Institutt for fysikk, NTNU
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Lecture notes in chemical physics

11.04. – 19.04. 2007

These notes represent a summary of the lectures in Chemical physics:

1. Quantum mechanical calculations on molecules

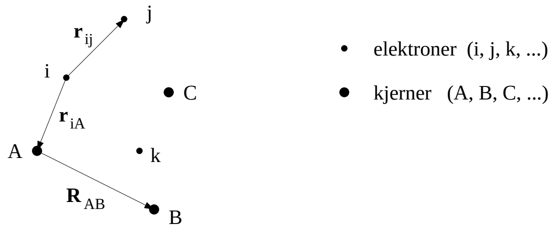
- The Born-Oppenheimer approximation
- The Hartree and the Hartree-Fock approximations
- The Hartree method
- The Hartree-Fock method
- LCAO: Linear Combination of Atomic Orbitals
- Geometry optimization, energy minimization
- Vibrational frequencies
- Chemical reactions and equilibria
- Quantum mechanical modeling of chemical reactions

2. Nomenclature in organic chemistry

3. Stereochemistry

Appendix: Molecular models from Spartan

1. Quantum mechanical calculations on molecules



In *principle*, we have a simple and well defined problem. We have a number of nuclei (A, B, ...) and a number of electrons (i, j, ...) in positions $\boldsymbol{R}_A$, $\boldsymbol{R}_B$, ..., $\boldsymbol{r}_i$, $\boldsymbol{r}_j$, ... The possible *states* Ψ of the complete *manybody system*, and the corresponding *energy eigenvalues* E are determined by the Schrödinger equation

$$H\Psi = E\Psi$$

Here,

$$H = K + V,$$

with quantum mechanical operator for kinetic energy,

$$K = \sum_i -\frac{\hbar^2}{2m}\nabla_i^2 + \sum_A -\frac{\hbar^2}{2M_A}\nabla_A^2$$

and potential energy,

$$V = \sum_{i<j} V_{ij} + \sum_{A<B} V_{AB} + \sum_{i,A} V_{iA} + V_{\text{ext}}$$

where the various interaction terms are

$$\begin{aligned} V_{ij} &= \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \\ V_{AB} &= \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R_{AB}} \\ V_{iA} &= \frac{-Z_A e^2}{4\pi\varepsilon_0 r_{iA}} \end{aligned}$$

whereas V_{ext} represents an external potential, e.g. due to an external electromagnetic field, if such a thing is present. In these expressions, $m =$ the electron mass, $M_A =$ the mass of nucleus nr A, and $Z_A =$ the atomic number of atom nr A.

To solve the Schrödinger equation for the manybody system means finding eigenfunctions Ψ_n and corresponding energy eigenvalues E_n. *The ground state*, then, is the Ψ that yields the lowest energy E. The wave functions Ψ will be manybody states that depend upon the electron coordinates $\boldsymbol{r}_i$ and the nuclear coordinates $\boldsymbol{R}_A$:

$$\Psi = \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{R}_1, \boldsymbol{R}_2, \ldots)$$

In general, exact solutions are not possible. Various types of *approximations* are necessary.

The Born-Oppenheimer approximation (Hemmer 7.4)
The nuclei are much heavier than the electrons: $M_A \gg m$. Hence, the nuclei will typically move much more slowly than the electrons: $v_A \ll v_e$. Then, it will be a reasonable approximation to assume that the nuclei are at rest when solving for the movement of the electrons. The Born-Oppenheimer approximation corresponds to solving the Schrödinger equation with fixed values for the nuclear coordinates $\boldsymbol{R}_A$. Then, we have

$$K = \sum_i -\frac{\hbar^2}{2m}\nabla_i^2$$

and

$$V = \left[\sum_{i<j} V_{ij} + \sum_{i,A} V_{iA}\right] + \left[\sum_{A<B} V_{AB} + V_{\text{ext}}\right].$$

Here, the terms in the first bracket depend upon the electron coordinates, whereas the terms in the second bracket do not.
After having solved the "electron problem", the nuclear movement may be investigated. The energy E, i.e., the ground state solution of $H\Psi = E\Psi$, now represents the *potential* that acts upon the nuclei. For example, the atoms in a molecule which is in (or near) an equilibrium configuration, will "feel" a potential approximately equal to that of a *harmonic oscillator*. Then, the atoms will oscillate back and forth, around their equilibrium positions, with certain *vibrational frequencies*. More about this later.

The Hartree and the Hartree-Fock approximations (Hemmer 9.3)
These approximations are based on the following idea: Treat the manybody system as a system of *independent* electrons moving in an *effective potential* $V(\boldsymbol{r})$, where $V(\boldsymbol{r})$ describes both the attraction due to the nuclei and the repulsion due to all the other electrons.

The Hartree method
(D. R. Hartree, 1897-1958, UK)
Assume that the electrons are in *single particle states* (or: *orbitals*) $\psi(\boldsymbol{r})$. Then, $|\psi_i(\boldsymbol{r}_i)|^2$ is the probability of finding electron nr i in the position $\boldsymbol{r}_i$, and $-e|\psi_i(\boldsymbol{r}_i)|^2$ represents the charge density in position $\boldsymbol{r}_i$ due to electron nr i.
Hence, the potential felt by electron nr j is

$$V(\boldsymbol{r}_j) = -\sum_A \frac{Z_A e^2}{4\pi\varepsilon_0 r_{jA}} + \sum_{i\neq j}\int \frac{e^2|\psi_i(\boldsymbol{r}_i)|^2}{4\pi\varepsilon_0 r_{ij}}\, d^3r_i$$

and the Schrödinger equation (SE) for electron nr j becomes

$$\left[-\frac{\hbar^2}{2m}\nabla_j^2 + V(\boldsymbol{r}_j)\right]\psi_j(\boldsymbol{r}_j) = E_j\psi_j(\boldsymbol{r}_j)$$

Here, the expression inside the brackets on the left side is the Hamiltonian H_j for electron nr j. Since H_j depends on the wave functions ψ_i ($i \neq j$) of all the other electrons, the problem must be solved *iteratively*:

- guess an initial potential $V^{(0)}(\boldsymbol{r})$

- solve the SE and determine wave functions $\{\psi_i\}^{(0)}$
- calculate a new potential $V^{(1)}(\boldsymbol{r})$ by letting the electrons occupy the wave functions $\{\psi_i\}^{(0)}$ with the lowest energy
- solve the SE and determine wave functions $\{\psi_i\}^{(1)}$
- calculate a new potential $V^{(2)}(\boldsymbol{r})\ \ldots$

and so on, until so-called *self-consistency*, which is achieved when

$$\{\psi_i\}^{(n)} \simeq \{\psi_i\}^{(n-1)}$$

with the desired accuracy. A method like this is usually called SCF (”Self Consistent Field”).

