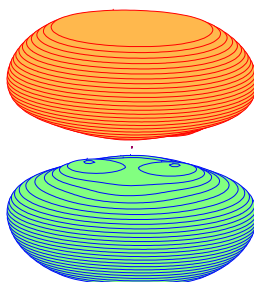
$2\sigma_u$ orbital (0.10 hartree)

$1\pi_u$ orbital (0.11 hartree)

$1\pi_u$ orbital (0.11 hartree)
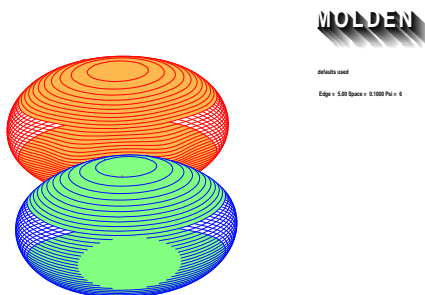
$3\sigma_g$ orbital (0.38 hartree)
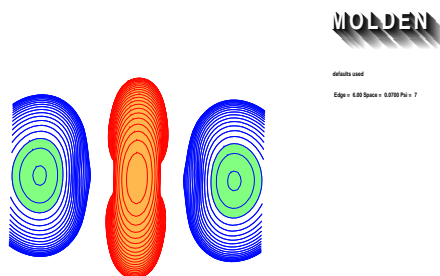
$1\pi_g$ orbital (0.42 hartree)
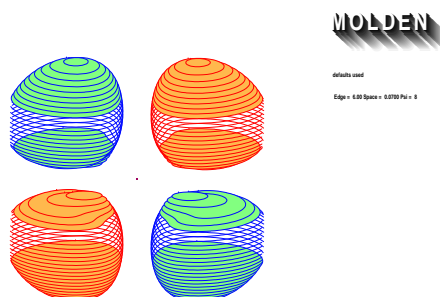
$1\pi_g$ orbital (0.42 hartree)
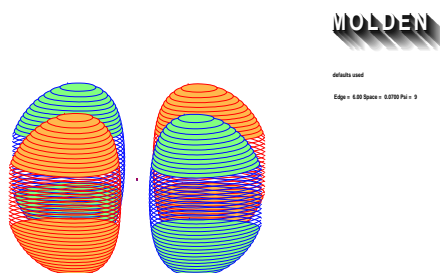
$3\sigma_u$ orbital (0.72 hartree)
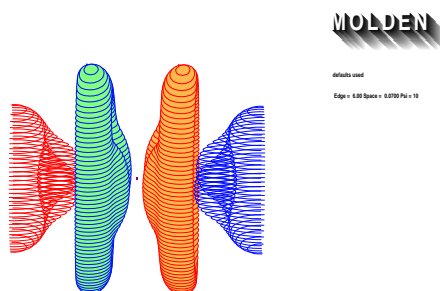
According to these results, energy ordering of the orbitals is:

$$1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u, 1\pi_u, 3\sigma_g, 1\pi_g, 3\sigma_u \cdots$$

Let us write these orbitals as linear combinations of the atomic orbitals like in case of H_2^+ and H_2 systems:

$$1\sigma_g = \frac{1}{\sqrt{2(1+S_1)}} (1s_A + 1s_B)$$

$$1\sigma_u = \frac{1}{\sqrt{2(1-S_1)}} (1s_A - 1s_B)$$

Similarly:

$$2\sigma_g = \frac{1}{\sqrt{2(1+S_2)}} (2s_A + 2s_B)$$

$$2\sigma_u = \frac{1}{\sqrt{2(1-S_2)}} (2s_A - 2s_B)$$

The next orbitals can be constructed from the $2p$ orbitals of atoms, considering also the symmetry (z is the molecular axis):
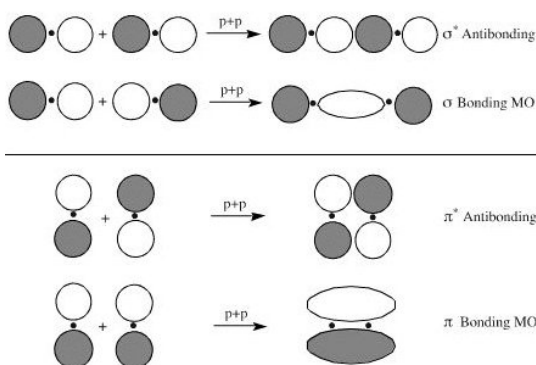
$$3\sigma_g = \frac{1}{\sqrt{2(1 - S_3)}} (2p_{zA} - 2p_{zB})$$

$$1\pi_u(x) = \frac{1}{\sqrt{2(1 + S_4)}} (2p_{xA} + 2p_{xB})$$

$$1\pi_u(y) = \frac{1}{\sqrt{2(1 + S_4)}} (2p_{yA} + 2p_{yB})$$

Similarly, for anti-bonding orbitals:

$$3\sigma_u = \frac{1}{\sqrt{2(1 + S_3)}} (2p_{zA} + 2p_{zB})$$

$$1\pi_g(x) = \frac{1}{\sqrt{2(1 - S_4)}} (2p_{xA} - 2p_{xB})$$

$$1\pi_g(y) = \frac{1}{\sqrt{2(1 - S_4)}} (2p_{yA} - 2p_{yB})$$

There is a problem with the energy ordering of orbitals: in case of H_2^+, the energy of the $1\pi_u$ orbital is lower than that of the $3\sigma_g$ orbital. The combination given above suggests the opposite order (see also General Chemistry).

Explanation: when forming linear combinations, not only one pair of atomic orbitals needs to be considered. For example:

$$1\sigma_g = c_{11} (1s_A + 1s_B) + c_{12} (2s_A + 2s_B) + c_{13} (2p_{zA} + 2p_{zB}) + \cdots$$
$$2\sigma_g = c_{21} (1s_A + 1s_B) + c_{22} (2s_A + 2s_B) + c_{23} (2p_{zA} + 2p_{zB}) + \cdots$$
$$3\sigma_g = c_{31} (1s_A + 1s_B) + c_{32} (2s_A + 2s_B) + c_{33} (2p_{zA} + 2p_{zB}) + \cdots$$

Obtaining the coefficients, we get that

$$c_{11} \approx \frac{1}{\sqrt{2(1 + S_1)}}, \quad c_{12} \approx c_{13} \approx 0$$

Thus, the simpler approximation above is valid in case of $1\sigma_g$. This can be explained since the energy of the $1s$ orbital is substantially lower than that of the others. The

same approximation is, however, less valid in case of the $2\sigma_g$ and $3\sigma_g$ orbitals, since their energies are closer, therefore they interact; the energy of the former lowers, that of the latter increases.

FIGURE

4.6.1. Construction of the states

First we occupy the orbitals according to the *Aufbau principle*. This gives the *configuration*. The wavefunction of the *state* can be characterized by its symmetry, which can be obtained as the direct product of the symmetry (irrep) of the occupied orbitals.
As example consider first H_2:
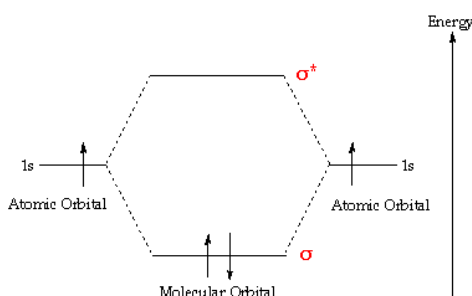
Configuration: $1\sigma_g^2$
Symmetry of the state: $\Sigma_g^+ \otimes \Sigma_g^+ = \Sigma_g^+$
Symbol of the state: $^1\Sigma_g^+$ (read as singlet sigma g plus)
Bond order: 1, since one bonding orbital is occupied by two electrons.

2nd example is He_2:
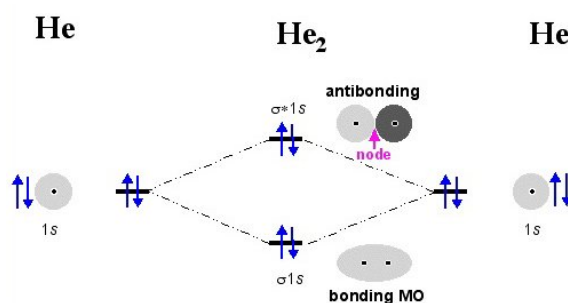
Configuration: $1\sigma_g^2 1\sigma_u^2$
Symmetry of the state: $\Sigma_g^+ \otimes \Sigma_g^+ \otimes \Sigma_u^+ \otimes \Sigma_u^+ = \Sigma_g^+$
Symbol of the state: $^1\Sigma_g^+$
Bond order: 0, since one bonding and one anti-bonding orbitals are occupied.

We observe that in case of doubly occupied orbitals, symmetry is always Σ_g^+. It is the totally symmetric irrep. This is true in general: fully occupied orbitals result in totally symmetric irrep. Therefore, it is enough to consider only open shells when obtaining the symmetry of the system.

For Li_2 and Be_2 we get the same picture as in General Chemistry. The first difference appears for B_2:

B_2: Configuration: $1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^2$.

The π_u orbital can host four electrons, therefore we have here open shell:

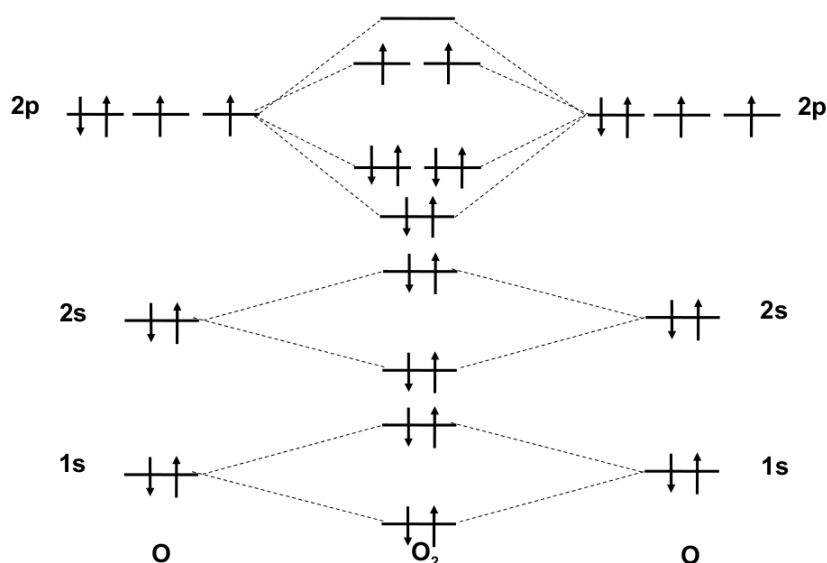Possible symmetries: $\Pi_u \otimes \Pi_u = \Sigma_g^+ \oplus \Sigma_g^- \oplus \Delta_g$

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

Energy ordering: $E_{^3\Sigma_g^-} < E_{^1\Delta_g} < E_{^1\Sigma_g^+}$

Bond order: ≈ 1, since the bonding orbitals are occupied with two electrons.

Problematic case:

O_2

Configuration: $1\sigma_g^1\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 3\sigma_g^2\ 1\pi_g^2$.

The π_g orbital can host four orbitals, i.e. this is again an open shell system:

Possible symmetries: $\Pi_g \otimes \Pi_g = \Sigma_g^+ \oplus \Sigma_g^- \oplus \Delta_g$

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

Ordering of energy: $E_{^3\Sigma_g^-} < E_{^1\Delta_g} < E_{^1\Sigma_g^+}$

Bond order: ≈ 2, since there are three bonding orbitals fully occupied ($3\sigma_g$, and $1\pi_u$ with six electrons, as well as an anti-bonding orbital with two electrons).

Oxygen is paramagnetic, triplet state!!!!

4.7. Electronic structure of AB-type diatomic molecules
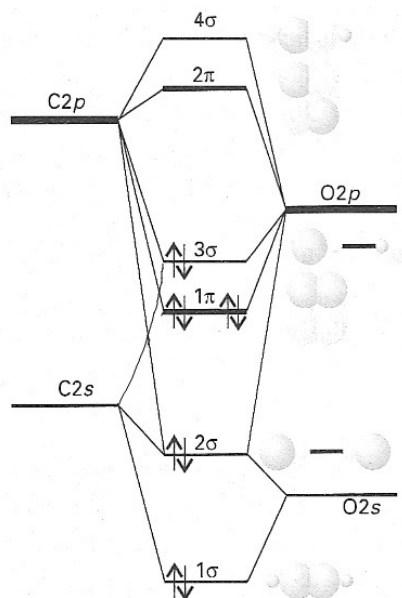
Problems:

- the orbital energies of the two atoms are not equal;

- stabilization of the bonding MO depends on this energy difference.

