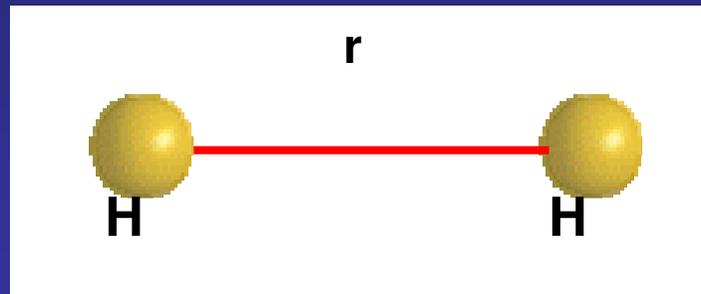


The H₂ molecule without convergence studies



Objectives:

- the (pseudo)total energy
- the bond length

Acknowledgment: exercise inspired on the first exercise of the Abinit tutorial (<http://www.abinit.org>)

H₂ molecule: example of a very simple input file

Go to the directory where the exercise of the H₂ molecule is included

Inspect the input file, h2.fdf

Examine in detail the different input variables, more information at

<http://www.icmab.es/siesta> and follow the link Documentations, Manual

```
SystemName          H2 molecule
SystemLabel         h2
NumberOfAtoms       2
NumberOfSpecies     1

%block ChemicalSpeciesLabel
  1 1 H      # Species index, atomic number, species label
%endblock ChemicalSpeciesLabel

AtomicCoordinatesFormat Ang
%block AtomicCoordinatesAndAtomicSpecies
  0.000  0.000  0.000  1
  1.000  0.000  0.000  1
%endblock AtomicCoordinatesAndAtomicSpecies
```

Number of different species and atoms present in the unit cell

List of different species

Position of the atoms

Example of a first-principles simulation: no input from experiment

Many variables will take the default value

```
SystemName          H2 molecule
SystemLabel         h2
NumberOfAtoms       2
NumberOfSpecies     1

%block ChemicalSpeciesLabel
  1 1 H      # Species index, atomic number, species label
%endblock ChemicalSpeciesLabel

AtomicCoordinatesFormat Ang
%block AtomicCoordinatesAndAtomicSpecies
  0.000 0.000 0.000 1
  1.000 0.000 0.000 1
%endblock AtomicCoordinatesAndAtomicSpecies
```

PAO.BasisSize	(Basis set quality)	DZP
MeshCutoff	(Fineness of real space integrations)	100 Ry
XC.Functional	(Exchange and correlation functional)	LDA
XC.Authors	(Flavour of the exchange and correlation)	CA
SpinPolarized	(Are we performing an spin polarized calc.)	.false.

... and many others. For a detailed list, see fdf.log after running the code.

H₂ molecule: the first run of Siesta (0.002 thousand of atoms)

Check that you have all the required files

A pseudopotential file (.vps or .psf) for every atomic specie included in the input file

For H within LDA, you can download it from the Siesta web page.

Run the code,

```
siesta < h2.fdf > h2.1.00.out
```

The name of the output file is free, but since we are running the H₂ molecule with an interatomic distance of 1 Å, this seems very sensible...

Wait for a few seconds... and then you should have an output

H₂ molecule: taking a glance to the output files

Let's make a tour on the different output files:

Inspect the output file, h2.1.00.out

How many SCF cycles were required to arrive to the convergence criterion?

How much is the total energy of the system after SCF?

How large is the unit cell automatically generated by Siesta?

How much is the electric dipole of the molecule (in electrons × bohr)?

For molecules,
$$\vec{p} = \int_{all\ space} \vec{r} \rho(\vec{r}) d\vec{r}$$

Inspect the output file where the forces are written, SystemLabel.FA

What is the value of the force on each atom, in eV/Å?

Is the system in the equilibrium configuration?

H₂ molecule: the interatomic distance

Goal: find the equilibrium structure of the molecule

Method 1:

- compute the **total energy** for different values of the interatomic distance,
- make a fit through the different points,
- determine the **minimum** of the fitting function.

Method 2:

- compute the **forces** for different values of the interatomic distance,
- make a fit through the different points,
- determine the **zero** of the fitting function.

