

5 Troubleshooting, Pitfalls, Traps

If you routinely use electronic structure methods, there is probably not one week passing without a run crashing, leaving you puzzled by a (sometimes mysterious) error message. Even if your run reaches the longed for **Normal termination**, this will not necessarily mean that your results are meaningful; the method that you used may in the end turn out to have been an inappropriate choice. This brief exercise deals with the most important error messages you may encounter.

5.1 How to Abort a Running Job

After submitting your job, you can *kill* it at any time by pressing **ctrl+c** in the window that the job was submitted in. However, this will not work if the job was submitted to the background using **&**. In these cases, use the command **top** to display all the running processes. In **top**, find out what the process ID or *PID* (first column) of the job is that you would want to kill. Then, in **top**, you may hit **k**, and **top** will ask for a PID to kill. Enter the PID of the desired process and hit enter. **Top** will then prompt for the kind of kill signal to send. There exist two important signals: *15* will let the process quit gracefully if possible, whereas *9* will just blindly kill it. It is often advisable to use *15* first and only send a process a *9* signal if it does not react to *15*.

5.2 Error Termination Of Gaussian...

You may download the inputs for this exercise from the webpage where you usually obtain the course script. Run the jobs and find out what is wrong with them. In your report, indicate what the source of the error message was and how you resolved the problem. Use the Gaussian manual on gaussian.com to find possible solutions to the error messages that the following inputs will induce (and do not forget that the assistants are there to help you if you have any questions):

- a) Run **allyl_radical.inp** to perform a single-point wavefunction optimisation for the allyl radical using the BLYP exchange-correlation functional.
- b) Run **N2_nosymm.inp** to perform a geometry optimisation of N_2 using the BP86 exchange-correlation functional.
- c) Run **O_nosymm.inp** to perform a single-point optimisation of the ^3O wavefunction using the B97-2 exchange-correlation functional (keyword: B972), turning off explicit orbital symmetries.
- d) Run **Cu_aqua.inp** to perform a single-point wavefunction optimisation of the $\text{Cu}[\text{H}_2\text{O}]^{2+}$ aqua complex (as observed in the gas phase) using **Symmetry=None** and the PBE exchange-correlation functional (keyword: PBE). *Hint*: Using the same approach as in the example of the oxygen atom will probably not work in this case.

6 Density Functional Theory - Comparison with (Post) Hartree-Fock Methods

All methods discussed so far evaluate the energy of a system based on its wavefunction Ψ ; a purely mathematical object that lacks any direct physical interpretation. In the next two sets of exercises, you will explore a formalism that is based on a physical observable, called *Density Functional Theory* (DFT). Rather than linking observables to abstract wavefunctions, DFT relates any observable to a physical, measurable quantity, the electron density ρ (*cf.* figure 1). In the next two sets of exercises, you will assess the performance of various state-of-the-art density functionals in the prediction of reaction enthalpies and geometric properties, and you will compare your results to both wavefunction theory and experimental data. The first exercise constitutes more of a practical introduction; you will be provided with more ample theoretical information on DFT in the following week.

6.1 Thermochemical Properties of an Aldol Reaction: Performance of DFT, HF and MP2

The approximation in wavefunction based methods lies in the restriction and truncation of the expansion of Ψ ; the Hamiltonian is exact. In DFT, instead, the approximate quantity is incorporated into the Hamiltonian. This approximate term is called the *exchange-correlation functional*, and without further elaborating on methodological details (we leave this for the oncoming week), you will now explore the performance of

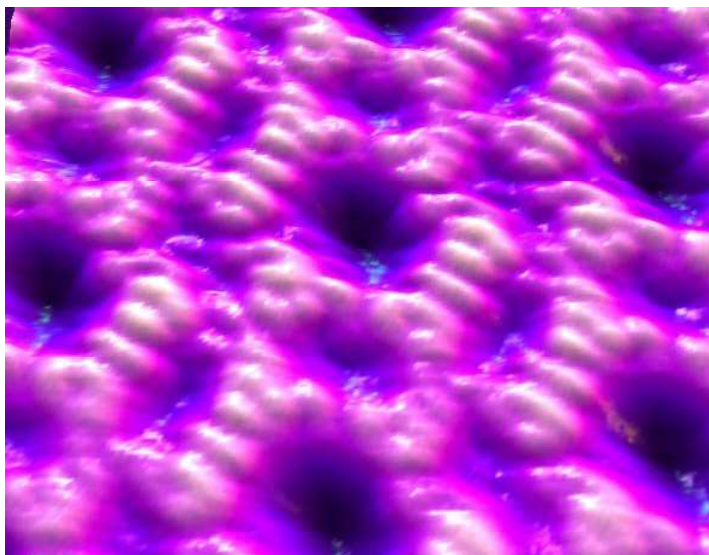
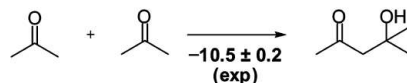


