Lab 4: Structure Optimizations, Hessian, Frequencies

Input files:
SCF.minimum_optimization.H2O.input
DFT.minimum_optimization.H2O.input
UHF.minimum_optimization.H2Oplus.input
SCF.minimization_plus_hessian.H2O.input
CASPT2.minimum_optimization.H2O.input
CASPT2.minimum_optimization_C2v.H2O.input

Introduction

In this lab we will do geometry optimizations, and frequency calculations. We will learn how to create the input and to find our way through the output. We will experience using the post processing utilities GV to analyse the results from the calculations.

Exercise 1: SCF optimization of water

In this exercise we will optimize a water molecule at the HF level of approximation.

Task 1:From the input identify which are the new features in the input that are new as compared to a point energy calculation. Note the shorthand in the input and that the gradient module (Alaska) is not explicitly referenced.

Task 2: Run the job (**molcas -f SCF.minimum_optimization.H2O.input**)! In the output identify
a) the number of macro iterations (*hint*: locate the string ”Energy Statistics”),
b) the final structure for which the energy was computed (*hint*: read carefully the text after the Energy Statistics section)

Task 3: Let us now use some of the resource files which were generated and also use some
additional keyword which can be useful in geometry optimizations.

1. Use GV to review the geometry optimization iteration by iteration! Hint: use the $Project.geo.molden file as input to GV and the Page-Up key (see Illustration 1).
2. Use GV to look at the molecular orbitals! *Hint*: use the $Project.grid file as input to GV (see Illustration 2).
3. Add the command “>export MOLCAS_PRINT=VERBOSE” to the top of the input and run the calculation again. What is the difference?
4. What happens if you use the OCCUPATION key word in the SCF input, does this affect the number of SCF and geometry iterations?
5. The optimization are done in so-called "force-constant-weighted" internal coordinates. There are also options to do the calculation in "standard" internal coordinates and Cartesian coordinates. Find these keyword (*hint*: molcas help slapaf), and try them. How did these changes affect the total number of iterations?
6. In the optimization a trust radius is used. Identify where you can find

the initial value of this parameter in the output, and how can you see if it is used. *Hint*: the trust radius is a parameter of the SLAPAF module (see Illustration 3). To see if it has been used look in the “Energy Statistics” section of the SLAPAF module and identify the presence of *s in the output (see Illustration 4). What happens if you set the initial value to 0.1 and 1.0 respectively (*hint*: Maxstep keyword)?

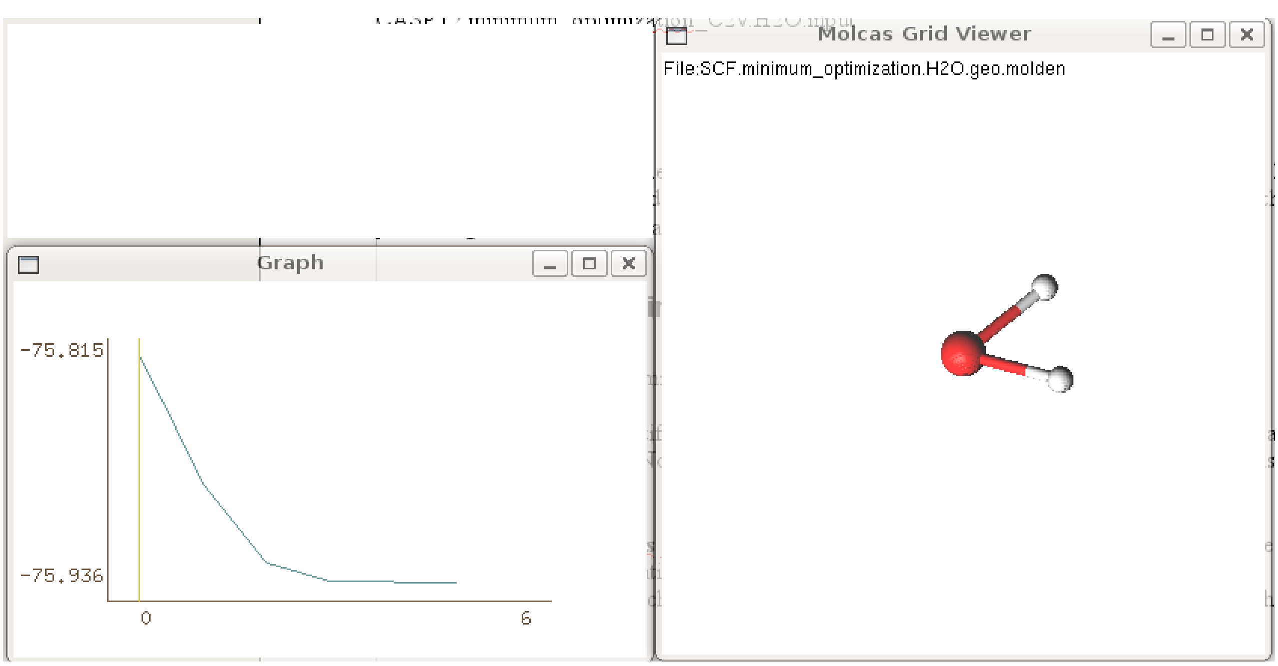

Illustration 1: View of geometry optimizaion by GV.

