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Lecture notes in chemical physics

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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

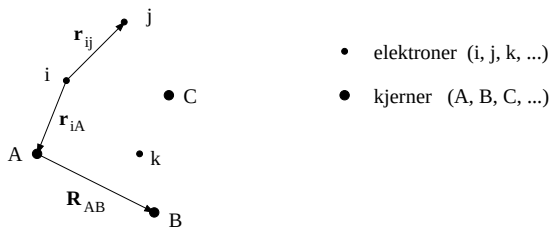
2. Nomenclature in organic chemistry (not relevant for exam 2012)

3. Stereochemistry

Appendix: Molecular models from Spartan

Last updated: March 22 2012.

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 to find eigenfunctions Ψ_n and corresponding energy eigenvalues E_n. *The ground state*, then, is the Ψ that results in the lowest energy E:

$$E_{\text{GS}} = \min E = \min \int \Psi^* H \Psi \, d\tau$$

Here, $\int \ldots d\tau$ means integral over all the spatial coordinates of the particles, and summation over variables that represent the spin of the particles. And we vary Ψ until the lowest possible energy E has been found.

Concerning the electron spin: Electrons are fermions with spin 1/2, and with two possible orientations, "up" or "down" (or: "+" or "-"). In this course, we will always study atoms, ions, and molecules that are so-called "closed shell" systems, i.e., the systems consists of an even numer of electrons that pairwise are described by the same orbital state, one with spin up and one with spin down. Hence, the total spin of the system is zero. And since our Hamiltonian does not contain any terms that depend upon the electron spin, we may simply disregard the spin in most of what follows. The only thing we must remember is that each single particle orbital state may be combined with two spin states (up and down), so that we may put two electrons into each single particle orbital. (This is the Pauli principle, more about that later.)
As is well known, finding a minimum of an ordinary function $f(x)$ implies to locate a so-called *stationary* point where the derivative of f is zero. In a similar manner, finding the ground state of a quantum mechanical manybody system implies locating a state Ψ which makes the value of the total energy E stationary. In other words, in the ground state of the system,

$$\frac{\delta}{\delta\Psi}\left(\int \Psi^* H\Psi \, d\tau\right) = 0.$$

This is an example of a *variational principle*. Another well known example is Fermat's principle from geometrical optics: the light travels along the path that minimizes the time of travel. The differentiation $\delta/\delta\Psi$ is not an ordinary derivative, but a so-called *functional derivative*, because the energy E is not an ordinary function of Ψ, but a *functional* of Ψ.
The wave functions Ψ are manybody states that depend both on 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 very simplest treatment of the electron–electron interaction: $V_{ij} = 0$
The major difficulty in various manybody problems is the interaction between the particles, in our case V_{ij}, i.e., the repulsion between the electrons. The simplest way to attack this problem is setting $V_{ij} = 0$. Such a drastic step will not give much of interest when it comes to the description of real systems like molecules, but it may serve as an illustration of how the *form* of the manybody states Ψ must be, *without* electron–electron interaction, but also *with* this interaction, in some situations.
With $V_{ij} = 0$, the hamiltonian becomes

$$H = \sum_i h_i + \sum_{A<B} V_{AB}.$$

Here,

$$h_i = -\frac{\hbar^2}{2m}\nabla_i^2 + \sum_A V_{iA}$$

is a single particle operator that only concerns electron nr i, and therefore only "operates upon" the coordinate $\boldsymbol{r}_i$. Now the Schrödinger equation becomes separable, and the manybody state Ψ may be written as a product of single particle states ψ:

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) = \psi_1(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2)\cdots\psi_N(\boldsymbol{r}_N).$$

We see that this is a solution simply by inserting it into

$$\sum_i h_i\Psi = \left(E - \sum_{A<B} V_{AB}\right)\Psi = \tilde{E}\Psi,$$

which is a slight rewriting of $H\Psi = E\Psi$. Insertion of the product form of Ψ results in N single particle equations,

$$h_i\psi_i = \varepsilon_i\psi_i \quad ; \quad i = 1, 2, \cdots, N$$

where ψ_i is an eigenfunction of h_i, with eigenvalue ε_i.
The ground state is then

$$\Psi_{\mathrm{GS}} = \psi_1(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2)\cdots\psi_N(\boldsymbol{r}_N),$$

with energy

$$E_{\mathrm{GS}} = \tilde{E} + \sum_{A<B} V_{AB} = \sum_{i=1}^{N}\varepsilon_i + \sum_{A<B} V_{AB}$$

Next questions: How to take the electron–electron interaction V_{ij} into account?

