CHE502 Chemical and Statistical Thermodynamics
Topic 3
Interactions, PES

URL: `http://theo.ism.u-bordeaux.fr/PBopp/vistec.2020.2021`

We have now enough knowledge and background to study the interactions
- inside molecules (eg bond stretches), **intRAmolecular interactions**
- between molecules (eg hydrogen bonds), **intERmolecular interactions**

In principle, these are the same, and they can be computed by the same methods (quantum chemistry)
The main difference is the order of magnitude of the energies involved:
Intramolecular energies are usually larger than intermolecular ones
even though there are very weak intramolecular interactions and quite strong intermolecular ones such as the hydrogen-'bond',
it is, in most cases, much 'harder' to break a 'bond' than to separate two molecules from each other (by a factor of 10 or 100 or so)

We now need to know:
How exactly (quantitatively) does the energy change when

- a molecular bond is stretched, an angle is changed, the molecules goes from cis to trans, and similar intramolecular changes
- one molecule comes close to another, one molecule is rotated with respect to another, and similar intermolecular changes

This is a huge task
We will study this here "in principle" based on quantum mechanics

Practically, there are many approximations that need to be made and many ways to find approximate solutions for the S-eq (eg ab-initio, DFT, ...)
This is well beyond the scope of this class

These studies are usually done with (more or less) black box programs.
Only few people bother to look 'inside the code', even if it is in principle possible for several popular codes
The most famous of the 'Quantum Chemistry programs' is called GAUSSIAN, created by John Pople (1925-2004) Nobel Prize for Chemistry 1998
There are many others

First set of assumptions:
A molecule consists of nuclei and electrons, so the S-eq for the molecule contains nuclear coordinates (the positions of the nuclei) and electron coordinates (3 variable per particles, neglecting spin)

– We assume that we can treat the electrons and the nuclei separately
The Born-Oppenheimer Approximation *read about it*

– We look first at the electrons, assuming thus that the nuclei do not move
We'll deal with the nuclei later

– It is not too hard to write the Hamiltonian $\hat{H}$ for a molecule with fixed positions of the nuclei
it is like the one for the hydrogen atom,
just more terms (eg electron-electron Coulomb interactions). **Do it!**

⇒ For our argument and to highlight the basic ideas and principles
we will use a diatomic molecule (H_2, O_2, HCl, ...)

- We fix the nuclei at some distance R from each other
  (other coordinates, eg the orientation in space, are not important here)

- We write $\hat{H}$ for the N electrons of the molecule
  and solve (with a computer program) the S-eq
  This is a $4N$-dimensional program since each electron has
  three spatial coordinates (eg x, y, z, and a spin coordinate
  We cannot discuss this (Slater determinant etc), the quantum chemistry programs
  take care of this

- What do we get?
  Like allays: wave functions ψ and energies E,
  each with many quantum numbers $(4N!)$
  But there will always be a lowest energy, the ground-state energy
  This is the one we are mostly interested in

Qualitatively, the microscopic picture of a molecule is:

- A number of nuclei 'swimming in a dense 'fog' of electrons
- The density of the fog is not constant, it is given by ψ^2
- The nuclei arrange themselves so that the total energy is one of the energy eigenvalues of the electronic Hamiltonian
- The nuclei are not fixed, they oscillate around 'equilibrium positions' ie geometries for which the electronic energy is minimal
- The ground state and the (electronic) excited states can thus lead to different molecular geometries

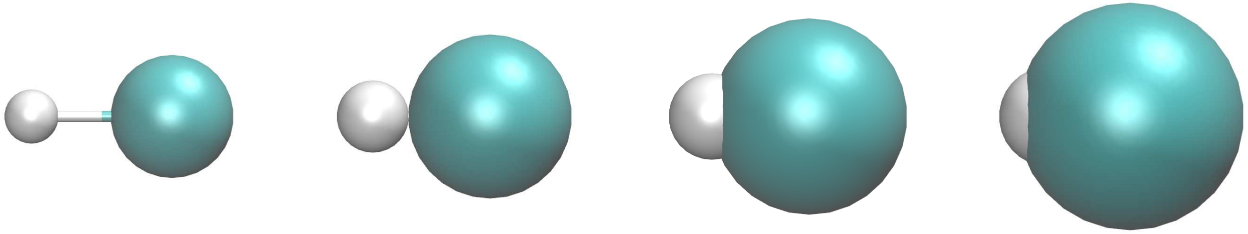
- ψ^2 is not constant, it is particularly high near the nuclei, and between nuclei, and decreases strongly at large distances

- Chemists have found it useful to decompose ψ (ψ^2) into various components, called "orbitals"
- Knowing these orbitals helps to understand the chemical behavior of a molecule

– A molecule thus does not have a 'size' or 'radius' or ....

molecular radii, or dimension, also graphic representations (eg colored spheres) are thus **approximations**

Which is the 'correct' HCl?