Method 3:

- use an automatic algorithm to minimize the energy

H₂ molecule: the interatomic distance using Method 1

Run again the code, changing the interatomic distance from 0.40 Å to 3.00 Å by steps of 0.10 Å

```
SystemName          H2 molecule
SystemLabel         h2
NumberOfAtoms       2
NumberOfSpecies     1

%block ChemicalSpeciesLabel
  1 1 H      # Species index, atomic number, species label
%endblock ChemicalSpeciesLabel

AtomicCoordinatesFormat Ang
%block AtomicCoordinatesAndAtomicSpecies
  0.000 0.000 0.000 1
  1.000 0.000 0.000 1
%endblock AtomicCoordinatesAndAtomicSpecies
```

Modify the input file,
changing the
position of this atom

Run the code, saving each output in a separate file

siesta < h2.fdf > h2.your_interatomic_distance.out

H₂ molecule: the interatomic distance using Method 1

Tabulate the total energy as a function of the interatomic distance

grep "Total =" h2.*.out > h2.distance.dat

Edit the h2.distance.dat file, and leave only two columns

Interatomic distance (Å)

Total energy (eV)

0.40	-23.866760
0.50	-27.849742
0.60	-29.650017
0.70	-30.376314
0.80	-30.538122
0.90	-30.390457
1.10	-29.669133
1.20	-29.227840
1.30	-28.777047
1.40	-28.334722
1.50	-27.911124
1.60	-27.510996
1.70	-27.137072
1.80	-26.791029
1.90	-26.472157
2.10	-25.914189
2.20	-25.671302
2.30	-25.454002
2.40	-25.255192
2.50	-25.077804
2.60	-24.918596
2.70	-24.772615
2.80	-24.648741
2.90	-24.533466
3.00	-24.429635

These numbers have been obtained with
siesta-3.0-b, compiled with the g95
compiler and double precision in the grid.

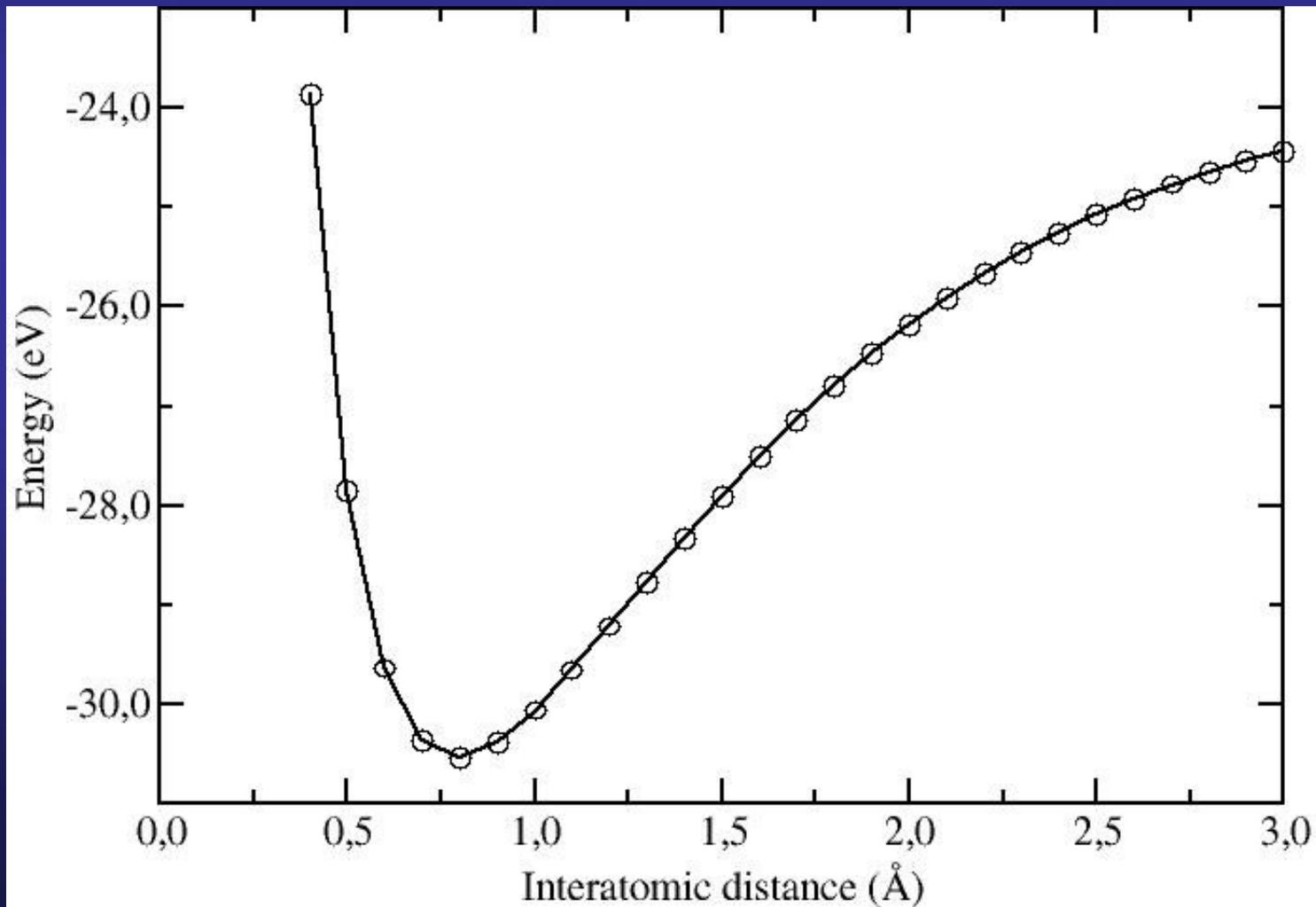
Numbers might change slightly depending
on the platform, compiler and compilation
flags

