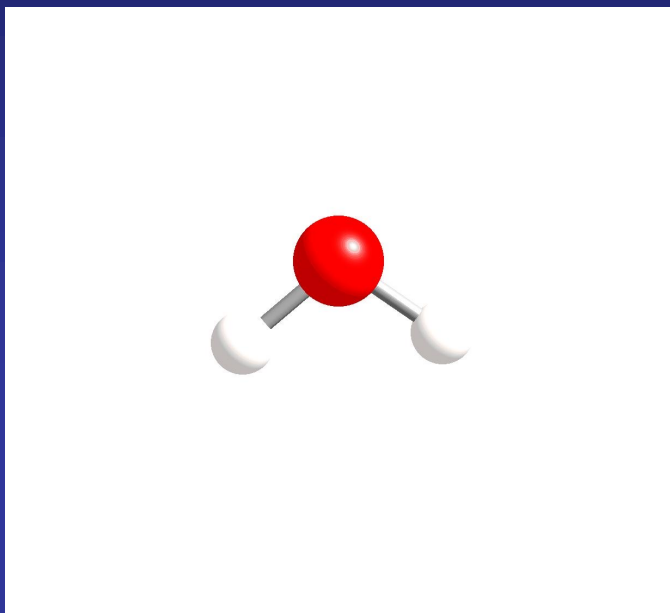


# The H<sub>2</sub>O molecule: converging the size of the simulation box



## Objectives

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

# H<sub>2</sub>O molecule: example of a very simple input file

Go to the directory where the exercise of the H<sub>2</sub>O 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 0      # 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

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

%block ChemicalSpeciesLabel
  1  8  0      # 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
```

|                      |  |                |
|----------------------|--|----------------|
| <b>PAO.BasisSize</b> | <b>(Basis set quality)</b>                         | <b>DZP</b>     |
| <b>XC.Functional</b> | <b>(Exchange and correlation functional)</b>       | <b>LDA</b>     |
| <b>XC.Authors</b>    | <b>(Flavour of the exchange and correlation)</b>   | <b>CA</b>      |
| <b>SpinPolarized</b> | <b>(Are we performing an spin polarized calc.)</b> | <b>.false.</b> |

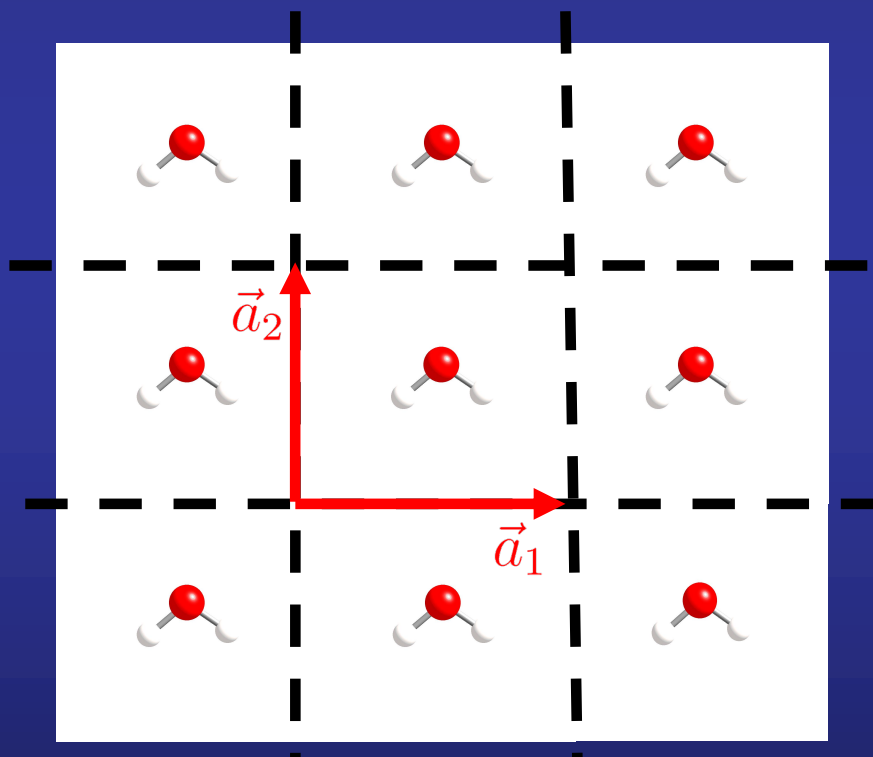
... and many others. For a detailed list, see fdf.log after running the code.