The Hartree-Fock method
(V. A. Fock, 1898-1974, USSR)
In the Hartree method, it is easy to obey the *Pauli principle* (Hemmer 8.5), i.e., no more than one electron in each single particle state, simply by constructing the potential in such a way that the lowest energy wave functions are filled with one electron in each.
In the *Hartree-Fock method*, one also makes sure the manybody state Ψ is *antisymmetric* with respect to an interchange of the coordinates of any two electrons. (Keywords here are product wave functions in the Hartree method, and Slater determinants in the Hartree-Fock method, but for details, we refer to later courses in quantum mechanics, e.g., TFY4210 Applied quantum mechanics.) In the exercises in Spartan, the SE is solved for various molecular systems with the Hartree-Fock method.

LCAO: Linear Combination of Atomic Orbitals
Now, assume we want to solve the SE for a molecule. The following idea then seems reasonable: Assume that the single particle states ψ_i in the molecule have certain similarities with (the well known) wave functions of the hydrogen atom.
After all,

$$\text{a molecule} = \text{atom} + \text{atom} + \text{atom} + \ldots$$

so why should we not be able to write

$$\text{a molecular state} = \text{atomic state} + \text{atomic state} + \text{atomic state} + \ldots ?$$

In other words, we try to write the molecular states, or rather *molecular orbitals* (MO), as linear combinations of atomic states known from the H atom, or at least functions very similar to them:

$$\psi_i = \sum_{\mu=1}^{M} c_{\mu i}\phi_\mu \quad , \quad i = 1, 2, \ldots$$

Here,

- ψ_i = molecular orbital nr i
- ϕ_μ = atomic state, or *basis function* nr μ

- $c_{\mu i}$ = molecular orbital coefficients, revealing to what extent the basis function ϕ_μ contributes to MO ψ_i

For each type of atom (i.e., H, He, Li, ...), one chooses (or constructs, or calculates) a *basis set* $\{\phi_\mu\}$, i.e., (orthogonal) basis functions $\phi_1, \phi_2, \ldots, \phi_M$.
Here, we may, as a rule of thumb, assume that a larger M (i.e. more basis functions in the basis set) will give us more accurate calculations. However, more basis functions means a heavier numerical job, of course.
Suppose the molecule has $2N$ electrons. The *ground state* is then given by the MO coefficients $\{c_{\mu i}\}$ ($\mu = 1, 2, \ldots, M$; $i = 1, 2, \ldots, N$) that yields N molecular orbitals $\psi_1, \psi_2, \ldots, \psi_N$ such that the energy becomes as small as possible.
Why N MOs for $2N$ electrons? Because the Pauli principle limits the number of electrons to 1 pr electron state. Each state consists of an orbital part (here: the MO) and a spin part. A given electron may have spin up or spin down, i.e., two possibilities. Hence, we may put 2 electrons in a particular MO, one with spin up and one with spin down. Hence, $2N$ electrons will occupy N MOs.
In programs like Spartan, it is common practice to use so-called *gaussian functions* as basis functions:

$$\phi(\boldsymbol{r}) = \phi(x, y, z) = Cx^a y^b z^c e^{-\alpha r^2}$$

Here, C is a normalization constant. From the H atom, we know the various wave functions, classified according to the value of the quantum number l for the angular momentum: s, p, and d orbitals correspond to $l = 0, 1, 2$ etc. The integral exponents a, b, c correspondingly yields

- s orbitals: $a = b = c = 0$
- p orbitals: $a = 1$ or $b = 1$ or $c = 1$ (p_x, p_y, p_z, respectively), the two others zero
- d orbitals: $a + b + c = 2$

etc. For a given value of l, we have $2l + 1$ possible states, one state for each value of the quantum number $m = -l, \ldots, l$ (Hemmer 5.4). That yields 1 s state and 3 p states. For the d states, $l = 2$, i.e., degeneracy equal to 5. With the gaussians degenerasjonsgrad lik 5. Med gaussfunksjonene

$$\phi(x, y, z) = Cx^a y^b z^c e^{-\alpha r^2},$$

one seems to have 6 possibilities ($a = 2$, $b = 2$, $c = 2$, $a = b = 1$, $a = c = 1$, $b = c = 1$). The 5 "correct" d orbitals, i.e., those known from the hydrogen atom, are obtained by using

$$\begin{aligned} \phi_{xy} &= xye^{-\alpha r^2} \\ \phi_{xz} &= xze^{-\alpha r^2} \\ \phi_{yz} &= yze^{-\alpha r^2} \end{aligned}$$

together with two linear combinations of the remaining three:

$$\begin{aligned} \phi_{x^2-y^2} &= \sqrt{\frac{3}{4}}\,(\phi_{xx} - \phi_{yy}) \\ \phi_{3z^2-r^2} &= \frac{1}{2}\,(2\phi_{zz} - \phi_{xx} - \phi_{yy}) \end{aligned}$$

(Here, we didn't care too much about normalization...) The final one,

$$\phi_{r^2} = \sqrt{5}\,(\phi_{xx} + \phi_{yy} + \phi_{zz})\,,$$

is spherically symmetric, i.e., its symmetry is that of an s orbital, so this is simply not a d orbital. In conclusion: The Spartan program *uses* all the 6 d-type basis functions, when constructing the 5 correct d orbitals. The sixth, ϕ_{r^2}, with s symmetry is not used.

