

Lab 5: Transition states, reaction paths, constraints

Input files:

CASSCF.minimum_optimization_restricted.H2O.input

DFT.minimum_optimization_restricted.H2O.input

DFT.transition_state.H2O.input

DFT.transition_state_restricted.H2O.input

reac.input

prod.input

ts.input

CASSCF.mep_excited_state.acrolein.input

.xyz files:

reac.xyz

prod.xyz

Introduction

In this lab we will study techniques for a) how to use constraints, b) how to fix internal coordinates, c) compute transition state optimization, d) transition state frequencies, e) intrinsic reaction coordinate (IRC) paths and f) how to compute minimum energy reaction (MEP) paths.

Exercise 1: Constrained water CASSCF optimization

In this exercise we will use constraints in the optimization. In this particular case we will constraint the angle HOH angle to 90. degree.

Task 1: Look in the input and identify where in the input the constraint is specified. *Hint:* look in the Gateway section of the input. Note that this constraint section could be in the Slapaf section too.

Task 2: Run the job and look in the SlapAf output, identify the value of the constraint at convergence (see Illustration 1). What was the value on the first iteration?

Task 3: The optimization in Task 2 was done with an ANO-S-MB basis set. We will now modify the input to at once use the result and proceed with optimization with a ANO-S-VDZP basis set. Do as follow a) copy the whole input and place the copy at the end of the input file, b) change the basis sets labels from ANO-S-MB to ANO-S-VDZP (for H and O), c) add the following two line

```
>COPY $Project.RunFile $Project.RunOld
```

```
>RM $Project.RunFile
```

in between the old input and the new input sections and finally d) add the keyword OLDFCM to the second input to the Slapaf module. Run the job. Identify that the second input did not use the input coordinates from the input file but rather read it from \$Project.RunOld and identify that the keyword OLDFCM meant that the force constant matrix (the Hessian) was read from the \$Project.RunOld. How many iterations to the second optimization?

```

ConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraints
ConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraints
Constraints
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C O N S T R A I N T S
Constraints
Constraints
Constraints
*****
A = ANGLE H1 O H2
VALUE
A = 90. DEGREE
*****

*****
* Values of the primitive constraints *
*****
A      : Angle=      75.8227   / Degree    1.323355 / rad

*****
* Values of the constraints / au or rad *
*****
Label      C      C0
Cns001     1.323355 1.570796

Constraints
ConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraints
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ConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraintsConstraints

```

Illustration 1: The constraint section in the Slapaf output of the 2nd iteration.

Task 4: Compute the PES along the HOH angle from 90 to 180 degree. Make a plot. Hint: use the FOREACH loop structure and the optimized structure for the previous constraint as the start for the next optimization. Instructions: a) place at the top of the input the following line

```
> FOREACH ANGLE in (90., 100., 110., 120., 130., 140., 150., 160., 170., 179.9999.)
```

b) at the end add the following three lines:

```
>COPY $Project,RunFile $Project:RunOld
```

```
>RM $Project.RunFile
```

```
>End Do
```

and c) substitute the hardwired value of 90.0 in the constrained input section with the variable \$ANGLE. Why should the last angle not be exactly 180. degrees? How many iterations was required for convergence for each individual constraint?

Task 5: Make a study in which you compute the energy curve as the water dissociate into H + OH. *Hint:* define one of the OH bonds to be constrained and do a series of calculations in which you extend the distance.

Exercise 2: Fixed water DFT optimization

Another way of doing optimizations in which a particular internal coordinate should have a specific value is the FIX option.

Task 1: Look at the input and identity the FIX option. Discuss advantage and disadvantage as compared to the method of exercise 1. *Hint:* what is the difference between the starting structure for a constrained geometry optimization and that one of a optimization with fixed internal coordinates?

Task 2: Run the job. Check that the fixed internal coordinate really has the same value for all iterations! *Hint:* you need to set MOLCAS_PRINT=VERBOSE to get this information in the output.

Task 3: Modify the input to be for a fixed angle. Run the job.