# H<sub>2</sub>O molecule with Periodic Boundary Conditions (PBC)

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

Strategy: **the supercell approach**

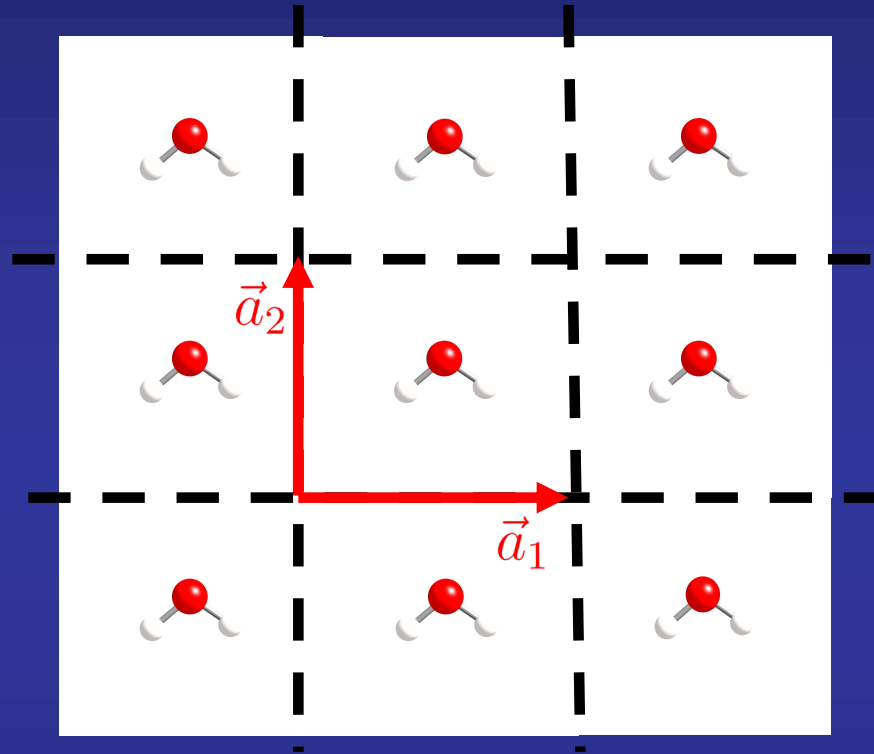
Introduce a vacuum region that should be large enough that periodic images corresponding to adjacent replicas of the supercell do not interact significantly.



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

# H<sub>2</sub>O 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<sub>2</sub>O 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<sub>2</sub>O molecule  
with the default unit cell,  
this seems very sensible...

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

# H<sub>2</sub>O 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):  
      7.818555    0.000000    0.000000  
      0.000000    6.218903    0.000000  
      0.000000    0.000000    6.153155  
  
outcell: Cell vector modules (Ang)   :    7.818555    6.218903    6.153155  
outcell: Cell angles (23,13,12) (deg):    90.0000    90.0000    90.0000  
outcell: Cell volume (Ang**3)       :    299.1839