If you examine the wave functions of the H atom, you will notice that they have exponentials of the form (Hemmer 5.7)

$$e^{-\alpha r}$$

and not

$$e^{-\alpha r^2}$$

The main reason for using the latter type, is that integrals like

$$\int \phi_\mu^* \phi_\mu \, d^3r$$

become simpler to solve. A disadvantage is that the chosen (gaussian) functions approach zero much too fast when r becomes large. Moreover, they have the wrong shape when $r \to 0$. Therefore, one must use more gaussian functions than functions of the type $\exp(-\alpha r)$ (so-called Slater orbitals) to achieve the same accuracy in the calculations.

In the exercises in Spartan, the so-called 3-21G basis set will be used. Then we include the following basis functions for the different atoms:

- H: 2 s orbitals: $1s$, $2s$
- C: 3 s and 2×3 p orbitals: $1s$, $2s$, $2p_x$, $2p_y$, $2p_z$, $3s$, $3p_x$, $3p_y$, $3p_z$
- Cl: 4 s, 3×3 p and 6 d orbitals: $1s$, $2s$, $2p_x$, $2p_y$, $2p_z$, $3s$, $3p_x$, $3p_y$, $3p_z$, $3d_{xx}$, $3d_{yy}$, $3d_{zz}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $4s$

For N and O, one uses the same number of functions as for C, i.e., 3 s and 2×3 p orbitals, a total of 9.

Example: In the molecule C_4H_7Cl, the MOs are written as linear combinations of $4{\cdot}9{+}7{\cdot}2{+}19 = 69$ basis functions. The number of electrons in this molecule is $4 \cdot 6 + 7 \cdot 1 + 17 = 48$. This means that the MOs $\Psi_1, \Psi_2, \ldots, \Psi_{24}$ are occupied by electrons (remember: 2 electrons in each MO), whereas MOs $\Psi_{25}, \ldots, \Psi_{69}$ are unoccupied (empty).

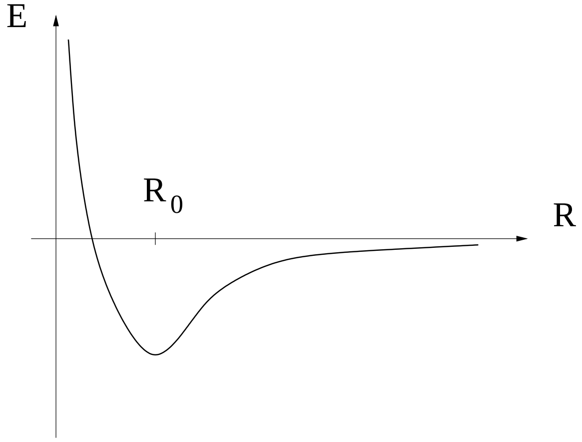
As mentioned earlier, the MOs $\{\Psi_i\}$ (or, the MO coefficients $\{c_{\mu i}\}$) are calculated iteratively, for example with the Hartree-Fock method.

Geometry optimization, energy minimization

Assume now that we have performed a Hartree-Fock calculation and found MOs $\{\Psi_i\}$ with corresponding energy eigenvalues $\{E_i\}$ for a number of atoms A in *fixed* positions $\{R_j\}$ ($j = 1, 2, \ldots, A$).

The next natural question may be: In which positions $\{R_{j0}\}$ will we find the atoms of the molecule in equilibrium? The equilibrium positions, and hence the *geometry* of the molecule, is determined by the requirement that the energy E of the system be as low as possible. The energy E depends parametrically on the atom positions $\{R_j\}$.

Example: Two-atomic molecule. The molecular geometry is then determined by a single coordinate, namely $R =$ the distance between the two atoms. The energy, as a function of the distance R, typically look something like this:



In other words, a strong repulsion if the interatomic distance becomes very small, and a weak attraction when the distance becomes large. Minimum energy corresponds to $R = R_0 =$ the equilibrium distance between the two atoms, i.e., the *bond length*. From the figure, we see that the equilibrium geometry is characterized by

$$\begin{aligned} E'(R_0) &= \left(\frac{dE}{dR}\right)_{R=R_0} = 0 \\ E''(R_0) &= \left(\frac{d^2E}{dR^2}\right)_{R=R_0} > 0 \end{aligned}$$

The bond length R_0 may be found by iteration. Assume that $E(R)$ may be approximated with a 2. order Taylor polynomial in the vicinity of $R = R_0$:

$$E(R) \simeq E(R_0) + (R - R_0)E'(R_0) + \frac{1}{2}(R - R_0)^2 E''(R_0)$$

Differentiation once and twice yields, respectively,

$$E'(R) \simeq E'(R_0) + (R - R_0)E''(R_0) = (R - R_0)E''(R_0)$$

and

$$E''(R) \simeq E''(R_0)$$

Solving with respect to R_0 yields

$$R_0 \simeq R - \frac{E'(R)}{E''(R_0} \simeq R - \frac{E'(R)}{E''(R)}$$

Hence, the following iteration scheme should work, assuming that we start with an R not too far away from R_0:

- guess an initial $R^{(1)}$
- calculate the corresponding energy $E(R^{(1)})$ and its derivative, $E'(R^{(1)})$, and second derivative, $E''(R^{(1)})$
- calculate a new length
$$R^{(2)} = R^{(1)} - \frac{E'(R^{(1)})}{E''(R^{(1)})}$$
- calculate the corresponding energy $E(R^{(2)})$ and its derivative, $E'(R^{(2)})$, and second derivative, $E''(R^{(2)})$
- calculate a new length
$$R^{(3)} = R^{(2)} - \frac{E'(R^{(2)})}{E''(R^{(2)})}$$

etc etc, until convergence is achieved. The old and new length in iteration step nr n is

$$R^{(n+1)} = R^{(n)} - \frac{E'(R^{(n)})}{E''(R^{(n)})},$$

and a *convergence criterion* must be specified, e.g.,

$$|R^{(n+1)} - R^{(n)}| < \delta,$$

where δ is a suitably chosen (small) length, e.g., 0.001 Å.

