

## EXERCISE 5

### BASIS SETS I: MOLECULES

This exercise is intended to illustrate the definition of basis sets with different numbers of orbitals and localization radii in SIESTA. It is based on the H<sub>2</sub>O molecule.

You will find three directories: *SZ*, *DZ* and *DZP*, in which you will find input files for a H<sub>2</sub>O molecule which will be solved with three different basis sets: single-Z, double-Z and double-Z plus polarization, respectively. The runs will consist in structural relaxations via Conjugate gradients, to find the equilibrium structure of the molecule for each of the bases utilized.

The bases are defined through these three lines:

```
PAO.BasisSize DZP
PAO.EnergyShift 500.0 meV
PAO.Splitnorm 0.15
```

where the first one defines the number of orbitals in the basis set (in this case, a double-Z plus polarization, which means two shells of s orbitals, two shells of p orbitals, and a polarization shell of d orbitals for oxygen, and two shells of s orbitals and one shell of polarization p orbitals for H); the second line indicates the energy shift parameter, that determines the cutoff radius of each of the orbitals; and the third one is the Split norm parameter, which defines the radius of the second-Z orbital in the case of double-Z bases.

You should do runs for each of the basis sets, changing the *PAO.EnergyShift* parameter, and look at the results as a function of basis size and localization radius (or energy shift).

In particular, you should look at:

- Total energy
- Bond lengths at the relaxed structure
- Bond angles at the relaxed structure
- CPU time
- Radius of each of the orbitals
- Shape of the orbitals

You have some files with results that you should be able to reproduce in the *Out* directories.

What is the best basis set that you have found? Why? How do the results compare with experiment? What do you consider a reasonable basis for the molecule, if you need an accuracy in the geometry of about 1%?? In order to assess convergence with respect to basis set size, should you compare the results with the experimental ones, or with those of a converged basis set calculation?

Tip 1.: In order to find the bond lengths and bond angles, it is helpful to use the *Molekel* program. Load the *h2o.ANI* file (which contains the coordinates of the molecule during the relaxation), and use the 'Geometry' option (left button of the mouse) to measure bond lengths and angles.

Tip 2.: You can see the radii of the orbitals in the output file, just after the line reading:  
printput: Basis input -----

Tip 3.: You can look at the shape of the orbitals by plotting the contents of the *ORB\** files generated by SIESTA.