```

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    0.585494   -0.000000  
siesta: Electric dipole (Debye) =   -0.000000    1.488176   -0.000000
```

# H<sub>2</sub>O molecule: convergence with the size of the supercell

Modify the input file, introducing explicitly the supercell

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

%block ChemicalSpeciesLabel
  1 8 0      # 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

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<sub>2</sub>O 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)

|       |             |
|-------|-------------|
| 8.00  | -466.099656 |
| 9.00  | -466.098788 |
| 10.00 | -466.098091 |
| 11.00 | -466.097596 |
| 12.00 | -466.097199 |
| 13.00 | -466.096878 |
| 14.00 | -466.096700 |
| 15.00 | -466.096541 |

These numbers have been obtained with siesta-5.1

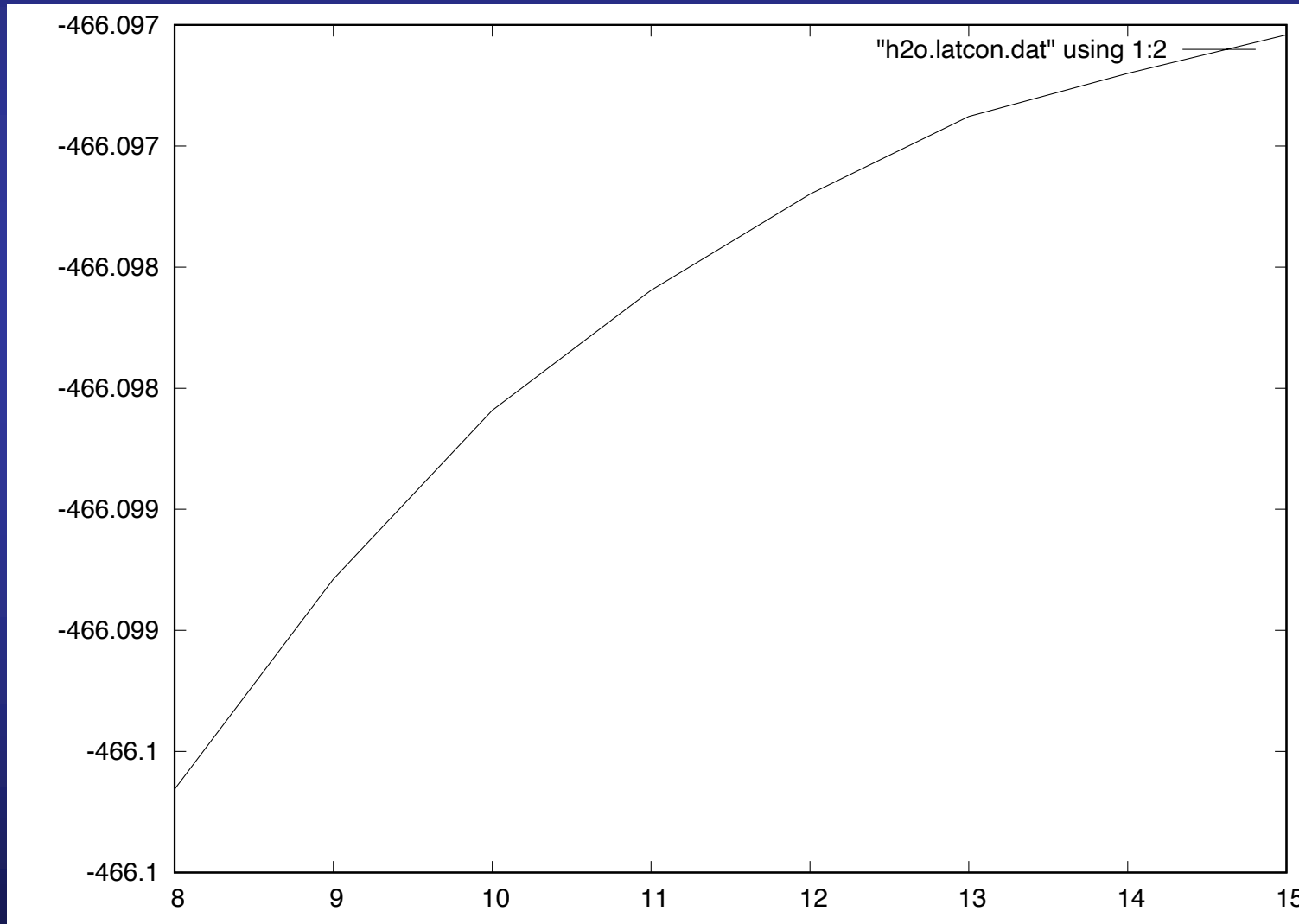
Numbers might change slightly depending on the platform, compiler and compilation flags

# H<sub>2</sub>O 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

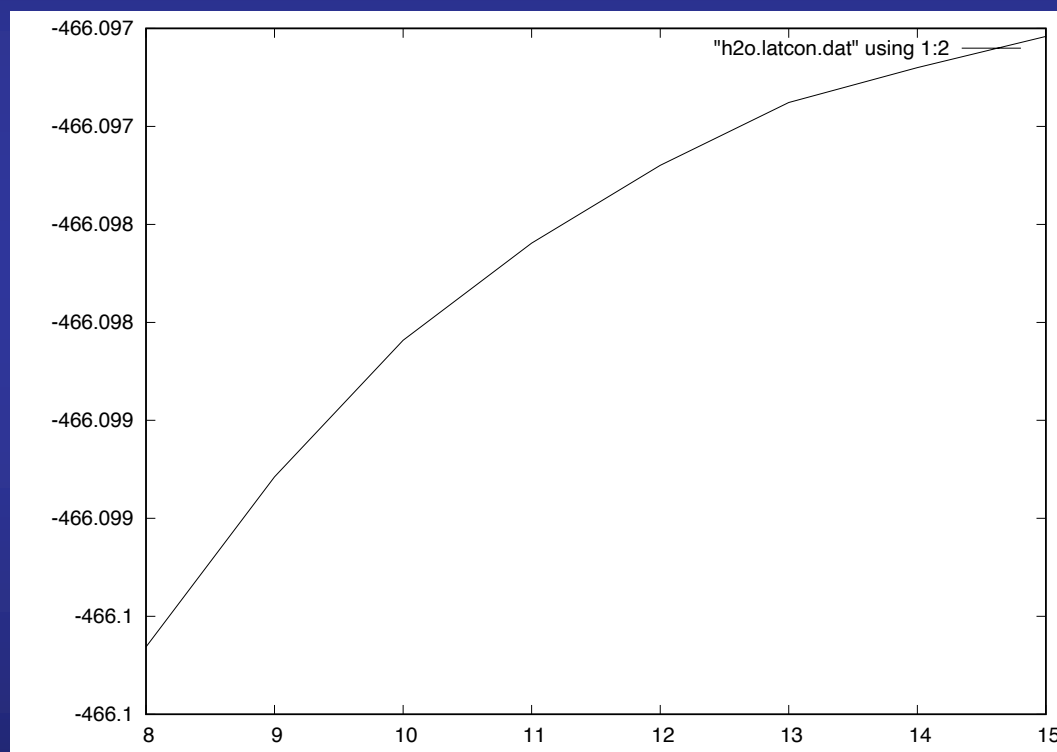