In a molecule with A atoms, the geometry will be determined by $3A$ coordinates, e.g., x_j, y_j and z_j for atom nr j ($j = 1, 2, \ldots, A$). A generalization of the method described above then becomes:
The molecular geometry is given by the vector

$$\boldsymbol{R} = (x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_A, y_A, z_A)$$

The relation between the old and the new geometry in iteration step nr n becomes

$$\boldsymbol{R}^{(n+1)} = \boldsymbol{R}^{(n)} - (\nabla E)^{(n)} \cdot \left(\boldsymbol{H}^{(n)}\right)^{-1}$$

with

$$\nabla E = \left(\frac{\partial E}{\partial x_1}, \frac{\partial E}{\partial y_1}, \frac{\partial E}{\partial z_1}, \ldots, \frac{\partial E}{\partial x_A}, \frac{\partial E}{\partial y_A}, \frac{\partial E}{\partial z_A}\right)$$

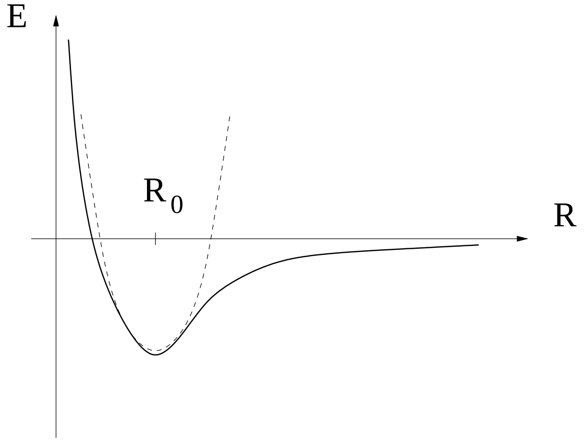
and the *Hessian matrix*

$$\boldsymbol{H} = \begin{bmatrix} \frac{\partial^2 E}{\partial x_1^2} & \frac{\partial^2 E}{\partial x_1 \partial y_1} & \cdots & \frac{\partial^2 E}{\partial x_1 \partial z_A} \\ \vdots & & & \vdots \\ \frac{\partial^2 E}{\partial z_A \partial x_1} & \cdots & \cdots & \frac{\partial^2 E}{\partial z_A^2} \end{bmatrix}$$

i.e., the matrix with matrix elements equal to the second derivative of the energy with respect to all possible combinations of two coordinates.

Vibrational frequencies

As mentioned earlier, the atoms in a molecule will oscillate back and forth around their equilibrium position. Again, it is illustrative to examine the simplest possible example, a two-atomic molecule:



We see that the two atoms of the molecule move in a potential $E(R)$ which, in the vicinity of equilibrium, to a good approximation may be regarded as *harmonic* (i.e., *quadratic*) (dashed curve in the figure):

$$E(R) \simeq \frac{1}{2}m\omega^2(R - R_0)^2$$

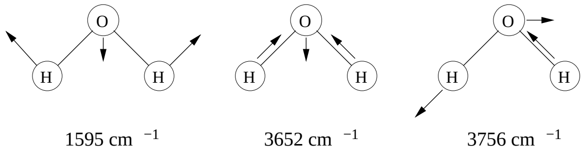
(m = the mass of the oscillator = the reduced mass = $m_1m_2/(m_1 + m_2)$ for a two-atomic molecule if we have atoms with mass m_1 and m_2) Then we know that the system will perform oscillations around the equilibrium distance R_0, with frequency $f = \omega/2\pi$. The vibrational frequency is determined by (the square root of) the *curvature* of the potential:

$$f = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{E''(R_0)}{m}}$$

We generalize (without details!) to an A-atomic molecule: The Hessian matrix $\boldsymbol{H}$ then contains all the information of the possible vibrational movements (so-called *normal modes*) and the corresponding vibrational frquencies in the molecule. *Diagonalization* of $\boldsymbol{H}$ yields eigenvalues that are proportional to ω_α^2 ($\alpha = 1, 2, \ldots, 3A$). The corresponding eigenvectors $\boldsymbol{A}_\alpha$ have elements $A_{\alpha i}$ ($i = 1, 2, \ldots, 3A$) that denote the amplitude of the displacement of the various atoms (in the $x-$, $y-$, and $z-$ directions) in the different normal modes α.
For a non-linear molecule (i.e., the atoms do not all lie on a straight line), 6 of the eigenvalues ω_α^2 will be zero. These correspond to pure translation (3 of them) and pure rotation (3 of them) of the whole molecule. In other words, there are $3A - 6$ vibrational modes for a molecule with A atoms.
For a linear molecule (e.g., CO_2 and C_2H_2), only 5 of the eigenvalues ω_α^2 will be zero: There are still 3 degrees of freedom associated with pure translation of the molecule, but only 2 degrees of freedom associated with rotation. (Rotation around the linear axis of the molecules does not

represent any kinetic energy, at least only a negligible kinetic energy, since the corresponding moment of inertia is zero, or at least very small.)

Example: The water molecule, H_2O, has 3 atoms. It is not linear, the angle H-O-H is ca 105 degrees. The number of degrees of freedom is 9. The number of vibrational modes is 9 - 6 = 3. The figure below denotes the wave number k (i.e., the wave number of an electromagnetic wave with frequency $f = c/\lambda = ck/2\pi$) and, with arrows, the corresponding movement of the three atoms in the molecule for each normal mode:



Notice that the vibrational movement is such that the center of mass of the molecule is always at rest.

Chemical reactions and equilibria

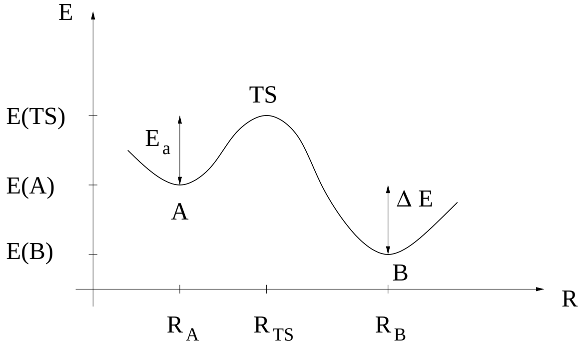
In connection with chemical reactions, we will typically be interested in two things:

- The kinetics: *How fast* is a chemical reaction?
- The thermodynamics: *To what extent* does the reaction proceed, from reactant(s) to product(s)? (I.e., provided we wait long enough...)