Therefore, the qualitative picture is not always enough, often quantitative considera-
tion is necessary.

Example: LiH (figure on the blackboard)
orbital energies: Li: -2.48 and -0.19 hartree, H: -0.5 hartree

Other example: CO molecule:

4.8. The Hartree-Fock method

4.8.1. Formulation of the Hartree-Fock equations

In MO theory determinant wave function is used. In case of diatomic molecules orbitals could be taken from a one-electron system H_2^+.

Problem:

- these are not the best orbitals for quantitative purposes;

- for more complicated molecules there is no reasonable one-electron problem.

Solution to this problem: look for optimal orbitals for each molecule.

But how? One can use variation principle: look for the determinant which gives the lowest energy. Since the determinant is built up from orbitals, in fact we look for the best orbitals.

What does it mean „the best orbitals"? According to the variational principle, these are the orbitals resulting the lowest energy determinant. Let us look for these orbitals!

Expression of energy (see earlier):

$$
\begin{aligned}
E &= \left\langle \Psi | \hat{H} | \Psi \right\rangle = \sum_i H_{ii} + \frac{1}{2} \sum_{ij} \left(J_{ij} - K_{ij} \right) \\
&= \sum_i \left\langle \phi_i | \hat{h} | \phi_i \right\rangle + \frac{1}{2} \sum_{ij} \left(\left\langle \phi_i(1)\phi_j(2) | \frac{1}{r_{12}} | \phi_i(1)\phi_j(2) \right\rangle - \left\langle \phi_i(1)\phi_j(2) | \frac{1}{r_{12}} | \phi_j(1)\phi_i(2) \right\rangle \right)
\end{aligned}
$$

which is a *functional of orbitals* $\{\phi_i\}$. Therefore one needs to look for the minimum of the functional with respect to the variation of the orbitals. Orbitals need to remain ortogonal in order to keep the above form of the energy valid (it is valid if the determinant is normalized) therefore boundary conditions need to be considered:

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

Thus, the functional to be varied is:

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

Without giving the details, the functional G has extremum for those orbitals which fulfill the following equation:

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

with

$$
\begin{aligned}
\hat{J}_j(1) &= \left\langle \phi_j(2) \Big| \frac{1}{r_{12}} \Big| \phi_j(2) \right\rangle_2 \\
\hat{K}_j | \phi_i(1) \rangle &= \left\langle \phi_j(2) \Big| \frac{1}{r_{12}} \Big| \phi_i(2) \right\rangle_2 | \phi_j(1) \rangle
\end{aligned}
$$

where integration is over the coordinates of the second electron.

Let us define the following operator:

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

With this (and by a transformation among orbitals) one gets the following equation:

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

This is the so called *Hartree-Fock equation*, which we obtained earlier as the generalization of the Hartree equation considering the indistinguishability of the electrons. Now we also get the form of the $\hat{U}^{HF}$ potential:

$$\hat{U}^{HF} = \sum_j \left(\hat{J}_j - \hat{K}_j \right),$$

i.e. the Hartree-Fock potential consists of the Coulomb ($\hat{J}_j$) and exchange ($\hat{K}_j$) operators.

Orbitals satisfying the *Hartree-Fock equation* are called *canonical orbitals*. Later we will discuss their porperties in detail, but we can recognize already that orbital energies are assiciated with them. It seems that n-electron problem is reduced to that of n independent one-electron systems. This is, however, not quite true: the Fock operator $\hat{f}$ is a one-particle operator, but – through $\hat{J}_j$ and $\hat{K}_j$ – it depends on all the occupied orbitals:

$$\hat{f} = \hat{f} \left(\left\{ \phi_i \right\} \right)$$

Therefore the solution of the equation can be performed through an iterative procedure we have discussed before:

$$\left\{ \phi_i^{(0)} \right\} \quad \rightarrow \quad \hat{f}^{(0)} \quad \rightarrow \quad \left\{ \phi_i^{(1)} \right\} \quad \rightarrow \quad \hat{f}^{(1)} \quad \rightarrow \quad ....$$

which is called the *SCF (Self-Consistent Field)* procedure. (The name comes from the fact that after convergence, the Fock operator built up from a set of orbitals results the same orbitals as its eigenfunctions.)

4.8.2. The Hartree-Fock-Roothaan method

Above we have derived the equations of the HF-method:

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

These are still complicated differential equations, which do not have analytic solution. We have to introduce a further approximation: let us look for the best orbitals in form of linear combination. In this case optimization of the orbitals means optimization of the coefficients of the linear combinations. In practice, atomic orbitals are used as basis, i.e. we use the *LCAO-MO* approximation:

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

with χ_a representing atomic orbitals. Insert these into the HF equations:

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

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

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

with $\underline{C}_i$ is the vector given by the C_{ai} coefficients corresponding to the ith MO. Collecting all $\underline{C}_i$ vectors into a matrix $\underline{\underline{C}}$, we have a compact form of *the Hartree-Fock-Roothaan (HFR)* equations:

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

This is a matrix eigenvalue equation, but the Fock matrix $\underline{\underline{F}}$ is still a function of the orbitals, or more precisely, their coefficients:

$$\underline{\underline{F}} = \underline{\underline{F}}\left(\hat{J}, \hat{K}\right) = \underline{\underline{F}}\left(\{\phi_i\}\right) = \underline{\underline{F}}\left(\{\underline{C}_i\}\right)$$

Therefore, the solution proceeds again in a SCF way.

In this the *Fock-matrix* is formed using the coefficient matrix $\underline{\underline{C}}$, then the *HFR* equations are solved, i.e. the Fock matrix is diagonalized. This results a new $\underline{\underline{C}}$ matrix which is used to build the new $\underline{\underline{F}}$, etc., the procedure is repeated until convergence.

4.8.3. Interpretation of the results of the Hartree-Fock method

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

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

In practice, orbitals are linear combination of atomic orbitals:

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

The wave function of the system is the determinant built from these orbitals:

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

The density matrix

According to the postulates, it is the probability density which has physical meaning:

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

which gives the probability of finding the first electron at position $\underline{r}_1$, the second at position $\underline{r}_2$, the third at $\underline{r}_3$, etc, while the nth at $\underline{r}_n$.

This is not really that we are interested in. Instead, we would like to know what is the probability of finding *an electron* at a given pont in space, $\underline{r}$, irrespective of the position of other electrons. This can be obtained with the following expression:

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

Notice that, except of the first electron, we integrate according to the position of all other electrons. The multiplier n in front of the expression comes from the fact that electrons can not be distinguished, so we added up the probability for all individual electrons. ρ is called *electron density*.

In case of determinental wave function, electron density can be given as the sum of the densities corresponding to individual orbitals.

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

In the second row orbitals have been expanded in the (AO) basis, in the last one the *density matrix $\underline{\underline{P}}$* has been introduced. The first line shows why this method is an *independent electron approximation*: density is given as the sum of the densities from individual orbitals.

Population analysis (according to Mulliken)

Integration of the electron density for the entire space gives the number of electrons:

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

In the last equation total electron density can be divided among basis functions:

- $P_{aa}S_{aa} = P_{aa}$ gives the charge corresponding to basis function χ_a;

- $P_{ab}S_{ab}$ gives the charge corresponding to the overlap $\chi_a\chi_b$.

From these one can construct atomic contributions:

- $\sum_{a\in A} P_{aa}S_{aa} = \sum_{a\in A} P_{aa}$ gives the charge on atom A;

- $\sum_{a\in A} \sum_{b\in B} P_{ab}S_{ab}$ gives the electron number corresponding to bond between atoms A and B (NOT BOND ORDER, THOUGH!).

Finally, the total (Mulliken) charge on atom A can be obtained by summing all contributions involving atom A:

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

Mulliken population analysis, despite of its theoretical weaknesses, is very popular. There are, however, other methods for population analysis, which are theoretically more precise, but at the same time more complicated. We can not deal with these in this course.

Orbital energy, total energy

The quantity ε_i in the Hartree-Fock equations is orbital energy. This is the expectation value of the *Fock operator* for orbital ϕ_i:

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

Summing all orbital energies of the occupied orbitals, we do *not* get the total energy of the system:

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

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

Ionization energy, Koopmans' principle

Consider a closed shell system (M), and remove one electron (M^+). For the latter system, we keep the orbitals unchanged. The energy of the molecule and ion can be given as:

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

Ionization energy is equal to the negative of the energy of the orbital where the electron has been removed from. This is the so called *Koopmans' principle*. This is a quite simple way to calculate ionization energy. Its accuracy is due to the cancellation of the errors of two approximations:

- determinental wave function (the so called electron correlation is neglected);

- orbitals are not optimized for the ion (orbital relaxation is neglected).

The same way one could also calculate electron affinity:

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

This is, however, a much worse approximation, since the empty orbital, which is occupied by the extra electron, is not well described (not included in the Fock operator, therefore its interaction with other electrons is not considered).

4.9. Electronic structure of water molecule

4.9.1. Qualitative MO treatment

Orbitals can be obtained from the Independent Particle Approximation (IPA), and occupy them according to orbital energies.

In practice: Hartree-Fock-Roothaan method (HF + LCAO-MO):

$$
\begin{aligned}
\text{wave function} : \Psi &= |\phi_1, \phi_2, ..., \phi_n| \\
\text{orbital} : \phi_i &= \sum_a C_{ai}\chi_a
\end{aligned}
$$

with χ_a being the basis functions.

Let us use the *minimal basis*, which only includes the functions of each occupied shells:
H: $1s_a$, $1s_b$ O: $1s$, $2s$, $2p_x$, $2p_y$, $2p_z$

Performing the calculations, we obtain the following orbitals:

$1a_1$ orbital (-20.52 hartree)
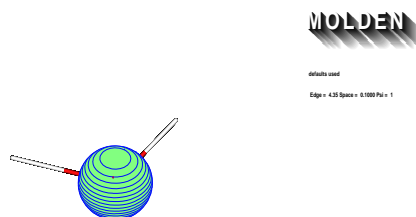
$1a_1$: $1s$

$2a_1$ orbital (-1.33 hartree)
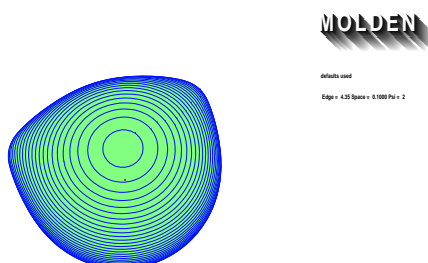
$2a_1$: $2s$ $(-2p_z)$+ $1s_a$+ $1s_b$ bonding

$1b_1$ orbital (-0.67 hartree)
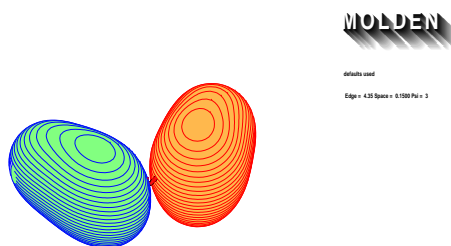
$1b_1$: $2p_y + 1s_a - 1s_b$ bonding

$3a_1$ orbital (-0.56 hartree)
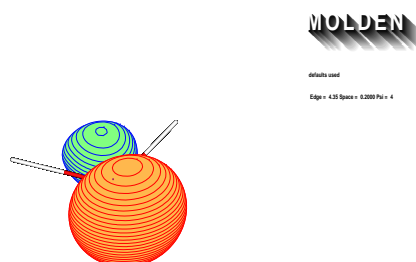
$3a_1$: $2p_z$ (+ 2s) non-bonding

$1b_2$ orbital (-0.52 hartree)
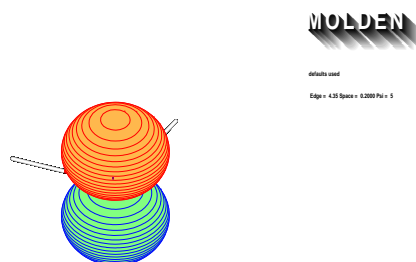
$1b_2$: $2p_x$ non-bonding

$4a_1$ orbital (0.33 hartree)
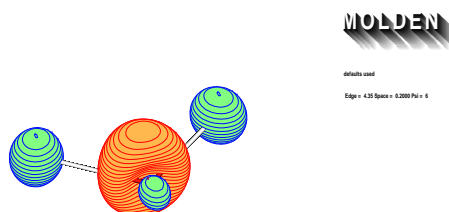
$4a_1$: $2s + 2p_z - 1s_a - 1s_b$ anti-bonding

