SIESTA School 2025

# Basis sets in SIESTA

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# Hands-on session:
# Basis sets optimization

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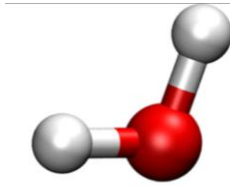
EXCELENCIA SEVERO OCHOA

# Recap from yesterday



```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/01-Eshift_SplitNorm

ls   ->    H.psml  O.psml  water.fdf
```

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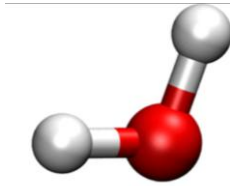
EXCELENCIA SEVERO OCHOA

# Recap from yesterday



```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/01-Eshift_SplitNorm

ls   ->    H.psml  O.psml  water.fdf

vi water.fdf
```

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EXCELENCIA SEVERO OCHOA

# Recap from yesterday

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/01-Eshift_SplitNorm

ls   ->    H.psml  O.psml  water.fdf

vi water.fdf
```

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

%block ChemicalSpeciesLabel
 1  8  O
 2  1  H
%endblock ChemicalSpeciesLabel

PAO.BasisSize       DZP
PAO.EnergyShift     0.01 Ry
PAO.SplitNorm       0.15

BasisPressure  0.02 GPa

XC.Functional       GGA
XC.Authors          PBE
MeshCutoff          300 Ry
SCF.Mixer.Weight    0.5
SCF.Mixer.History   10

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 15.0 Ang
%block LatticeVectors
 1.0 0.0 0.0
 0.0 1.0 0.0
 0.0 0.0 1.0
%endblock LatticeVectors
```

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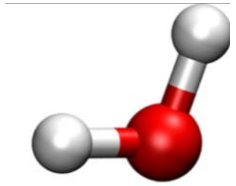
# Exercise 1.1



```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/01-Eshift_Split

ls   ->    H.psml  O.psml  water.fdf

vi water.fdf

mkdir ex1 && cp H.psml O.psml water.f

siesta < water.fdf > water.out

vi water.out
```

```
atom: ________________________________________________________________________

prinput: Basis input

PAO.BasisType split

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

%block PAO.Basis                 # Define Basis set
# WARNING: This information might be incomplete!
O                     2                    # Species label, number of l-shells
 n=2   0   2                         # n, l, Nzeta
   3.532      2.297
   1.000      1.000
 n=2   1   2 P   1                   # n, l, Nzeta, Polarization, NzetaPol
   4.257      2.746
   1.000      1.000
H                     1                    # Species label, number of l-shells
 n=1   0   2 P   1                   # n, l, Nzeta, Polarization, NzetaPol
   5.201      3.508
   1.000      1.000
%endblock PAO.Basis
```

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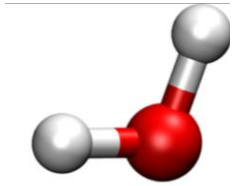
# Exercise 1.1



```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/01-Eshift_SplitNorm

ls   ->    H.psml  O.psml  water.fdf

vi water.fdf

mkdir ex1 && cp H.psml O.psml water.fdf ex1/ && cd ex1/

siesta < water.fdf > water.out

vi water.out

grep “E + p_basis” water.out  ->  (Free)E + p_basis*V_orbitals      =       -482.064557 eV
```

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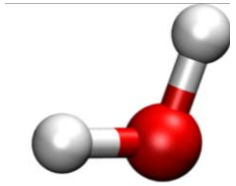
EXCELENCIA SEVERO OCHOA

# Exercise 1.1



```
siesta < water.fdf > water.out

vi water.out

grep “E + p_basis” water.out   ->   (Free)E + p_basis*V_orbitals      =       -482.064557 eV
```

Cat h2o.BASIS_ENTHALPY ->

```
Basis enthalpy [eV] :   -482.064557447372 47
Basis Harris enthalpy [eV] :   -482.064557579977 47
Free energy [eV] :   -482.132769320656 73
Harris energy [eV] :   -482.132769453261 69
Orbital volume [Ang**3] :    546.437347686564 18
Average basis pressure [eV/Ang**3] :    1.248301814892 1527E-004
Average basis pressure [GPa] :    2.000000000000 000E-002
```

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# Exercise 1.2

Do the same but modifying water.fdf for different values of the EnergyShift:

- 0.01 Ry
- 0.001 Ry
- 0.0001 Ry

```
mkdir ex2 && cp H.psml O.psml water.fdf ex2/ && cd ex2/

mkdir 0.01Ry 0.001Ry 0.0001Ry

cp H.psml O.psml water.fdf 0.01Ry/

cd 0.01Ry/

siesta < water.fdf > water.out
```

Now do the same for the other two values

# Exercise 1.2

Do the same but modifying water.fdf for different values of the EnergyShift:

- 0.01 Ry
- 0.001 Ry
- 0.0001 Ry

```
mkdir ex2 && cp H.psml O.psml water.fdf ex2/ && cd ex2/

mkdir 0.01Ry 0.001Ry 0.0001Ry

cp H.psml O.psml water.fdf 0.01Ry/

cd 0.01Ry/

siesta < water.fdf > water.out
```