Let us examine a chemical reaction

$$A \rightleftharpoons B$$

Here, A may represent one or more reactants, and B may correspondingly represent one or more products. The energy E of the system will typically be as in the figure below, along some kind of *reaction coordinate* R:



Here, R may e.g. be the distance between two atoms, such that a bond is broken when R is increased from R_A to R_B. The reaction proceeds via a (local) energy maximum, the so-called *transition state*, denoted as TS.

The speed of the reaction (the kinetics) is determined by the *activation energy* (the energy barrier)

$$E_a = E(TS) - E(A)$$

in that the *reaction rate* k will depend exponentially upon the ratio between E_a and the available thermal energy $k_B T$:

$$k \sim e^{-E_a/k_B T}$$

Provided we wait long enough, a *thermodynamic equilibrium* will be established between reactant(s) A and product(s) B. The equilibrium is determined by the energy difference

$$\Delta E = E(A) - E(B)$$

in that the ratio between concentrations $[A]$ and $[B]$ will depend exponentially upon the ratio between ΔE and $k_B T$:

$$\frac{[A]}{[B]} = e^{-\Delta E/k_B T}$$

Comment: Above, we are rather sloppy when we refer to the "energy". For instance, we say nothing about what kind of experimental conditions we have, whether the pressure or the volume is kept constant and so on. Such details will determine which energy function is the relevant one: the enthalpy, the Helmholtz free energy, or the Gibbs free energy, cf courses like TMT4110 Chemistry, Thermal physics, and Statistical physics. Let us here avoid all such details and simply assume that $E(R)$ reflects the relevant energetic conditions, both with respect to the kinetics and with respect to the thermodynamics.

Quantum mechanical modeling of chemical reactions

Several strategies are possible if we wish to model a chemical reaction with quantum mechanical methods. Here, only *one* method is described. It is based on identifying a sensible reaction coordinate R, and then change this stepwise, starting from the reactant geometry A. Let us illustrate the method with a concrete example (see exercise 2).

Chemical reaction that we want to model:

$$\mathrm{ClCH_3} + \mathrm{Br^-} \rightarrow \mathrm{BrCH_3} + \mathrm{Cl^-}$$

Here, the anion $\mathrm{Br^-}$ will "attack" the C atom from "behind", such that the bond between C and Cl is broken while a new bond between Br and C is formed.

The reactant A will be a "complex", with $\mathrm{Br^-}$ "coordinated" to the $\mathrm{CH_3Cl}$ molecule, with a certain equilibrium distance R_A between $\mathrm{Br^-}$ and C. The product B will be a similar complex, but this time with $\mathrm{Cl^-}$ coordinated to the $\mathrm{CH_3Br}$ molecule, and with a (shorter) distance R_B between Br and C.

We choose the Br-C distance as reaction coordinate and change it stepwise, from the initial value R_A to the final value R_B. Let the step size be ΔR.

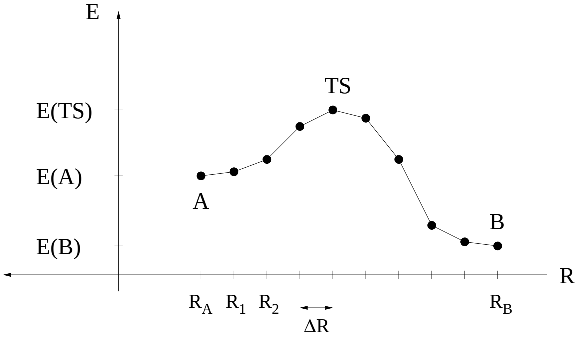
First, an unconstrained geometry optimization of the coordinated complex A is performed. This gives us the equilibrium distance R_A and the corresponding energy E_A.

Next, the Br-C distance is changed to $R_1 = R_A - \Delta R$ and *kept fixed*, while the rest of the geometry of the system is optimized. This gives us the point (R_1, E_1) on the energy curve $E(R)$.

And in this way we continue. In step nr n, we have $R_n = R_A - n \cdot \Delta R$, and when all other degrees of freedom have been optimized, we obtain the point (R_n, E_n) on the energy curve. In step nr N, with

$$N = \frac{R_A - R_B}{\Delta R},$$

we have $R_N = R_A - N \cdot \Delta R = R_B$, i.e., we have modeled through the reaction, all the way to the product B, which is here the $BrCH_3$ molecule, with Cl^- coordinated to the C atom.
A plot of E as a function of R_j will look something like this (note: decreasing R to the right in the figure):



The activation energy is now calculated to be

$$E_a = E(TS) - E(A)$$

whereas

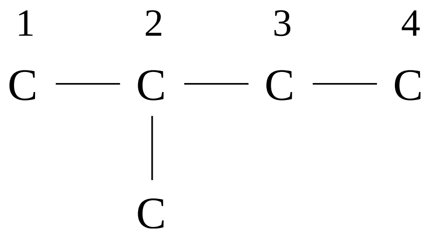
$$\Delta E = E(A) - E(B)$$

We start and end in energy minima A and B, characterized by a *positive curvature* of the energy curve $E(R)$. In general, an energy minimum will be characterized by *only positive eigenvalues* of the Hessian matrix $\boldsymbol{H}$.

The reaction proceeds via a local energy maximum TS, characterized by a *negative curvature* of the energy curve $E(R)$. In general, such a transition state will be characterized by *one negative eigenvalue* of the Hessian matrix $\boldsymbol{H}$. (While the remaining eigenvalues are positive.)

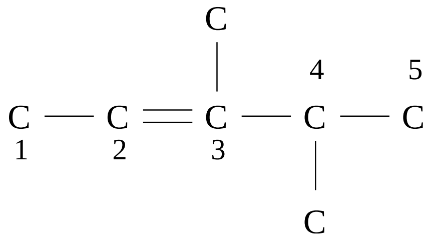
2. Nomenclature in organic chemistry

Let us start with a couple of simple examples (assumed to be known from TMT4110 Chemistry):



Appendix, Figure 1

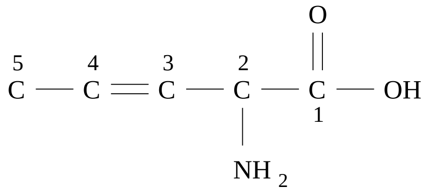
We identify the longest carbon chain and number the atoms in this chain such that the most important substituent is placed on the lowest possible number. Then we have here a *butane*, with a *methyl* substituent in position 2. Hence, the compound is 2-methyl-butane.