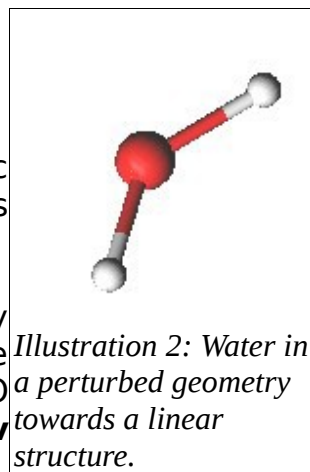
Exercise 3: Water DFT transition state optimization (TS option)

Transition states are more difficult to find as compared to normal optimizations. In this particular example we are using the most simplest way (using the TS option) of finding the transition state of linear water. The starting structure is that of water slightly perturbed away from its equilibrium structure (the x-coordinate of the oxygen is set to 0.75, see Illustration 2). *If one starts with the equilibrium structure the gradient is zero and the optimization procedure will terminate at once! The perturbation is in the direction of dissociation. Why? Since we are looking for the linear transition structure we have opened up the structure.*

Task 1: Run the job and look at the output.

Task 2: Make a input file and compute the harmonic frequencies of the TS structure. Monitor the normal modes with GV.

Task 3: The success of this approach can easily fail! Modify the x-coordinate of the oxygen to 0.25 and try to find the TS! What did you get? *Hint:* cd to DFT.transition.state.H2O and use GV to monitor the optimization (**molcas gv DFT.transition.state.H2O.geo.molden**).



Exercise 4: Water DFT transition state optimization (FindTS option)

This example is doing the same as above ($x=0.25$), however it is using a slightly different approach (using the FindTS option in connection with a constrained optimization). Compare the input with that of Exercise 3.

Task 1: Run the job and compare the number of iterations as found in Exercise 3 (*hint:* look at the last “Energy Statistics” output).

Task 2: Take as the starting geometry that of fully optimized H₂O (you will have to generate that structure yourself! *Hint:* take the input used in Exercise 3 and remove the TS keyword). Run the TS optimization.

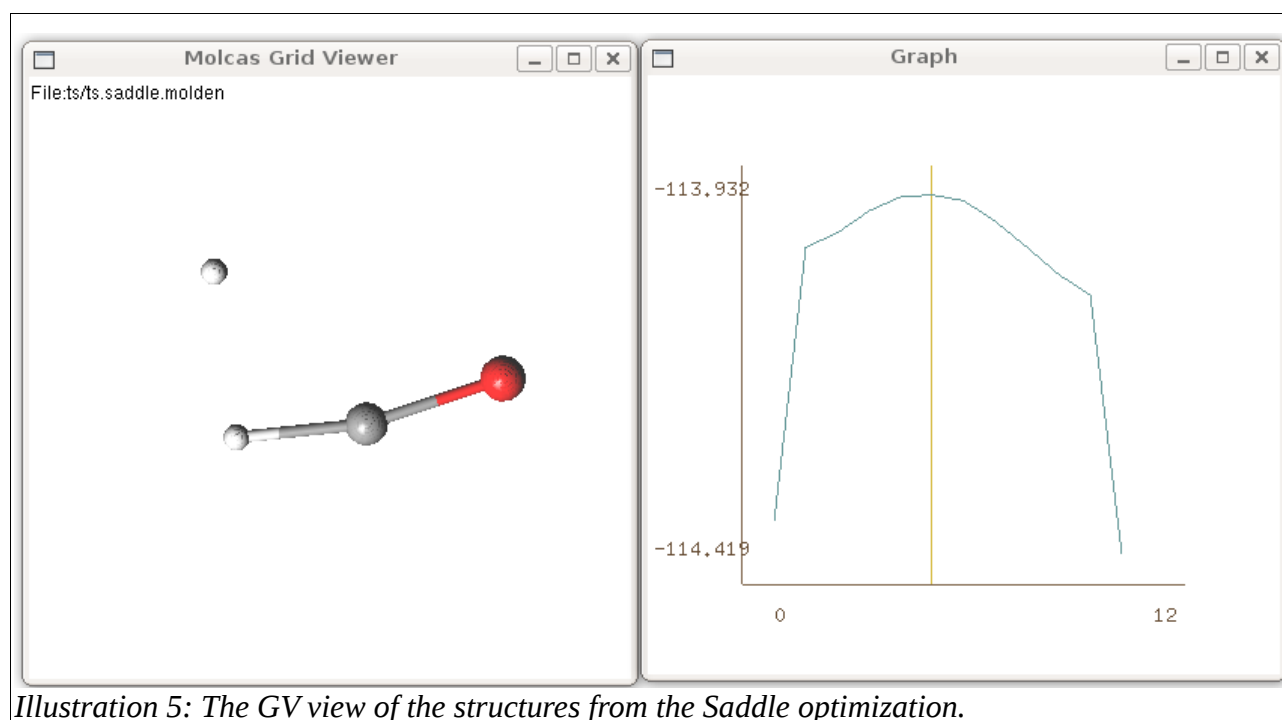
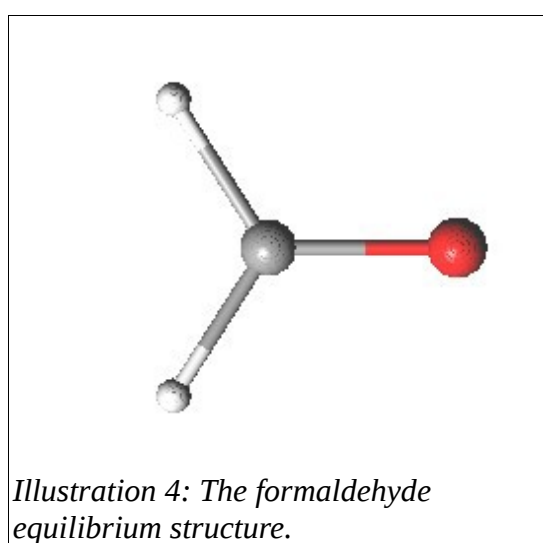
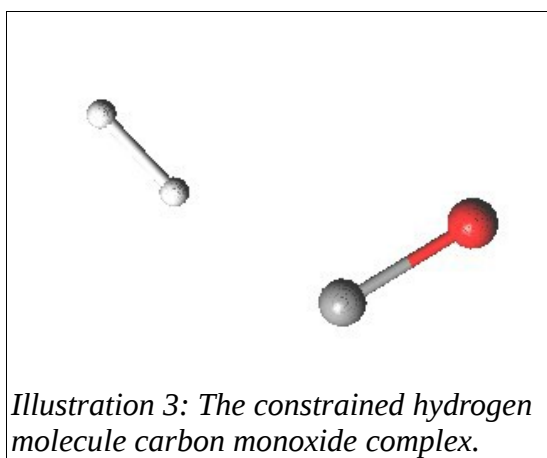
Task 3: Let us assume that you didn't really know where the TS was. Would you get the TS if you guess 160. or 140. degree (**hint:** do the calculation in Task 1 with different values specified for the constraint).