# H<sub>2</sub>O molecule: the most important point:

## 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<sub>2</sub>O. Why?



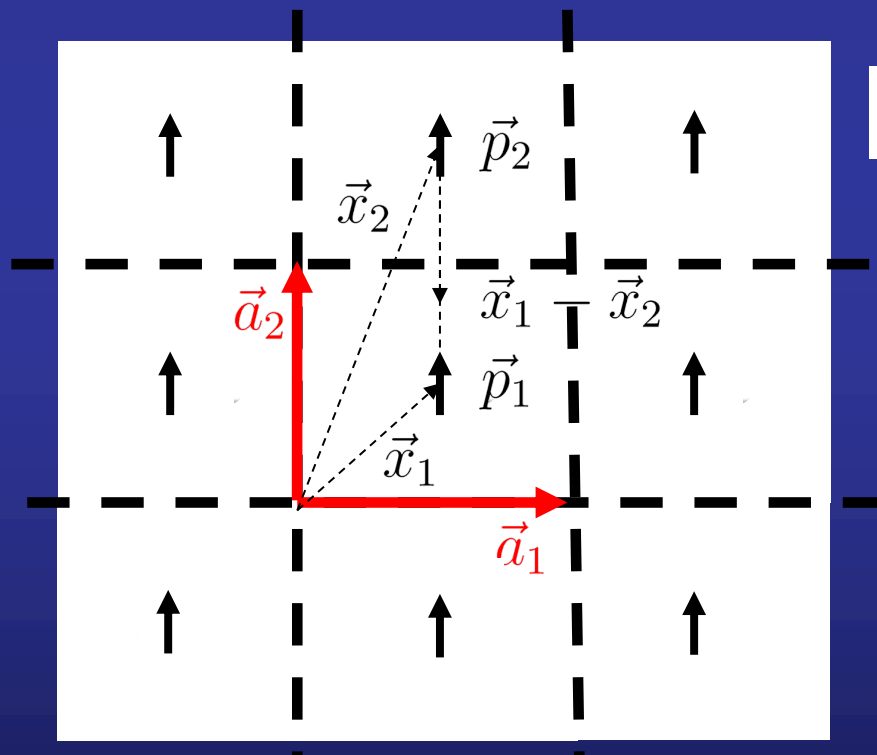
**Water molecule has a dipole**

|                                 |   |           |          |           |
|---------------------------------|---|-----------|----------|-----------|
| siesta: Electric dipole (a.u.)  | = | -0.000000 | 0.585494 | -0.000000 |
| siesta: Electric dipole (Debye) | = | -0.000000 | 1.488176 | -0.000000 |

# H<sub>2</sub>O molecule: the most important point, analyze the results

When calculating the energy of an aperiodic system using periodic boundary conditions, one is interested only in the energy,  $E_0$  in the limit  $L \rightarrow \infty$ , where  $L$  is the linear dimension of the supercell. The energy calculated for a finite supercell  $E(L)$  differs from  $E_0$ , because of the spurious interactions of the aperiodic charge density with its images in neighboring cells

To estimate  $E_0$  from the calculated  $E(L)$ , we need to know the asymptotic behaviour of the energy on  $L$