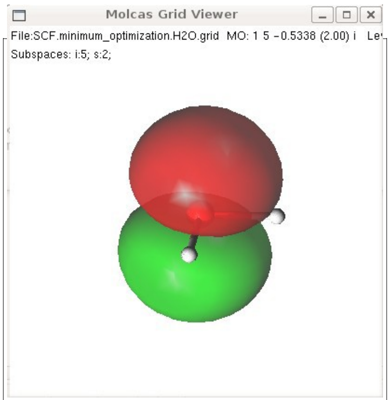

Illustration 2: Orbital view using GV.

```
()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()
                                  MOLCAS executing module SLAPAF with 1024 MB of memory
                                              at 13:52:52 Sat Apr 25 2009
()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()


 Max iterations:                        200
 Convergence test a la Schlegel.
 Convergence criterion on gradient/para.<=: 0.3E-03
 Convergence criterion on step/parameter<=: 0.3E-03
 Convergence criterion on energy change <=: 0.1E-05
 Max norm of step:      0.30E+00

 Line search is performed


 -Optimization for minimum.
  Optimization method: RS-RFO.

 -Initial Hessian guessed by Hessian Model Function (HMF).
  HMF augmented with weak interactions.

 -Hessian update method: Broyden-Fletcher-Goldfarb-Shanno
  Max number of points in Hessian update:  5

 -Relaxation will be done in nonredundant internal coordinates, based on
  force constant weighted redundant internal coordinates.
```

Illustration 3: Parameters of the geometry optimization as printed by the SlapAf module.

```
()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()
                        MOLCAS executing module SLAPAF with 1024 MB of memory
                                  at 13:52:52 Sat Apr 25 2009
()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()()


 Max iterations:                          200
 Convergence test a la Schlegel.
 Convergence criterion on gradient/para.<=: 0.3E-03
 Convergence criterion on step/parameter<=: 0.3E-03
 Convergence criterion on energy change <=: 0.1E-05
 Max norm of step:      0.30E+00

 Line search is performed


 -Optimization for minimum.
  Optimization method: RS-RFO.

 -Initial Hessian guessed by Hessian Model Function (HMF).
  HMF augmented with weak interactions.

 -Hessian update method: Broyden-Fletcher-Goldfarb-Shanno
  Max number of points in Hessian update:  5

 -Relaxation will be done in nonredundant internal coordinates, based on
  force constant weighted redundant internal coordinates.
```

Illustration 4: The Energy Statistics setion of the SlapAf module.

Exercise 2: UHF H2O+ and DFT H2O optimization

In this exercise we will play around with optimizations with other types of wave functions.

Task 1:Look at the input files and take notice on how you can change between different wave function models.