$2b_1$ orbital (0.49 hartree)
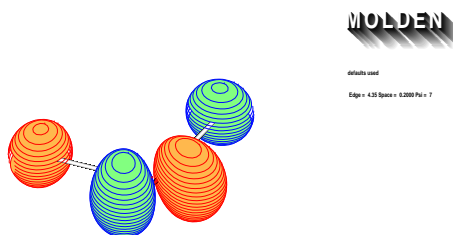
$2b_1$: $2p_y - 1s_a + 1s_b$ anti-bonding

Configuration: $(1a_1)^2 (2a_1)^2 (1b_1)^2 (3a_1)^2 (1b_2)^2$
State: $^1A_1$ (orbitals are fully occupied $\Rightarrow$ total symmetric singlet)

Excited states:
  configuration: $(1a_1)^2 (2a_1)^2 (1b_1)^2 (3a_1)^2 (1b_2)^1 (4a_1)^1$
  $B_2 \otimes A_1 = B_2 \Rightarrow$ state: $^3B_2$ or $^1B_2$

  configuration: $(1a_1)^2 (2a_1)^2 (1b_1)^2 (3a_1)^2 (1b_2)^1 (2b_1)^1$
  $B_2 \otimes B_1 = A_2 \Rightarrow$ state: $^3A_2$ or $^1A_2$

Considering symmetry

In IEA/LCAO-MO there are seven atomic orbitals → seven MO's → 7x7 problem.
Symmetry: C$_{2v}$
seven basis functions → seven symmetry-adapted basis functions
mathematically: basis is reducible → transform it into irreducible representation

Character table:

C_{2v}	E	C_2	$\sigma_v(yz)$	$\sigma_v(xz)$
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

Formula for the reduction:

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

with

h: order of the group;

N_k: order of the class;

$\chi^i(k)$: character if the ith irrep corresponding to class k;

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

With this:
$n_{A1} = \frac{1}{4}(1\cdot1\cdot7 + 1\cdot1\cdot1 + 1\cdot1\cdot5 + 1\cdot1\cdot3) = 4$
$n_{A2} = \frac{1}{4}(1\cdot1\cdot7 + 1\cdot1\cdot1 + 1\cdot(-1)\cdot5 + 1\cdot(-1)\cdot3) = 0$
$n_{B1} = \frac{1}{4}(1\cdot1\cdot7 + 1\cdot(-1)\cdot1 + 1\cdot1\cdot5 + 1\cdot(-1)\cdot3) = 2$
$n_{B2} = \frac{1}{4}(1\cdot1\cdot7 + 1\cdot(-1)\cdot1 + 1\cdot(-1)\cdot5 + 1\cdot1\cdot3) = 1$

Thus: $\Gamma_{basis} = 4\ A_1 \oplus 2\ B_1 \oplus 1\ B_2$

The above expression tells us that there are four a$_1$, two b$_1$, and b$_2$ orbitals.

Which basis functions form the MOs?

Remember: the operator projecting into the space of the ith irrep is:

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

with $\hat{R}$ is the symmetry operation, $\chi^i(\hat{R})$ is its character with respect to irrep i.

For example:

$$P_{A_1} \, 1s_a = 1s_a + 1s_b + 1s_a + 1s_b = 2(1s_a + 1s_b)$$

The final results:

a_1: 1s, 2s, $2p_z$, $(1s_a + 1s_b)$ dimension 4x4
b_1: $2p_y$, $(1s_a - 1s_b)$ dimension 2x2
b_2: $2p_x$ dimension 1x1

One can perform the calculations in the symmetry adapted basis. This will result in the same orbitals discussed above, however, symmetry blocks can be treated separately.

Localized orbitals

How do bonding orbitals look like? There are two bonding orbitals, both of them extend over all three atoms.

Chemical intuition suggests different bonds!

Remember: „orbitals have no physical meaning", the determinant does not change if we transform occupied orbitals among themselves.

Thus, one can consider the linear combination of these two orbitals:

$2a_1$ $1b_1$

$2a_1 - 1b_1$ $2a_1 + 1b_1$
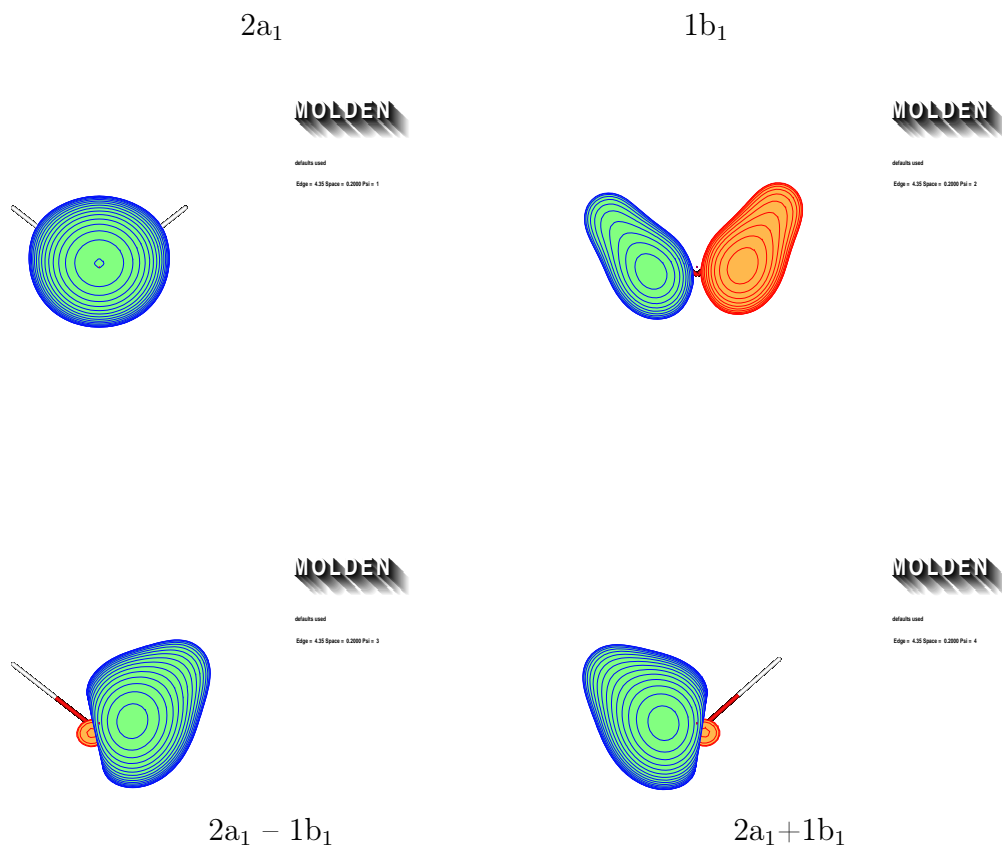
We obtain two bonding orbitals which correspond to chemical intuition, each representing one OH bond!

Now consider the two non-bonding orbitals:

$3a_1$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $1b_2$

$3a_1 + 1b_2$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $3a_1 - 1b_2$
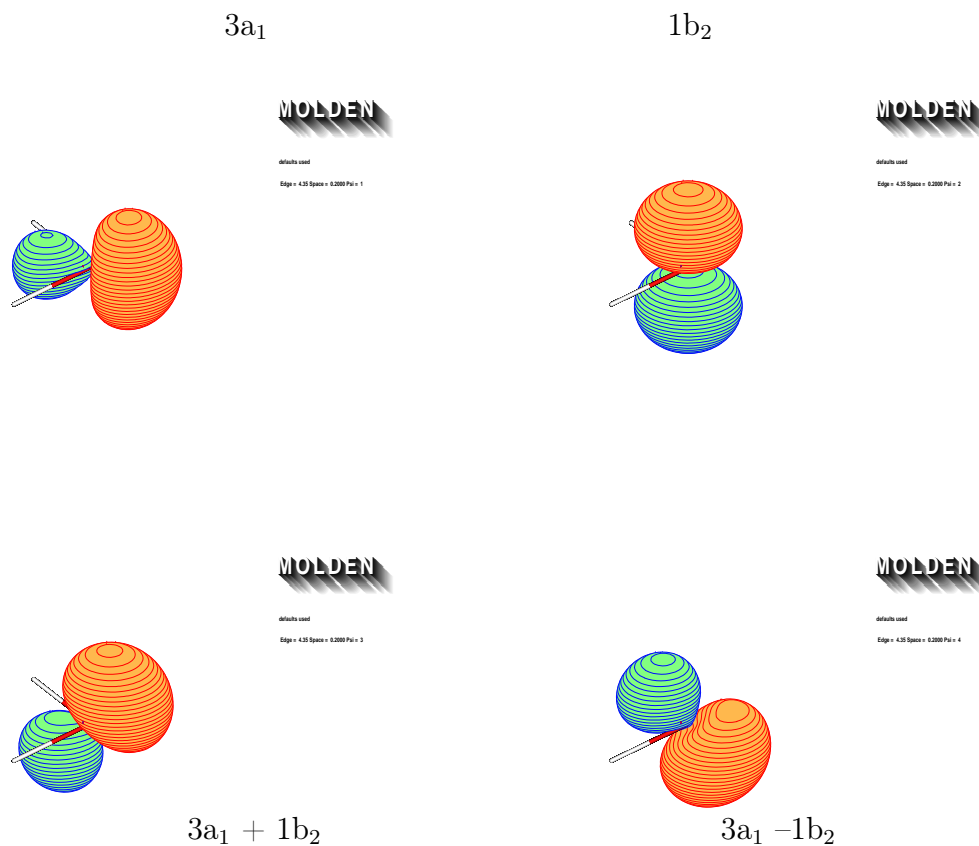
We obtained two non-bonding orbitals which correspond to chemical intuition (two lone pairs on oxygen).

Comparison of localized and canonic orbitals:

	canonic	localized
orbital energy	yes	no
symmetry	yes	no
bond between pair of atoms	no	yes
lone pair on atom	no	yes

4.9.2. „Hybrid orbitals" (details see later)

We would like to construct localized orbitals directly from the basis functions.

We know that basis functions span a space, therefore any linear combination of basis functions will span the same space, while the description of the problem in this new basis is unchanged.

Construct so called *hybrid* orbitals, which point into the direction of the bonds:
$h_1 = 2p_z + 2p_y$ orbital:
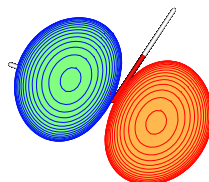
$h_2 = 2p_z - 2p_y$ orbital:
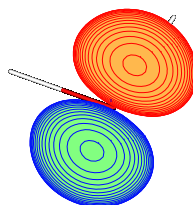
Mix in also some 2s component:
$h_1' = h_1 + 2s$
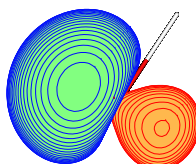
$h_2' = h_2 + 2s$
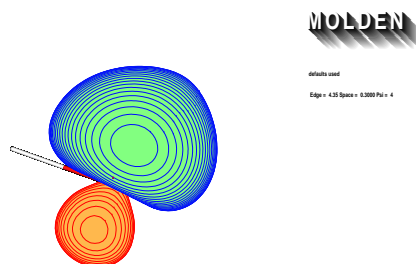
(There is of course a third orbital: $h_3' = 2s - h_1 + h_2$)

These already point along the bonds, so that we can construct the desired pairs:

$h_1' + 1s_a$ first bond
$h_2' + 1s_b$ second bond

Important: when constructing hybrid orbitals, we already use the „results", since the hybrids point where we expect the bond to be.

For example: h_1 and h_2 do not point exactly along the bond:
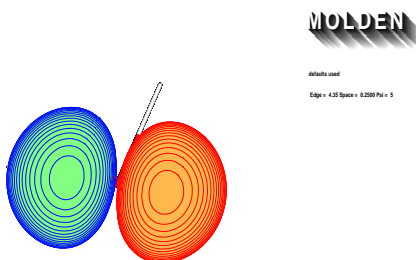
Let us as change the relative weight of the p_y and p_z orbitals:

MOLDEN

defaults used

Edge = 4.35 Space = 0.2500 Psi = 6
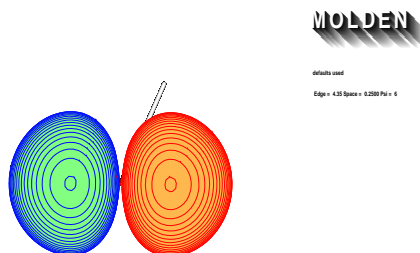
The figure shows that increasing $2p_z$ contribution rotates the hybrid orbitals. Below this will have an important consequence!