G. Makov and M. C. Payne,  
Phys. Rev. B 51, 4014 (1995)

Water molecule has a dipole

|                                 |   |           |          |           |
|---------------------------------|---|-----------|----------|-----------|
| siesta: Electric dipole (a.u.)  | = | -0.000000 | 0.585494 | -0.000000 |
| siesta: Electric dipole (Debye) | = | -0.000000 | 1.488176 | -0.000000 |

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

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

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

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

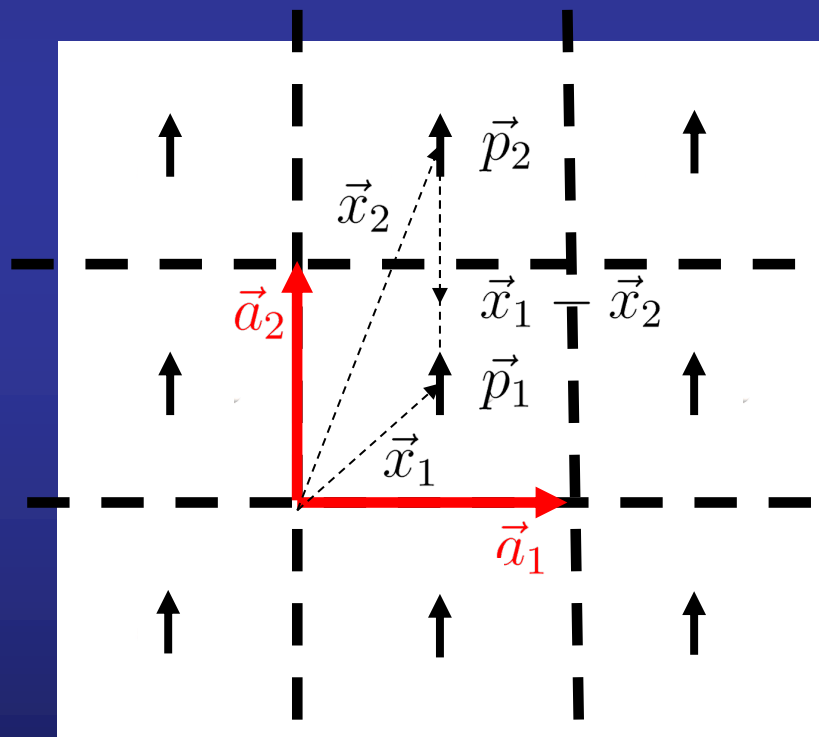
$\hat{n}$  unit vector along  $(\vec{x}_1 - \vec{x}_2)$

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

# H<sub>2</sub>O molecule: the most important point, analyze the results

To estimate  $E_0$  from the calculated  $E(L)$ , we need to know the asymptotic behaviour of the energy on  $L$

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



But this dependence is not enough.  