Now do the same for the other two values & compare the basis enthalpy and total energy

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# Exercise 1.2

Do the same but modifying water.fdf for different values of the EnergyShift:

- 0.01 Ry
- 0.001 Ry
- 0.0001 Ry

```
mkdir ex2 && cp H.psml O.psml water.fdf ex2/ && cd ex2/

mkdir 0.01Ry 0.001Ry 0.0001Ry

cp H.psml O.psml water.fdf 0.01Ry/

cd 0.01Ry/

siesta < water.fdf > water.out
```

Now do the same for the other two values & compare the basis enthalpy and total energy

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# Exercise 1.2

```
ls * -> 0.01Ry/ 0.001Ry/  0.0001Ry/

grep "E + p_basis" */water.out          ->      0.01Ry    -482.064557 eV
                                                0.001Ry   -482.435979 eV
                                                0.0001Ry  -482.344446 eV
```

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# Exercise 1.2

```
ls * -> 0.01Ry/ 0.001Ry/  0.0001Ry/

grep "E + p_basis" */water.out          ->      0.01Ry    -482.064557 eV
                                                0.001Ry   -482.435979 eV
                                                0.0001Ry  -482.344446 eV


grep “Total = " */water.out             ->      0.01Ry    -482.132769 eV
                                                0.001Ry   -482.588034 eV
                                                0.0001Ry  -482.624963 eV
```

Role of `BasisPressure`: Control the length of the orbitals

- The energy of the system is lower, but the orbitals are too long.

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# Exercise 1.3

Set the value of EnergyShift to: 0.001 Ry

```
mkdir ex3 && cp H.psml O.psml water.fdf ex3/ && cd ex3/

mkdir 0.45  0.55 0.65

cp H.psml O.psml water.fdf 0.45/

cd 0.45/

siesta < water.fdf > water.out
```

Now do the same for the other two values & compare the basis enthalpy and total energy

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# Exercise 1.3

```
ls * -> 0.45/ 0.55/  0.65/

grep "E + p_basis" */water.out          ->          0.45      -482.696472 eV
                                                    0.55Ry    -482.741379 eV
                                                    0.65Ry    -482.621525 eV
```

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# Exercise 1.3

```
ls * -> 0.45/ 0.55/  0.65/

grep "E + p_basis" */water.out          ->          0.45      -482.696472 eV
                                                    0.55Ry    -482.741379 eV
                                                    0.65Ry    -482.621525 eV


grep “Total = " */water.out             ->          0.45      -482.696472 eV
                                                    0.55Ry    -482.741379 eV
                                                    0.65Ry    -482.621525 eV
```

Role of `PAO.SplitNorm`: Control the value of the matching radii

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# Exercise 1.3

```
ls * -> 0.45/ 0.55/  0.65/

grep "E + p_basis" */water.out          ->          0.45     -482.696472 eV
                                                    0.55     -482.741379 eV
                                                    0.65     -482.621525 eV


grep “Total = " */water.out             ->          0.45     -482.696472 eV
                                                    0.55     -482.741379 eV
                                                    0.65     -482.621525 eV


grep “Orbital " */*.BASIS_ENTHALPY      ->          0.45      1133.4670869288188 Ang^3
                                                    0.55      1125.4349550834477 Ang^3
                                                    0.65      1120.3374442047921 Ang^3
```

Role of `PAO.SplitNorm`: Control the value of the matching radii

- It does not have a big impact on the total orbital volume (if compared to the `PAO.EnergyShift`)

# Before moving to Exercise 2

## Advanced way to the BasisPressure (new feature in v5.4):

```
%block BasisPressure.Specs
  H   0.02   GPa   # Hydrogen
  Z 8 0.0003 GPa   # Oxygen
%endblock BasisPressure.Specs/
```

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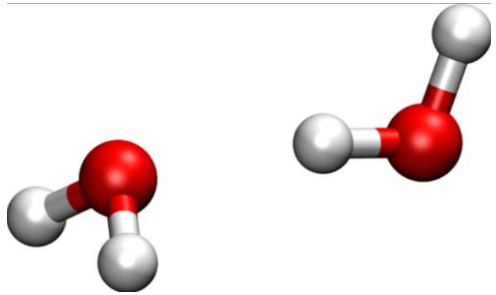
# Exercise 2: Binding energy of a water dimer (round 1)

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$



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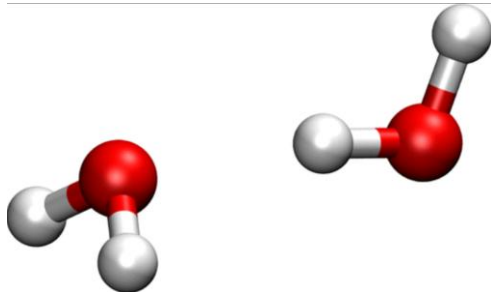
# Exercise 2: Binding energy of a water dimer (round 1)

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$



```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/02-WaterDimer
```

```
ls ->    H.psml  O.psml  dimer.fdf monomer.fdf
```

