

# General Recap

# Reminders

**Fill the survey!!!**

[https://siesta-project.org/siesta/events/SIESTA\\_School-2023/Sessions.html](https://siesta-project.org/siesta/events/SIESTA_School-2023/Sessions.html)

[https://siesta-project.org/siesta/events/SIESTA\\_School-2023/MN4.html](https://siesta-project.org/siesta/events/SIESTA_School-2023/MN4.html)

<https://docs.siesta-project.org/projects/siesta/en/school-2023/tutorials/index.html>

12.30	Introduction	Basis Set Optimization	Geometry Optimization	Polarization, Born Charges	Siesta Solvers		
13.00	SIESTA Theory		Molecular Dynamics	Wannierization	TranSIESTA		
13.30	Pseudopotentials					Phonons	SISL
14.00	A First Contact	Break	Break	Break			
14.30		K-Points, Mesh, SCF	Phonons	Spin, SO			
15.00						Break	Break
15.30					Break	Break	
16.00	Break	Analysis I	Analysis II	Analysis III	Build/Deploy		
16.30	Basis Sets				Analysis I	Analysis II	Analysis III
17.00							

# Reminders


Before doing a calculation with SIESTA, there are a few things we should do:

- Test the pseudopotentials
- Test the basis sets (today!)
- Converge the mesh cut-off for calculations (today!)
- Converge the k-point sampling (today!)

# Basis set optimization

19/09/2023 - Federico Pedron

# Key concepts

 **siesta**<sup>TM</sup> can automatically generate basis sets, or you can provide whatever radial function you want.

Basis functions become strictly zero beyond a certain radius, *rcut*.

For multiple-z basis, the second-z orbital is equal to the first-z orbital beyond a matching radius *rmatch*.

# Global basis set options

**Cardinality:** amount of basis functions per atom (SZ, SZP, DZ, DZP, TZP).

```
PAO.BasisSize  DZP
```

**Energy-shift:** controls the cut-off radii of all atoms in a cohesive way.

```
PAO.EnergyShift 0.01 Ry
```

**Split Norm:** controls the matching radii for all multiple-zeta orbitals.

```
PAO.Splitnorm  0.15
```

# Global basis set options

**Soft confinement:** Use a soft confinement potential when creating the basis orbitals.

```
PAO.SoftDefault T
```

**Polarization style:** Controls the way polarization orbitals are created.

```
PAO.OldStylePolOrbs F
```



Playing with water

## First tests with water (geometry optimization)

Copy your tutorial files from `/gpfs/projects/nct00/nct00003/TUTORIALS/day2/`

In the tutorials for `day2` go to **01-BasisSets-Global**, and copy the run script from `/gpfs/projects/nct00/nct00003/SCRIPTS/runmn.sh`.

Take note of how the **total energy (from output)**, **bond lengths (h2o.BONDS file)**, and **total time (from h2o.times)** change in this cases:

- 1) When changing the basis set between **SZ, SZP, and DZP**. Use an energy shift of **100 meV**.
- 2) For **DZP**, changing the energy shift between **5 meV, 100 meV, and 500 meV**.

If you have time, test the effect of the following options:

- OldStylePolOrbs (T or F)
- PAO.SoftDefault (T or F)

# Budgeting

Both increasing the cardinality (SZ -> SZP -> DZP -> TZP) and reducing the energy-shift increase the quality of results and the computational costs.

Costs are affected differently though:

- **Cardinality** increases the cost of **diagonalization** ( $\sim N^3$ )
- **Energy shift/Cut-off radius** increase the cost of **grid operations** ( $\sim N$ ).

For **small systems** (a few N), **grid operations** are the dominant part of the calculation. Meanwhile, for **large systems** (large N), **diagonalization** becomes dominant.

This means that for very large systems (300-800 atoms), increasing the cut-off radii does not greatly increase computational costs.

# TIP: Visualizing orbital shapes

## How-to -> Visualization -> Visualizing Orbital Shapes

<https://docs.siesta-project.org/projects/siesta/en/latest/how-to/visualization/orbitals.html>

The screenshot shows the left-hand navigation menu of the Siesta Documentation website. At the top is the 'Siesta Documentation' logo with the version 'latest'. Below it is a search bar labeled 'Search docs'. The main menu is divided into several sections: 'Tutorials', 'How-to guides' (which is expanded to show 'Building Siesta', 'Visualization', and 'Other'), 'Technical reference', and 'Background information'. The 'Visualization' section is further expanded to show 'Analysis tools' and 'Visualizing orbital shape', which is the current page.