Furthermore, these interactions induce changes in the aperiodic charge density itself, which depends on  $L$

In other words, the dipole also depends on  $L$

If the molecule has a permanent dipole, then the induced dipole will be  $O(L^{-3})$  because the field generated by a dipole decays as  $L^{-3}$

# H<sub>2</sub>O molecule: convergence of the dipole moment

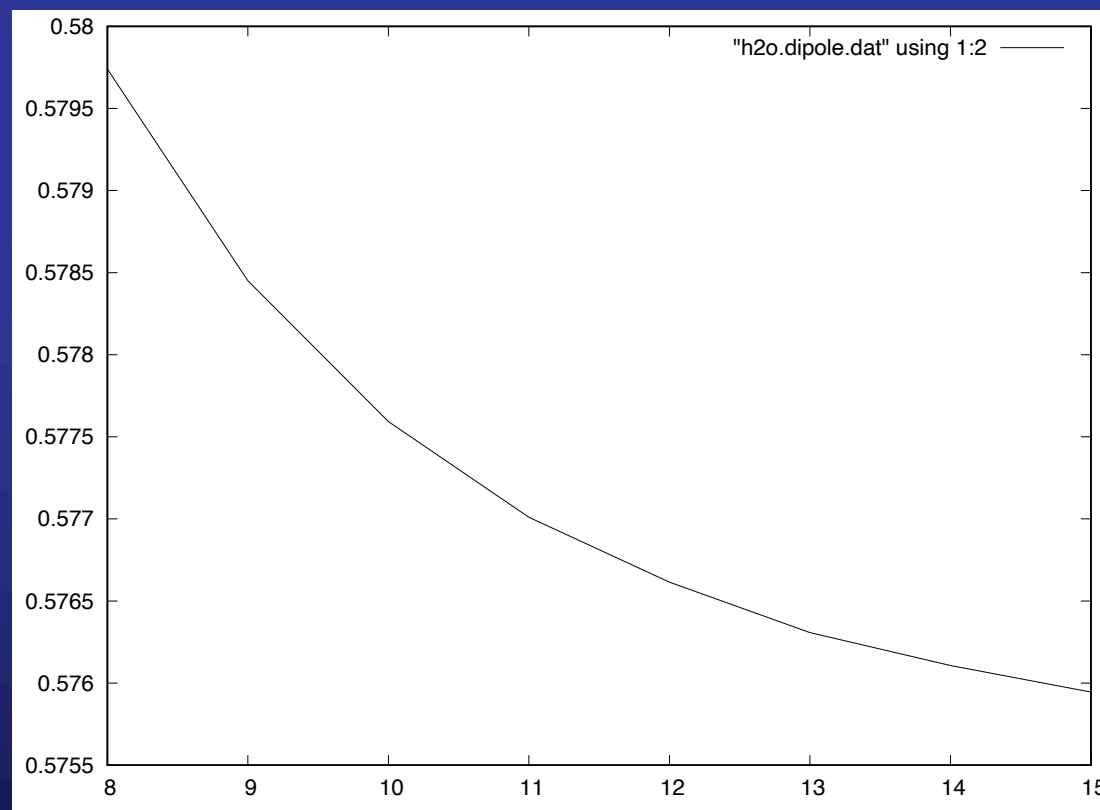
```
grep "Electric dipole (a.u.)" h2o*.out > h2o.dipole.dat
```

Edit h2o.dipole.dat and leave only the lattice constant and the components of the dipole moment (with the particular orientation of our molecule, only the *y* component does not vanish).

**gnuplot**

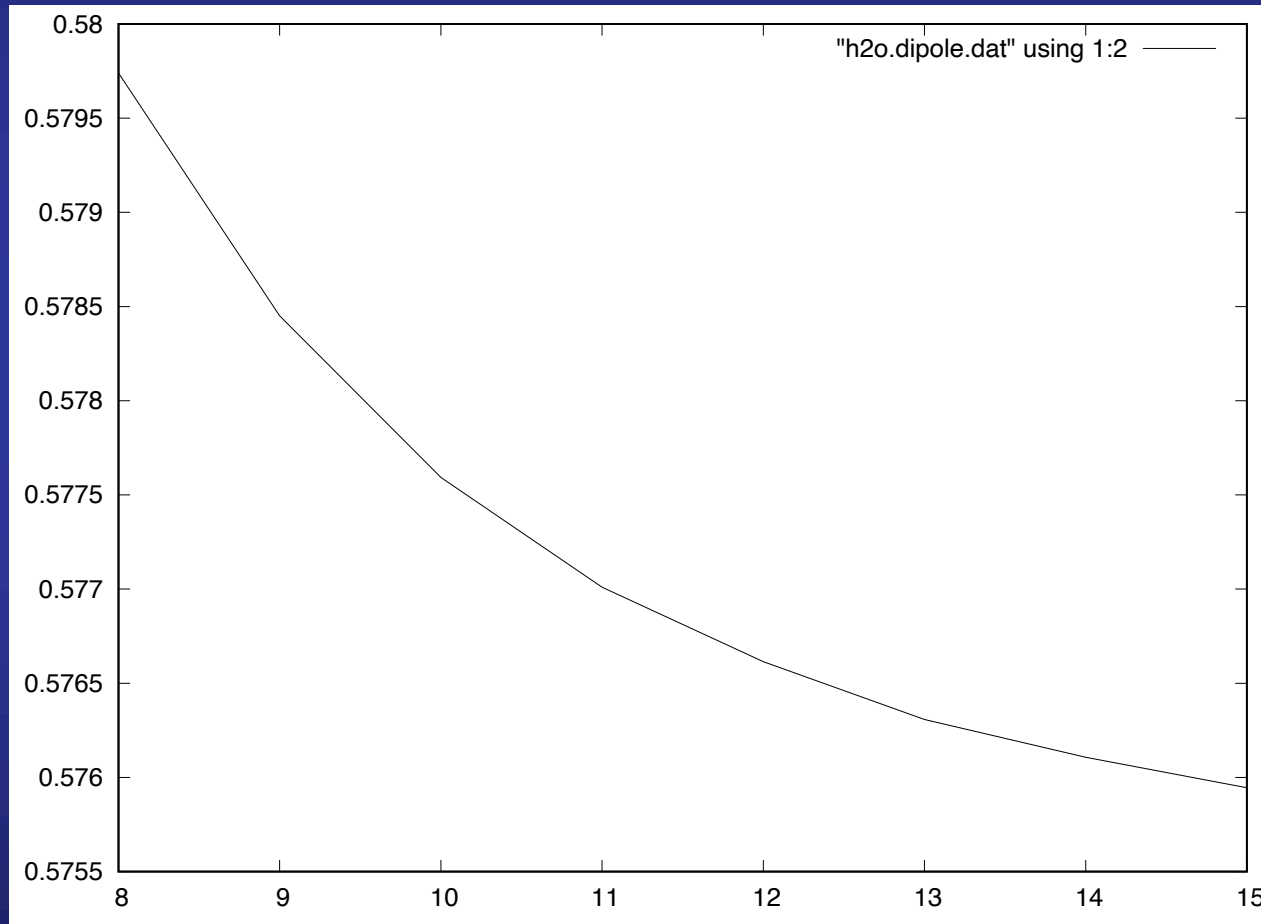
```
plot "h2o.dipole.dat" using 1:2 with lines
```

| Lattice constant (Å) | Electric dipole (a.u.) |
|----------------------|------------------------|
| 8.00                 | 0.579740               |
| 9.00                 | 0.578451               |