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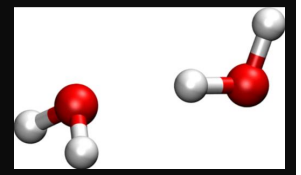
# Exercise 2: Binding energy of a water dimer (round 1)

$$E_{binding} = E_{dimer} - E_{monomer}$$

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/02-WaterDimer

ls ->    H.psml  O.psml  dimer.fdf monomer.fdf

vi dimer.fdf
```

```
##
SystemName          Water dimer
SystemLabel         2h2o
NumberOfAtoms       6
NumberOfSpecies     2

XC.Functional       GGA
XC.Authors          PBE

SCF.Mixer.Weight    0.5
SCF.Mixer.History   10
MeshCutoff          300 Ry

%block ChemicalSpeciesLabel
 1  8  O
 2  1  H
%endblock ChemicalSpeciesLabel

AtomicCoordinatesFormat  Ang
%block AtomicCoordinatesAndAtomicSpecies
 0.000000    0.000000    0.000000 2
 0.000000    0.000000    1.522047 2
 2.341468    0.000000    0.760784 2
 3.795635    0.459564    0.760954 2
 0.436628    0.395162    0.761024 1
 3.251445   -0.331791    0.760767 1
%endblock AtomicCoordinatesAndAtomicSpecies

LatticeConstant 25.0 Ang
%block LatticeVectors
1.0 0.0 0.0
0.0 1.0 0.0
0.0 0.0 1.0
%endblock LatticeVectors

PAO.EnergyShift     0.01 Ry
PAO.SplitNorm       0.15
```



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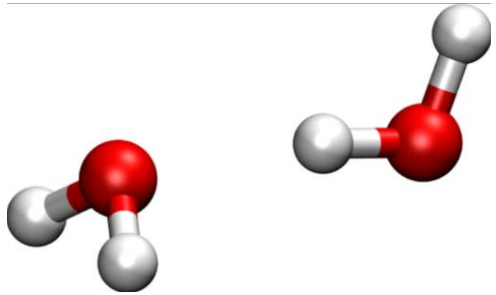
# Exercise 2: Binding energy of a water dimer (round 1)

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$



```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/02-WaterDimer

ls ->    H.psml  O.psml  dimer.fdf monomer.fdf

vi dimer.fdf

mkdir run1 && cp H.psml  O.psml  dimer.fdf monomer.fdf run1/ && cd run1/

Run the calculations for dimer and monomer

Energies?? (using grep)
```

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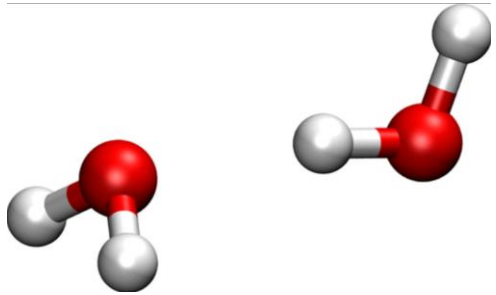
# Exercise 2: Binding energy of a water dimer (round 1)

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$



```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/02-WaterDimer

ls ->    H.psml  O.psml  dimer.fdf monomer.fdf

vi dimer.fdf

mkdir run1 && cp H.psml  O.psml  dimer.fdf monomer.fdf run1/ && cd run1/

Run the calculations for dimer and monomer

Energies?? (using grep)
```

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# Exercise 2: Binding energy of a water dimer (round 1)

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$

```
mkdir run1 && cp H.psml  O.psml  dimer.fdf monomer.fdf run1/ && cd run1/

Run the calculations for dimer and monomer

Energies run1?? (using grep)

Now run the calculation using the values obtained previously for
PAO.SplitNorm and PAO.EnergyShift!

mkdir run2 && cp H.psml  O.psml  dimer.fdf monomer.fdf run2/ && cd run2/

Run the calculations for dimer and monomer

Energies run2??
```

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# Exercise 2: Binding energy of a water dimer (round 1)

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$

Compare the energies of run1 and run2. Are they different?

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EXCELENCIA SEVERO OCHOA

# Exercise 2: Binding energy of a water dimer (round 1)

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$

Compare the energies of run1 and run2. Are they different? Yes they are!

| | | | | |
|---|---|---|---|---|
| run1 | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -964.717861<br>-482.136281 | $E_b$ = -445 meV |
| run2 | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -966.016972<br>-482.884135 | $E_b$ = -248 meV |

**Is our default basis set bad??**

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# Exercise 2: Binding energy of a water dimer (round 1)

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$

Compare the energies of run1 and run2. Are they different? Yes they are!

| | | | | |
|---|---|---|---|---|
| run1 | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -964.717861<br>-482.136281 | $E_b$ = -445 meV |
| run2 | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -966.016972<br>-482.884135 | $E_b$ = -248 meV |

**Is our default basis set bad??**

Not really… Basis Set Superposition Error (BSSE)
…round 2

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# Manual optimization of the cut-off radii

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# Exercise 3: Optimizing the first ζ

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/03-OptimizeFirstZeta

ls ->    H.psml  O.psml  water.fdf

vi water.fdf
```

```
PAO.EnergyShift     0.001 Ry

%block PAO.Basis
H 1
 n=1 0 2 P 1
  0.0 0.0
O 2
 n=2 0 2
  0.0 0.0
 n=2 1 2 P 1
  0.0 0.0
%endblock PAO.Basis

BasisPressure  0.02 GPa
```