Appendix, Figure 2

Here, the longest carbon chain has 5 C atoms. We put numbers such that the double bond comes at the lowest possible number. This yields a pent-2-ene (or: 2-pentene), with methyl substituents in positions 3 and 4. Hence, the name is 3,4-dimethyl-pent-2-ene (or: 3,4-dimethyl-2-pentene).

But how to figure out the fact that this compound,



Vedlegg, Figur 3

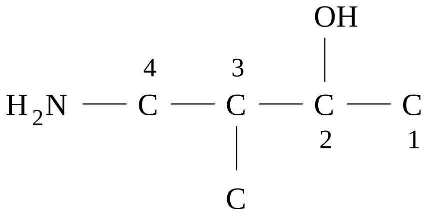
should have the name 2-amino-pent-3-enoic acid? We need some rules. The name of the compound consists of 3 parts:

- One or several prefixes, including numbering
- The main skeleton
- The suffix

First, we identify the *suffix*. The rules say that we should choose the *functional group* in the molecule with the *highest priority*, according to Table 1 (below). The *main skeleton* is then determined by the longest carbon chain. The *prefix* of the name must finally contain information about all the substituents (except the one promoted to suffix, of course), including their position. The *numbering* is done so that the suffix sits at the lowest possible number on the carbon skeleton. One could ask if the carbon atom in, say, the carboxylic acid group -COOH should be counted when naming the skeleton. The answer is yes, also if the suffix is an ester, an amide, a nitrile, an aldehyde, a ketone etc.

Let us look at some more examples.

Example 1:

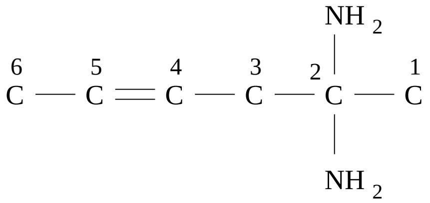


Appendix, Figure 4

This could be an alcohol or an amine. According to Table 1, alcohol has higher priority than amine, so it must be an alcohol. The skeleton is C-C-C-C, i.e., butane. We have two substituents, one methyl (CH_3) and one amino ((NH_2) gorup. We number the skeleton so that the suffix group sits at the lowest possible number. Here, this implies putting -OH on carbon nr 2. Hence, the methyl group is in position 3, and the amino group in position 4. The name is

3-methyl-4-amino-butan-2-ol
(or 3-methyl-4-amino-2-butanol)

Example 2:

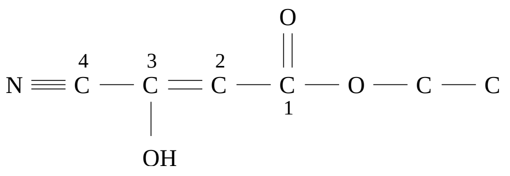


Appendix, Figure 5

The functional group with highest priority is -NH_2, and since we have two of them, this becomes a diamine. The skeleton has 6 C atoms, with a double bond between nr 4 and 5. The amino groups should sit on the lowest possible numbers, here nr 2. That's it, so the name is

hex-4-ene-2,2-diamine
(or 4-hexene-2,2-diamine)

Example 3:



$\mathrm{N \equiv \overset{4}{C} - \underset{|\atop OH}{\overset{3}{C}} = \overset{2}{C} - \underset{1}{\overset{O \atop ||}{C}} - O - C - C}$

Appendix, Figure 6

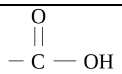
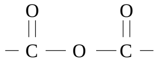
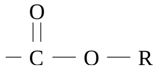
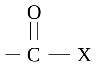
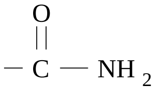
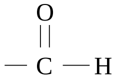
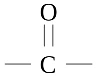
Highest priority for the group -COOR, with R = C_2H_5, i.e. ethyl. So the compound is an ester, and the name should end with -oate or -ate. (If we had R = H, we would have had a carboxylic acid.) The carbon skeleton starts with the carbon atom of the ester group and consists of 4 C atoms, with a double bond between nr 2 and 3. Hence, this is a but-2-enoate (or: 2-butenoate), and with R = ethyl, this becomes an ethyl-but-3-enoate. Between ”ethyl” and ”but-2-enoate”, we must say something about the substituents. Here, we have a hydroxy group in position 3 and a nitrile group in position 4. So, I believe the name must be

Ethyl-4-cyano-3-hydroxy-but-2-enoate
(or Ethyl-4-cyano-3-hydroxy-2-butenoate)

The substituents (here, cyano and hydroxy) in *alphabetical* order, which I forgot to mention.

This page will be an appendix to the questions at the exam.

Table: Some functional groups, ranked according to decreasing priority

Rank	Main group	Functional group	Prefix	Suffix
1	Carboxylic acid	-COOH  $-\overset{O}{\overset{\|}{C}}-OH$	(carboxy-)	-oic acid
2	Carboxylic acid anhydride	-CO–O–CO-  $-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$		-oic anhydride
3	Ester †	-COOR  $-\overset{O}{\overset{\|}{C}}-O-R$		-oate
4	Carboxylic acid halide †	-COX  $-\overset{O}{\overset{\|}{C}}-X$	halocarbonyl-	-oyl halide
5	Amide	-CONH$_2$  $-\overset{O}{\overset{\|}{C}}-NH_2$	amido-	-amide
6	Nitrile	-CN $-C\equiv N$	cyano-	-nitrile
7	Aldehyde	-COH  $-\overset{O}{\overset{\|}{C}}-H$	oxo-	-al
8	Ketone	-CO-  $-\overset{O}{\overset{\|}{C}}-$	oxo-	-one
9	Alcohol	-OH	hydroxy-	-ol
10	Thiol	-SH	mercapto-	-thiol
11	Amine	-NH$_2$	amino-	-amine
12	Imine	>C=N-	imino-	-imine
13	Alkene	-C=C-		-ene
14	Alkyne	-C≡C-		-yne
15	Alkane	-C–C-		-ane

Secondary groups (no priority)	Functional group	Prefix	Suffix
Ether	-C–O–C-	alkoxy-	-ether
Halide †	-X	halo- (e.g. chloro-)	
Nitro	-NO$_2$	nitro-	