| 10.00                | 0.577593               |
| 11.00                | 0.577010               |
| 12.00                | 0.576615               |
| 13.00                | 0.576308               |
| 14.00                | 0.576107               |
| 15.00                | 0.575945               |



# H<sub>2</sub>O molecule: convergence of the dipole moment

If the molecule has a permanent dipole, then the induced dipole will be  $O(L^{-3})$  because the field generated by a dipole decays as  $L^{-3}$



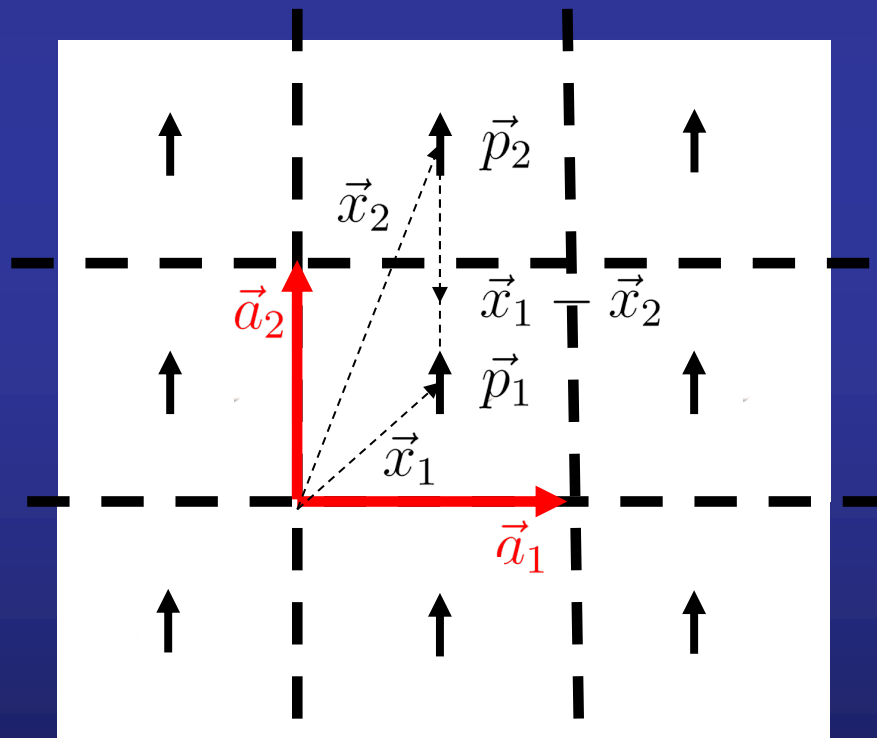
$$\vec{p}(L) = \vec{p}_0 + \frac{\vec{c}}{L^3}$$

$\vec{p}_0$  , and  $\vec{c}$  fitting parameters

# H<sub>2</sub>O molecule: the most important point, analyze the results

To estimate  $E_0$  from the calculated  $E(L)$ , we need to know the asymptotic behaviour of the energy on  $L$

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



If we replace  $p$  by  $p(L)$ , then the leading contribution to the electrostatic energy reflecting the (dipole-induced)-dipole interaction is of the order of  $O(L^{-6})$