Task 2: Run the jobs and identify the total number of iterations. How should

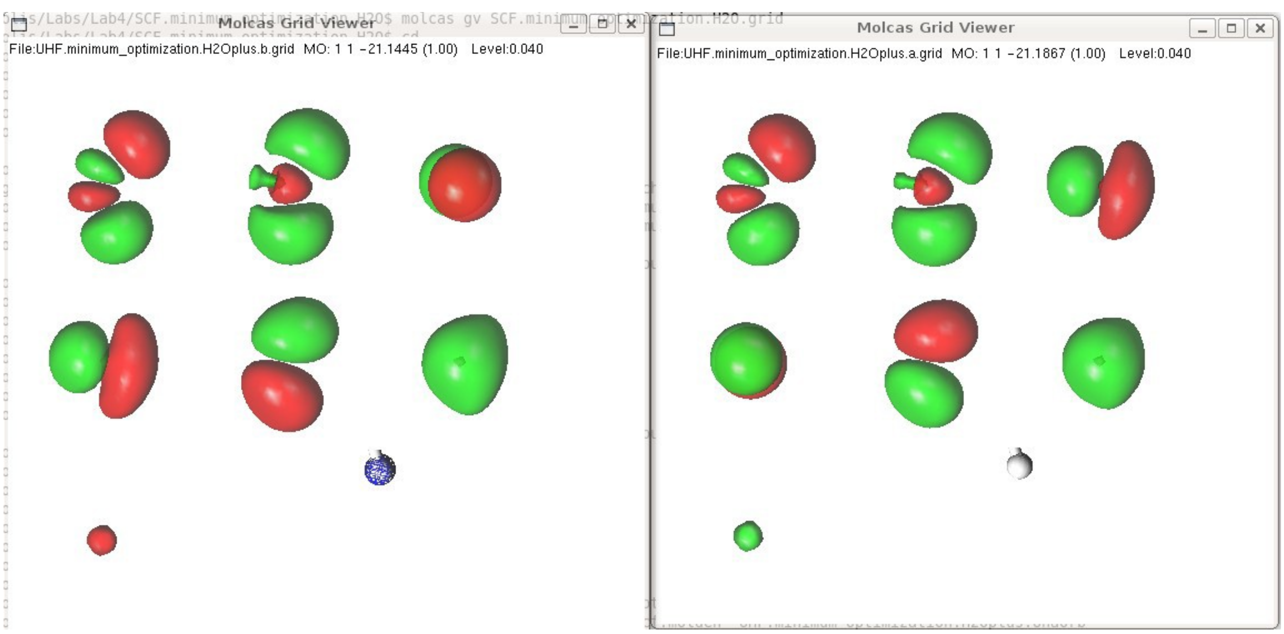

Illustration 5: UHF alpha and beta orbitals as viewed with GV.

you modify the input to get the printout from all interactions (hint: look at previous exercise)?

Task 3: For the UHF use GV to compare the alpha and beta orbitals (see Illustration 5)!

Exercise 3: water SCF minimization and frequencies

In this exercise we will go one step further and directly make a frequency calculation after the completed geometry optimization.

Task 1: Look at the input and identify the additional input which is needed to make a frequency calculation (**hint**: look at the end of the input, see Illustration 6),

Task 2: Run the job and identify
a) which modules in MOLCAS are used,
b) the frequencies (see Illustration 7),
c) the isotopic shift for single substitution, and
d) if there is some thermodynamical information.

Task 3: How do you compute isotopic shifts for double substitutions? *Hint*: consult the manual or ”molcas help” for the MCKINLEY and MCLR module. Note that the MCKINELY module normally starts up the MCLR module automatically. When you want to specify an explicit MCLR input you have to override this feature!

```
 &GATEWAY
Title
 H2O minimum optimization
Basis set
O.ANO-S...2s1p.
O        0.000000  0.000000  0.000000 Angstrom
End of basis
Basis set
H.ANO-S...1s.
H1       0.758602  0.000000  0.504284 Angstrom
H2       0.758602  0.000000 -0.504284 Angstrom
End of basis

>>> Set maxiter 100
>>> Do while

 &SEWARD
 &SCF; Title="H2O minimum optimization"
 &SLAPAF &END

>>> EndDo

 &Grid_It
 &MCKINLEY
```

Illustration 6: Input for SCF optimization and frequency calculation.

Task 4: Use GV to inspect the normal modes of the vibrations! Hint: use the $Project.freq.molden file. What is ”wrong” with the rotations and translations?

Task 5 (if you have time): Modify the input to use the Cholesky decomposition technique! Compare the computed frequencies! Try also to compute the structure and frequencies for a B3LYP DFT functional!

Exercise 4: CASPT2 water optimization

In this exercise we will do a geometry optimization for a module for which we do not have analytic gradients.

Task 1: Look at the input and identify the various components.

Task 2: Run the job! Can you identify the numerical differentiation section in the output?

Task 3:Remove the keyword ”Frozen=1” and rerun. How many orbitals are frozen in the CASPT2? Run it again but now with no frozen orbitals.

		1	2	3	4	5	6
Freq.		0.00	0.01	0.02	6.48	8.75	9.66
Intensity:		0.293E-18	0.415E-19	0.269E-07	0.260E+03	0.875E+02	0.148E-15
O	x	0.00000	0.23563	0.00000	0.00000	0.00000	0.00000
O	y	0.23563	0.00000	0.00000	-0.08365	0.00000	0.00000
O	z	0.00000	0.00000	0.23563	0.00000	0.04855	0.00000
H1	x	0.00000	0.23563	0.00001	0.00000	0.57356	0.00000
H1	y	0.23563	0.00000	0.00000	0.66377	0.00000	0.70436
H1	z	0.00000	0.00000	0.23563	0.00000	-0.38528	0.00000
H2	x	0.00000	0.23563	-0.00001	0.00000	-0.57356	0.00000
H2	y	0.23563	0.00000	0.00000	0.66377	0.00000	-0.70436
H2	z	0.00000	0.00000	0.23563	0.00000	-0.38528	0.00000