» How-to guides » Visualizing orbital shape

[Edit on GitLab](#)

## Visualizing orbital shape

### Using the ioncat/ionplot tools to process .ion files

You can look at the shape of the orbitals by plotting the contents of the .ion files produced by Siesta. These files are not easily readable, but the 'ioncat' program can extract the relevant pieces of information, and the "ionplot" script can drive 'ioncat' to plot the desired graphs. For example:

```
ionplot -o 1 0
```

will plot the orbital with number "1" in the O.ion file.:

```
ioncat -i 0
```

will print the numbers of the representative orbitals of each nlz shell (i.e., disregarding the 'm' quantum number, which does not affect the radial part):

```
ioncat -o 1 0
```

will output the data for the first orbital in O.ion.

Typing `ioncat -h` produces a display of the full set of options for the program:

# Optimizing a Basis Set

# Exploring the PAO.Basis block

We have each species and all orbitals with different (n,l) separated.

For water:

H -> 1s

O -> 2s, 2p

```
%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
```

Number of different orbital (n,l)

n and l: n=1, l=0, which means 1s

P 1 = add one set of polarization orbitals. DZP basis.

Number of zetas: DZ basis?

# Exploring the PAO.Basis block

We have each species and all orbitals with different (n,l) separated.

For water:

H -> 1s

O -> 2s, 2p

```
%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
```

First Z cut-off radius

Second Z matching radius

# Basis Enthalpy

- We want to get a good energy for a set of orbitals.
- We don't want those orbitals to get needlessly large.



$$\text{Basis Enthalpy} = E_{\text{total}} + \text{“} \mathbf{P}_{\text{basis}} \cdot V_{\text{orbitals}} \text{”}$$



# Basis Enthalpy

- Not a real physical magnitude, we choose it as a input value.

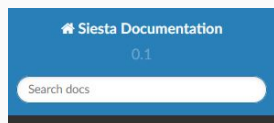
BasisPressure 0.2 GPa

- The **0.2 GPa** default works well for most cases, but for first- and second-row elements, it might result in very short orbitals. Use **0.02 GPa** instead.

# Getting practice...

In the **day2**, go to **02-BasisSet-Optimization**.

Get to the **Basis set optimization** tutorial, and follow the first two practical sections: **Optimizing the First-Zeta cutoff radii**, and **Optimizing the Second-Zeta matching radii**.



- Tutorials
  - Setting up the local working environment for the tutorial exercises
- Basics of Siesta
  - A first encounter with Siesta
  - First crystals
  - Pseudopotentials
  - Basis sets
- Basis set optimization
  - General Concepts
  - Basis Enthalpy
  - The Water molecule
  - Optimizing the first-zeta cut-off radii
  - Optimizing the second-zeta matching radii
  - Calculating the binding energy of a water dimer
  - The Basis Set Superposition Error
  - Optional: Optimizing the polarization

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### Note

Before doing this tutorial, we encourage you to do and review the more [general tutorial on basis sets](#).

## Basis set optimization

Using the default basis sets generated by SIESTA might be enough for some applications, but doing some degree of manual optimization of the basis sets may help to achieve better results with similar computational costs. This is especially advisable when dealing with extremely large systems, where going for high basis set cardinality (triple-zeta, quadruple-zeta) is not really an option.

### Have you set up the local environment?

If not, [do that now](#) before proceeding.

### Note

This tutorial shows just one possible method to optimize your basis sets. Different people tend to use different techniques, there is no "one true way". This method does, however, work reliably across different kinds of systems.

# Testing the Basis Set

# Testing the optimized basis

How do we know if we effectively have a better basis set than the default?