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

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

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 $V^{(2)}(\boldsymbol{r})$ ...

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"). Note that the Hartree equations are on the same mathematical form as the ones we had without any interactions whatsoever. Hence, the Hartree method also results in the simple product form for the manybody states Ψ.

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. (*Two* electrons in each, one with spin up and one with spin down, if we are only dealing with the orbital part of the wave function.)
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. Since the value of the spin

is half-integer, more precisely 1/2, electrons are particles called *fermions*, and a state that describes two or more fermions, must change sign if two of them interchange coordinates.
We remember from mathematics that a *determinant* changes sign if we interchange two rows (or columns). We also remember, perhaps, that a determinant is zero if two rows (or columns) are linearly dependent. For example, the determinant is zero if two rows are identical.
John C. Slater realized that these properties of determinants could be useful when dealing with manybody states, and he suggested to write them as a determinant, where element (i, j) equals $\psi_i(\boldsymbol{r}_j, s_j)$, i.e., single particle state nr i for electron nr j – with spatial coordinate $\boldsymbol{r}_j$ and spin coordinate s_j. We simplify the notation by writing

$$\psi_i(\boldsymbol{r}_j, s_j) = \psi_i(j).$$

Then, the *Slater determinant* that describes the N–electron state $\Psi(1, 2, \cdots, N)$ is:

$$\Psi(1, 2, \cdots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \cdots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \cdots & \psi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(1) & \psi_N(2) & \cdots & \psi_N(N) \end{vmatrix}.$$

Let us be convinced that such a determinant fulfills the various requirements for a many electron state:

- Ψ is antisymmetric (we use $N = 2$ as an example):

$$\begin{aligned} \Psi(1, 2) &= \frac{1}{\sqrt{2}} [\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)] \\ \Psi(2, 1) &= \frac{1}{\sqrt{2}} [\psi_1(2)\psi_2(1) - \psi_1(1)\psi_2(2)] = -\Psi(1, 2) \end{aligned}$$

- The Pauli principle is automatically built in: If two single particle states ψ_i and ψ_j are identical, this means that row nr i and row nr j are equal, and then the determinant is zero, i.e., $\Psi = 0$. In other words: Two electrons cannot occupy the same single particle state. Note: Here, we have included the electron spin variable in the discussion, and hence there may be no more than one electron in each single particle state ψ. However, nothing prevents ψ_i and ψ_j fraom having identical *orbital parts*, provided they have different *spin parts*, one with spin up and one with spin down. If this is the case, ψ_i and ψ_j correspond to one and the same *molecular orbital* (MO), of which we will talk more below.

- Ψ is correctly *normalized* if it is built up of orthogonal and normalized ("orthonormal") single particle states ψ_i. We will not show this in detail here, but I guess it looks reasonable with the factor $1/\sqrt{N!}$ since Ψ contains all together $N!$ terms.

A few additional comments:

- Why isn't the Hartree–Fock solution the exact solution of such a manyfermion problem? Because a single Slater determinant is not the most general manybody function $\Psi(1, 2, \cdots, N)$. You could e.g. construct a linear combination of many Slater determinants. If such a state gives you a lower total energy for the system, it is by definition a better approximation to the exact ground state.

- There are alternative methods for attacking manybody problems. One common method is so-called *density functional theory* (DFT). In DFT, one starts by expressing the total energy of the system as a functional of the particle density n, i.e.,

  $$E = E[n]$$

  For many real problems in physics and chemistry, DFT provides a better description of experimental data than does the Hartree–Fock method. At the same time, DFT is a numerically faster method than Hartree–Fock.