**New!**

```
PAO.BasisSize       DZP
PAO.EnergyShift     0.01 Ry
PAO.SplitNorm       0.15

BasisPressure  0.02 GPa
```

**Old!**

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# Exercise 3.1: Optimizing 1s of H

```
PAO.EnergyShift     0.001 Ry

%block PAO.Basis
H 1
 n=1 0 2 P 1
  0.0 0.0
O 2
 n=2 0 2
  0.0 0.0
 n=2 1 2 P 1
  0.0 0.0
%endblock PAO.Basis

BasisPressure  0.02 GPa
```

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/03-OptimizeFirstZeta

ls ->    H.psml  O.psml  water.fdf

vi water.fdf
```

Do a series of calculations changing the value of rc for the 1s orbital of H (from 4.0 to 6.0 Bohr by 0.5 Bohr steps) – create a directory (e.g. H1s)

The first calculation should look like:

```
PAO.EnergyShift     0.001 Ry

%block PAO.Basis
H 1
 n=1 0 2 P 1
  4.0 0.0
O 2
 n=2 0 2
  0.0 0.0
 n=2 1 2 P 1
  0.0 0.0
%endblock PAO.Basis

BasisPressure  0.02 GPa
```

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# Exercise 3.1: Optimizing 1s of H

```
PAO.EnergyShift     0.001 Ry

%block PAO.Basis
H 1
 n=1 0 2 P 1
  0.0 0.0
O 2
 n=2 0 2
  0.0 0.0
 n=2 1 2 P 1
  0.0 0.0
%endblock PAO.Basis

BasisPressure  0.02 GPa
```

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/03-OptimizeFirstZeta

ls ->    H.psml  O.psml  water.fdf

vi water.fdf
```

Do a series of calculations changing the value of rc for the 1s orbital of H (from 4.0 to 6.0 Bohr by 0.5 Bohr steps) (By hand or with a script)

The first calculation should look like:

```
PAO.EnergyShift     0.001 Ry

%block PAO.Basis
H 1
 n=1 0 2 P 1
  4.0 0.0
O 2
 n=2 0 2
  0.0 0.0
 n=2 1 2 P 1
  0.0 0.0
%endblock PAO.Basis

BasisPressure  0.02 GPa
```

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EXCELENCIA SEVERO OCHOA

# Exercise 3.1: Optimizing 1s of H

```
PAO.EnergyShift     0.001 Ry

%block PAO.Basis
H 1
 n=1 0 2 P 1
  0.0 0.0
O 2
 n=2 0 2
  0.0 0.0
 n=2 1 2 P 1
  0.0 0.0
%endblock PAO.Basis

BasisPressure  0.02 GPa
```

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/03-OptimizeFirstZeta

ls ->    H.psml  O.psml  water.fdf

vi water.fdf
```

Do a series of calculations changing the value of rc for the 1s orbital of H (from 4.0 to 6.0 Bohr by 0.5 Bohr steps)

Which is the optimized value? (Looking at the basis enthalpy)

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EXCELENCIA SEVERO OCHOA

# Exercise 3.1: Optimizing 1s of H

```
PAO.EnergyShift     0.001 Ry

%block PAO.Basis
H 1
 n=1 0 2 P 1
  0.0 0.0
O 2
 n=2 0 2
  0.0 0.0
 n=2 1 2 P 1
  0.0 0.0
%endblock PAO.Basis

BasisPressure  0.02 GPa
```

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/03-OptimizeFirstZeta

ls ->    H.psml  O.psml  water.fdf

vi water.fdf
```

Do a series of calculations changing the value of rc for the 1s orbital of H (from 4.0 to 6.0 Bohr by 0.5 Bohr steps)

Which is the optimized value? (Looking at the basis enthalpy)

```
water-4.0.out:     (Free)E + p_basis*V_orbitals        =        -482.533803 eV
water-4.5.out:     (Free)E + p_basis*V_orbitals        =        -482.552463 eV
water-5.0.out:     (Free)E + p_basis*V_orbitals        =        -482.511975 eV
water-5.5.out:     (Free)E + p_basis*V_orbitals        =        -482.480837 eV
water-6.0.out:     (Free)E + p_basis*V_orbitals        =        -482.463814 eV
```

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# Exercise 3.2 and 3.3: Opt. the other orbitals

We change the value of the first-ζ for the 1s orbital of H and do the same procedure for the O's orbitals.

