


Basis set optimization

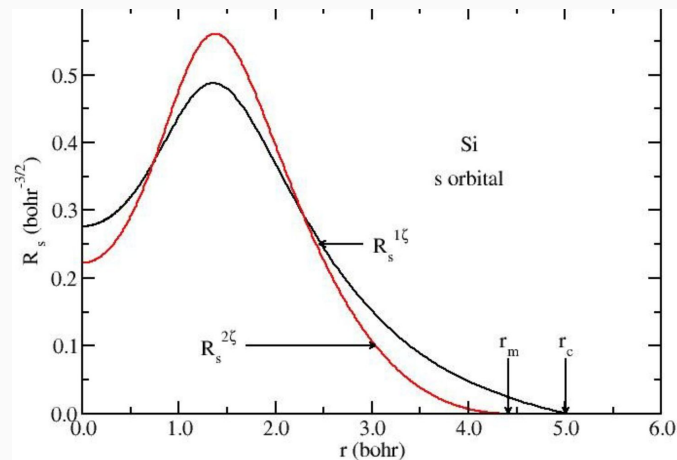
13/03/2024 - Federico Pedron

Key concepts

 can automatically generate basis sets, or you can provide whatever radial function you want.

Basis functions become strictly zero beyond a certain radius, r_{cut} .

For multiple-z basis, the second-z orbital is equal to the first-z orbital beyond a matching radius r_{match} .



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

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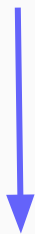
```
%block PAO.Basis
H 1
  n=1 0 2 P 1
      0.0 0.0
O 2
  n=2 0 2
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  n=2 1 2 P 1
      0.0 0.0
%endblock PAO.Basis
```

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...

Go to **03-BasisSets**, and visit:

<https://docs.siesta-project.org/projects/siesta/en/latest/tutorials/basic/basis-optimization/index.html>

Follow the first two practical sections: **Optimizing the First-Zeta cutoff radii**, and **Optimizing the Second-Zeta matching radii**.

The screenshot shows the Siesta Documentation website. The top navigation bar includes 'Siesta Documentation' and '0.1'. A search bar is present. The left sidebar contains a navigation menu with categories: 'Tutorials', 'Basics of Siesta', and 'Basis set optimization'. The 'Basis set optimization' category is expanded, showing sub-items: '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', and 'Optional: Optimizing the polarization'. The main content area shows the 'Basis set optimization' tutorial page. It includes a 'Note' section with the text: 'Before doing this tutorial, we encourage you to do and review the more general tutorial on basis sets.' Below this is the title 'Basis set optimization' and a paragraph: '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.' To the right of this paragraph is a box titled 'Have you set up the local environment?' with the text: 'If not, do that now before proceeding.' Below the main text is another 'Note' section: '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?

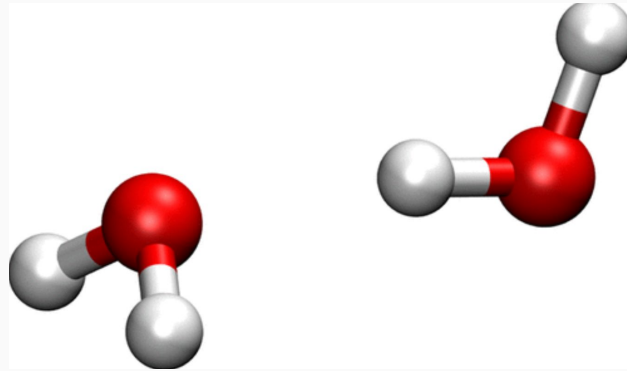
At least, three things are important to check:

- Costs
- Quality
- **Transferability**

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

Binding energy of a water dimer

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



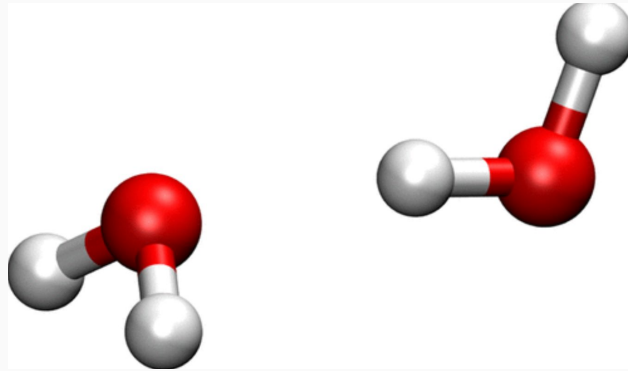
Testing the optimized basis

Run the third part of the tutorial, *Calculating the binding energy of a water dimer*.

Did we get better results with our optimized basis set?

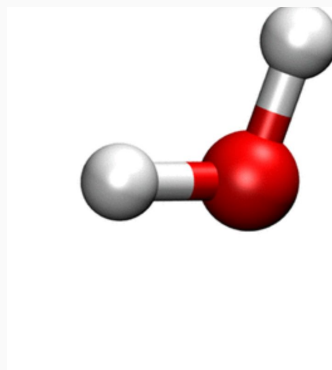
Appendix: Ghost atoms

Basis Set Superposition Error



Basis Set Superposition Error

POOF!



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

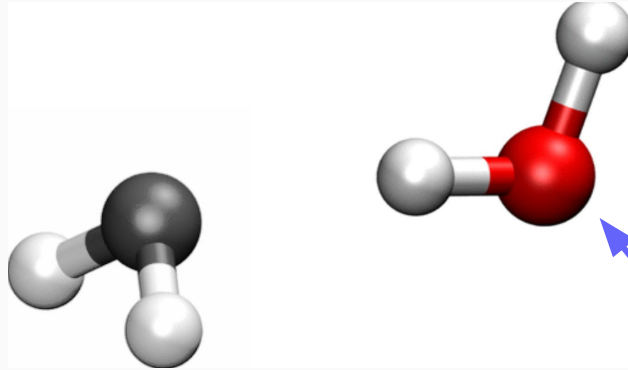
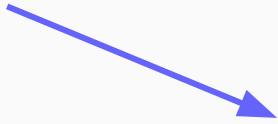
Ghost atoms

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

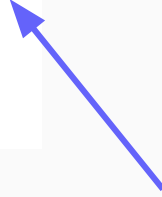
We do not add electrons or nuclei to the calculation!

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.