

# Density functional theory of crystals and molecules with FPLO

Tutorial at the QUANTY workshop in Heidelberg

Tuesday 24<sup>th</sup> September, 2024

This is a set of tutorials we will (partially) discuss during the QUANTY workshop in Heidelberg. For time reasons we will together do example 1.1 and then go to problem set 2. Feel free to team up with others and look at the other examples (forces in 1.2 and 1.3, band weights in 1.4, 1.5 and impurities in 1.6) as well.

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## 1 Convergence of k-summation

Evaluate the total energy and the density of states of f.c.c. aluminum versus the k-point number. Use a lattice constant of 7.53 Bohr radii (close to the equilibrium lattice constant in LDA-PW 92). Use a strict convergence criterion (Density AND Energy). Use default settings else. Carry out four calculations with a subdivision of the Brillouin zone into 12 (default), 24, 48, and 96 intervals in each direction.

This task aims at providing a feeling for the dependence of total energy and details of the DOS on the k-point sampling. Hints:

- (i) Create a new sub-directory for each calculation. Call the sub-directories k12, k24, k48, k96. Call the output files 'out'. You may speed up the calculation for the k=96 setting by using a converged charge density from one of the other calculations as input charge density:  

```
[parent directory] cp k12/= .dens k96/= .dens
```

after convergence of the calculation running in k12.
- (ii) You can check the convergence of the iterations by using the shell script 'grit':  

```
[parent directory] grit k
```

yields a list of the distance between the final-iteration density vector and the previous density vector for all calculations running in the sub-directories k\*.
- (iii) You can extract the total energies (in Hartree) from the output files by using the shell script 'grEE':

[parent directory] grEE k

yields a list of the final-iteration total energies of k\*out. How many k-points do you need to get the total energy converged at a level of  $E/k_B$  of 1 Kelvin?

- (iv) If the calculations are converged, you can switch on the input option ‘CALC DOS’ and re-run. Use:

[parent directory] xfbp k12/+dos.total k96/+dos.total

to compare the densities of states for different k-point samplings. How many k-points do you need to get the DOS converged to about 10% accuracy?

## 2 Molecules

In FPLO, molecules can be treated on the same footing as bulk systems. In this tutorial, we will calculate the ground state of two simple molecules, H<sub>2</sub>O and a Ni<sub>2</sub> dimer. We will also learn to use the force module to optimize the structure. The force module is also applicable to bulk systems. To save time, we will practice it with molecules.

### 2.1 Ground state of the water molecule using the force module

- In the ‘Symmetry’ menu, first select ‘structure type’ and set it to ‘Molecule’
- In the ‘spacegroup’ option, one can either choose spacegroup no. 1 or a suitable point group option for H<sub>2</sub>O. H<sub>2</sub>O has point group  $C_{2v}$  (space group: 25) with two mirror planes and a 2-fold rotation axis. Using the point group symmetry is computationally more efficient and sufficient.
- Choose your preferred unit of length: Ångström or Bohr radii. For our example, we will use Ångström.
- Next input are the atomic positions. If you have chosen spacegroup 1, then one needs to provide all three atomic positions. If you have chosen spacegroup 25, then one needs to provide the positions for oxygen and only one of the hydrogen atoms. The second hydrogen position is generated by the symmetry operations of the chosen point group. For example, O at (000); H1 at (1 0 -0.5) and H2 at (-1.05 0 -0.6). Please note that we have provided neither the correct O-H bond length nor the correct H-O-H bond angle here. Our goal is to optimize the structure to obtain the ground state.
- All the other options in the ‘Symmetry’ menu are not used for a molecule calculation.
- Please set the maximum number of iterations to 200
- Use convergency criterion ‘Density OR Energy’
- Next, please go to sub-menu ‘Forces’ (using the space bar and then selecting F). Here, set the ‘Force Mode’ to ‘Site geometry optimization’.
- Now, we are finished with the setup of the calculation. Run ‘fplo’ and pipe the output to a file (named ‘out’).

- The force convergency can be checked by typing: `grep '|force| out` (shorter `grep '|fo' out`).
- The correct solution is obtained when the O-H bond length is 0.9746 Ångström and the H-O-H bond angle is 104.54 degrees.

After force minimization, the positions of the atoms in the 'Symmetry' menu are automatically updated with the optimized values from the last iteration. If you face convergency problems, one option is to increase the temperature and try again. Use the 'Brillouin-Zone' sub-menu option to change the temperature value. The temperature influences the total energy, the optimal structure, the spin moments and so on. A meaningful value for the temperature depends on what makes physical sense. If the temperature is larger than the level separation at the chemical potential some physical quantities get altered (very sensitive is the orbital moment/magnetic anisotropy). In such cases one can start with large temperatures, converge it and then start a sequence of calculations in which the temperature is more and more decreased, in steps, which depend on the stability of the calculation. The second option is to use the 'LCiterat' iteration scheme from to iteration sub-menu.

Magnetic molecules have many spin multiplet states that are close in energy. During the course of a calculation (ex. geometry optimization), the system might jump from one spin multiplet state to another. In order to avoid such a scenario, it is safer to use the fixed-spin-moment module to fix the spin state. We will use this procedure for the next exercise.