To keep things clean: Create a directory for each orbital!

```
PAO.EnergyShift     0.001 Ry

%block PAO.Basis
H 1
 n=1 0 2 P 1
  4.5  0.0
O 2
 n=2 0 2
  0.0 0.0
 n=2 1 2 P 1
  0.0 0.0
%endblock PAO.Basis

BasisPressure  0.02 GPa
```

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# Exercise 3.2 and 3.3: Opt. the other orbitals

We change the value of the first-ζ for the 1s orbital of H and do the same procedure for the O's orbitals. (From 4.5 Bohr to 7.5 Bohr)

To keep things clean: Create a directory for each orbital!

```
PAO.EnergyShift     0.001 Ry

%block PAO.Basis
H 1
 n=1 0 2 P 1
  4.5  0.0
O 2
 n=2 0 2
  0.0 0.0
 n=2 1 2 P 1
  0.0 0.0
%endblock PAO.Basis

BasisPressure  0.02 GPa
```

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# Exercise 3.2 and 3.3: Opt. the other orbitals

We change the value of the first-ζ for the 1s orbital of H and do the same procedure for the O's orbitals. (From 4.5 Bohr to 7.5 Bohr)

To keep things clean: Create a directory for each orbital!

Results...

O-*2s*

O-*2p*

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# Exercise 3.2 and 3.3: Opt. the other orbitals

We change the value of the first-ζ for the 1s orbital of H and do the same procedure for the O's orbitals. (From 4.5 Bohr to 7.5 Bohr)

To keep things clean: Create a directory for each orbital!

Results...

O-*2s*

```
water-4.5.out:    (Free)E + p_basis*V_orbitals  =      -482.554540 eV
water-5.0.out:    (Free)E + p_basis*V_orbitals  =      -482.567785 eV
water-5.5.out:    (Free)E + p_basis*V_orbitals  =      -482.570432 eV
water-6.0.out:    (Free)E + p_basis*V_orbitals  =      -482.568240 eV
water-6.5.out:    (Free)E + p_basis*V_orbitals  =      -482.563629 eV
water-7.0.out:    (Free)E + p_basis*V_orbitals  =      -482.558274 eV
water-7.5.out:    (Free)E + p_basis*V_orbitals  =      -482.552222 eV
```

O-*2p*

```
water-4.5.out:    (Free)E + p_basis*V_orbitals  =      -482.267679 eV
water-5.0.out:    (Free)E + p_basis*V_orbitals  =      -482.451362 eV
water-5.5.out:    (Free)E + p_basis*V_orbitals  =      -482.551777 eV
water-6.0.out:    (Free)E + p_basis*V_orbitals  =      -482.603669 eV
water-6.5.out:    (Free)E + p_basis*V_orbitals  =      -482.626368 eV
water-7.0.out:    (Free)E + p_basis*V_orbitals  =      -482.631294 eV
water-7.5.out:    (Free)E + p_basis*V_orbitals  =      -482.625763 eV
```

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# Exercise 3.2 and 3.3: Opt. the other orbitals

We change the value of the first-ζ for the 1s orbital of H and do the same procedure for the O's orbitals. (From 4.5 Bohr to 7.5 Bohr)

To keep things clean: Create a directory for each orbital!

Results...

O-*2s*

```
water-4.5.out:    (Free)E + p_basis*V_orbitals  =      -482.554540 eV
water-5.0.out:    (Free)E + p_basis*V_orbitals  =      -482.567785 eV
water-5.5.out:    (Free)E + p_basis*V_orbitals  =      -482.570432 eV
water-6.0.out:    (Free)E + p_basis*V_orbitals  =      -482.568240 eV
water-6.5.out:    (Free)E + p_basis*V_orbitals  =      -482.563629 eV
water-7.0.out:    (Free)E + p_basis*V_orbitals  =      -482.558274 eV
water-7.5.out:    (Free)E + p_basis*V_orbitals  =      -482.552222 eV
```

O-*2p*

```
water-4.5.out:    (Free)E + p_basis*V_orbitals  =      -482.267679 eV
water-5.0.out:    (Free)E + p_basis*V_orbitals  =      -482.451362 eV
water-5.5.out:    (Free)E + p_basis*V_orbitals  =      -482.551777 eV
water-6.0.out:    (Free)E + p_basis*V_orbitals  =      -482.603669 eV
water-6.5.out:    (Free)E + p_basis*V_orbitals  =      -482.626368 eV
water-7.0.out:    (Free)E + p_basis*V_orbitals  =      -482.631294 eV
water-7.5.out:    (Free)E + p_basis*V_orbitals  =      -482.625763 eV
```

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# Exercise 3: Optimizing the first ζ

Final PAO.Basis block:

```
%block PAO.Basis
  H 1
    n=1 0 2 P 1
        4.5 0.0
  O 2
    n=2 0 2
        5.5 0.0
    n=2 1 2 P 1
        7.0 0.0
%endblock PAO.Basis
```

Which is the shortest orbital? Which is the largest?

Is it what you expected?