- In the Spartan exercises in this course, we use 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

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

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:

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

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

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

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: $1s$, $2s$, $2p_x$, $2p_y$, $2p_z$, $3s$, $3p_x$, $3p_y$, $3p_z$, $3d_{xx}$, $3d_{yy}$, $3d_{zz}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $4s$, $4p_x$, $4p_y$, $4p_z$

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.

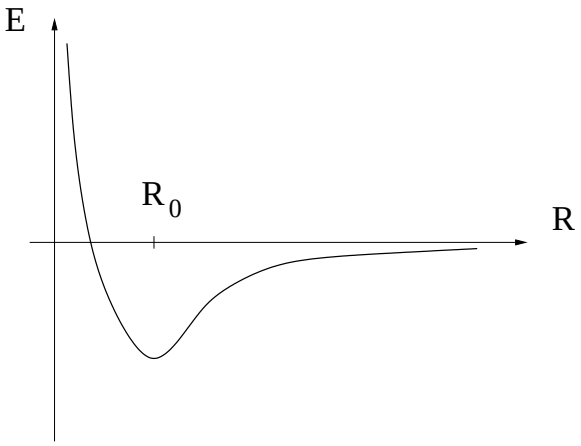
Example: In the molecule C_4H_7Cl, the MOs are written as linear combinations of $4{\cdot}9{+}7{\cdot}2{+}19 = 69$ basis functions. The number of electrons in this molecule is $4 \cdot 6 + 7 \cdot 1 + 17 = 48$. This means that the MOs $\Psi_1, \Psi_2, \ldots, \Psi_{24}$ are occupied by electrons (remember: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

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

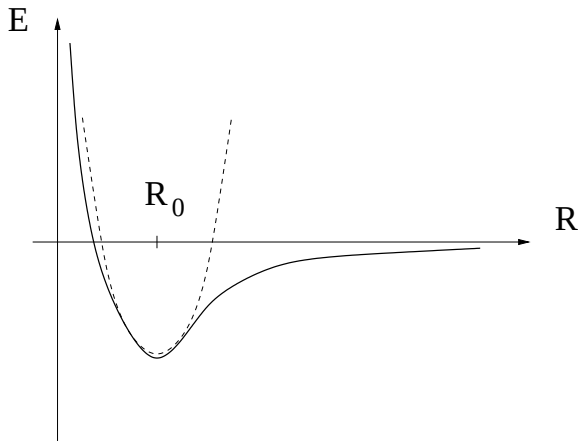
and the *Hessian matrix*

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

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 = $m_1 m_2/(m_1 + m_2)$ 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:

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

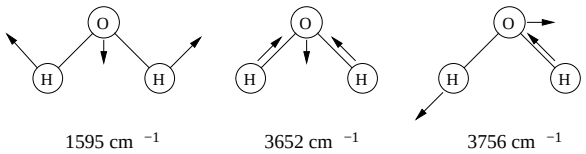
We generalize (without many details!) to an A-atomic molecule: The Hessian matrix $\boldsymbol{H}$ then contains all the information of the possible vibrational movements (so-called *normal modes*) and the corresponding vibrational frquencies in the molecule. More precisely: *Diagonalization* of the *mass–weighted* Hessian matrix, $\boldsymbol{F} = \boldsymbol{M}^{-1/2}\boldsymbol{H}\boldsymbol{M}^{-1/2}$, i.e., solution of the eigenvalue problem

$$\boldsymbol{F}\boldsymbol{A} = \lambda \boldsymbol{A},$$

provides eigenvalues $\lambda_\alpha = \omega_\alpha^2$ ($\alpha = 1, 2, \ldots, 3A$). Here, $\boldsymbol{M}$ is a diagonal ($3A \times 3A$) matrix with elements $M_{11} = M_{22} = M_{33} = m_1$, with m_1 equal to the mass of atom nr 1, $M_{44} = M_{55} = M_{66} = m_2$, with m_2 equal to the mass of atom nr 2, and so on. 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. (The ground state of a linear molecule is cylindrically symmetric with respect to the linear axis of the molecule. Then, within quantum mechanics, it does not make sense to speak about rotation around this axis, just as it does not make sense to speak about rotation of a spherically symmetric atom.)

