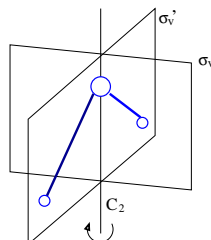


# Calculating Molecules with FPLO

In FPLO, molecules can be treated on the same footing like bulk systems. In this tutorial, we will calculate the ground state of two simple molecules,  $\text{H}_2\text{O}$  and  $\text{Ni}_2$  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.

## 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  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}$  has point group  $\text{C}_{2v}$  (space group: 25) with two mirror planes and a 2-fold rotation axis (please see the picture below). 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 (0 0 0); 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 is 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.

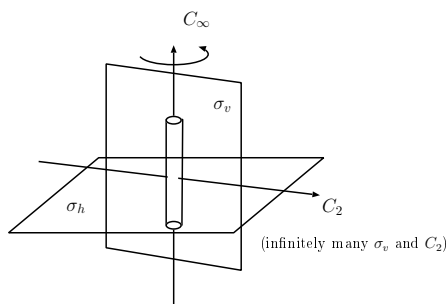
After force minimization, the positions of the atoms in the “Symmetry” menu are automatically updated with the optimized values from the last iteration. If you face convergency problems, one option is to increase the temperature and try again. Use the ‘Brillouin-Zone’ sub-menu option to change the temperature 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 the 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 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  $D_{\infty h}$  point group symmetry. None of the space groups have this point group symmetry. Therefore, we use the  $D_{nh}$  sub group of the  $D_{\infty h}$  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.)