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# Exercise 3: Optimizing the first ζ

Final PAO.Basis block:

```
%block PAO.Basis
  H 1
    n=1 0 2 P 1
        4.5 0.0
  O 2
    n=2 0 2
        5.5 0.0
    n=2 1 2 P 1
        7.0 0.0
%endblock PAO.Basis
```

DO THE OPTIMIZATION IN A RECURSIVE WAY

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# Exercise 4: Optimizing the second ζ

From exercise 3 our PAO.Basis block looks like:

```
%block PAO.Basis
  H 1
    n=1 0 2 P 1
        4.5 0.0
  O 2
    n=2 0 2
        5.5 0.0
    n=2 1 2 P 1
        7.0 0.0
%endblock PAO.Basis
```

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# Exercise 4: Optimizing the second ζ

From exercise 3 our PAO.Basis block looks like:

```
%block PAO.Basis
  H 1
    n=1 0 2 P 1
        4.5 0.0
  O 2
    n=2 0 2
        5.5 0.0
    n=2 1 2 P 1
        7.0 0.0
%endblock PAO.Basis
```

Matching radius for the second ζ

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# Exercise 4: Optimizing the second ζ

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/04-OptimizeSecondZeta

ls ->    H.psml  O.psml  water.fdf

vi water.fdf
```

```
PAO.EnergyShift     0.001 Ry

%block PAO.Basis
H 1
 n=1 0 2 P 1
  4.5 0.0
O 2
 n=2 0 2
  5.5 0.0
 n=2 1 2 P 1
  7.0 0.0
%endblock PAO.Basis

BasisPressure  0.02 GPa
```

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# Exercise 4: Optimizing the second ζ

```
PAO.EnergyShift     0.001 Ry

%block PAO.Basis
H 1
 n=1 0 2 P 1
  4.5 0.0
O 2
 n=2 0 2
  5.5 0.0
 n=2 1 2 P 1
  7.0 0.0
%endblock PAO.Basis

BasisPressure  0.02 GPa
```

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/04-OptimizeSecondZeta

ls ->    H.psml  O.psml  water.fdf

vi water.fdf
```

Do a series of calculations changing the value of matching radius for:

- Exercise 4.1: 1s orbital of H (from 1.5 Bohr to 3.0 Bohr by 0.5 Bohr increases)
- Exercise 4.2: 2s orbital of O (from 2.5 Bohr to 4.0 Bohr by 0.5 Bohr increases)
- Exercise 4.3: 2p orbital of O (from 2.5 Bohr to 4.0 Bohr by 0.5 Bohr increases)

Remember: Create a separate folder for each of the orbitals!

Which is the optimized value? (Looking at the basis enthalpy)

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# Exercise 4: Optimizing the second ζ

- Exercise 4.1: 1s orbital of H (from 1.5 Bohr to 3.0 Bohr by 0.5 Bohr steps)
- Exercise 4.2: 2s orbital of O (from 2.5 Bohr to 4.0 Bohr by 0.5 Bohr steps)
- Exercise 4.3: 2p orbital of O (from 2.5 Bohr to 4.0 Bohr by 0.5 Bohr steps)

To keep things clean: Create a directory for each orbital!

Results...

H-*1s-2ζ*

```
water-1.5.out:    (Free)E + p_basis*V_orbitals  =  -482.666780 eV
water-2.0.out:    (Free)E + p_basis*V_orbitals  =  -482.829897 eV
water-2.5.out:    (Free)E + p_basis*V_orbitals  =  -482.777909 eV
water-3.0.out:    (Free)E + p_basis*V_orbitals  =  -482.666422 eV
```

O-*2s-2ζ*

```
water-2.5.out:    (Free)E + p_basis*V_orbitals  =  -482.831605 eV
water-3.0.out:    (Free)E + p_basis*V_orbitals  =  -482.832936 eV
water-3.5.out:    (Free)E + p_basis*V_orbitals  =  -482.816571 eV
water-4.0.out:    (Free)E + p_basis*V_orbitals  =  -482.809207 eV
```

O-*2p-2ζ*

```
water-2.5.out:    (Free)E + p_basis*V_orbitals  =  -482.815772 eV
water-3.0.out:    (Free)E + p_basis*V_orbitals  =  -482.833345 eV
water-3.5.out:    (Free)E + p_basis*V_orbitals  =  -482.825561 eV
water-4.0.out:    (Free)E + p_basis*V_orbitals  =  -482.818233 eV
```

# Exercise 4: Optimizing the second ζ

Final PAO.Basis block:

```
%block PAO.Basis
  H 1
    n=1 0 2 P 1
        4.5 2.0
  O 2
    n=2 0 2
        5.5 3.0
    n=2 1 2 P 1
        7.0 3.0
%endblock PAO.Basis
```