H₂ molecule: the interatomic distance using Method 1

Plot the total energy versus interatomic distance

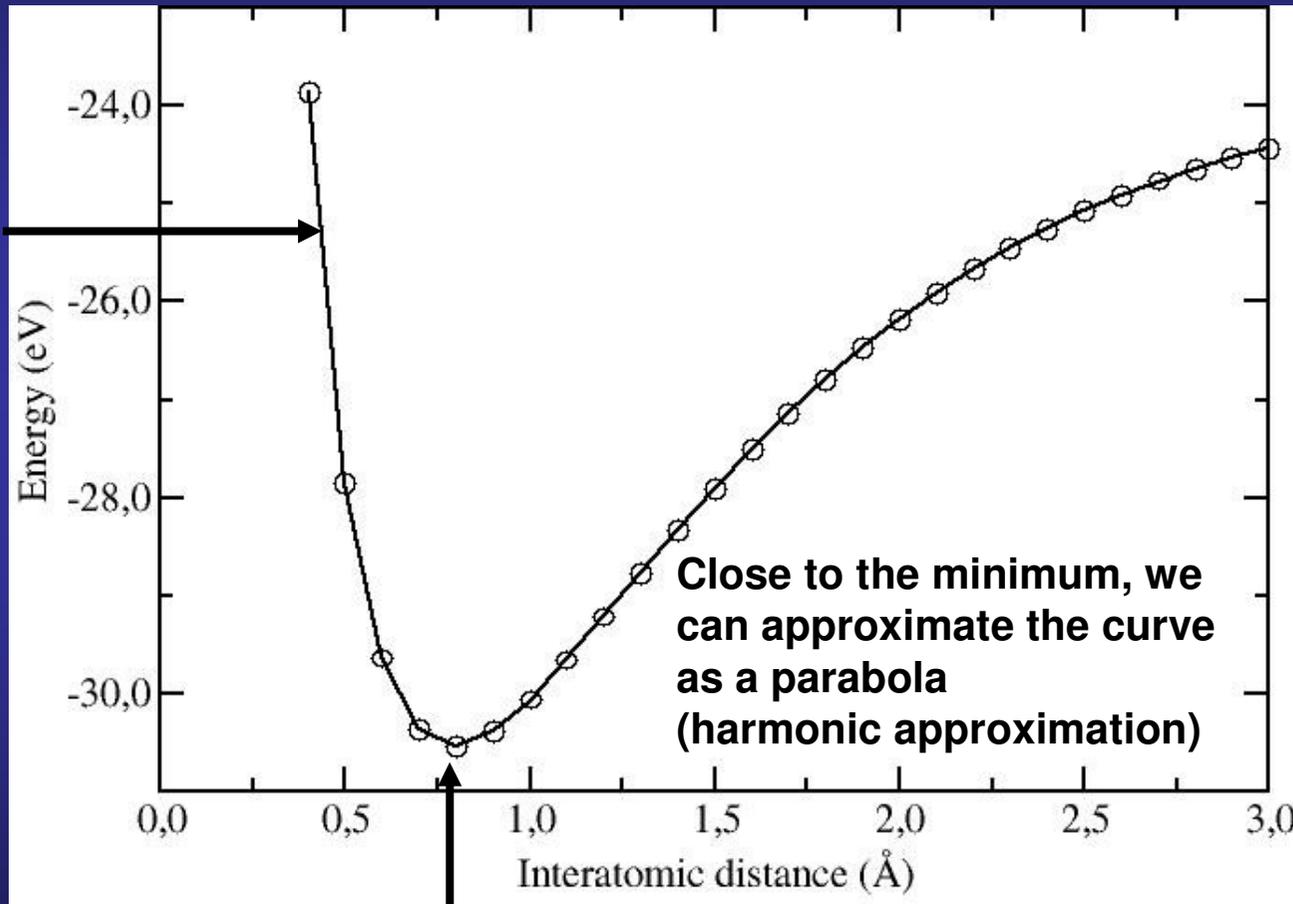
gnuplot

plot "h2.distance.dat" using 1:2 with lines



H₂ molecule: the most important point: analyze the results

When atoms or molecules get too close, they repel each other with a very large repulsion



For non-polar molecules, the interaction at very large distances is an attraction, and varies inversely as the sixth power of the distance

$$E \propto r^{-6}$$

(Thought LDA does not capture Van-der-Waals interaction)

Minimum at the equilibrium distance, around 0.8 Å (For comparison, Abinit 0.805 Å)

At this point, the forces on the atoms vanish ($\vec{F} = -\frac{\partial E}{\partial \vec{R}}$)