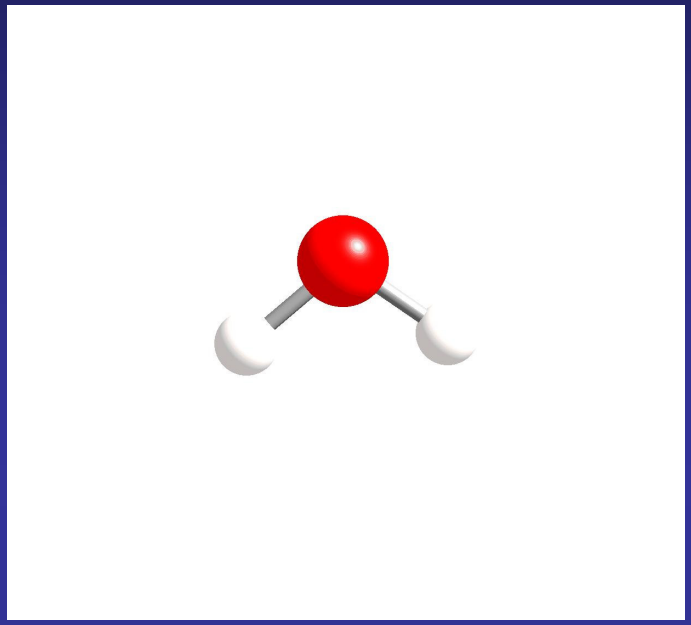
The H_2O molecule: converging the size of the simulation box