Task 4: We note that the TS is of higher symmetry. How could you find the TS in yet a third way? *Hint:* make a normal geometry optimization but with input such that the water molecule is constrained by symmetry to be linear.

Exercise 5: $H_2 + CO \leftrightarrow H_2CO$ TS optimization (Saddle method)

In this example we will find the TS of the formation of formaldehyde from hydrogen and carbon monoxide using the Saddle method to find the TS. Note that the Saddle method in principle is a series of constrained optimization. This will result in a large total number of iterations. For that purpose we set MAXITER to the value of 200 or large when we do the TS optimization (Task 2). Once we have found the TS we will verify it with IRC and frequency calculations.

Task 1: The Saddle method needs the energies and the associated structures at either side of the TS. Run the react.input to find the structure of the $H_2\cdots CO$ complex (see Illustration 3). Note that this complex is not bound and that we use constraints to find a suitable structure at this side of the TS. Here we have selected a constraint which drags one of the hydrogens in towards the carbon. This will hopefully generate a structure which is in the correct reaction channel.



Task 2: Do the same for the product (prod.input), formaldehyde (see Illustration 4).

Task 3: Take the energies and structures from **Task 1** and **Task 2** and put them into the RP-Coor input section in the file ts.input. Run the job. Monitor the Saddle structures with GV after completion (**molcas gv ts.saddle.molden**, see Illustration 5).

Task 4: Modify the input so that an automatic IRC calculation will be performed after the TS optimization. Instructions: a) copy the whole input and place the copy at the end of the input file, b) in the second part of the input remove the RP-Coord section from the input, c) copy the RunFile to RunOld and remove RunFile (see Exercise 1: Task 3), and finally d) add the keyword IRC to the input of the second Slapaf input section. Run the job (this will take some while so proceed with Exercise 6 while you wait for the result!). View the IRC with GV (see Illustration 6, 7 and 8).

Task 5: Modify the input again to compute the vibrational frequencies. View the normal modes with GV.