Figure 1: STM image of the electron density of a self-assembled layer of benzenedicarboxylic acid isomers at a liquid-solid interface. *J. Phys. Chem. B*, **2014**, 108, 13652.

various exchange-correlation functionals of differing complexity in the prediction of a reaction enthalpy. By doing this, you will also learn how to create chemical structures in Molden.

Aldol Reaction of Acetone

Consider an organic chemistry classic, the Aldol reaction between two molecules of acetone (*J. Phys. Chem. A*, **2009**, 113, 10376).



The value for the reaction enthalpy at 0 K, ΔH_{0K} , is found to be -10.5 kcal mol⁻¹ based on experimental data. The reaction enthalpy at 0 K is simply given by the differences in potential energy between reactants and products.

Creating Molecules in Molden

For larger molecules, the creation of an approximate xyz file that can be used as the molecular input coordinates is impossible. In these cases, one may refer to the drawing ability of Molden. First, we may want to create coordinates for acetone. Run Molden without a file to read:

`molden`

and click on **ZMAT Editor** (it is advisable to do this in the **Ball & Stick** drawing mode). Then, click on **Substitute atom by Fragment** and select CH4. The screen will now show a methane molecule, starting from which you may create your target species. Click on one of the hydrogens, such that it is marked by a red ball. By selecting **Substitute atom by Fragment** again, you may now substitute this atom by a -HC=O carbonyl group. Click on the new hydrogen atom of the carbonyl group and substitute it by a methyl group -CH3. The molecule is now completely constructed and the coordinates are ready to be saved. In the main *Molden Control*, click on **Write**, select **xyz**, and specify a filename of your choice. The coordinates are now saved to an xyz file, which is a common format to exchange molecules between different programs. Do not close Molden at this point.

You are now ready to create the product structure. As you wish to calculate the structure as given in the reaction mechanism, you must be careful not to randomly replace atoms, but to adhere to the desired geometry (it turns out that the product conformation you are about to construct is the minimum energy conformation). As we wish the hydroxyl group of the product to be hydrogen-bonding to the carbonyl group, we first have to rotate one of the methyl groups so that its hydrogen is in plane with the carbonyl group. It is easiest to do this by cleverly choosing a hydrogen atom. It may be more convenient to do the following for the methyl group you added last. By clicking on one of the hydrogens, it will be highlighted in the Z-matrix. If you click on the dihedral angle instead of the element symbol in the Z-matrix editor, you will see to which atom(s) the

current selection is connected, as illustrated in figure 2.

Probably, two of the three hydrogens will be specified by a dihedral with respect to one hydrogen of the same methyl group, the carbon atom of the methyl group, and the neighbouring carbon. We do not want to change any of these parameters, as they internally fix the structure of the methyl group, and we simply want to rotate the methyl group without changing its internal structure. Find out which of the hydrogen dihedrals is given with respect to the oxygen of the carbonyl group. Click on this dihedral, delete the current value of 180° , and replace it by a value of 0° . This will cause the methyl group to rotate. You may now select the same hydrogen again, and substitute it by an other methyl group. The carbon atom of this methyl group will now be in plane with the carbonyl group. Again, the methyl group will probably need to be rotated such that the final hydroxyl group that you will construct lies in plane as well. Proceed as before: Select the hydrogen of the methyl group that determines the rotation of the whole group, *i.e.* the one which has a dihedral that is specified with respect to the carbonyl C (again, click on the value of the dihedral to see which atoms are involved). Change this dihedral angle to 0° as well, such that the desired atoms are now all in plane. Then, you may substitute the in-plane hydrogen by a hydroxyl group. This hydroxyl group should be hydrogen bonding to the carbonyl. You will thus have to change the value of the dihedral that specifies the O-H bond. If you click on the dihedral, you will see that it is defined in terms of all the neighbouring carbons. Change the value from 180° to 0° again, and you will end up with the desired chelating structure. In the end, all that is left to do is

