

## EXERCISE 6

### **BASIS SETS II: CRYSTALS**

This exercise is intended to illustrate the optimization of the range of the basis set orbitals for a bulk system. In the bulk, the convergence with respect to basis set range is much faster than in molecules, since the basis does not need to reproduce the exponential decay into vacuum

The system in which we will work is bulk bcc-Fe. This is a difficult system, for many reasons. First, it needs core corrections for a proper description of the magnetism. Second, LDA does not yield the right ground state structure, and GGA is therefore necessary. Third, since the d-orbitals are very compact, and core corrections are present, a large *MeshCutoff* is necessary for proper convergence. Finally, metallic character with a large density of states at the Fermi level makes it necessary to use a fine **k**-point sampling. The input files have been built to take into account these stringent conditions.

First, go to directory *SZ-OptRc*. Here, you have the input file *fe.fdf*. See that the basis set is defined explicitly using the block *PAO.Basis*. It is a Single-Z basis with both s and d orbitals localized to within  $r_c=4.0$  Bohr.

We want to see which is the optimal radius for each of the orbitals in the Fe atom. We will do it in a simple way. First, maintaining the d orbitals to  $r_c=4.0$  Bohr, change the radius of the s orbitals from 4.0 up to 8.0 Bohrs in increments of, lets say, 0.5 Bohrs. Plot the energy as a function of  $r_c$ . You will see that the energy converges quite quickly with  $r_c$ , and even it shows a minimum!.

Now, pick the value of  $r_c$  for the s orbital that gives the minimum energy, and do the same procedure changing the  $r_c$  of the d orbital. Plot the result and find the optimal radius for the d orbital. Observe the results, and try to understand what's going on.

In *SZ-OptRc/Opt/rc.ps* you have a graph with the results that you should be able to reproduce.

Once that you have optimized the radii, lets go to the directory *Props*. Here, you have input files with different sizes of basis: SZ, DZ and DZP. The radius of the first-Z is chosen close to the optimal one found before. Use these files to compute some physical properties of Fe, and see how they change as a function of the basis set. You can look at the equilibrium lattice constant, the total spin, the bulk modulus, etc. Choose your favorite property and try to get it!!!!