4.9.3. VB treatment

In case of the H_2 molecule we have seen that in VB theory one forms electron pairs from unpaired electrons. The spatial part of the wave function reads:

$$\Psi_{HL}^{spatial} \;\; = \;\; 1s_A(1)\; 1s_B(2) + 1s_A(2)\; 1s_B(1)$$

It follows that we need only consider unpaired electrons.

In case of water, the contributing atomic configurations are:
O: $1s^2\; 2s^2\; 2p^4 \;\rightarrow 1s^2\; 2s^2\; 2p_x{}^2\; 2p_y\; 2p_z$
H: $1s$
Open shells:
O: $2p_y$ and $2p_z$
H: $1s_a$ and $1s_b$

Thus we can form two pairs (spatial pairs):
$f_{11}(1,2)=1s_a(1)2p_z(2) + 1s_a(2)2p_z(1)$
$f_{12}(3,4)=1s_b(3)2p_y(4) + 1s_b(4)2p_y(3)$
From these one can obtain the wave function of four electrons (spatial part):
$\Phi_A(1,2,3,4)= f_{11}(1,2) \cdot f_{12}(3,4)$

One can, however, pair these also in another way:
$f_{21}(1,2)=1s_a(1)2p_y(2) + 1s_a(2)2p_y(1)$
$f_{22}(3,4)=1s_b(3)2p_z(4) + 1s_b(4)2p_z(3)$
From these one can obtain the wave function of four electrons (spatial part):
$\Phi_B(1,2,3,4)= f_{21}(1,2) \cdot f_{21}(3,4)$

(There is one more possibility:
$f_{31}(1,2)=1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)$
$f_{32}(3,4)=2p_z(3)2p_y(4) + 2p_z(4)2p_y(3)$
but this is redundant, see e.g. the book of Levine).

The Heitler-London wave function:

$\Psi_{HL}(1,2,3,4)=c_A\Phi_A(1,2,3,4)+ c_B\Phi_B(1,2,3,4)$,
where coefficients can be obtained variationally: $c_A=-c_B$

Problem: since we used $2p_z$ and $2p_y$ orbitals, the bond angle is 90°!!!!!
Correction:
i.) consider also ionic terms (for the repulsion of H atoms)
ii.) use hybridization – place the unpaired electrons to such orbitals which show the right bond angle.

VB wave function with hybrid orbitals:
   O: h_1' and h_2'
   H: $1s_a$ and $1s_b$
   (h' hybrids are shown above!)
   $f'_{11}(1,2)=1s_a(1)h_1'(2) + 1s_a(2)h_1'(1)$
   $f'_{12}(3,4)=1s_b(3)h_2'(4) + 1s_b(4)h_2'(3)$
   These are all we need since, as can be seen from the figure, overlaps are small in case of other pairings (e.g. between $1s_a$ and h_2').

$$\Psi_{HL}(1,2,3,4) \quad = \quad f'_{11}(1,2) \cdot f'_{12}(3,4)$$

Graphically:
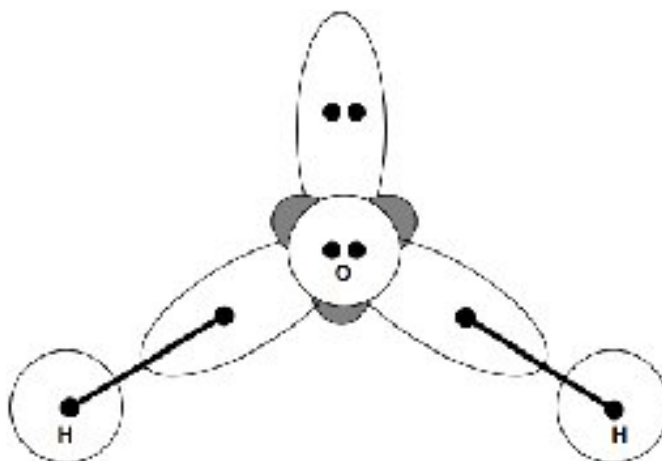
As we have seen, the angle of hybrid orbitals can be adjusted, therefore we can obtain the correct structure!
   This means that for a good result one needs to know the structure in advance :).

1. For a qualitative treatment this is enough: Lewis structures are based on this theory (see later).

2. For a quantitative treatment: generalized VB (GVB) method can be used.

Generalized VB wave function:

In case of water molecule:
$\Psi_{GVB}(1,2,3,4)= c_A\{(g_1(1)g_2(2) + g_1(2)g_2(1)) (g_3(3)g_4(4) + g_3(4)g_4(3))\} +$
$c_B\{(g_1(1)g_3(2) + g_1(2)g_3(1)) (g_2(3)g_4(4) + g_2(4)g_4(3))\}$
$g_i=\Sigma_a c_{ia}\chi_a$ These are ATOMIC ORBITALS!!!!!!

Coefficients c_A, c_B and c_{ia} can be obtained variationally. Thus one takes into account that during bond formation, orbitals of the atoms might change.

Advantage:

- „ab initio", meaning that no information on structure is used;

- chemical intuition OK;

- quantitative.

Disadvantage: computationally demanding (atomic orbitals are not orthogonal).

4.10. Qualitative description of the electronic structure of molecules using VB theory based on hybrid orbitals

4.10.1. Methane molecule

Atomic configurations:

H: 1s
C: $1s^2$ $2s^2$ $2p^2$

We know that the carbon atom forms four equivalent bonds. But how, if

- it has only two unpaired electrons;

- these are on the three components of the $2p$ orbital?

How do we get four equal bonds?

Solution:

1. „promotion" (excitation): $2s^2$ $2p^2 \rightarrow 2s^1$ $2p^3$

2. hybridization: from the $2s$ and three components of the $2p$ orbitals: „**sp^3 hybridization**"

$h_1 = 2s + 2p_x + 2p_y + 2p_z$
$h_2 = 2s - 2p_x - 2p_y + 2p_z$
$h_3 = 2s - 2p_x + 2p_y - 2p_z$
$h_4 = 2s + 2p_x - 2p_y - 2p_z$
These orbitals point to the corners of a tetrahedron:
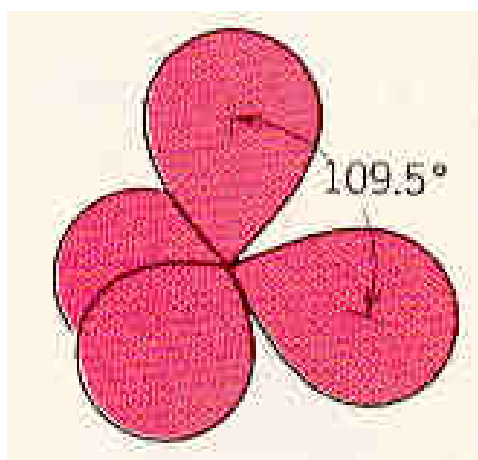
sp^3 hybrid orbitals

A fictive process before the formation of bonds:

$2s^2 2p^2 \rightarrow$ promotion $\rightarrow 2s^1 2p^3 \rightarrow$ hybridization $\rightarrow h^4$ configuration
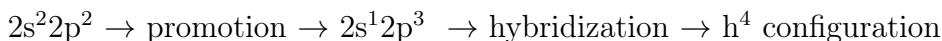
Note: h^4 results in the same spherical electron density than sp^3.

Now we can form electron pairs:

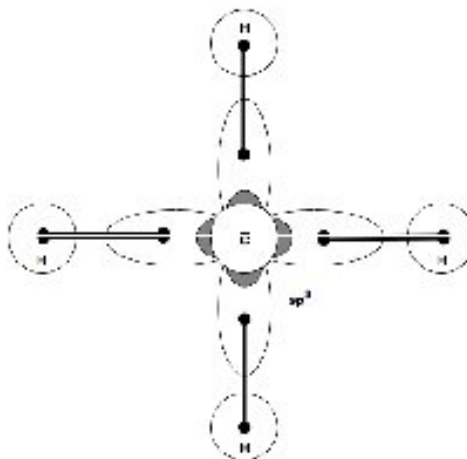$f_1(1,2) = h_1(1)1s_a(2) + h_1(2)1s_a(1)$
$f_2(3,4) = h_2(3)1s_b(4) + h_2(4)1s_b(3)$
$f_3(5,6) = h_3(5)1s_c(6) + h_3(6)1s_c(5)$
$f_4(7,8) = h_4(7)1s_d(8) + h_4(8)1s_d(7)$

$\Phi_{HL}(1,2,\ldots,8) = f_1(1,2) \cdot f_2(3,4) \cdot f_3(5,6) \cdot f_4(7,8)$

We do not need other configuration, since only these orbitals point towards each other. Graphically:

Thus using the fact that there are four equivalent bonds in methane, VB theory predicts four bonds pointing towards the corners of a tetrahedron.
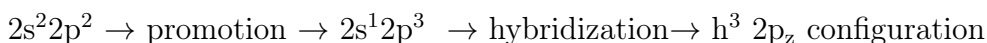
4.10.2. Ethene molecule

Atomic configurations are as above. Now, however, one wants to form not four, rather three identical bonds (two CH and one CC bonds):

Other hybridization: $2s\ 2p_x\ 2p_y\ \rightarrow$ three orbitals
The $2p_z$ orbital is unchanged.
„sp^2 hybridization"

The fictive process before forming the bonds:

$2s^2 2p^2 \rightarrow$ promotion $\rightarrow 2s^1 2p^3 \rightarrow$ hybridization$\rightarrow h^3\ 2p_z$ configuration
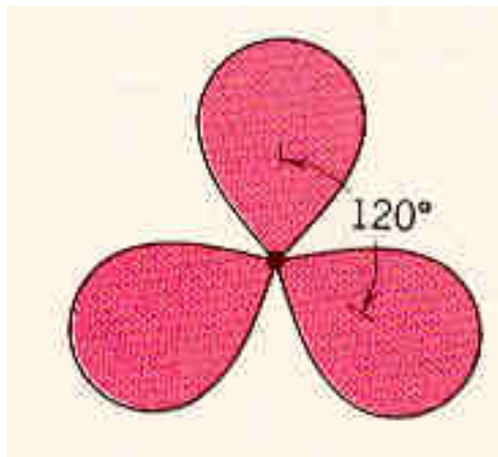
$h_1 = 2s + 2p_x + 2p_y$
$h_2 = 2s - 2p_x - 2p_y$
$h_3 = 2s - 2p_x + 2p_y$

These orbitals point towards the corners of a triangle:

sp^2 hybrid orbitals

The unpaired electrons are on the following orbitals:

$1s_a$, $1s_b$, $1s_c$, $1s_d$, h_{11}, h_{21}, h_{31}, $2p_{z1}$, h_{12}, h_{22}, h_{32}, $2p_{z2}$

Now we can form the electron pairs:

$f_{CH1}(1,2) = h_{11}(1)1s_a(2) + h_{11}(2)1s_a(1)$
$f_{CH2}(3,4) = h_{21}(3)1s_b(4) + h_{21}(4)1s_b(3)$
$f_{CH3}(5,6) = h_{12}(5)1s_c(6) + h_{12}(6)1s_c(5)$
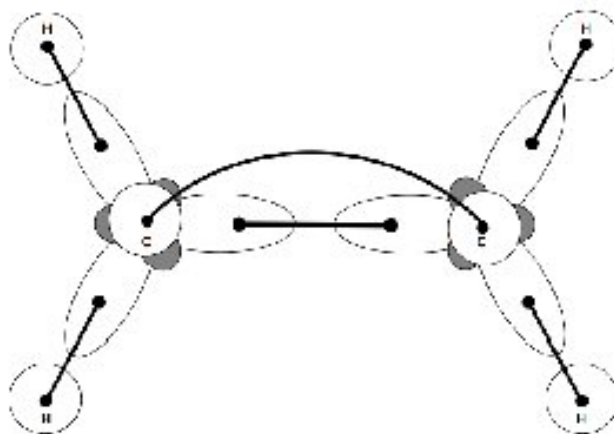$f_{CH4}(7,8) = h_{22}(7)1s_d(8) + h_{22}(8)1s_d(7)$
$f_{CC1}(9,10) = h_{31}(9)h_{32}(10) + h_{31}(10)h_{32}(9)$
$f_{CC2}(11,12) = 2p_{z1}(11)2p_{z2}(12) + 2p_{z1}(12)2p_{z2}(11)$ $\qquad$ Π bond

$\Phi_{HL}(1,2,\ldots,12) = f_{CH1}(1,2) \cdot f_{CH2}(3,4) \cdot f_{CH3}(5,6) \cdot f_{CH4}(7,8) \cdot f_{CC1}(9,10) \cdot f_{CC2}(11,12)$

Other resonance is not possible.
Graphically:

Thus, there is one bond between each neighbouring C and H atoms, while there is a double bond between carbon atoms.