Objectives

- study the convergence of the properties with the size of the unit cell

H_2O molecule: example of a very simple input file

Go to the directory where the exercise of the H_2O molecule is included

Inspect the input file, h2o.fdf

Examine in detail the different input variables, more information at

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

```
SystemName          Water molecule
SystemLabel         h2o
NumberOfAtoms       3
NumberOfSpecies     2

%block ChemicalSpeciesLabel
 1  8  O      # Species index, atomic number, species label
 2  1  H
%endblock ChemicalSpeciesLabel

AtomicCoordinatesFormat  Ang
%block AtomicCoordinatesAndAtomicSpecies
 0.000   0.000   0.000  1
 0.757   0.586   0.000  2
-0.757   0.586   0.000  2
%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

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```

PAO.BasisSize	(Basis set quality)	DZP
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.

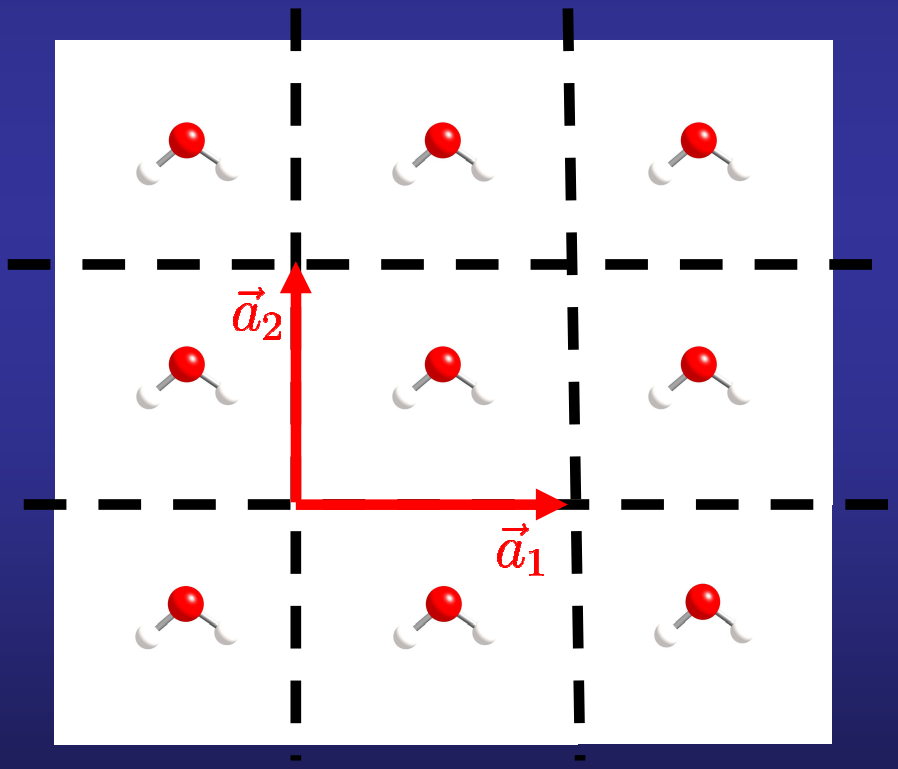
… and many others. For a detailed list, see fdf.log after running the code.

H_2O molecule with Periodic Boundary Conditions (PBC)

Although our system is aperiodic (a molecule), Siesta still does use PBC

Strategy: the supercell approach

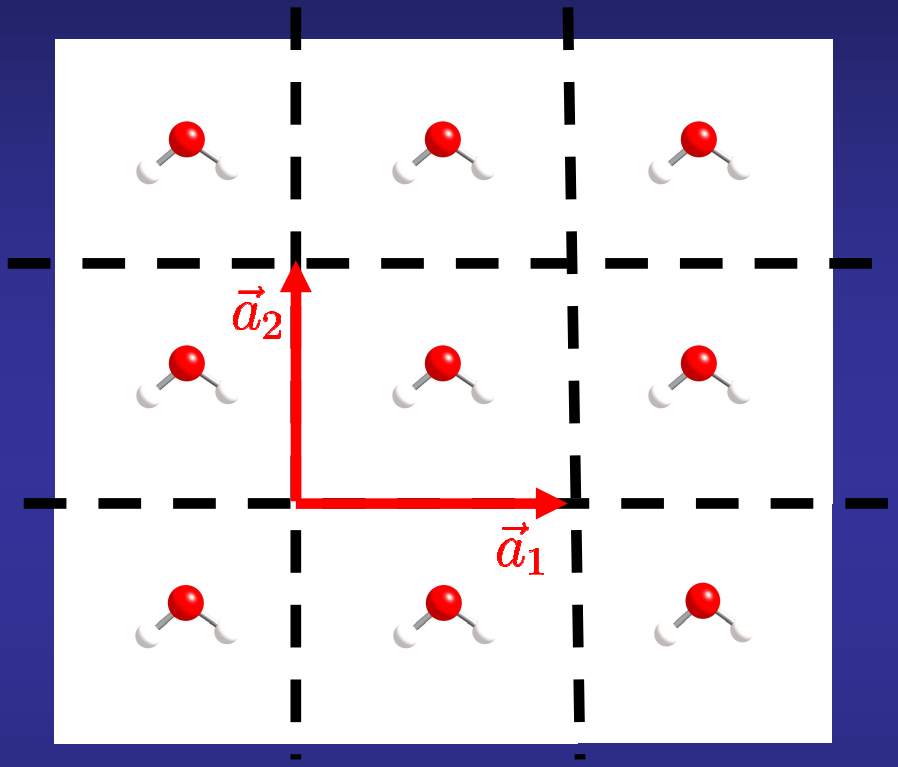
Introduce a vacuum region that should be large enough that periodic images corresponding to adjacent replicas of the supercell do not interact significantly.



Make sure that the required physical and chemical properties are converged with the size of the supercell

H_2O molecule with Periodic Boundary Conditions (PBC)

The default unit cell



The lattice vectors will be diagonal, and their size will be the minimum size to include the system without overlap with neighboring cells, plus a buffer layer (10%)

H_2O molecule: the first run of Siesta (we are doing better, 0.003 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 and O within LDA, you can download it from the Siesta web page.

Run the code,

siesta < h2o.fdf > h2o.default.out

The name of the output file is free, but
since we are running the H_2O molecule
with the default unit cell,
this seems very sensible…

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

H_2O molecule with Periodic Boundary Conditions (PBC)

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

Inspect the output file, h2o.default.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?