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.

A little warning before we move on: The term *degrees of freedom* is not used in a unique manner in all of physics and chemistry. We have used it to be synonymous with the number of spatial dimensions available for each "building block" (i.e. each atom) in the system at hand. Hence, a molecule with A atoms moving in 3 spatial dimensions simply have $3A$ degrees of freedom. In Thermal physics, in connection with heat capacity of e.g. ideal gases, a slightly different definition is used. Here, "the number of degrees of freedom" means the number of quadratic terms in the energy function of the system, where both kinetic and potential energy terms are counted (of course). Then, a two-atomic molecule has *seven*, and not six, degrees of freedom: Three for translation of the molecule (kinetic energy $mv_x^2/2 + mv_y^2/2 + mv_z^2/2$), two for rotation around the two axes perpendicular to the linear axis of the molecule, and *two* for the vibration along the molecular axis, one for kinetic energy and one for potential energy. In the general formulation of Mechanics, each particle in the system has two degrees of freedom for each spatial dimension, one for the position and one for the momentum of the particle. Hence, all together twelve degrees of freedom for a two-atomic molecule.

Chemical reactions and equilibria

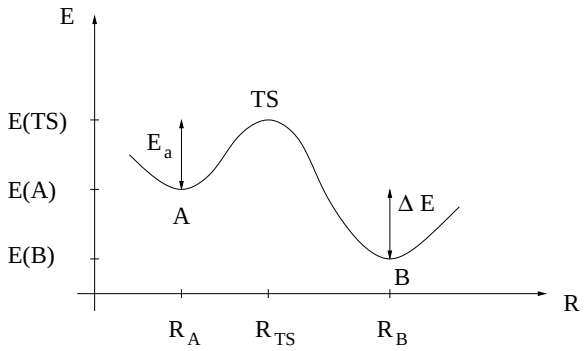
In connection with chemical reactions, we will typically be interested in two things:

- 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_BT:

$$k \sim e^{-E_a/k_BT}$$

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_BT:

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

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).

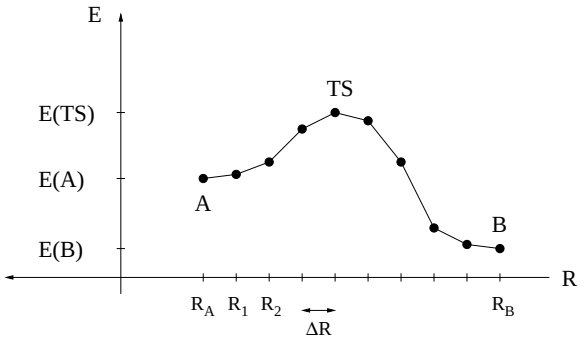
Chemical reaction that we want to model:

$$ClCH_3 + Br^- \rightarrow BrCH_3 + Cl^-$$

Here, the anion 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 Br^- "coordinated" to the CH_3Cl molecule, with a certain equilibrium distance R_A between Br^- and C. The product B will be a similar complex, but this time with Cl^- coordinated to the 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

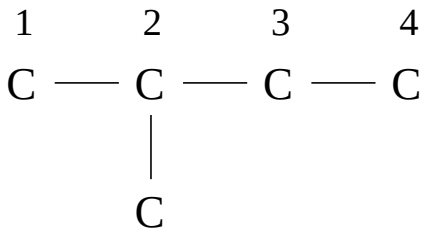
$$\Delta E = E(A) - E(B)$$

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.)