† X = a halogen (F, Cl, Br, or I), R = (usually) an alkyl group (C_nH_{2n+1})

Naming organic compounds:

[Prefix(es) including numbering] - [Main skeleton] - [Suffix]

- Suffix: functional group with highest rank
- Main skeleton: longest connected carbon chain
- Prefix(es) incl numbering: all substituents on the main skeleton

3. Stereochemistry

Stereochemistry is about compounds with the same chemical formula, but compounds that are not identical. We speak of different *isomers*.
We classify isomers as

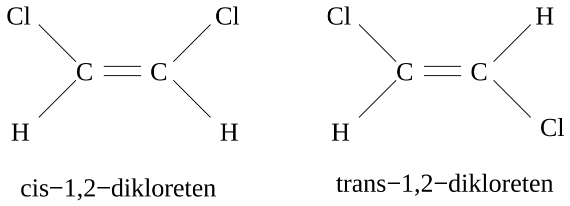
- constitutional isomers: different order of the atoms/substituents
- stereo isomers: same order, but different spatial positions of the atoms/substituents

For example: 1-butene and 2-butene are different constitutional isomers of C_4H_8. Here, we will take a closer look at stereo isomers.

Stereo isomers may be divided into two groups:

- Enantiomers: compounds that are each others mirror images
- Diastereomers: compounds that are not each others mirror images

Example of diastereomers: *cis*- and *trans*-compounds:

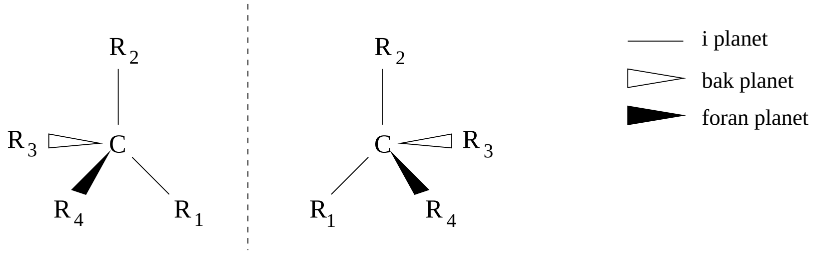


Appendix, Figure 7

The figure above illustrates *cis*-1,2-dichloroethene (left) and *trans*-1,2-dichloroethene (right). The names are latin and means "on this side" (cis) and "on the other side" (trans), respectively. An alternative nomenclature for cis and trans is Z and E, respectively, from German: zusammen and entgegen.

Of greatest interest for a physicist are the so-called enantiomers. The reason is that such compounds are *optically active*: If one of the enantiomers rotate the plane of polarization of plane polarized electromagnetic waves in a certain direction (e.g. to the right), the other enantiomer (the mirror image of the first one) will rotate the plane of polarization in the opposite direction (e.g. to the left). A gas with 50 % of each of the two enantiomers will not rotate the plane of polarization. Deviations from equal concentrations may be measured by sending plane polarized light through the gas.

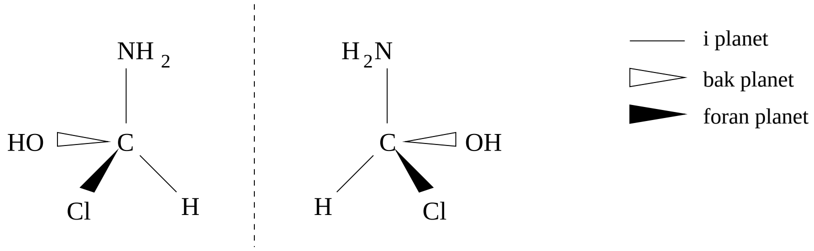
We will not go into the microscopical explanation of this optical effect. However, we will take a look at the general structure of such compounds. Common for them is the presence of an sp^3 hybridized carbon atom with four different substituents R_1, R_2, R_3, and R_4:



Notice the notation given to the right in the figure, to illustrate whether a given substituent lies in, in front of, or behind the paper plane. With four different substituents, it is not possible to superimpose these two compounds. (Something which *is* possible if only 3, 2, or 1 substituents are different.) We call the central C atom in such compounds a *chiral center*.

To tell the enantimers apart, we need some kind of notation: First, rank the 4 substituents according to standard rules (higher atom number gives higher priority and so on), such that R_1 has the lowest priority etc. Next, imagine looking down the C-R_1 axis. Go from R_4 to R_3 to R_2. If you go clockwise, you have an R isomer (R for rectus - right). If you go counterclockwise, you have an S isomer (S for sinister - left).
According to this convention, we have, in the figure above, an R enantiomer to the left and an S to the right.

An example:



Appendix, Figure 8

Both molecules have the formula $HCNH_2OHCl$ and the name amino-chloro-methanol. However, the two molecules are not identical - they are each others mirror images. Ranking the 4 substituents by decreasing atom number yields Cl $>$ OH $>$ NH_2 $>$ H. If we look down the C-H bond of the molecule to the left, we see that we much go *clockwise* from Cl to OH to NH_2. Hence, this is the R isomer. Doing the same with the molecule to the right, we find that we must go counterclockwise. So, this is the S isomer.

TFY4215 Kjemisk fysikk og kvantemekanikk Våren 2007
Chemical physics

Appendix to the lecture notes

Molecular models produced in Spartan
(color code in Figure 9)