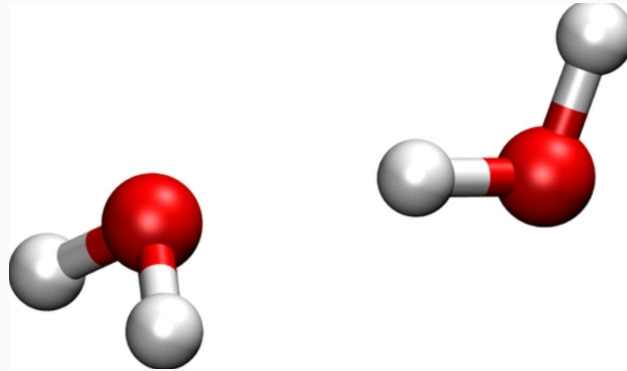
At least, three things are important to check:

- Costs
- Quality
- **Transferability**

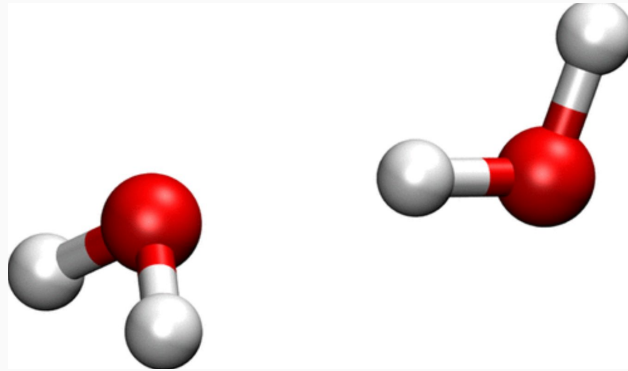
We need to test this in a slightly **different system!**

# Binding energy of a water dimer

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

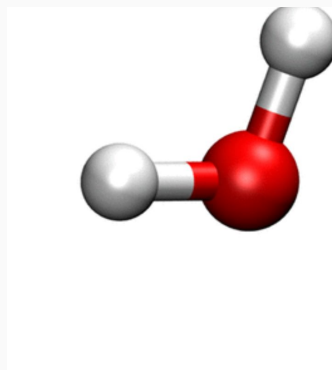


# Basis Set Superposition Error



# Basis Set Superposition Error

**POOF!**



We lost the basis functions for the second molecule! What if they are important?

# Basis Set Superposition Error

Who ya gonna call?

**Ghost atoms!**





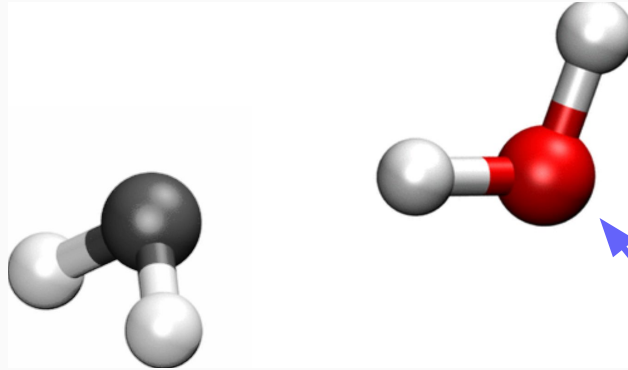
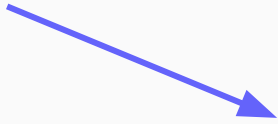
# Ghost atoms

We add the basis functions that would belong to an atom, if the atom were there.

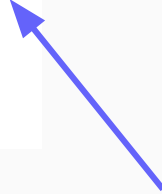
We do not add electrons or nuclei to the calculation!

# Ghost atoms

Ghost



Afraid of no ghosts



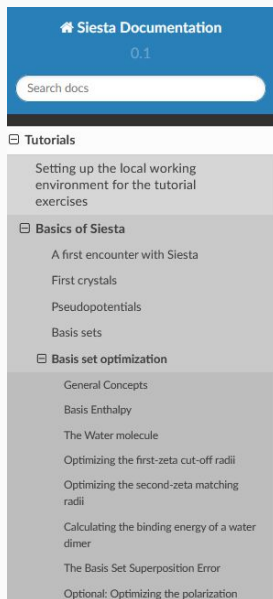
# Ghost atoms

To add ghost atoms, we just create a new species with **negative atomic number**.

```
NumberOfSpecies      4
%block ChemicalSpeciesLabel
  1  8  0
  2  1  H
  3 -8  O_ghost
  4 -1  H_ghost
%endblock ChemicalSpeciesLabel
```

Yes, this means we have to duplicate the pseudopotential files and add extra terms to the PAO.Basis block.

Go again to the **Basis set optimization** tutorial, and follow the following two practical sections: **Calculating the binding energy of a water dimer**, and **The Basis Set Superposition Error**.



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