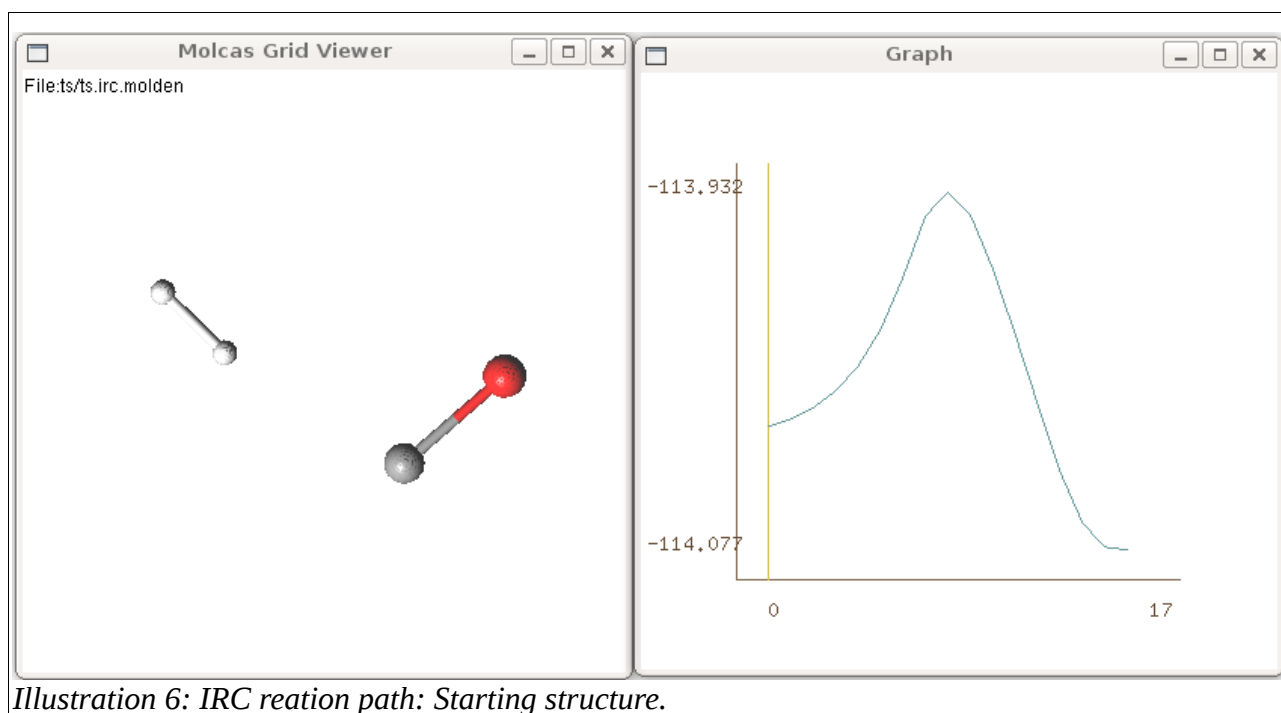


Illustration 6: IRC reaction path: Starting structure.