4.10.3. Ethine molecule

Here carbon atoms form bonds with only two other atoms.

Other hybridization: $2s\ 2p_z\ \rightarrow$ two hybrid orbitals.
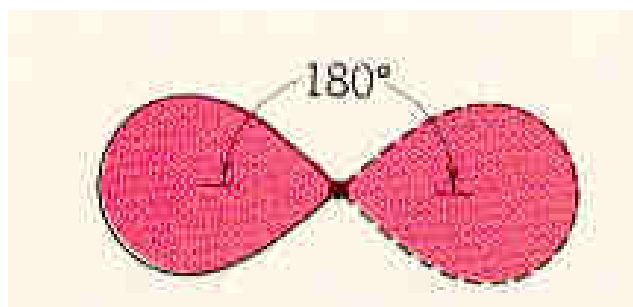$2p_x$ and $2p_y$ orbitals are unchanged.
„sp hybridization"

The fictive process before forming the bonds:

$2s^2 2p^2 \rightarrow$ promotion $\rightarrow 2s^1 2p^3\ \rightarrow$ hybridization $\rightarrow h^2\ 2p_x{}^1\ 2p_y{}^1$ configuration
$h_1 = 2s + 2p_z$
$h_2 = 2s - 2p_z$
These orbitals are along one line.

sp hybrid orbitals

Unpaired electrons are on the following orbitals:

$1s_a$, $1s_b$, h_{11}, h_{21}, $2p_{x1}$, $2p_{y1}$, h_{12}, h_{22}, $2p_{x2}$, $2p_{y2}$

Now we can form electron pairs:

$f_{CH1}(1,2) = h_{11}(1)1s_a(2) + h_{11}(2)1s_a(1)$
$f_{CH2}(3,4) = h_{12}(3)1s_b(4) + h_{12}(4)1s_b(3)$
$f_{CC1}(5,6) = h_{21}(5)h_{22}(6) + h_{21}(6)h_{22}(5)$
$f_{CC2}(7,8) = 2p_{x1}(7)2p_{x2}(8) + 2p_{x1}(8)2p_{x2}(7)$ Π bond
$f_{CC2}(9,10) = 2p_{y1}(9)2p_{y2}(10) + 2p_{y1}(10)2p_{y2}(9)$ Π bond
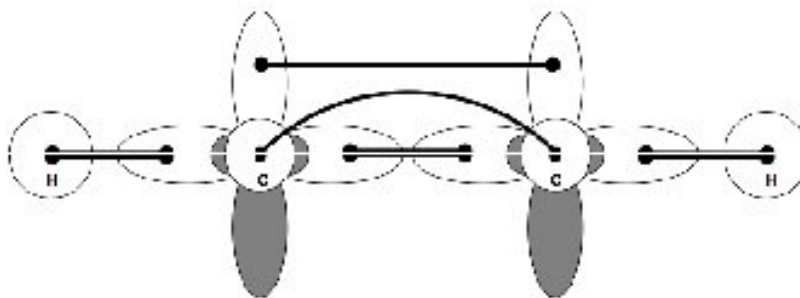
$\Phi_A(1,2,\ldots,10) = f_{CH1} \cdot f_{CH2} \cdot f_{CC1} \cdot f_{CC2} \cdot f_{CC3}$

Other resonance is not possible.

Graphically:

Thus, there are single bonds between the neighbouring C and H atoms and a triple bond between carbon atoms.

4.10.4. Ammonia molecule
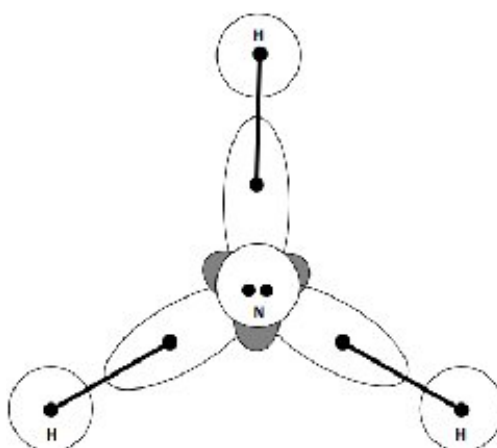
Atomic configuration:
  H: 1s
  N: $1s^2$ $2s^2$ $2p^3$

The nitrogen atom forms bonds with three hydrogen atoms.
According to the above consideration, this can happen with sp^2 hybridization:

$2s^2 2p^3 \rightarrow$ promotion $\rightarrow 2s^1 2p^4$ $\rightarrow$ hybridizatio$\rightarrow h^3$ $2p^2_z$ configuration

This results in a planar structure. We know, however that ammonia is not planar. Graphically:

Now let us try also sp^3 hybridization:
  $2s^2 2p^3 \rightarrow$ promotion $\rightarrow 2s^1 2p^4$ $\rightarrow$ hybridization$\rightarrow h^5$ configuration

Pyramidal structure with the non-bonding pair on the top!

Which one is the right structure? Without calculating energy, this question can not be answered. The pyramidal structure is lower in energy, therefore it is the most stable one. In fact, tha planar one is a saddle point on the potential energy surface.

4.10.5. Allyl radical

C atom: sp^2 hybridization

Unpaired electrons:
$1s_a$, $1s_b$, $1s_c$, $1s_d$, $1s_e$, h_{11}, h_{21}, h_{31}, $2p_{z1}$, h_{12}, h_{22}, h_{32}, $2p_{z2}$, h_{13}, h_{23}, h_{33}, $2p_{z3}$

Possible electron pairs::
$f_{CH1}(1,2) = h_{11}(1)1s_a(2) + h_{11}(2)1s_a(1)$
$f_{CH2}(3,4) = h_{21}(3)1s_b(4) + h_{21}(4)1s_b(3)$
$f_{CH3}(5,6) = h_{12}(5)1s_c(6) + h_{12}(6)1s_c(5)$
$f_{CH4}(7,8) = h_{13}(7)1s_d(8) + h_{13}(8)1s_d(7)$
$f_{CH5}(9,10) = h_{23}(9)1s_e(10) + h_{23}(10)1s_e(9)$
$f_{CC1}(11,12) = h_{31}(11)h_{22}(12) + h_{31}(12)h_{22}(11)$
$f_{CC2}(13,14) = h_{32}(13)h_{33}(14) + h_{32}(14)h_{33}(13)$

There remain three $2p_z$ orbitals and three electrons. Therefore only one more bond is possible:
$f_{\Pi1}(15,16) = 2p_{z1}(15)2p_{z2}(16) + 2p_{z1}(16)2p_{z2}(15)$ and $2p_{z3}(17)$
$f_{\Pi2}(15,16) = 2p_{z3}(15)2p_{z2}(16) + 2p_{z3}(16)2p_{z2}(15)$ and $2p_{z1}(17)$

The last electron remains unpaired.

The two possible resonance structures are:
$\Phi_A(1,2,\ldots 17) = f_{CH1}(1,2) \cdot f_{CH2}(3,4) \cdot f_{CH3}(5,6) \cdot f_{CH4}(7,8) \cdot f_{CH5}(9,10) \cdot f_{CC1}(11,12) \cdot f_{CC2}(13,14) \cdot f_{\Pi1}(15,16) \cdot 2p_{z3}(17)$

$\Phi_B(1,2,\ldots.17) = f_{CH1}(1,2) \cdot f_{CH2}(3,4) \cdot f_{CH3}(5,6) \cdot f_{CH4}(7,8) \cdot f_{CH5}(9,10) \cdot f_{CC1}(11,12) \cdot f_{CC2}(13,14) \cdot f_{\Pi2}(15,16) \cdot 2p_{z1}(17)$

$\Psi_{VB} = c_A\Phi_A + c_B\Phi_B$

Summarized: we have found single bonds between the neighbouring C and H atoms, single bonds between C atoms and a partial Π bond involving all three carbon atoms, as well as a delocalized unpaired electron.

4.10.6. Rules for constructing Lewis structures

Rules (see General Chemistry):
  1. count valence electrons;
  2. draw single bonds around the central atom;
  3. on the terminal atoms, add non-bonding electron pairs to match octets;

4. put the remaining electrons in form of non-bonding pairs on the central atom;

5. if there is no octet around the central atom, form double bonds by moving the non-bonding pairs of the terminal atoms into bonding position;

6. determine the formal charges on the atom, and make sure that charge separation is minimal.

Explanation based on VB theory:

ad 2: with hybridization we form bonds between the central and terminal atoms;

ad 3: on the terminal atoms, we fill up the hybrid and non-bonding orbitals with electrons;

ad 4: repeat this on the central atom;

ad 5: form Π bonds;

ad 6: resonance structures.

Thus we have shown that the rules obtaining Lewis structures is based on a VB theory using hybrid orbitals.

Octet rule: there are four orbitals (2s + 2p) in the second shell, if all orbitals are occupied by two electrons, altogether eight electrons can be accommodated.
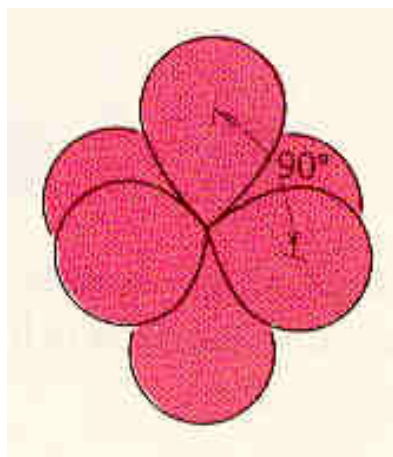
4.10.7. Hybridization

Types:

1. sp^3 $\rightarrow$ tetrahedral (see figure above);

2. sp^2 $\rightarrow$ triangle (see figure above);

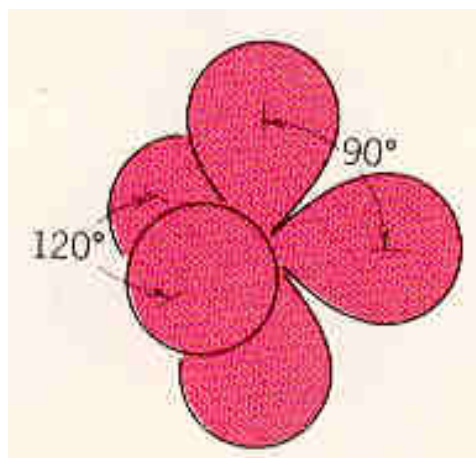3. sp $\rightarrow$ linear (see figure above);

In case of transition metal complexes, also d orbitals contribute. For example:

sp^3d^2 hybridization $\rightarrow$ octahedral complex

sp^2d^2 hybrid orbitals

sp^{3}d hybridization $\rightarrow$ trigonal-bipyramidal complex

sp^{3}d hybrid orbitals

Concerning hybrid orbitals, it is important to note that:

1. the result is included in the process since we form such combinations which point into the required direction;

2. hybridization itself is a simple basis transformation without any physical meaning.

4.11. The Hückel method

For larger molecules the description by the MO theory becomes complicated. In some cases it is enough to consider only a subset of orbitals. For example, in case of conjugated molecules, we only consider the $2p$ orbitals perpendicular to the molecular plane.