```
outcell: Unit cell vectors (Ang):
        7.286412    0.000000    0.000000
        0.000000    5.746952    0.000000
        0.000000    0.000000    5.621012

outcell: Cell vector modules (Ang)   :    7.286412    5.746952    5.621012
outcell: Cell angles (23,13,12) (deg):     90.0000     90.0000     90.0000
outcell: Cell volume (Ang**3)        :    235.3780
```

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

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

```
siesta: Electric dipole (a.u.)  =    0.000000    0.557123    0.000000
siesta: Electric dipole (Debye) =    0.000000    1.416067    0.000000
```

H_2O molecule: convergence with the size of the supercell

Modify the input file, introducing explicitly the supercell

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LatticeConstant   8.0 Ang
%block LatticeVectors
  1.0  0.0  0.0
  0.0  1.0  0.0
  0.0  0.0  1.0
%endblock LatticeVectors
```

Define the supercell here

Run the code, changing the lattice constant from 8.00 Å to 15.00 Å in steps of 1.0 Å. Save each input file in a separate file.

siesta < h2o.fdf > h2o.your_lattice_constant.out

H_2O molecule: convergence with the size of the supercell

Tabulate the total energy as a function of the lattice constant

grep “Total =” h2o.*.out > h2o.latcon.dat

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

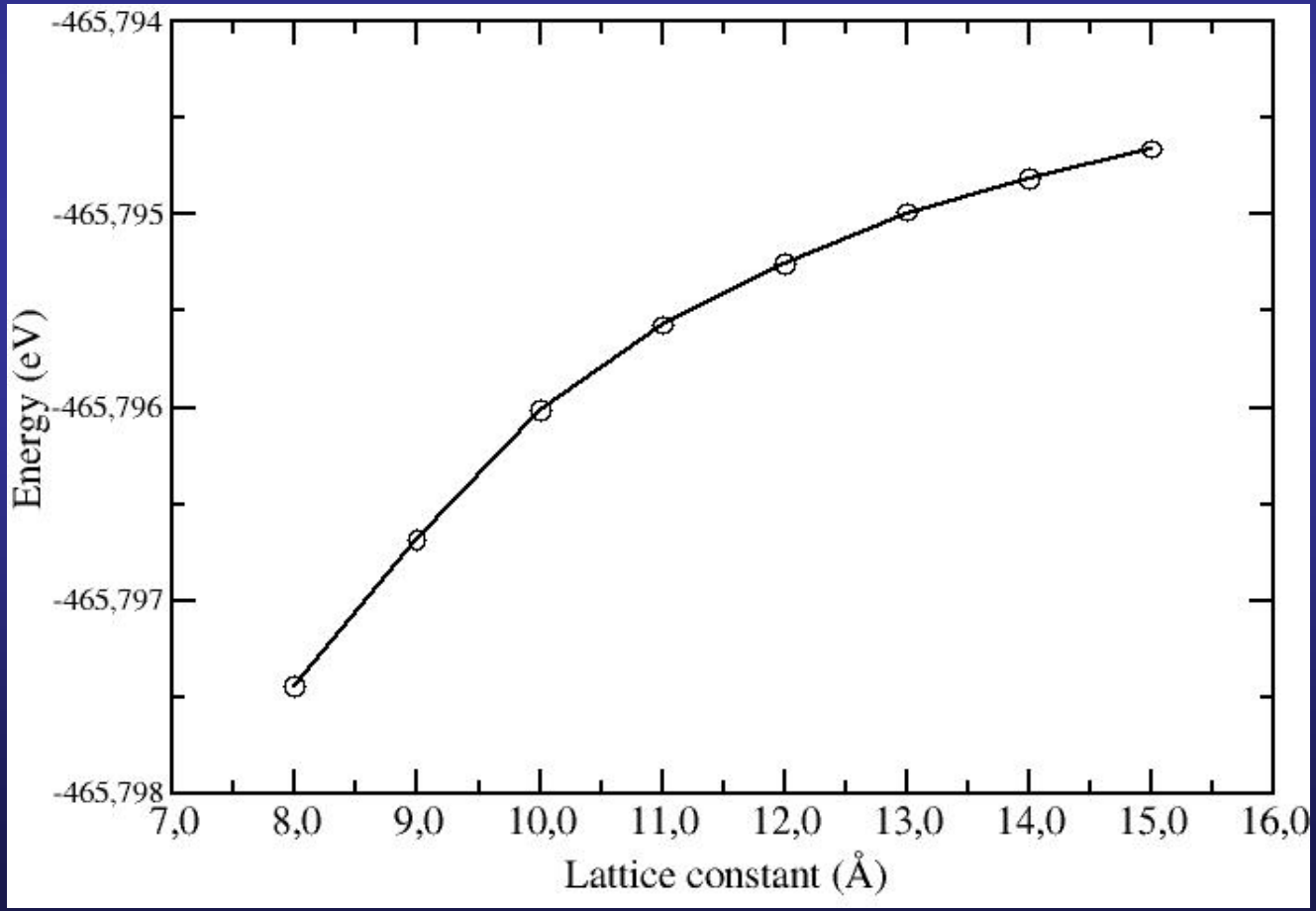
Lattice constant (Å)	Total energy (eV)
8	-465.797449
9	-465.796688
10	-465.796018
11	-465.795577
12	-465.795259
13	-465.794992
14	-465.794812
15	-465.794665

