QUANTUM CHEMISTRY WITH *GAUSSIAN* : A *VERY* BRIEF INTRODUCTION (PART 2)

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This tutorial continues introduction to *Gaussian* [2]. Here we concentrate on single point energy calculations on a molecules of water and formaldehyde, geometry optimization, frequencies and normal modes. For more detailed discussion please see [2, 1]. Basic knowledge of Unix/Linux and *Gaussian* is assumed. See for example previous tutorials [4, 5]. Estimated time to complete this tutorial is 1.5 hrs.

1. Software

One will need: text editor, ssh client, molecule builder and viewer.
Suggestions:
Molecule builder: *Avogadro* (http://sourceforge.net/projects/avogadro/files/)
Molecule viewer: *Molden* (http://www.cmbi.ru.nl/molden/molden.html)
Mac:
Text editors: TextEdit, Vim,
SSH client: built in Terminal , scp or Fugu for file transfers
PC:
Text editor: Notepad, vim
SSH client: putty, WinSCP for file transfer

2. Formaldehyde single point energy and molecular orbitals with MP2

Install *Avogadro* on your computer, if needed.
Open *Avogadro* and Select Element: `Carbon(6)`
Click once anywhere is the main window and watch an atom of carbon to appear and four hydrogens being added.
Select Element: `Oxygen(8)` and click on one of the hydrogens. It will be converted into an oxygen atom with a hydrogen atom.
Select Bond: double and pull from the oxygen towards carbon. Double bond will be formed and hydrogen removed.
Prepare *Gaussian* input file: Open `Extensions`, *Gaussian*.
Note: the coordinates are already listed in the *Gaussian* Input plugin.
Enter title: `CH2O SP MP2`

Date: March 16, 2010.

Select: `Calculation:` Single Point Energy, `Theory level:` MP2, `Basis:` 6-31G(d), `Charge:` 0, `Multiplicity:` 1.

To use the Z matrix form select `Format` Z-matrix. Please make sure to understand the way Z-matrix is generated from Cartesian coordinates. Briefly, it is a way to describe molecular structure using internal coordinates. First line introduces the starting atom. Second line contains the second atom and the bond distance to the first. Third line gives the bond length to the first and the angle formed by this bond and the bond between two previous atoms. Fourth line adds the value of the dihedral angle between two planes: formed by atoms one through three and the current atom and atoms one and two.

Click: `Generate` button.

Save as: `CH2O-SPE-MP2.com`

Open the newly created CH2O-SPE-MP2.com file in a text editor of your choice.

Add in the end of the first line `Pop=Reg formcheck` to request information about molecular orbitals to be printed.

Copy *Gaussian* input file to triton using `scp` command.

`> ssh triton`

Make a directory `ch2oSP` in your home directory.

Copy *Gaussian* input file to triton using `scp` command.

Note: please see the Unix/Linux Primer if you need to refresh your knowledge of the OS.

Setup your environment:

`> source /share/apps/gaussian/g09_login.csh`

Start Gaussian job with prepared files:

`> g09 < CH2O-SPE-MP2.com > CH2O-SPE-MP2.log`

Note: `<` is the "pipe" flag to direct the input file to *Gaussian* and the output into .log file.

3. *Gaussian* OUTPUT: BASIC ANALYSIS

Open `CH2O-SPE-MP2.log` in a text editor and locate the following: Input data, Standard orientation, Number of basis functions used, Single point energy, Symmetry, Mulliken charges.

Note: energy values are reported for MP2 and for lower-level HF.

Note: energy is reported in A.U. Recall 1 hartree is 627.51 kcal/mol.

3.1. **Find data in the output without opening.** Close the output file and use `grep` to find the energy value, *without* opening the file. This can become important for larger systems, as the size of the output file will grow very fast.

Note: the checkpoint `Test.FChk` was produced. This is an ASCII file which has MO information. Please see the previous tutorial *Gaussian*: Intro for a reminder of how to display MOs with *Avogadro*.

4. Geometry optimization

Here we consider geometry optimization as a search for mimina on the potential energy surface. Optimization methods calculate the second derivative of the energy with respect to the coordinates. Matrix of forces (Hessian) is updated for each new conformation.