4.11.1. Approximations

1. $\sigma - \pi$ separation: neglect of the interaction between σ (in plane) and π electrons;

2. $\hat{H}$ operator:

$$\hat{H} = \sum_i^{\pi\ el} \hat{h}^{eff}(i)$$

3. Wave function: product form (no determinant!!!), spatial orbitals are double occupied:

$$\Psi(1, 2, 3, ...2n) = u_1(1)\alpha(1)u_1(2)\beta(2)u_2(3)\alpha(3) \dots u_n(2n)\beta(2n)$$

Consequence: eigenvalue equations: $\hat{h}^{eff} u_i = \varepsilon_i u_i$ \qquad Energy: $E = 2\sum_i^n \varepsilon_i$

4. Basis: minimal basis: on all C atoms a single $2p_z$ orbital ($p_1,\ p_2,\ ....p_n$)

5. Molecular orbitals can thus be obtained from a matrix eigenvalue equation with the overlap of the basis functions neglected: $\underline{\underline{h}}^{eff}\underline{c} = \varepsilon\underline{c}$

6. Matrix elements (diagonal elements are α, between neighbours β, 0 otherwise):

$$\begin{aligned}
\langle p_1|\hat{h}^{eff}|p_1\rangle &= \alpha \\
\langle p_2|\hat{h}^{eff}|p_2\rangle &= \alpha \\
&\vdots \\
\langle p_n|\hat{h}^{eff}|p_n\rangle &= \alpha \\
\langle p_1|\hat{h}^{eff}|p_2\rangle &= \beta \\
\langle p_1|\hat{h}^{eff}|p_3\rangle &= 0 \\
&\vdots \\
\langle p_1|\hat{h}^{eff}|p_n\rangle &= 0 \\
\langle p_2|\hat{h}^{eff}|p_3\rangle &= \beta \\
\langle p_2|\hat{h}^{eff}|p_4\rangle &= 0 \\
&\vdots \\
\langle p_{n-1}|\hat{h}^{eff}|p_n\rangle &= \beta
\end{aligned}$$

To solve is the eigenvalue equation of the following matrix:

$$\underline{h} = \begin{pmatrix} \alpha & \beta & 0 & 0 & \ldots & 0 \\ \beta & \alpha & \beta & 0 & \ldots & 0 \\ 0 & \beta & \alpha & \beta & \ldots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \ldots & \alpha \end{pmatrix}$$

4.11.2. Ethene

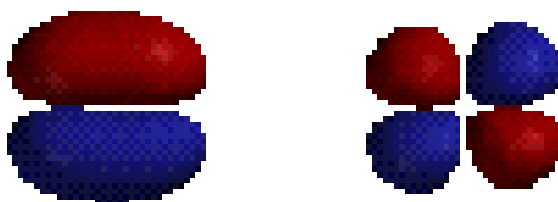$$\underline{\underline{h}}^{eff} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

Eigenvalue equation to solve:

$$\underline{\underline{h}}^{eff}\underline{c}(i) = \varepsilon\underline{c}(i)$$

$$\begin{pmatrix} \alpha - \varepsilon & \beta \\ \beta & \alpha - \varepsilon \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

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

We get:

$$\varepsilon_1 = \alpha + \beta \qquad c_1 = c_2 = \frac{1}{\sqrt{2}}$$

$$\varepsilon_2 = \alpha - \beta \qquad c_1 = -c_2 = \frac{1}{\sqrt{2}}$$

Eigenfunctions:

Energy diagram:

Total energy:

$$E = 2\alpha + 2\beta$$

4.11.3. Butadiene

$$\underline{\underline{h}} = \begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix}$$

A 4x4 problem, requires the solution of a fourth order equation. It is problematic by hand...

However, one can consider the symmetry!

Point group: C_{2h}: only „π" irreps need to be considered, others do not include any basis functions: B_g and A_u

Character table:

C_{2h}	E	C_2	i	σ_h
A_g	1	1	1	1
B_g	1	-1	1	-1
A_u	1	1	-1	-1
B_u	1	-1	-1	1
Γ	4	0	0	-4

The last row of the table denoted by Γ includes the characters of the reducible representation spanned by the four p functions.

Resolve into irreps:

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

(notations see at the water example).

$$n_{B_g} = \frac{1}{4} \Big(1 \cdot 1 \cdot 4 + 0 + 0 + 1 \cdot (-1) \cdot (-4) \Big) = 2$$

$$n_{A_u} = \frac{1}{4} \Big(1 \cdot 1 \cdot 4 + 0 + 0 + 1 \cdot (-1) \cdot (-4) \Big) = 2$$

Thus:

$$\Gamma = 2B_g \oplus 2A_u$$

The symmetry adapted functions can be determined by using the projection operators:

$$P_i = \sum_{\hat{R}} \chi^i_{\hat{R}} \hat{R}$$

$$A_u: \quad s_{a_u}(1) = \frac{1}{\sqrt{2}}(p_1 + p_4) \qquad s_{a_u}(2) = \frac{1}{\sqrt{2}}(p_2 + p_3)$$

$$B_g: \quad s_{b_g}(1) = \frac{1}{\sqrt{2}}(p_1 - p_4) \qquad s_{b_g}(2) = \frac{1}{\sqrt{2}}(p_2 - p_3)$$

The h^{eff} matrix on this basis:

$$
\begin{aligned}
\langle s_{a_u}(1)|\hat{h}^{eff}|s_{a_u}(1)\rangle &= \frac{1}{2}\langle p_1 + p_4|\hat{h}^{eff}|p_1 + p_4\rangle = \frac{1}{2}2\alpha = \alpha \\
\langle s_{a_u}(2)|\hat{h}^{eff}|s_{a_u}(2)\rangle &= \frac{1}{2}\langle p_2 + p_3|\hat{h}^{eff}|p_2 + p_3\rangle = \frac{1}{2}(2\alpha + 2\beta) = \alpha + \beta \\
\langle s_{a_u}(1)|\hat{h}^{eff}|s_{a_u}(2)\rangle &= \frac{1}{2}\langle p_1 + p_4|\hat{h}^{eff}|p_2 + p_3\rangle = \frac{1}{2}2\beta = \beta \\
\langle s_{b_g}(1)|\hat{h}^{eff}|s_{b_g}(1)\rangle &= \frac{1}{2}\langle p_1 - p_4|\hat{h}^{eff}|p_1 - p_4\rangle = \frac{1}{2}2\alpha = \alpha \\
\langle s_{b_g}(1)|\hat{h}^{eff}|s_{b_g}(1)\rangle &= \frac{1}{2}\langle p_2 - p_3|\hat{h}^{eff}|p_2 - p_3\rangle = \frac{1}{2}(2\alpha - 2\beta) = \alpha - \beta \\
\langle s_{b_g}(1)|\hat{h}^{eff}|s_{b_g}(2)\rangle &= \frac{1}{2}\langle p_1 - p_4|\hat{h}^{eff}|p_2 - p_3\rangle = \frac{1}{2}2\beta = \beta
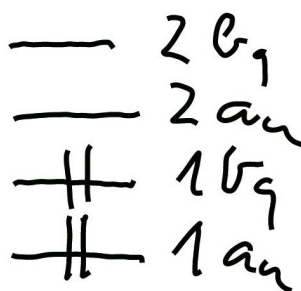\end{aligned}
$$

There are two matrices to be diagonalized:
Symmetry A_u:

$$
\underline{\underline{h}}^{A_u} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha + \beta \end{pmatrix} \quad \rightarrow \quad \varepsilon_{1,3} = \alpha + \frac{1 \pm \sqrt{5}}{2}\beta
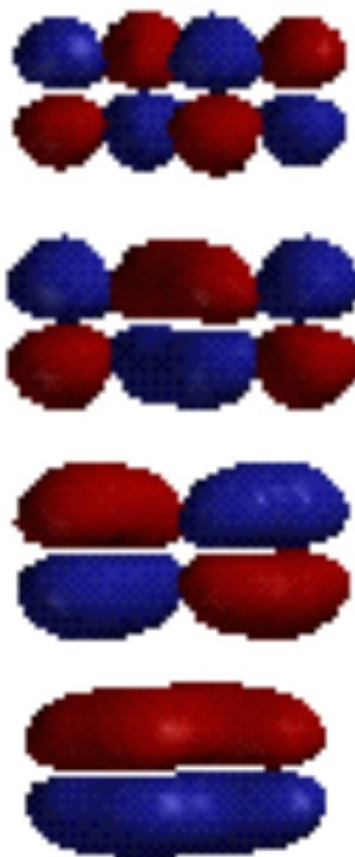$$

Symmetry B_g:

$$
\underline{\underline{h}}^{B_g} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha - \beta \end{pmatrix} \quad \rightarrow \quad \varepsilon_{2,4} = \alpha - \frac{1 \mp \sqrt{5}}{2}\beta
$$

Energy diagram:

Eigenfunctions:

Configuration: $(1a_u)^2(1b_g)^2$
State: ^1A_g
Total energy: $E_{butadiene} = 4\alpha + 4.48\beta$
Delocalization energy: $E_{butadiene} - 2E_{ethene} = (4\alpha + 4.48\beta) - (4\alpha + 4\beta) = 0.48\beta$

We can perform population analysis, as well. For this the coefficients are:

$1a_u$: $c_1 = 0.37$, $c_2 = 0.60$, $c_3 = 0.60$, $c_4 = 0.37$
$1b_g$: $c_1 = 0.60$, $c_2 = 0.37$, $c_3 = -0.37$, $c_4 = -0.60$

$P_{12} \cdot S_{12} = 2(0.37 \cdot 0.60 + 0.37 \cdot 0.60)S_{12} = 0.89S_{12}$
$P_{23} \cdot S_{23} = 2(0.60 \cdot 0.60 - 0.37 \cdot 0.37)S_{23} = 0.22S_{23}$

Question: what would we get for cis-butadiene?

4.11.4. Benzene

$$\underline{\underline{h}} \;=\; \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

It is a 6x6 problem, but we can again use symmetry.

Pointgroup: D_{6h}: only „π" irreps, no basis functions in the other ones.

Resolve into irreps:

$$\Gamma(p_1, p_2, p_3, p_4, p_5, p_6) = A_{2u} \oplus B_{2g} \oplus E_{1g} \oplus E_{2u}$$

None of the irreps appears twice $\Rightarrow$ the matrix in this basis is diagonal.
The symmetrized basis functions, which are already eigenfunctions:

$$A_{2u}: \quad a_{2u} = \frac{1}{\sqrt{6}}(p_1 + p_2 + p_3 + p_4 + p_5 + p_6)$$

$$B_{2g}: \quad b_{2g} = \frac{1}{\sqrt{6}}(p_1 - p_2 + p_3 - p_4 + p_5 - p_6)$$

$$E_{1g}: \quad e_{1g}(1) = \frac{1}{\sqrt{12}}\Big((2p_1 - p_3 - p_5) - (2p_4 - p_6 - p_2)\Big)$$

$$e_{1g}(2) = \frac{1}{2}\Big((p_3 - p_5) - (p_6 - p_2)\Big)$$

$$E_{2u}: \quad e_{2u}(1) = \frac{1}{\sqrt{12}}\Big((2p_1 - p_3 - p_5) + (2p_4 - p_6 - p_2)\Big)$$
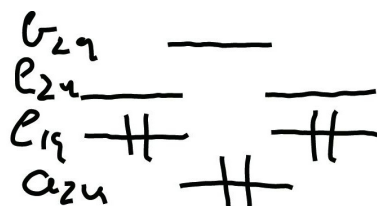
$$e_{2u}(2) = \frac{1}{2}\Big((p_3 - p_5) + (p_6 - p_2)\Big)$$

The corresponding energy can be calculated from the expectation value:

$$A_{2u}: \quad \varepsilon_1 = \frac{1}{6}\langle a_{2u}|\hat{h}^{eff}|a_{2u}\rangle$$

$$= \frac{1}{6}\langle (p_1 + p_2 + p_3 + p_4 + p_5 + p_6)|\hat{h}^{eff}|(p_1 + p_2 + p_3 + p_4 + p_5 + p_6)\rangle$$
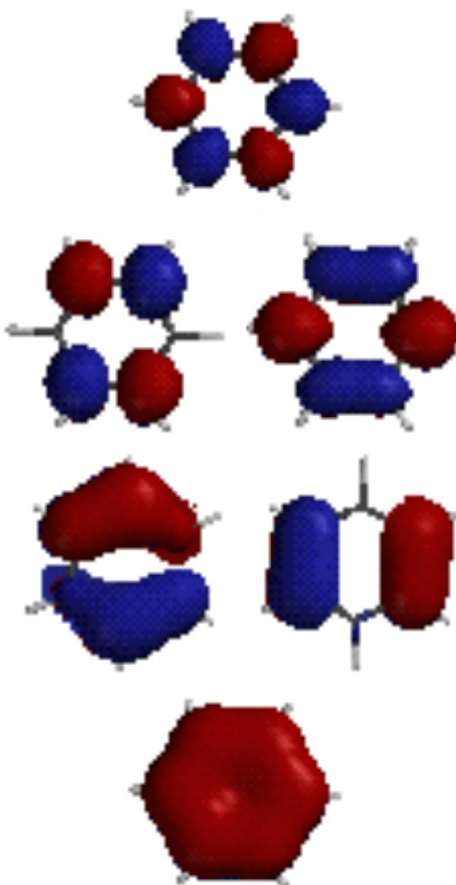
$$= \alpha + 2\beta$$