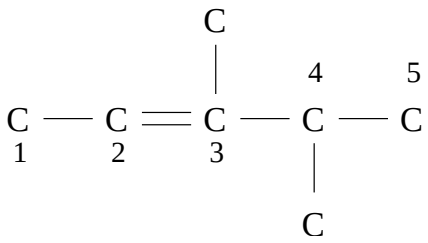
2. Nomenclature in organic chemistry (not relevant for exam)

Let us start with a couple of simple examples:



Appendix, Figure 1

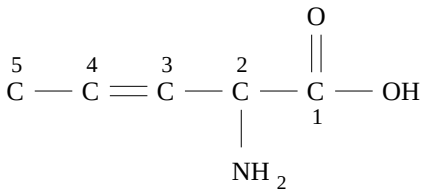
We identify the longest carbon chain and number the atoms in this chain such that the most important substituent is placed on the lowest possible number. Then we have here a *butane*, with a *methyl* substituent in position 2. Hence, the compound is 2-methyl-butane.



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

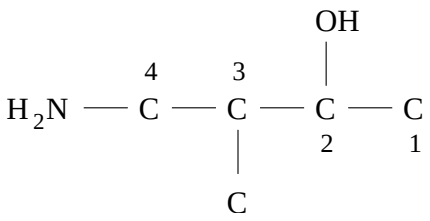
should have the name 2-amino-pent-3-enoic acid? We need some rules. The name of the compound consists of 3 parts:

- 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, and in alphabetical order. 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:

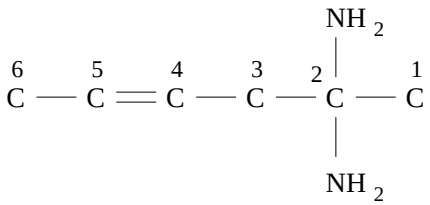


Appendix, Figure 4

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:

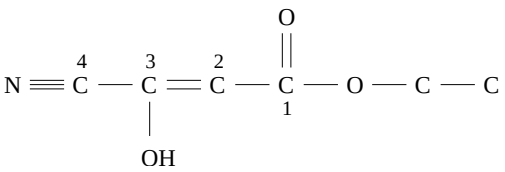


Appendix, Figure 5

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:



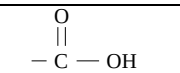
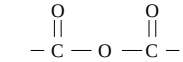
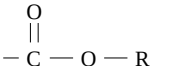
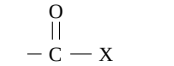
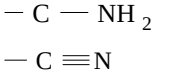
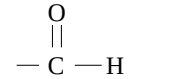
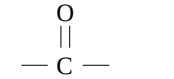
Appendix, Figure 6

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.)

Table: Some functional groups, ranked according to decreasing priority

Rank	Main group	Functional group	Prefix	Suffix
1	Carboxylic acid	-COOH 	(carboxy-)	-oic acid
2	Carboxylic acid anhydride	-CO–O–CO- 		-oic anhydride
3	Ester †	-COOR 		-oate
4	Carboxylic acid halide †	-COX 	halocarbonyl-	-oyl halide
5	Amide	-$CONH_2$	amido-	-amide
6	Nitrile	-CN 	cyano-	-nitrile
7	Aldehyde	-COH 	oxo-	-al
8	Ketone	-CO- 	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, numbered so that the suffix group sits on the lowest possible number
- Prefix(es) incl numbering: all substituents on the main skeleton, in alphabetical order

3. Stereochemistry (most of this is not exam relevant, but lectured material about enantiomers and optically active compounds is relevant for the exam)

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

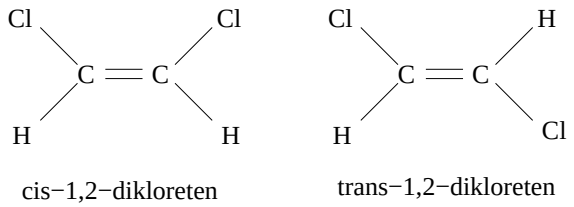
- constitutional isomers: different order of the atoms/substituents
- stereo isomers: same order, but different spatial positions of the atoms/substituents

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:

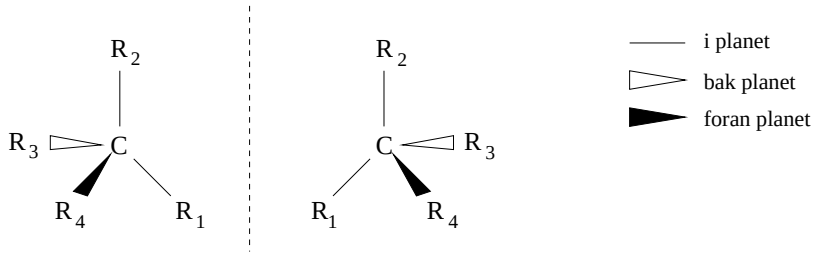


Appendix, Figure 7

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.