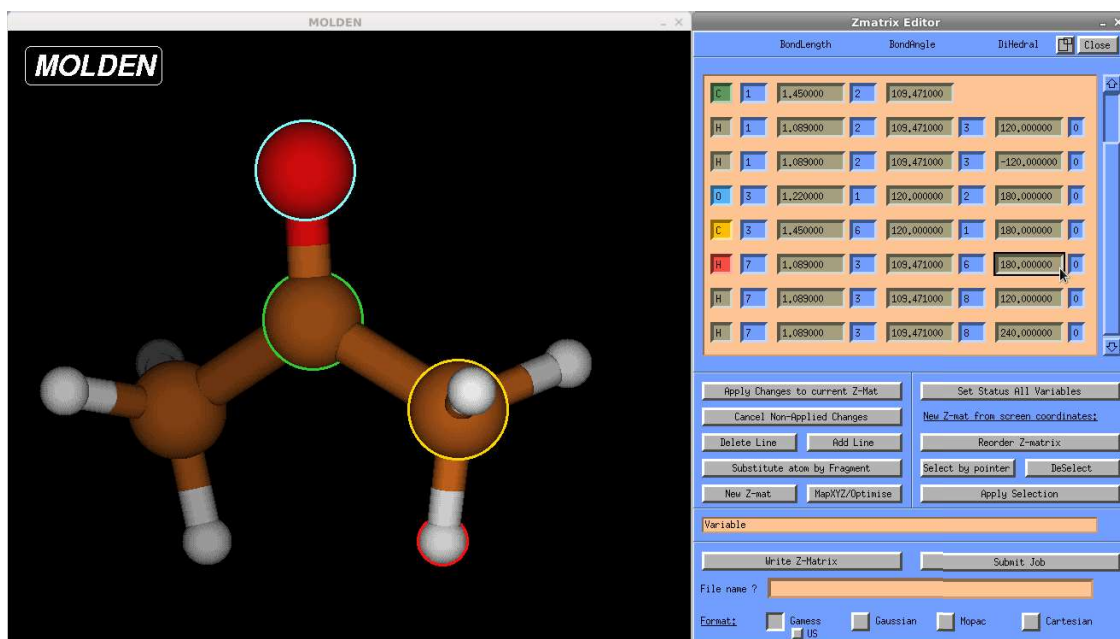


Figure 2: Visualising connectivities in the Z-matrix editor.

to substitute the remaining hydrogen atoms with one methyl group each. Then, save the coordinates of your product structure to a new xyz file.

- a) Take a screenshot of your product structure and enclose it in your report.

Copy your xyz files to .com files with the same name, then open them in vi. You will see that an xyz file has a very simple structure, namely a number that specifies the number of atoms, a blank line (which may be used as a comment line), followed by the coordinates in xyz format. Delete the first two lines of the .com file and provide the additional information needed for a Gaussian input file based on the existing coordinates. As a reminder, the format for a Gaussian input file is:

```
%NProcShared=2
%Mem=1GB
%Chk=CHECKPOINTNAME
#P METHOD/BASIS_SET Opt
```

COMMENT

CHARGE MULTIPLICITY

LIST OF XYZ COORDINATES

Of course, there must be a blank line at the end. Because the following calculations will take some considerable time, you will be split in groups, each optimising the energy at different levels of theory.

- b) Your assistants will assign to each of you one or two level(s) of theory. Create the corresponding Gaussian input files using the 6-31+G(d,p) basis. For MP2 calculations, you should start from a HF geometry and the Checkpoint file using %OldChk=, indicating Guess=Read as well as Geom=Checkpoint in the route section. Submit your jobs to Gaussian one at a time, then complete the following table with the information from your fellow students.

Method	$E_{reactant}$ [a.u.]	$E_{product}$ [a.u.]	ΔH_{0K} [kcal mol ⁻¹]
Exp.	n/a	n/a	-10.5
Ψ based:			
HF			
MP2			
ρ based:			
BLYP			
mPW1PW91			
B97-2			
M06-2X			

- c) What kind of basis set did you use? On which atoms will polarisation and diffuse functions be included?
- d) Comment on the performance of the wavefunction based methods and DFT for this reaction. Can you imagine why some DFT methods perform better than others? How does DFT compare to MP2 and HF? Would you expect the exchange-correlation functionals to give similar errors in different systems?
- e) An often cited target for the development of exchange-correlation functionals is an error below *chemical accuracy*, *i.e.* within 1 kcal mol⁻¹ of the accurate result. A coupled-cluster based scheme called CBS-QB3 predicted $\Delta H_{0K} = -9.2$ kcal mol⁻¹ for this reaction. In light of this, explain the accuracy of the results that you obtained.
- f) Why is it important to construct the starting material and the product in a specific conformation, although one is carrying out a geometry optimisation for both species?