H_2O molecule: convergence with the size of the supercell

Plot the total energy versus the lattice constant

gnuplot

plot “h2o.latcon.dat” using 1:2 with lines

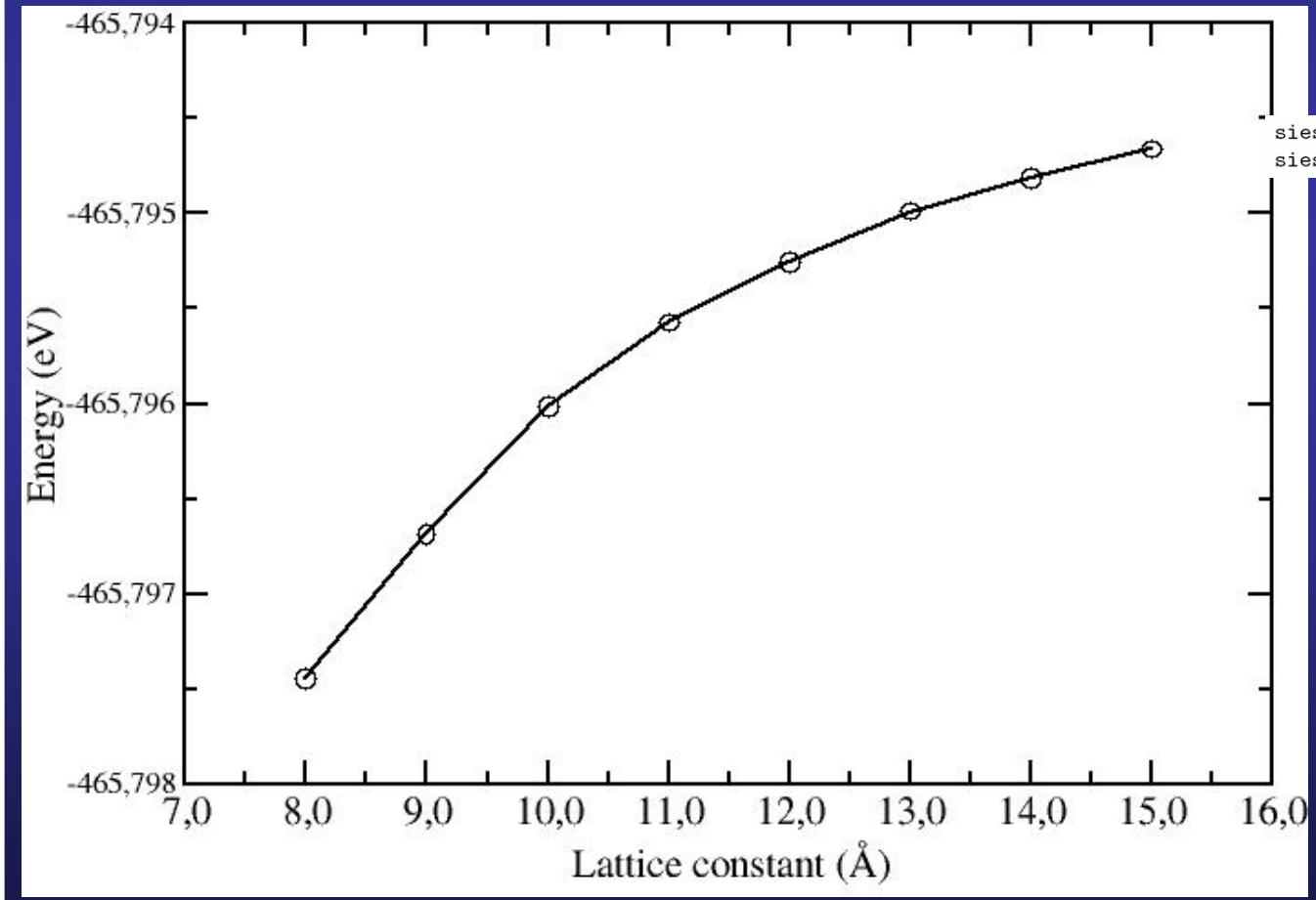


H_2O molecule: the most important point:

Analyze the results

Ideally, for a molecule any property should be independent of the size of the simulation box…

…but this is not the case (at least for the energy) in the case of H_2O. Why?



Water molecule has a dipole

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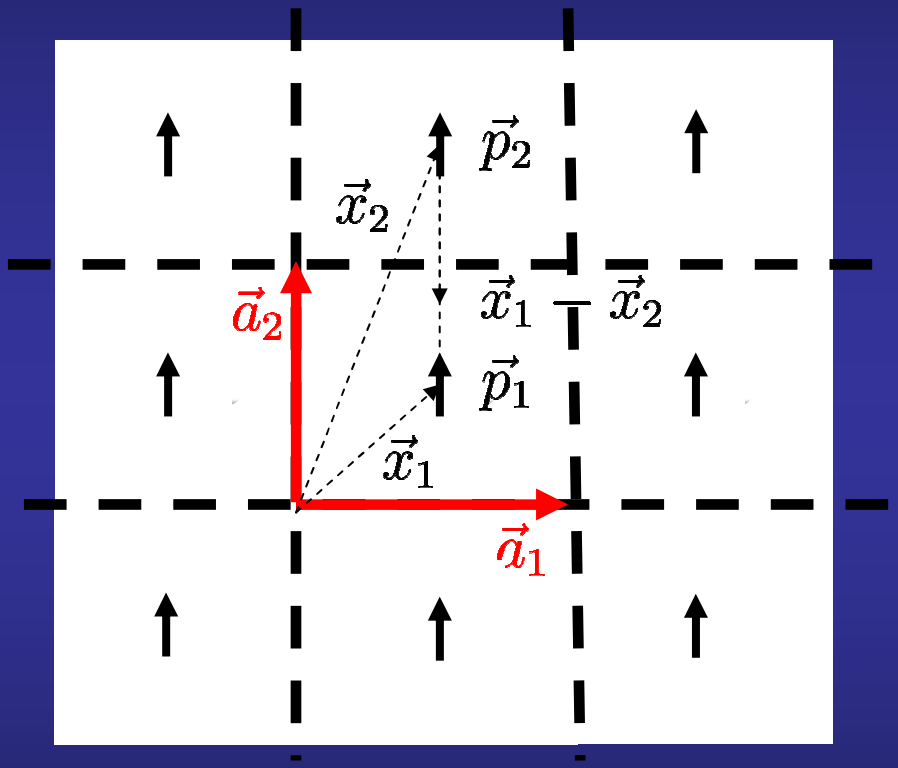

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The electrostatic interaction between dipoles decay as R^{-3}, with R the separation between dipoles

$$W_{12} = \frac{\vec{p}_1 \cdot \vec{p}_2 - 3(\hat{n} \cdot \vec{p}_1)(\hat{n} \cdot \vec{p}_2)}{R^3}$$

$\vec{p}_1$ puntual dipole located at $\vec{x}_1$

$\vec{p}_2$ puntual dipole located at $\vec{x}_2$

$\hat{n}$ unit vector along $(\vec{x}_1 - \vec{x}_2)$

$R = |\vec{x}_1 - \vec{x}_2|$

In order to minimize spurious effect, the supercell has to be chosen large enough that these interactions do not have a significant influence on the properties under scrutiny