For other symmetries, similarly:

$$E_{1g}: \quad \varepsilon_2 = \frac{1}{12}\langle e_{1g}(1)|\hat{h}^{eff}|e_{1g}\rangle = \alpha + \beta$$

$$E_{2u}: \quad \varepsilon_3 = \frac{1}{12}\langle e_{2u}(1)|\hat{h}^{eff}|e_{2u}\rangle = \alpha - \beta$$

$$B_{2g}: \quad \varepsilon_4 = \frac{1}{6}\langle b_{2g}(1)|\hat{h}^{eff}|b_{2g}\rangle = \alpha - 2\beta$$

Energy diagram:

Eigenfunctions:

Configuration $(a_{2u})^2(e_{1g})^4$
State: $^1A_{1g}$
Energy: $E = 6\alpha + 8\beta$
Delocalization energy: $E_{benzene} - 3E_{ethene} = (6\alpha + 8\beta) - 6(\alpha + \beta) = 2\beta$

Mulliken population analysis:
  Density matrix:

$$P_{ab} = 2 \cdot \sum_i^{occupied} c_{ai}c_{bi}$$

Atomic charge in case of the Hückel method:

$$\sum_{a \in A} \sum_{b \in A} P_{ab} S_{ab} \;=\; P_{aa} = 2 \sum_{i}^{occupied} c_{ai} c_{ai}$$

For atom 1:

$$2 \cdot P_{11} \;=\; 2 \cdot \Big(\underbrace{\frac{1}{\sqrt{6}} \frac{1}{\sqrt{6}}}_{a_{2u}} + \underbrace{\frac{2}{\sqrt{12}} \cdot \frac{2}{\sqrt{12}}}_{e_{1g(1)}} + \underbrace{0 \cdot 0}_{e_{1g(2)}} \Big) = 1$$

Electron density corresponding to the bond in case of the Hückel method:

$$\sum_{a \in A} \sum_{b \in B} P_{ab} S_{ab} \;=\; P_{ab} \cdot S_{ab}$$

For bond between atoms 1 and 2:

$$P_{12} \cdot S_{12} \;=\; 2 \cdot \Big(\underbrace{\frac{1}{\sqrt{6}} \frac{1}{\sqrt{6}}}_{a_{2u}} + \underbrace{\frac{2}{\sqrt{12}} \cdot \frac{1}{\sqrt{12}}}_{e_{1g(1)}} + \underbrace{0 \cdot \frac{1}{2}}_{e_{1g(2)}} \Big) S_{12} = \frac{2}{3} S_{12}$$

For bond between atoms 2 and 3:

$$P_{23} \cdot S_{23} \;=\; 2 \cdot \Big(\underbrace{\frac{1}{\sqrt{6}} \frac{1}{\sqrt{6}}}_{a_{2u}} + \underbrace{\frac{1}{\sqrt{12}} \cdot \frac{-1}{\sqrt{12}}}_{e_{1g(1)}} + \underbrace{\frac{1}{2} \cdot \frac{1}{2}}_{e_{1g(2)}} \Big) S_{23} = \frac{2}{3} S_{23}$$

4.12. Electronic structure of transition metal complexes

System:

- „transition metal": atom or positively charged ion
  $\rightarrow$ open shell, can take additional electrons

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

Two theories:

- Cristal field theory: only symmetry

- Ligand field theory: simple MO theory

Questions to answer:

- why are they stable?

- why is the typical color?

- why do they have typical ESR spectrum?

### 4.12.1. Cristal field theory (Bethe, 1929)

Basic principle:

- 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 neighbouring 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

This theory is purely based on symmetry!!

Example: $[Ti(H_2O)_6]^{3+}$
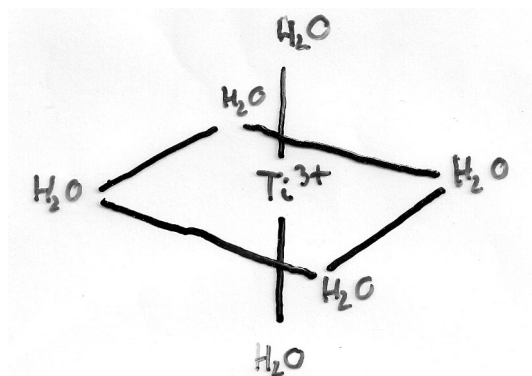
Pointgroup: O_h
Character table of the pointgroup O_h:

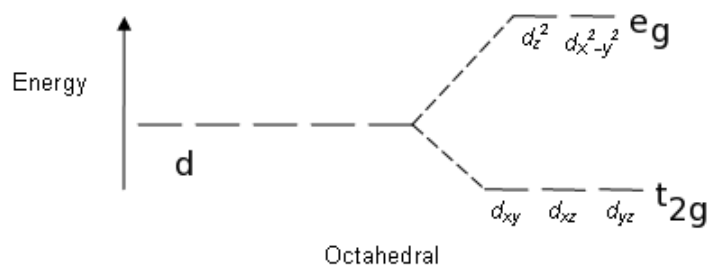| O_h	I	$8C_3$	$6C_2$	$6C_4$	$3C_2=(C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz,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

Lower symmetry, five d functions form a reducible representation:

$$\Gamma(5\ functions) = T_{2g} + E_g$$
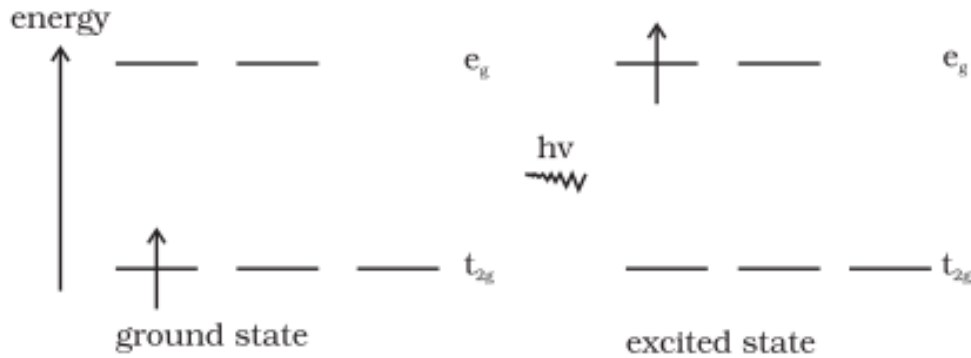$$T_{2g} : d_{z^2}, d_{x^2-y^2} \qquad E_g : d_{xy}, d_{xz}, d_{yz}$$
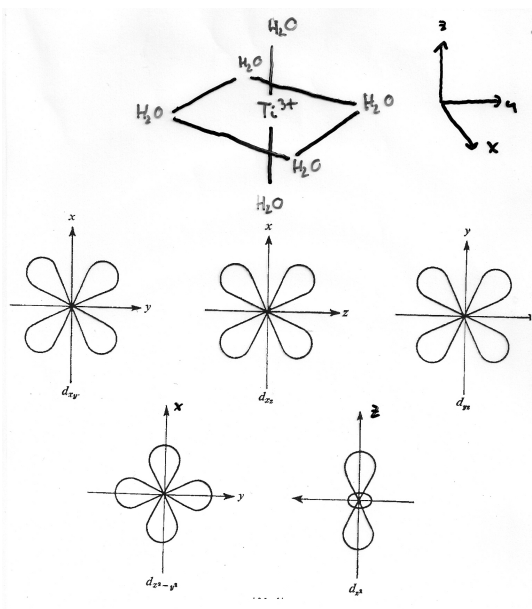
Energy levels:

Degree of splitting:

- Theory does not say a word about this

- However: $6 \cdot \Delta_{t_{2g}} = 4 \cdot \Delta_{e_g}$, i.e. average energy does not change!
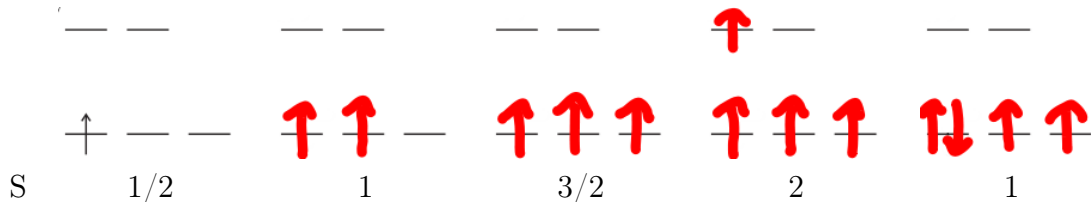
$[Ti(H_2O)_6]^{3+}$ in more detail:

Ti: $...3d^2 4s^2$

Ti^{3+}: $...3d^1$

configuration:	d^1	$(t_{2g})^1$	$(e_g)^1$
State:	^2D	$^2T_{2g}$	^2E_g

atom   complex

ground state   excited state

Energy difference between ground and excited states is small $\rightarrow$ violet color (20400 cm^{-1})

How does this work for more electrons? Use the Aufbau-principle:

| S | 1/2 | 1 | 3/2 | 2 | 1 |

From the fourth electron, occupation depends on whether Δ or the exchange interaction (K) is larger:

- if $\Delta > K$, the electron goes to the lower level (complex with small spin)

- if $\Delta < K$, the electron goes to the higher level (complex with large spin)

Strong cristal field: splitting is large enough so that the low spin case will be more stable.
Weak cristal field: the splitting is small and the high spin case will be more stable

Experiment: ESR spectroscopy (see later)

4.12.2. Ligand field theory

Basic principle: MO theory

- the orbitals of the central atom interact with the orbitals of the ligands $\rightarrow$ bonding and anti-bonding orbitals are formed

- symmetry is again important: which orbitals do mix?

Basis:

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

- ligands (closed shell): s-type orbital per ligand („superminimal basis")
  (sometimes eventually also π orbitals)
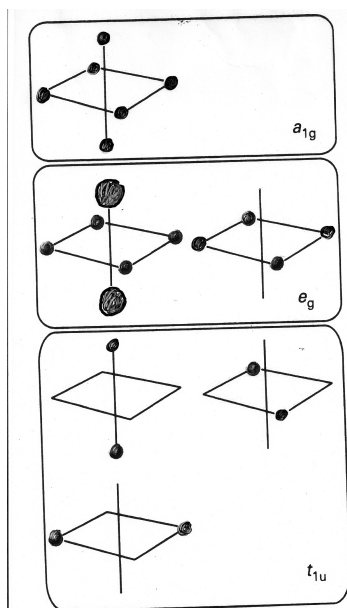
Symmetrized basis:
    according to the pointgroup of the complex, we split it into irreducible representations.