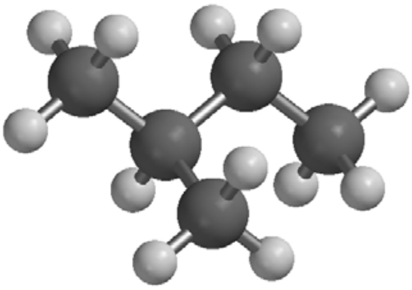


Figure 1: 2-methyl-butane, C_5H_{12}

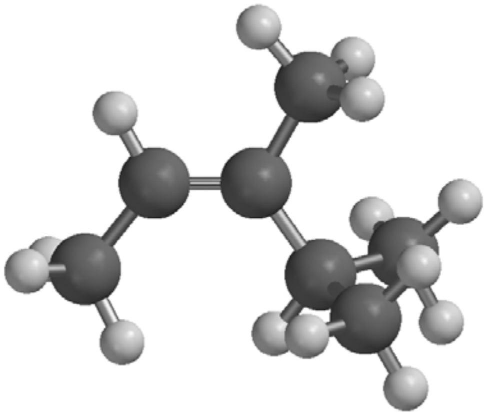


Figure 2: 3,4-dimethyl-2-pentene, C_7H_{14}

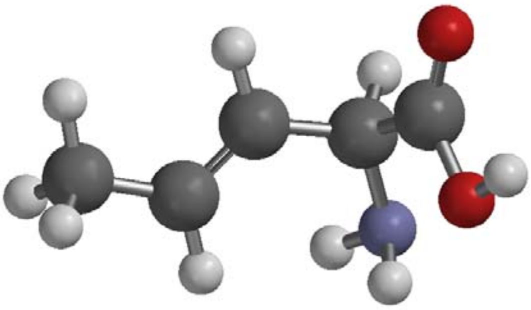


Figure 3: 2-amino-3-pentenoic acid, $C_4H_6NH_2COOH$

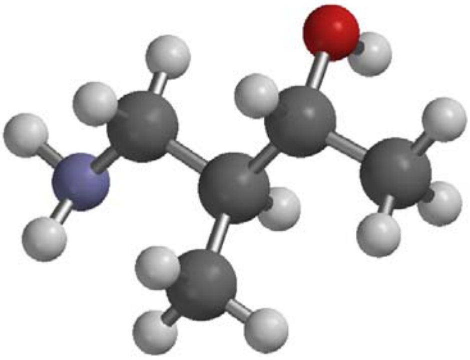


Figure 4: 4-amino-3-methyl-2-butanol, $NH_2C_5H_{10}OH$

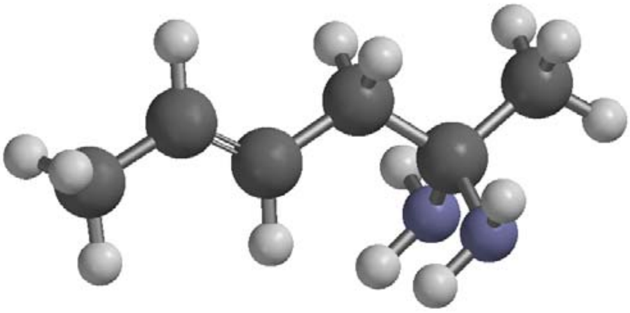


Figure 5: 4-hexene-2,2-diamine, $(NH_2)_2C_6H_{10}$

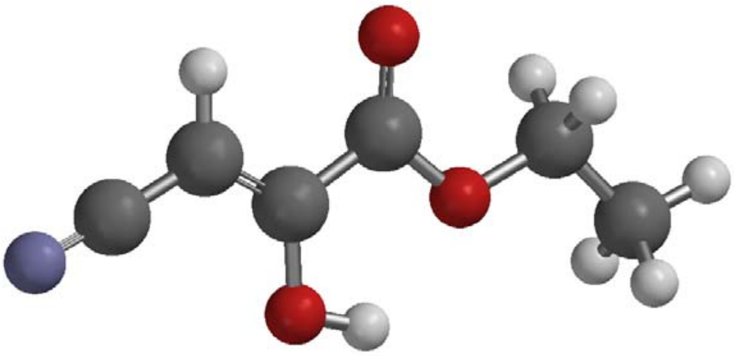


Figure 6: Ethyl-4-cyano-3-hydroxy-2-butenoate, $NC_3HOHCOOC_2H_5$

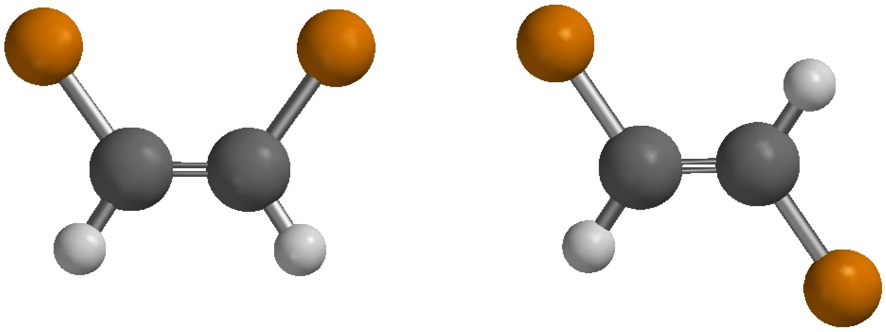


Figure 7: cis- and trans-1,2-dichloroethene, $C_2H_2Cl_2$

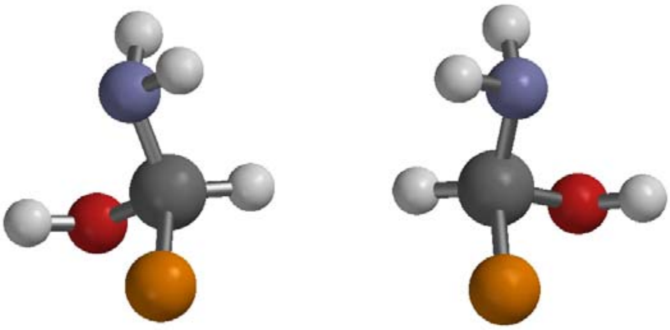


Figure 8: R- and S-amino-chloro-methanol, $HCNH_2OHCl$ (R to the left)

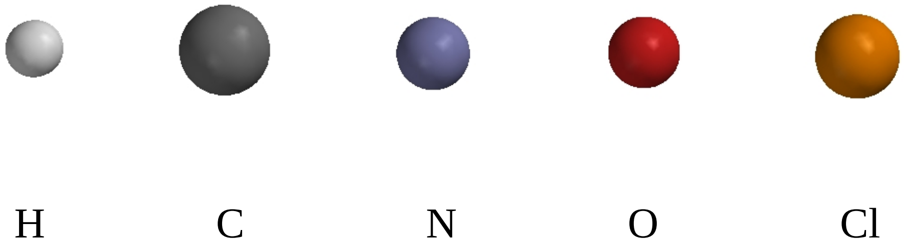


Figure 9: Color code