		7	8	9
Freq.		1637.08	3538.73	3816.09
Intensity:		0.540E+02	0.746E+01	0.139E+02
O	x	-0.06933	-0.04680	0.00000
O	y	0.00000	0.00000	0.00000
O	z	0.00000	0.00000	-0.06811
H1	x	0.55018	0.37135	0.40884
H1	y	0.00000	0.00000	0.00000
H1	z	-0.39406	0.58381	0.54051
H2	x	0.55018	0.37135	-0.40884
H2	y	0.00000	0.00000	0.00000
H2	z	0.39406	-0.58381	0.54051

Illustration 7: Frequency section. Frequencies in cm-1 and intensities in km/mol.

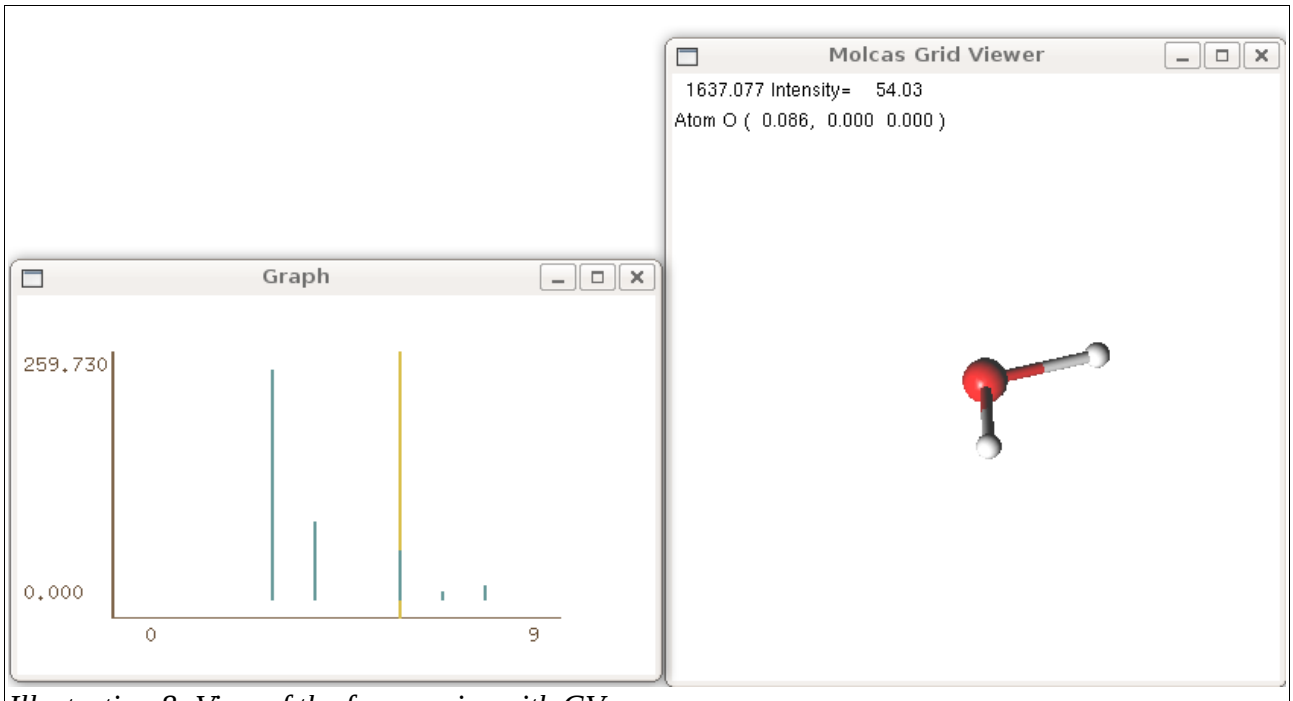

Illustration 8: View of the frequencies with GV.

Task 4:Modify and compute frequencies! Compare CASPT2 and B3LYP frequencies. Btw, how many frequencies are reported in the case of numerical frequencies?

Exercise 5: CASPT2 water optimization with symmetry (if time permits)

This exercise is similar to 4 but here we will use symmetry.

Task 1: Run the job and compare the number of displacements that are used with and without symmetry.

Task 2: Modify the input so that you use only the X or the Z symmetry operator(hint: find the SYMMETRY keyword and eliminate one or the other symmetry operator. Remember to make sure that coordinates and commands to the wave functions are correct with respect to the reduced symmetry). Rerun and check that you get the correct result.