$$E(L) = E_0 + \frac{a}{L^3} + \frac{b}{L^6}$$

Direct dipole-dipole interaction

(Dipole-induced) - dipole interaction

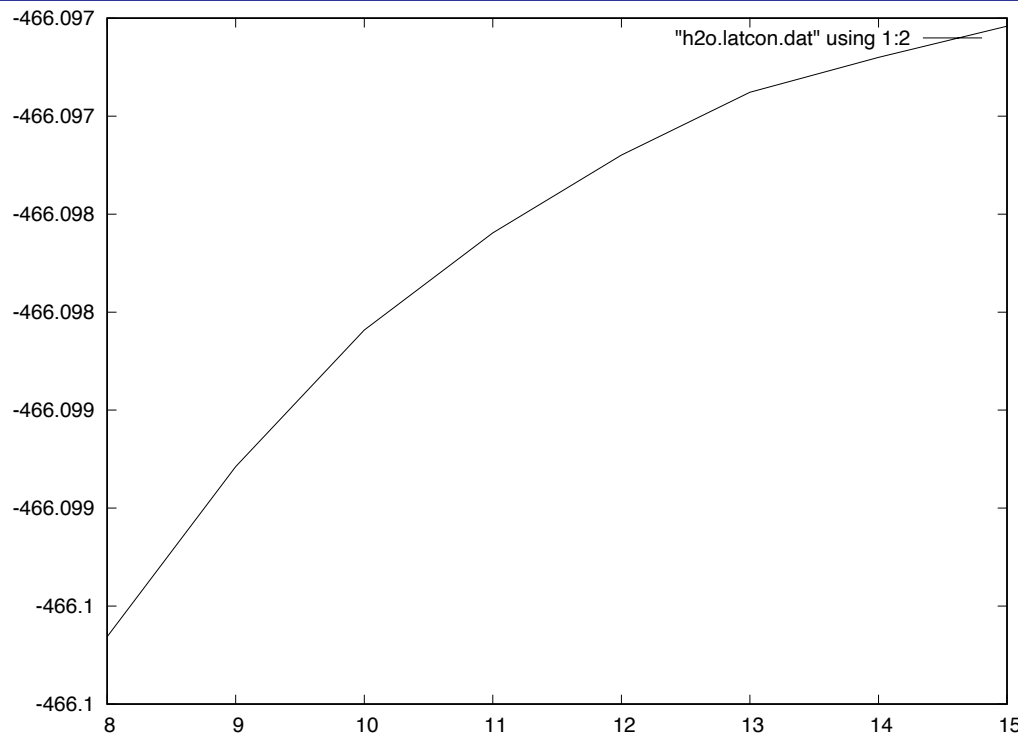
$E_0$  ,  $a$  , and  $b$  fitting parameters



# H<sub>2</sub>O molecule: the most important point, analyze the results

To estimate  $E_0$  from the calculated  $E(L)$ , we need to know the asymptotic behaviour of the energy on  $L$

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



If we replace  $p$  by  $p(L)$ , then the leading contribution to the electrostatic energy reflecting the (dipole-induced)-dipole interaction is of the order of  $O(L^{-6})$

$$E(L) = E_0 + \frac{a}{L^3} + \frac{b}{L^6}$$

Direct dipole-dipole interaction

(Dipole-induced) - dipole interaction

$E_0$ ,  $a$ , and  $b$  fitting parameters

$E_0$  is the energy we are interested in

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