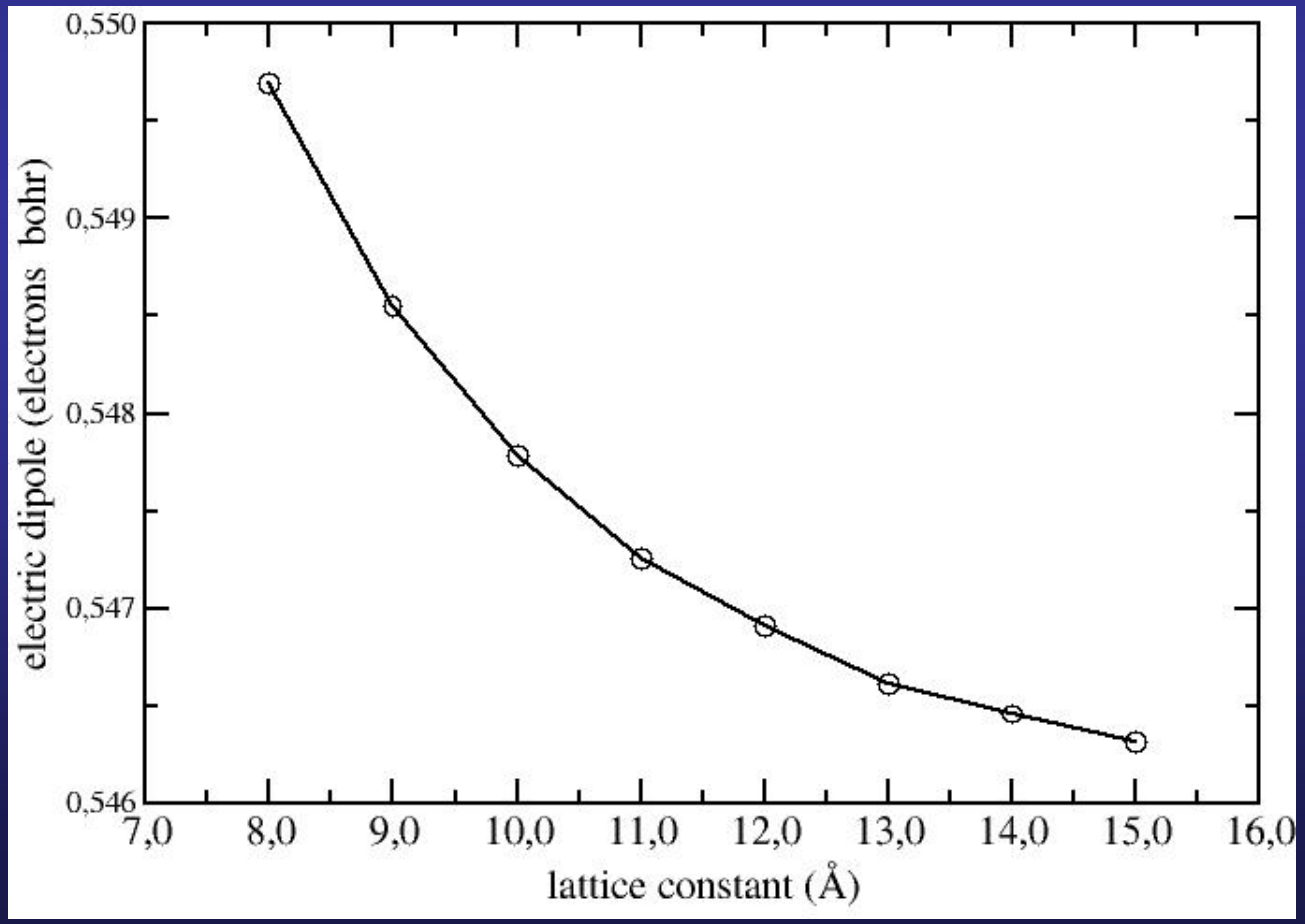
H_2O molecule: convergence of the dipole moment

grep “Electric dipole (a.u.)” h2o.*.out > h2o.dipole.dat

Edit h2o.dipole.dat and leave only the lattice constant and the components of the dipole moment

gnuplot

plot “h2o.dipole.dat” using 1:3 with lines



What is the accuracy required in your problem?

The answer to this question determines when a simulation can be considered “converged”