## 2.2 Ground state of Ni<sub>2</sub> dimer using both fixed- spin-moment and force modules

The goal of this exercise is to find the correct spin state of the Ni<sub>2</sub> dimer. Therefore, we will perform self-consistent calculations for different spin moment values using the 'fixed-spin-moment' option. For simplicity, please use different directories for different total spin moments (in this example: `mom0` for  $0\mu B$ , `mom2` for  $2\mu B$ , and `mom4` for  $4\mu B$ ). For each spin moment, we will simultaneously optimize the length of the dimer using the force module. The following steps must therefore be repeated for each spin moment.

- Set up the structure using spacegroup 1 (one could also take into account some point group symmetry, for example spacegroup 123. Ni<sub>2</sub> dimer has a  $D_{inf h}$  point group symmetry. None of the space groups have this point group symmetry. Therefore, we use the  $D_{nh}$  sub group of the  $D_{inf h}$  point group). Ni1 at (0 0 1.5) and Ni2 at (0 0 -1.5) in spacegroup 1, otherwise only the first position has to be given. Please note that the unit of length used here is Bohr radii. We are starting with a Ni-Ni bond length of 3 Bohr radii.
- Turn ON the 'spin polarization' option (spin sorts).
- Increase the number of iterations to 200.
- Use the convergency criterion 'Density OR Energy'.

- Turn ON the fixed-spin-moment option and set the choice of spin moment.
- Turn ON the force module and set it to 'Site geometry optimization'.
- Run 'fplo'.
- The correct solution having the lowest energy is: Ni-Ni bond length 3.873 Bohr radii and a total spin moment of  $2\mu_B$ .

Note that the bond length of the Ni<sub>2</sub> dimer is increasing with increasing spin moment values. This is a result of the Pauli exclusion principle. When the spins of the two Ni atoms are aligned parallel to each other, larger the moment on each of the Ni atom, larger are their mutual repulsion due to Fermi statistics. This in turn leads to larger Ni-Ni separation.

Note that in molecules with even electron number only even spin moments (in Bohr magnetons) are allowed; in molecules with odd electron number only odd spin moments. (This only holds as long as spin-orbit coupling is disregarded.)

### 3 Structure optimization of Al

In this problem we will find the theoretical lattice parameters of Al. One can optimize the atomic positions within a unit cell by calculating forces and do a site geometry optimization. In Al there is only one atom per unit cell and its position is given by symmetry to be (0 0 0). So there are no internal positions to optimize. The forces on the Al atom are by symmetry exactly equal to zero.

In order to optimize the lattice constants we need to run several self-consistent calculations with different lattice constants. We then can plot the total energy as a function of the lattice parameters.

- How do the theoretical lattice parameters of Al depend on the functional used?
- How do the theoretical lattice parameters of Al depend on using full relativistic, scalar relativistic or non-relativistic functionals?
- How do the theoretical lattice parameters of Al compare to experiment? You can find experimental structures here: <https://icsd.fiz-karlsruhe.de/search/basic.xhtml> .

### 4 Partial density of states

The electronic structure of Al can be explained using a free electron theory with weak periodic potential or starting from local atomic orbitals and making a tight binding model. Calculate and plot the partial density of states for the Al *s* and Al *p* orbitals.

In order to calculate the DOS you need to go to FPLO and activate in the options menu (press -) the calc dos (press 0) option. This will calculate the total DOS, but also the partial DOSes.

In order to plot the comparison you can use  
 xfbp +dos.total +dos.total.l001 +dos.total.l002

## 5 Band-structure

In order to investigate the electronic structure further it is useful to look at the energy momentum distribution of the electronic eigenstates of Al. In this problem we will calculate the band-structure of Al and look at the partial  $s$  and  $p$  weight of the bands and their momentum dependence.

open fedit and press the space bar to get extra menu options. Go to the menu Bandplot (press B). Press B again to activate Bandstructure plot. We also want to look at the partial weights of the bands, so also set Weights on (press W). Have a look at the other options in this menu. Especially at the path calculated in k-space.

Once you saved the changes, rerun fplo (and save the output for example in out.band)

You can now plot the bands with  
xftp +band

the file +bweights contains the partial weights of the bands, i.e. if it is an s or p band. You can plot this with the command  
xftp +bweights In order to add the weight of the band go to the menu Edit - Sets. In the new popup window go to Weights. Now make the 3s red and the 3p blue.

## 6 Doping of Silicon

Calculate the effect of N, P and As doping in Silicon. We will use the experimental structure parameters of Si. You can find experimental structures here: <https://icsd.fiz-karlsruhe.de/search/basic.xhtml> . Enter "Si" in the field Composition under Chemistry and enter "1" in the field Number of Elements. Be careful to use the correct structure. First calculate the DOS and band-structure of pure Si and make sure you understand the bands. Once you have a converged calculation for Si generate a supercell with 8 Si atoms. You can use the conventional Cubic unit cell for this.

- (i) Compare the density of states and the band-structure for Si calculated using the space group  $F_{d-3m}$  and using the conventional cubic unit cell with 8 atoms.
- (ii) Replace one atom in the cubic unit cell with either N, P or As. (make 3 separate calculations). Make sure the unit cell has 7 Si and one substituted atom. Converge the calculation to a self consistent solution and calculate the density of states.
- (iii) Calculate the partial N, P and As density of states
- (iv) Compare the Density of states for the 4 calculations, i.e. pure Si compared to either N, P or As doped Si. Discuss the physical meaning of the results.