The rest of the notes are relevant for the exam!
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.

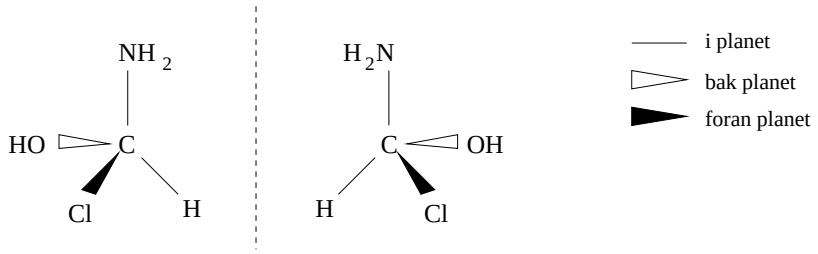
We will not go much into the microscopical explanation of this optical effect, but a "classical" explanation, based on the refractive index of the medium, has been included below. At first, however, we take a closer look at the general structure of such compounds. Common for them is the presence of an 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.

Explanation of why chiral molecules are optically active.
When electromagnetic waves propagate through a medium, this implies an oscillating electric field $\boldsymbol{E}$ and magnetic field $\boldsymbol{B}$ that influence the charges in the molecules, and result in oscillating electric and magnetic dipoles, which in turn represent *their* contributions to the total electric and magnetic field. As is well known from wave physics (and let us here assume linear and non-dispersive media, for simplicity), the net effect of this seemingly complicated interaction between the incoming wave and the medium, is expressed by a change in the velocity of the

electromagnetic wave, from the value c in vacuum, to the value $v = c/n$ in the medium at hand. Here, n is the refractive index of the medium.
Let us now make the following – rather plausible – assumption: For a medium that consists of chiral molecules, i.e., molecules that are either "right handed" or "left handed", the refractive index is different for a right circularly and a left circularly polarized electromagnetic wave:

$$n_R \neq n_L$$

We will not attempt to prove this here, but simply note that it can be verified experimentally, and that is can be shown theoretically by (not quite trivial) quantum mechanical calculations. Furthermore, a right circularly polarized wave must be "seen" by an R-isomer in the same way as a left circularly polarized wave is seen by an S-isomer, and vice versa. In other words,

$$n_R^R = n_L^S$$

and

$$n_R^S = n_L^R$$

so that

$$\Delta n(R) \equiv n_R^R - n_L^R = -\Delta n(S) \equiv -(n_R^S - n_L^S)$$

Here, the notation is like this: n_α^j denotes the refractive index for an α-circularly polarized e.m. wave ($(\alpha = R, L)$ when the medium consists of the j-isomer (j =R,S).
Next, we assume that the incident wave is linearly polarized, e.g. with its polarization along x, and with propagation along z:

$$\boldsymbol{E}(z,t) = \hat{x}\, E_0 \cos(kz - \omega t)$$

We may regard this wave as a superposition of a right circularly and a left circularly polarized wave,

$$\boldsymbol{E}_R(z,t) = [\hat{x}\, E_0 \cos(kz - \omega t) - \hat{y}\, E_0 \sin(kz - \omega t)]/2$$

and

$$\boldsymbol{E}_L(z,t) = [\hat{x}\, E_0 \cos(kz - \omega t) + \hat{y}\, E_0 \sin(kz - \omega t)]/2$$