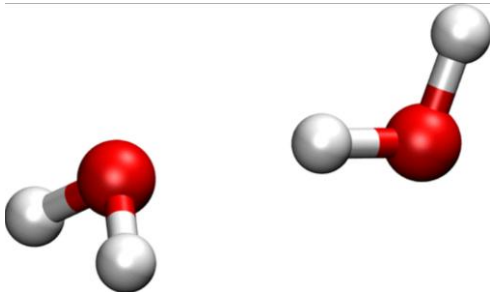
DO THE OPTIMIZATION IN A RECURSIVE WAY

ALWAYS CHECK CONVERGENCE

# Exercise 5: Binding energy of the water dimer

Now let's put everything together…

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$



# Exercise 5: Binding energy of the water dimer

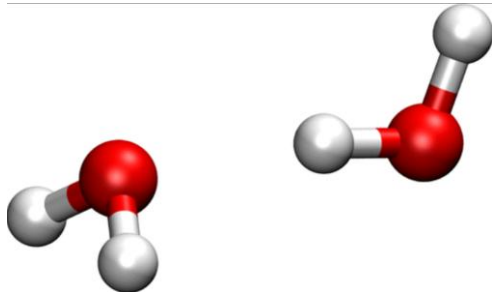
Now let's put everything together…

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/05-OptimizedWaterDimer

ls ->    H.psml  O.psml  dimer.fdf  monomer.fdf

vi dimer.fdf
```

```
%block PAO.Basis
  H 1
    n=1 0 2 P 1
        4.5 2.0
  O 2
    n=2 0 2
        5.5 3.0
    n=2 1 2 P 1
        7.0 3.0
%endblock PAO.Basis
```

siesta

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$

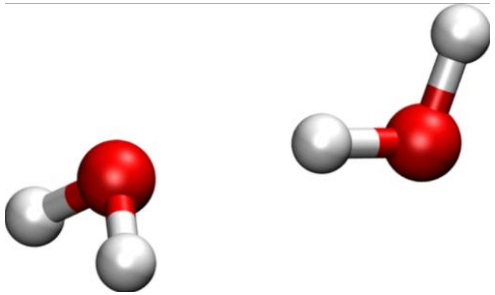


# Exercise 5: Binding energy of the water dimer

From the past we have:

| | | | | |
|---|---|---|---|---|
| run1<br>default | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -964.717861<br>-482.136281 | $E_b$ = -445 meV |
| run2<br>Rough opt | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -966.016972<br>-482.884135 | $E_b$ = -248 meV |

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$

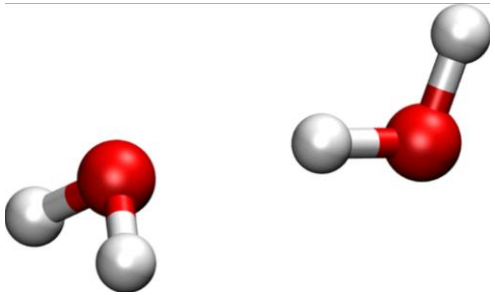


# Exercise 5: Binding energy of the water dimer

And now:

| | | | | |
|---|---|---|---|---|
| run1<br>default | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -964.717861<br>-482.136281 | $E_b$ = -445 meV |
| run2<br>Rough opt | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -966.016972<br>-482.884135 | $E_b$ = -248 meV |
| run3<br>Optimized | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -966.119097<br>-482.936001 | $E_b$ = -247 meV |

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$



# Exercise 6: Optimizing the polarization orbitals

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/06-PolarizationOrbitals

ls ->    H.psml  O.psml  water.fdf

vi water.fdf
```

```
PAO.EnergyShift     0.001 Ry

%block PAO.Basis
H 2
 n=1 0 2
  4.5 2.0
 n=2 1 1 Q 0.0
  4.5
O 3
 n=2 0 2
  5.5 3.0
 n=2 1 2
  7.0 3.0
 n=3 2 1 Q 0.0
  7.0
%endblock PAO.Basis

BasisPressure  0.02 GPa
```

- We need to add an extra orbital
- The polarization orbitals have the same cut-off radii as the orbital they are polarizing
- Charge confinement method (change the value of Q)

$$V(r;Q) = Q/r^2$$

Charge confinement potential

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# Exercise 6: Optimizing the polarization orbitals

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/06-PolarizationOrbitals

ls ->    H.psml  O.psml  water.fdf

vi water.fdf
```

```
PAO.EnergyShift     0.001 Ry

%block PAO.Basis
H 2
 n=1 0 2
  4.5 2.0
 n=2 1 1 Q 0.0
  4.5
O 3
 n=2 0 2
  5.5 3.0
 n=2 1 2
  7.0 3.0
 n=3 2 1 Q 0.0
  7.0
%endblock PAO.Basis

BasisPressure  0.02 GPa
```

- We need to add an extra orbital
- The polarization orbitals have the same cut-off radii as the orbital they are polarizing
- Charge confinement method (change the value of Q)

$$V(r;Q) = Q/r^2$$

Charge confinement potential

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# Exercise 6: Optimizing the polarization orbitals

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/06-PolarizationOrbitals

ls ->    H.psml  O.psml  water.fdf

vi water.fdf
```

Do a series of calculations changing the value of matching radius for:

- Excercise 6.1: 2p orbital of H (from 3.5 to 6.0 by 0.5 steps)
- Excercise 6.2: 3d orbital of O (from 5.0 to 8.0 by 0.5 steps)

Remember: Create a separate folder for each of the orbitals!

Which is the optimized value? (Looking at the basis enthalpy)

# Exercise 6: Optimizing the polarization orbitals

- Exercise 6.1: 2p orbital of H (from 3.5 to 6.0 by 0.5 steps)
- Exercise 6.2: 3d orbital of O (from 5.0 to 8.0 by 0.5 steps)

To keep things clean: Create a directory for each orbital!