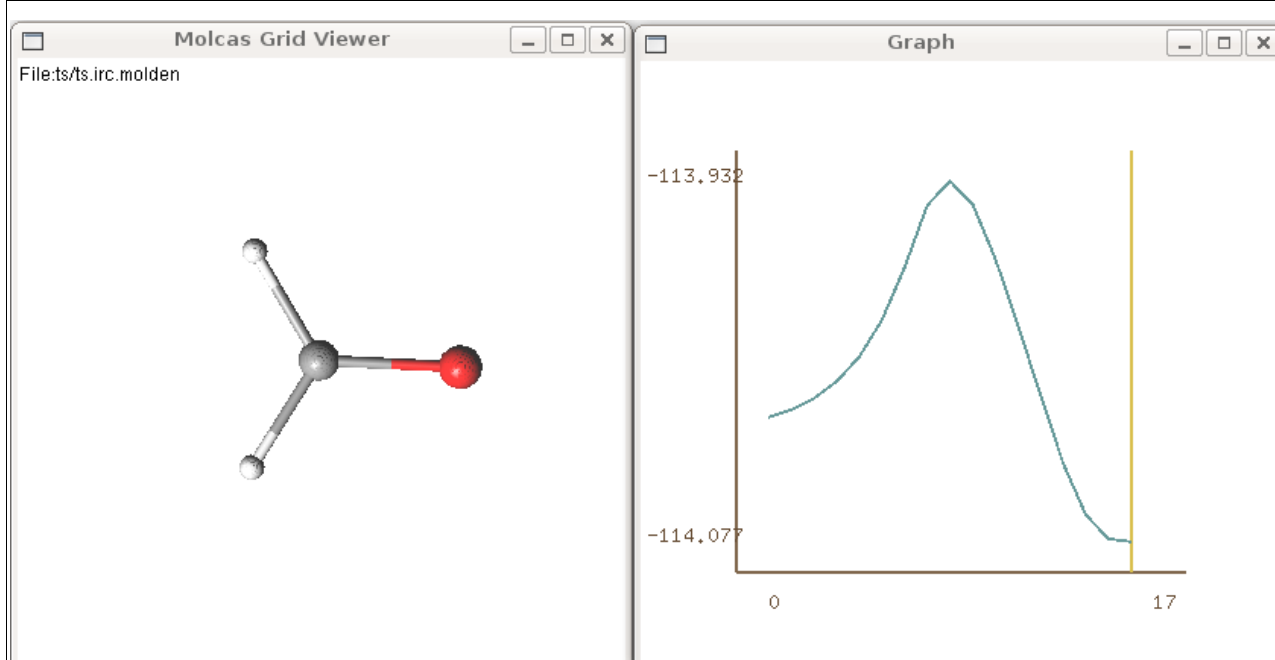


Illustration 7: IRC reaction path: product structure.

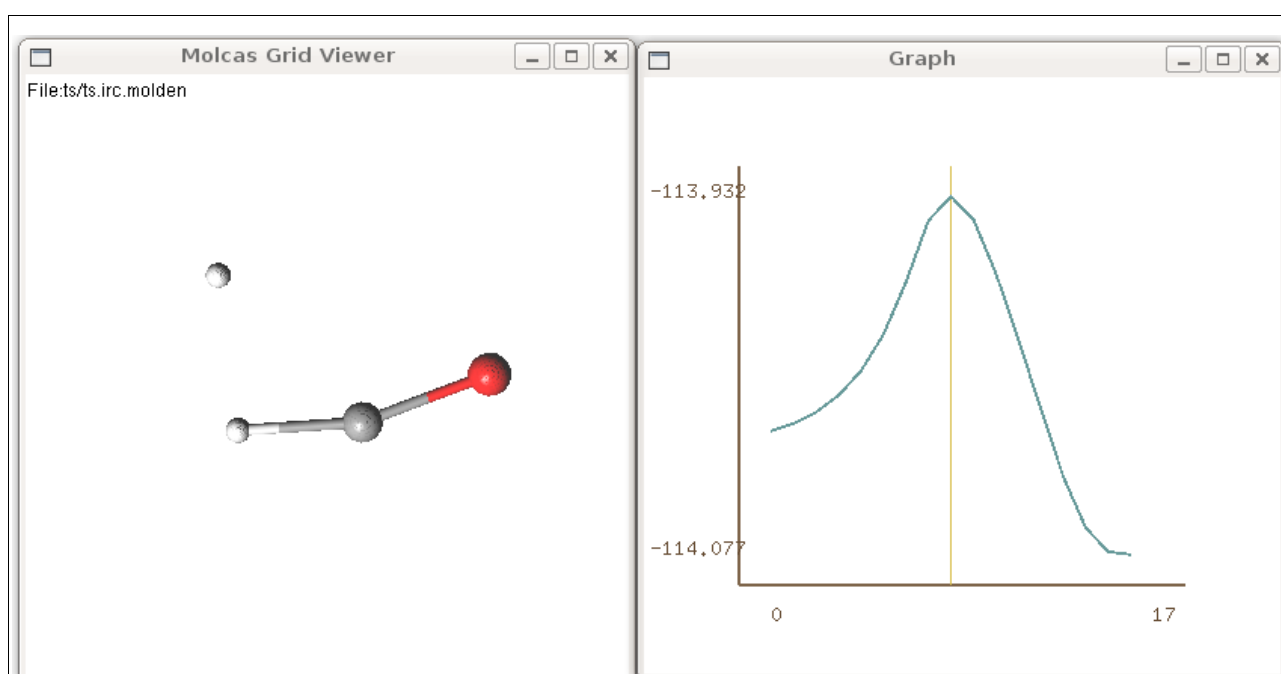


Illustration 8: IRC reaction path: TS structure.

Exercise 6: Acrolein CASSCF MEP optimization

In this example we will compute the minimum energy path (MEP) from the FC region of the first excited state of acrolein. The starting structure in the input is that of acrolein in equilibrium in the GS.

Task 1: Look at the input and note the differences as compared to a normal optimization. *Hint:* look in the input section for the SLAPAF module. Run the job and monitor the MEP with GV after completion (see Illustration 9). *Hint:* used the \$Project.mep.molden file.