respectively. Then, we see that we may write

$$\boldsymbol{E}(z,t) = \boldsymbol{E}_R(z,t) + \boldsymbol{E}_L(z,t)$$

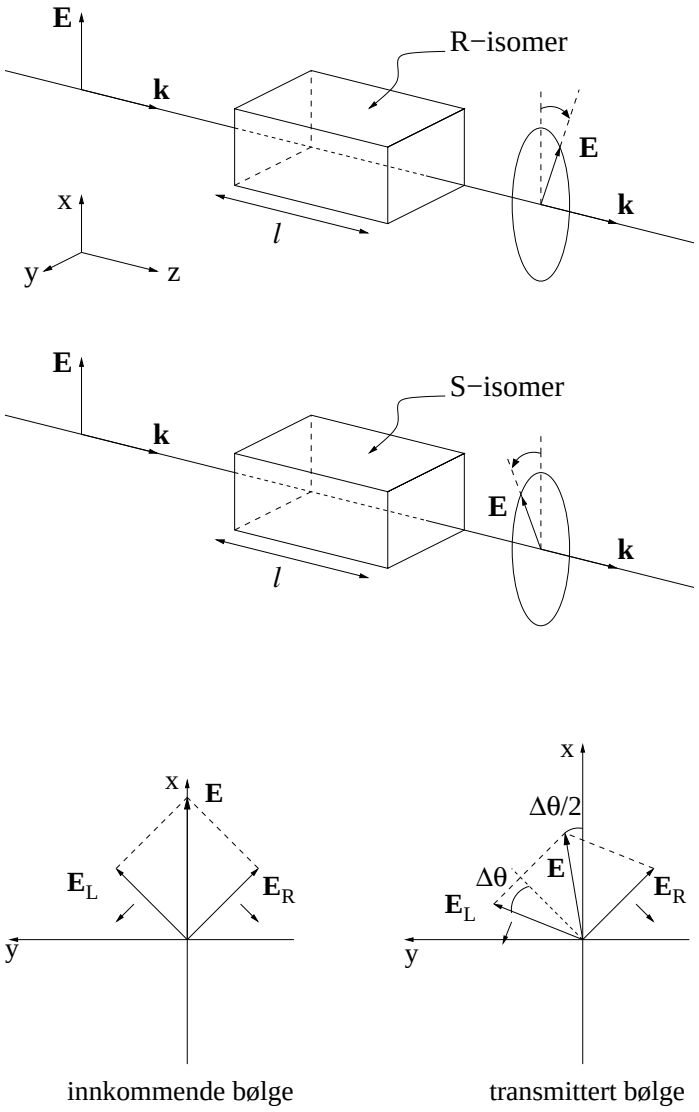
Since the refractive index is different for the two circularly polarized components, they will not have the same speed through the medium. Let us denote by l the path length through the medium. The two circularly polarized components will not spend the same time traversing the box with the medium, and the time difference is

$$\Delta t = t_R - t_L = \frac{l}{v_R} - \frac{l}{v_L} = (n_R - n_L)\,\frac{l}{c}$$

This corresponds to a phase difference $\Delta\theta$ between the two circularly polarized components, given by

$$\Delta\theta = \omega\Delta t = ck\Delta t = c\frac{2\pi}{\lambda}\Delta t = \frac{2\pi l}{\lambda}\,(n_R - n_L)$$

Hence, the transmitted wave is stil a linearly polarized wave, where the polarization is no longer along x, but rotated an angle $\Delta\theta/2$ with respect to the x axis.



Since R and L interchange roles when the R-isomer is replaced by the S-isomer, it is clear that the only difference between a medium with R-isomers and a medium with S-isomers is precisely the sign of the accumulated phase difference $\Delta\theta$. If we have a so called racemic mixture, i.e., 50% of the R- and the S-isomer, there will be no net rotation of the polarization direction. Deviations from a racemic mixture may be detected by observing a rotated polarization direction in the transmitted wave.

Exercise: Show that if $\boldsymbol{E}_L$ and $\boldsymbol{E}_R$ have obtained a mutual phase difference $\Delta\theta$ upon transmission through the medium, then the polarization of $\boldsymbol{E} = \boldsymbol{E}_L + \boldsymbol{E}_R$ has rotated an angle $\Delta\theta/2$. Hint: Use trigonometric relations for "sums of cosines and sines" from Rottmann.