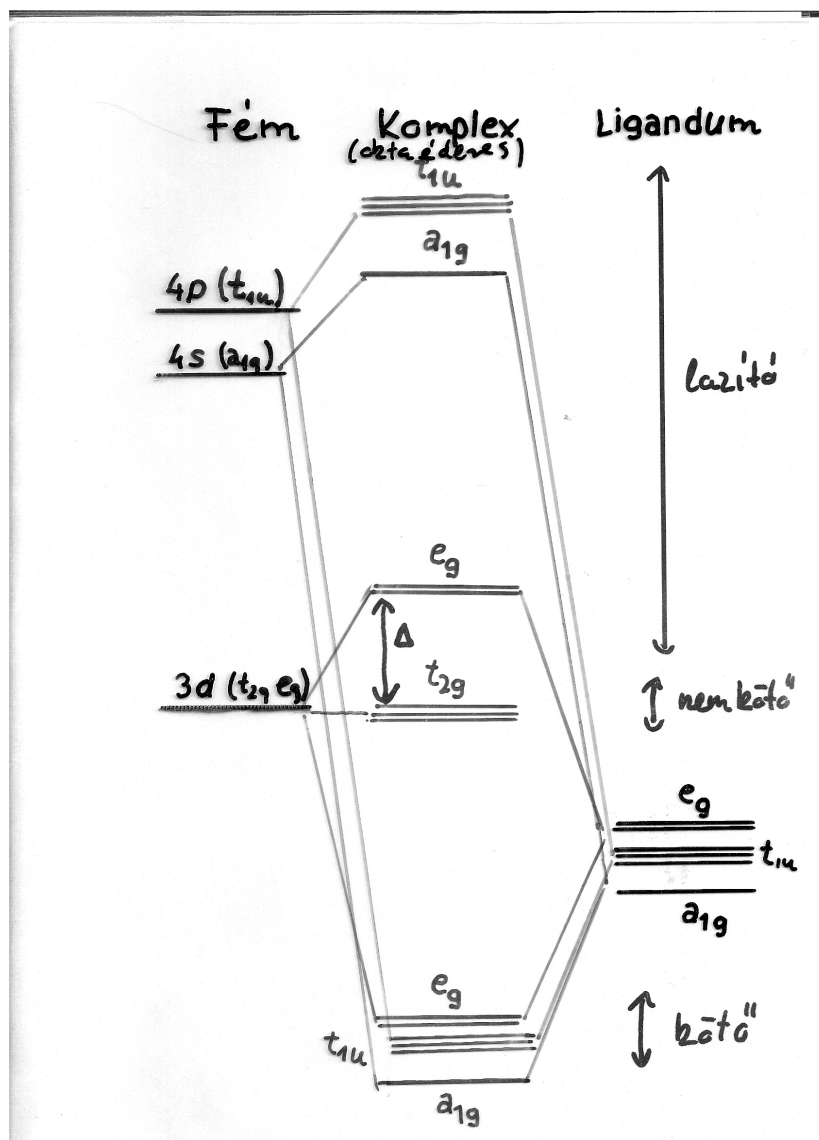Example: Octahedral complex (O_h point group)
Basis:

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

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

Symmetry adapted orbitals of ligands (6 water molecules):

MO diagram:

One has to put 1+12 electrons on these orbitals:

   configuration: $(a_{1g})^2, (t_{1u})^6, (e_g)^4, (t_{2g})^1$

   Occupancy is the same as in cristal field theory, but

- the energy of the t_{2g} orbital does not change with respect to atomic orbital, while that of the e_g orbital grows

- stabilization of the complex is due to the stabilization of the orbitals of the ligands

Other example: tetrahedral complex (e.g.. $[CoCl_4]^{2-}$, $[Cu(CN)_4]^{3-}$):
Character table of the pointgroup T_d

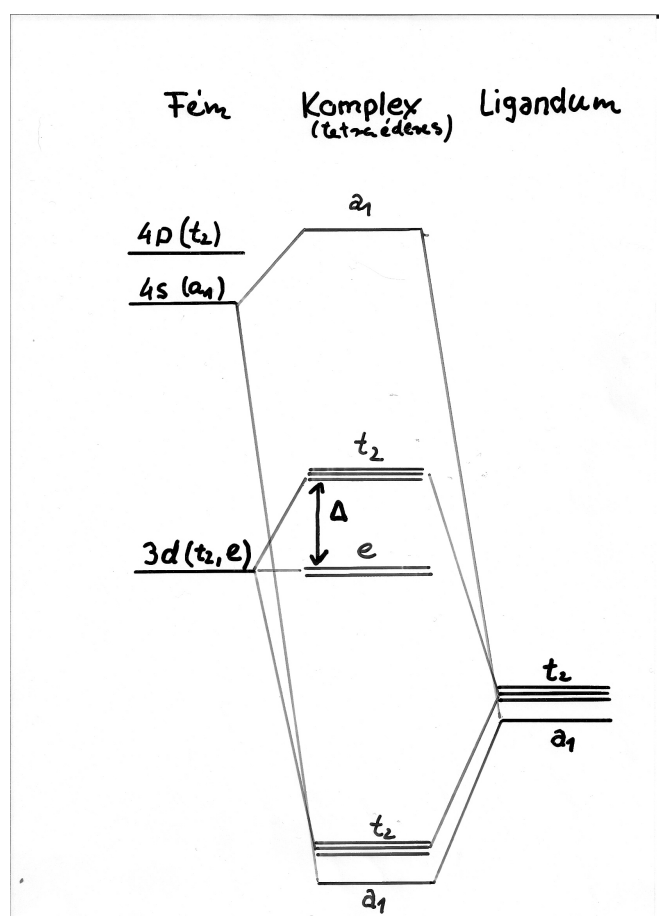| T_d	I	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2,$ $x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)
Γ	4	1	0	0	2		

Reductions:

$$\Gamma(3d) = E \oplus T_2$$
$$\Gamma(4s) = A_1$$
$$\Gamma(4p) = T_2$$
$$\Gamma(ligands) = A_1 \oplus T_2$$

MO diagram:

Appendix

Az energia kifejezése determináns hullámfüggvénnyel

A Hamilton-operátort bontsuk nulla-, egy- és kételektron tagokra:

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

Az egyszerűség kedvéért dolgozzunk két elektronnal (2x2-es determináns):

$$E = \left\langle \Psi(1,2)|\hat{H}|\Psi(1,2)\right\rangle$$

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\Big(\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)\Big) \qquad \langle\varphi_i|\varphi_j\rangle = \delta_{ij}$$

Kezdjük $\hat{H}_0$-lal. Ez, nem hatván az elektronok koordinátáira, konstans:

$$\begin{aligned}
\left\langle \Psi|\hat{H}_0|\Psi\right\rangle &= \sum_{A<B}\left\langle\Psi\Big|\frac{1}{r_{AB}}\Big|\Psi\right\rangle = \sum_{A<B}\frac{1}{r_{AB}}\langle\Psi|\Psi\rangle\\
&= \sum_{A<B}\frac{1}{r_{AB}}\left\langle\frac{1}{\sqrt{2}}\Big(\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)\Big)\Big|\frac{1}{\sqrt{2}}\Big(\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)\Big)\right\rangle\\
&= \sum_{A<B}\frac{1}{r_{AB}}\frac{1}{2}\Big[\quad \langle\varphi_1(1)\varphi_2(2)|\varphi_1(1)\varphi_2(2)\rangle\\
&\qquad\qquad\qquad - \langle\varphi_1(1)\varphi_2(2)|\varphi_2(1)\varphi_1(2)\rangle\\
&\qquad\qquad\qquad - \langle\varphi_2(1)\varphi_1(2)|\varphi_1(1)\varphi_2(2)\rangle\\
&\qquad\qquad\qquad + \langle\varphi_2(1)\varphi_1(2)|\varphi_2(1)\varphi_1(2)\rangle\Big]\\
&= \sum_{A<B}\frac{1}{r_{AB}}\frac{1}{2}\Big[1 - 0 - 0 + 1\Big] = \sum_{A<B}\frac{1}{r_{AB}}
\end{aligned}$$

Ellenőriztük tehát hogy a 2x2-es Slater-determináns valóban normált.

Folytassuk az egyelektron-taggal:

$$\begin{aligned}
\left\langle \Psi|\hat{H}_1|\Psi\right\rangle &= \left\langle \Psi\Big|\sum_i \hat{h}(i)\Big|\Psi\right\rangle\\
&= \frac{1}{2}\left\langle\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)\Big|\hat{h}(1)\Big|\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)\right\rangle\\
&\quad + \frac{1}{2}\left\langle\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)\Big|\hat{h}(2)\Big|\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)\right\rangle\\
&= \frac{1}{2}\Big[\ \left\langle\varphi_1(1)\varphi_2(2)\Big|\hat{h}(1)\Big|\varphi_1(1)\varphi_2(2)\right\rangle \quad\rightarrow\quad \langle\varphi_1|\hat{h}|\varphi_1\rangle\langle\varphi_2|\varphi_2\rangle = h_{11}
\end{aligned}$$

$$-\left\langle \varphi_1(1)\varphi_2(2)\middle|\hat{h}(1)\middle|\varphi_2(1)\varphi_1(2)\right\rangle \quad \rightarrow \quad \langle\varphi_1|\hat{h}|\varphi_2\rangle\,\langle\varphi_2|\varphi_1\rangle = 0$$

$$-\left\langle \varphi_2(1)\varphi_1(2)\middle|\hat{h}(1)\middle|\varphi_1(1)\varphi_2(2)\right\rangle \quad \rightarrow \quad \langle\varphi_2|\hat{h}|\varphi_1\rangle\,\langle\varphi_1|\varphi_2\rangle = 0$$

$$+\left\langle \varphi_2(1)\varphi_1(2)\middle|\hat{h}(1)\middle|\varphi_2(1)\varphi_1(2)\right\rangle \Big] \quad \rightarrow \quad \langle\varphi_2|\hat{h}|\varphi_2\rangle\,\langle\varphi_1|\varphi_1\rangle = h_{22}$$

$$+ \text{ ugyanez a } \hat{h}(2)-\text{re}$$

$$= \frac{1}{2}\left(h_{11} + h_{22}\right) + \frac{1}{2}\left(h_{11} + h_{22}\right) = h_{11} + h_{22}$$

Általános esetben tehát:

$$\left\langle \Psi\middle|\hat{H}_1\middle|\Psi\right\rangle = \sum_i h_{ii}$$

Végül a kételektron-tag:

$$
\begin{aligned}
\left\langle \Psi|\hat{H}_2|\Psi\right\rangle &= \left\langle \Psi\middle|\frac{1}{r_{12}}\middle|\Psi\right\rangle \\
&= \frac{1}{2}\Big[\quad \left\langle \varphi_1(1)\varphi_2(2)\middle|\frac{1}{r_{12}}\middle|\varphi_1(1)\varphi_2(2)\right\rangle \qquad \rightarrow \qquad J_{12} \\
&\qquad -\left\langle \varphi_2(1)\varphi_1(2)\middle|\frac{1}{r_{12}}\middle|\varphi_1(1)\varphi_2(2)\right\rangle \qquad \rightarrow \qquad K_{21} = K_{12} \\
&\qquad -\left\langle \varphi_1(1)\varphi_2(2)\middle|\frac{1}{r_{12}}\middle|\varphi_2(1)\varphi_1(2)\right\rangle \qquad \rightarrow \qquad K_{12} \\
&\qquad -\left\langle \varphi_2(1)\varphi_1(2)\middle|\frac{1}{r_{12}}\middle|\varphi_2(1)\varphi_1(2)\right\rangle \Big] \qquad \rightarrow \qquad J_{21} = J_{12} \\
&= J_{12} - K_{12}
\end{aligned}
$$

Általános esetben (mert $J_{ii} = K_{ii}$):

$$\left\langle \Psi\middle|\hat{H}_2\middle|\Psi\right\rangle = \sum_{i<j}\left(J_{ij} - K_{ij}\right) = \frac{1}{2}\sum_{ij}\left(J_{ij} - K_{ij}\right)$$

Ha a spineket is nézzük ($\varphi_1 =: u_1\alpha,\ \varphi_2 = u_1\beta$):

$$
\begin{aligned}
J_{12} &= \left\langle u_1\alpha(1)u_1\beta(2)\middle|\frac{1}{r_{12}}\middle|u_1\alpha(1)u_1\beta(2)\right\rangle = \tilde{J}_{11}(\neq 0) \\
K_{12} &= \left\langle u_1\alpha(1)u_1\beta(2)\middle|\frac{1}{r_{12}}\middle|u_1\beta(1)u_1\alpha(2)\right\rangle \\
&= \left\langle u_1(1)u_1(2)\middle|\frac{1}{r_{12}}\middle|u_1(1)u_1(2)\right\rangle \langle\alpha(1)\beta(2)|\beta(1)\alpha(2)\rangle = 0
\end{aligned}
$$

Kicserélődés tehát csak azonos spinű elektronok között lehet.
Példaként tekintsük a H_2 molekula alapállapotát ($\varphi_1 = u_1\alpha,\ \varphi_2 = u_1\beta$):

$$E_0 = h_{11} + h_{22} + J_{12} = 2\tilde{h}_{11} + \tilde{J}_{11}$$

A triplet gerjesztett állapotban ($\varphi_1 = u_1\alpha$, $\varphi_2 = u_2\alpha$) pedig:

$$
\begin{aligned}
K_{12} &= \left\langle u_1\alpha(1)u_2\alpha(2)\left|\frac{1}{r_{12}}\right|u_2\alpha(1)u_1\alpha(2)\right\rangle \\
&= \left\langle u_1(1)u_2(2)\left|\frac{1}{r_{12}}\right|u_2(1)u_1(2)\right\rangle\left\langle\alpha(1)\alpha(2)\Big|\alpha(1)\alpha(2)\right\rangle = \tilde{K}_{12}
\end{aligned}
$$

$$
E_1 = h_{11} + h_{22} + J_{12} - K_{12} = \tilde{h}_{11} + \tilde{h}_{22} + \tilde{J}_{12} - \tilde{K}_{12}
$$

Tehát nem tűnik el a kicserélődés, szemben a szinglet gerjesztett állapottal.

Ezzel magyarázható a Hund-szabály.