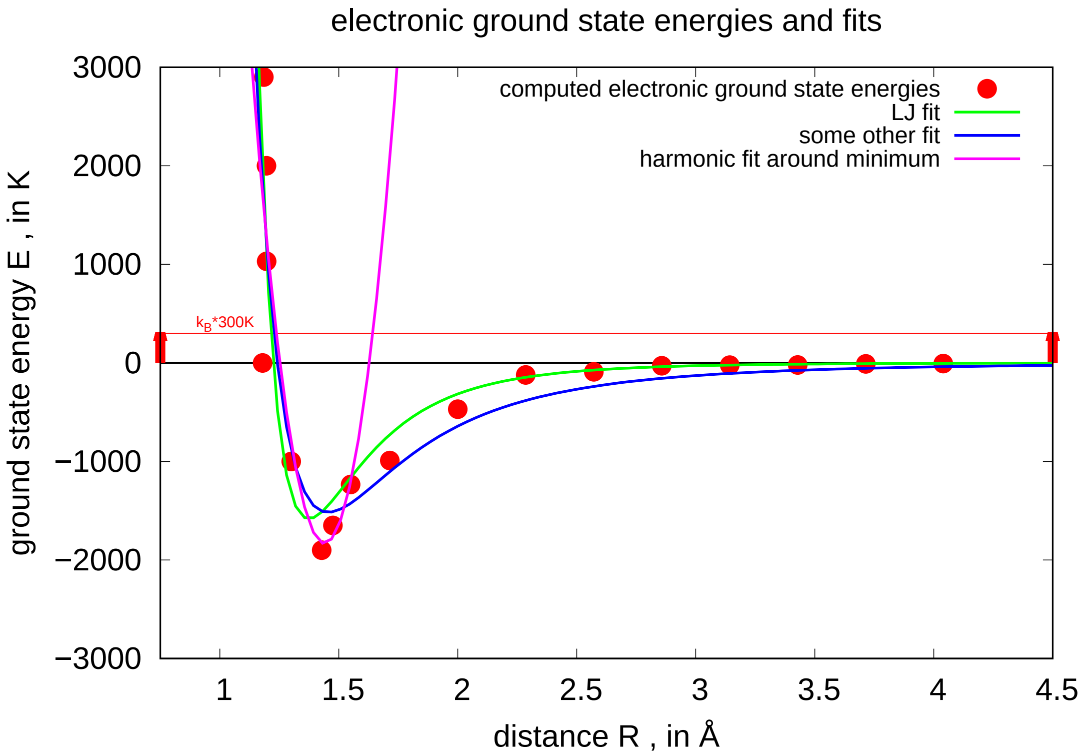


Answer: none. The one on the right is probably the closest one

So we make many calculations, one for each distance R, and plot in each case the lowest energy (a number) that we find as a function of R, see next page
(*of course we find also higher energies (excited states), but we assume they are quite far away above the ground state energy (outside our plot) and we will not consider them.*)

Now to make use of these numbers (energies) in further calculations (such as statistical mechanics) we need to find a reasonable mathematical representation.
We do this usually by fitting (*see section on fitting later in this class*) some 'reasonable' function to these energies, getting in this way
a function $V(R)$ that approximates these energies
$V(R)$ is called the **Potential Energy Surface (PES)**

For bigger molecules it is more complicated, because there are more distances (bonds), some angles, etc, The fits become more difficult (see example below), but the principle remains **exactly the same**



Red points: Ground state energies of the electrons, other lines: various more or less good fits. The little red arrows show the energy $E = k_{\mathrm{B}} \cdot 300$ K, ie the thermal energy at 'room temperature'.

So our 'bonding energy' is roughly 7 times this energy, which is not a very strong bond, as we shall see later.

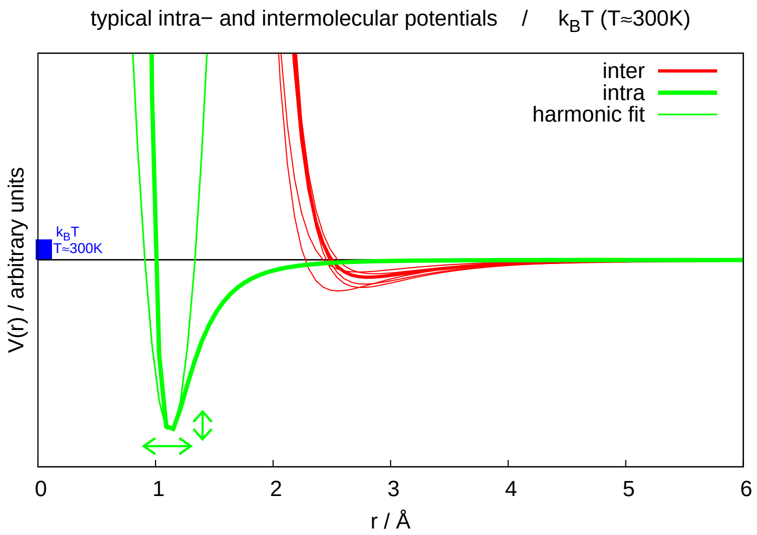
(*Roughly speaking, it has a 1 in 1000 chance to break.*
If you had a class on 'kinetics' you'll know why.)