Results...

H-polarized

```
water-3.5.out:    (Free)E + p_basis*V_orbitals  =    -482.523463 eV
water-4.0.out:    (Free)E + p_basis*V_orbitals  =    -482.533292 eV
water-4.5.out:    (Free)E + p_basis*V_orbitals  =    -482.535352 eV
water-5.0.out:    (Free)E + p_basis*V_orbitals  =    -482.531367 eV
water-5.5.out:    (Free)E + p_basis*V_orbitals  =    -482.522689 eV
water-6.0.out:    (Free)E + p_basis*V_orbitals  =    -482.510356 eV
```

O-*polarized*

```
water-5.0.out:    (Free)E + p_basis*V_orbitals  =    -482.868356 eV
water-5.5.out:    (Free)E + p_basis*V_orbitals  =    -482.880011 eV
water-6.0.out:    (Free)E + p_basis*V_orbitals  =    -482.884055 eV
water-6.5.out:    (Free)E + p_basis*V_orbitals  =    -482.883230 eV
water-7.0.out:    (Free)E + p_basis*V_orbitals  =    -482.879307 eV
water-7.5.out:    (Free)E + p_basis*V_orbitals  =    -482.873390 eV
water-8.0.out:    (Free)E + p_basis*V_orbitals  =    -482.866172 eV
```

# Extra: Final calculation of the binding energy

Final PAO.Basis block:

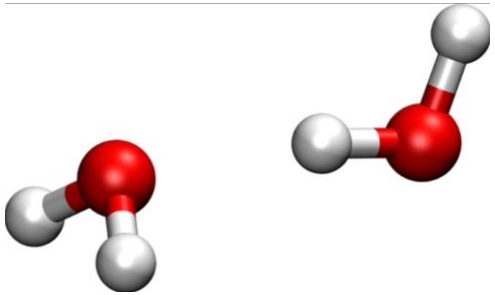
```
%block PAO.Basis
H 2
 n=1 0 2
  4.5 2.0
 n=2 1 1 Q 4.5
  4.5
O 3
 n=2 0 2
  5.5 3.0
 n=2 1 2
  7.0 3.0
 n=3 2 1 Q 6.0
  7.0
%endblock PAO.Basis
```

DO THE OPTIMIZATION IN A RECURSIVE WAY

ALWAYS CHECK CONVERGENCE

# Extra: Final calculation of the binding energy

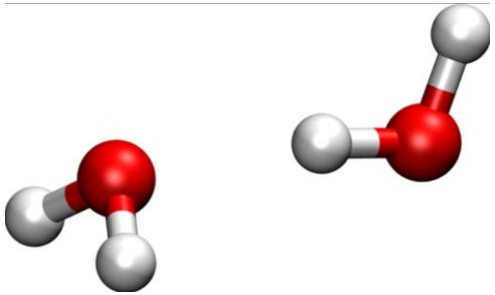
$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$



# Exercise 6: Optimizing the polarization orbitals

```
/user/path/siesta-docs/work-files/tutorials/basic/

cd basis-optimization/06-PolarizationOrbitals

mkdir binding-energy

copy the monomer.fdf and dimer.fdf (and the pseudos) to binding-energy

Run the calculations for both systems.

Results...
```

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$

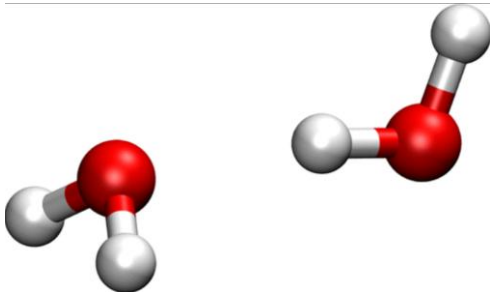


# Extra: Final calculation of the binding energy

From the past:

| | | | | |
|---|---|---|---|---|
| run1<br>default | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -964.717861<br>-482.136281 | $E_b$ = -445 meV |
| run2<br>Rough opt | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -966.016972<br>-482.884135 | $E_b$ = -248 meV |
| run3<br>Optimized | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -966.119097<br>-482.936001 | $E_b$ = -247 meV |

$$E_{binding} = E_{dimer} - 2 \cdot E_{monomer}$$



# Extra: Final calculation of the binding energy

And now:

| | | | | |
|---|---|---|---|---|
| run1<br>default | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -964.717861<br>-482.136281 | $E_b$ = -445 meV |
| run2<br>Rough opt | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -966.016972<br>-482.884135 | $E_b$ = -248 meV |
| run3<br>Optimized | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -966.119097<br>-482.936001 | $E_b$ = -247 meV |
| run4<br>Fully Optimized | dimer.out:siesta:<br>monomer.out:siesta: | Total =<br>Total = | -966.215237<br>-482.985858 | $E_b$ = -243 meV |

# Powered by…

Projects PID2022-142162NB-I00 and RYC2023-044383-I financed by:

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**Questions?**