Example of a more complex PES

We look at the intramolecular energies of water, H_2O. We have two O-H bonds of about 1 Å length each and an H-O-H angle of about 105 degrees.

Now to do our calculations
(1) we fix the Oxygen and one H, and we move the other H along the direction of the 'bond'
We will get energies like the red points in the plot and can try to make a fit
(2) If we fix this H-atom and move the other, we should of course get exactly the same result
because of the c_2v symmetry of the molecule
(3) We keep the O-H distances fixed and change the angle
(4) If now we first move one H to a slightly different position (eg by stretching its bond
a bit, or by slightly changing the angle), will we get the same result?
or if we stretch the two bonds at the same time, will we get exactly twice the result
from (1)?
Answer of course: No. The '.bonds' are not really independent of each other
But it is actually not so difficult to find fit functions that can represent this
reasonably well

Spectroscopists have known this for a long time from the IR and Raman spectra of molecules, so we will use their insights here (→ normal modes)

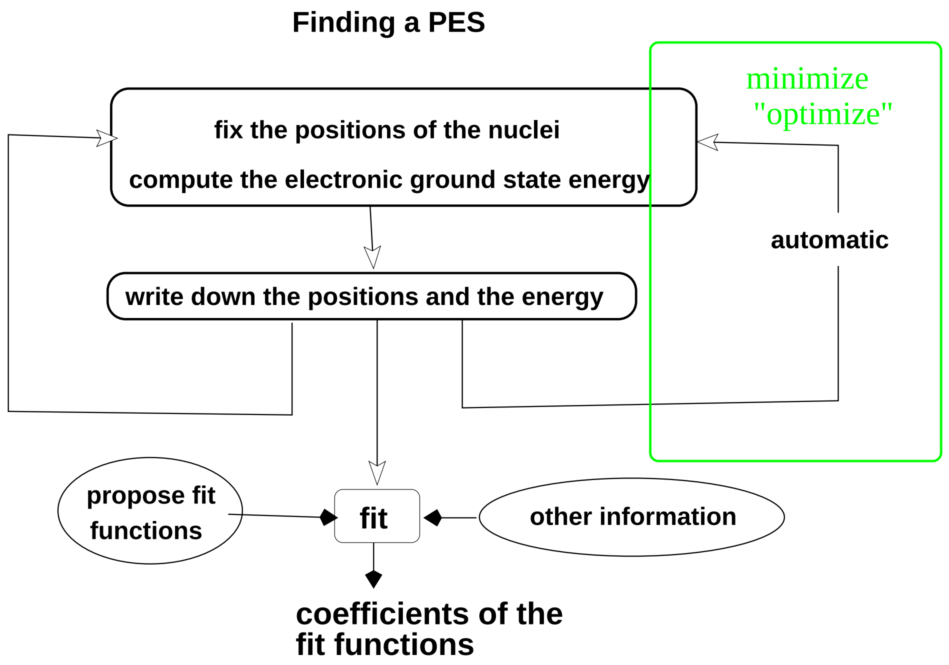


The figure compares again a typical intramolecular with a typical intermolecular PES.
The intramolecular one (green) is deeper and has its minimum at a shorter distance
The intermolecular one (red) is shallower and has its minimum at a larger distance
Compared to the previous plot, you see that it was a quite weak intramolecular bond indeed

→ The intermolecular interaction is weak ($\approx k_{\mathrm{B}}T$)
neighboring molecules will thus not stay together for a long time
→ The intramolecular is such that neighboring molecules will stay together for a long time (forever)

Different functions are thus usually used to fit **intra**- and **inter**molecular PES

Making these fits and developing expressions for the PES makes up a large part of **molecular modeling** (→ che501)
A set of such expressions, which fully describe a particular molecule (or system of molecules) is called an **interaction model** or simply **model**
The term **force field** is also used



Finding a PES

fix the positions of the nuclei

compute the electronic ground state energy

minimize
"optimize"

automatic

write down the positions and the energy

propose fit functions

fit

other information

coefficients of the fit functions

We will study some technical aspects in some more detail of 'model(l)ing' in CHE501 in spring

Final remark

In classes or books about simulations, modeling or statistical mechanics, but also in many applications, these model-PES seem to appear out of thin air, to be somehow God-given and are not questioned.
Now you know where they come from