Convergence criteria in *Gaussian*:
- The force components are less than 0.00045;
- The root-mean-square of the forces are less than 0.0003;
- Displacement for the next step is less than 0.0018;
- The root-mean-square of the displacement for the next step is less than 0.0012.

Note: please comment on why convergence criteria contain conditions on force and coordinate. Think of examples of potential energy surface where one criterium alone would not suffice.

4.1. **Prepare input file for geometry optimization of a formaldehyde molecule.**
Using *Avogardo* follow the steps above for single point energy calculation with the exception of selecting `Calculation:` Geometry Optimization.

Note: `Opt` was added to the input file.

Transfer .com file to triton and run the calculation.

4.2. **Analysis of the output file.** Open the .log file and locate the following information:
- Did optimization converged? Hint: search for `YES`
- If yes, how many steps were required to converge?
- Predicted energy for the optimized structure?
- Locate final optimized structure. Hint: look for the statement: Stationary point found.
- Reflect on which bonds, angles, dihedrals changed.

4.3. **Visualizing geometries using *Molden*.** Note: Use `ssh -C` to connect to `triton` to speed this up.

Type `gmolden` in your terminal on `triton` to start the program.

Note: `molden` will start the Xwindows version and whereas `gmolden` will start the OpenGL one.

Click `Read` button and select your .log output file. Choose `Draw Mode:` Solid -¿ Ball and Stick.

To see how conformations changes during minimization, click `Select Point: Next`. Click through to the final structure. Click `Forces` and go through frames once again to see how forces changed during this process.

5. Frequency and normal mode calculations

Frequencies are functions of second derivative of the energy with respect to the nuclear positions. Second derivatives can be computed analytically: Hartree-Fock (`HF`), density functional theory (e.g. `B3LYP`), second-order Moller-Plesset (`MP2`), and CASSCF (`CASSCF`) or numerically.

Gaussian is capable of computing the vibrational spectra of molecule on ground and excited states.

5.1. **Frequency calculation for a water molecule.** Prepare input file using *Avogardo* and select `Calculation:` Frequencies. Chose `RHF` for `Theory`.

Submit job to triton and study resulting output file.

5.2. **Results of the frequency calculation.** Locate frequencies and intensities. Compare to the experimental results.

Note: output frequencies are in cm^{-1}.

Note: due to a systematic error in this calculation use empirical scale factor to multiply the resulting frequencies: `0.8929` for `HF/6-31(d)` and `0.9427` for `MP2/6-31(d)`, see [3].

Comment on why the accuracy of `MP2/6-31(d)` is higher.

Locate normal mode displacements. Hint: they are listed after the `IR Inten`.

Note: one needs the `Standard orientation` printed in the beginning of the output file to visualize the displacements.

Note: if the molecule is planar one coordinate, usually `X`, initially will be set to zero for all atoms. Complete the following if you have time, otherwise see next section on how to use *Molden* on how to visualize normal modes. Sketch normal modes on a sheet of paper. Use the displacements with the largest magnitudes as a guide to which atoms move the most. Additionally see which atoms move closer together.

5.3. **Visualizing normal modes and spectrum using *Molden*.** Note: Use `ssh -C` to connect to `triton` to speed this up.

Type `gmolden` in your terminal on `triton` to start the program.

Note: `molden` will start the Xwindows version and whereas `gmolden` will start the OpenGL one.

Click `Read` button and select your .log output file. Choose `Draw Mode:` Solid -¿ Ball and Stick.

To see normal modes, click `Frequencies: Norm.  Modes`. New window `Molden Frequency Select` will allow you to choose which mode to see. Try them all one by one.

Note: there is a window with the calculated spectrum. You can use it to print and save the frequencies.

5.4. **Frequencies and normal modes for a formaldehyde molecule.** Repeat previous calculation for formaldehyde. Display the normal modes using *Molden*. Look at the representation of normal modes in the output file and see whether you can describe the motions by just studying the matrices.

5.5. **Frequencies and normal modes using `MP2`.** Repeat frequency and normal modes calculations for a formaldehyde molecule using `MP2` for `Theory`. Comment on the differences of results, if any.

6. Summary

This tutorial covered material using *Gaussian* for single point energy, geometry optimization, frequency and normal modes.

7. Contact

If you found errors/typos or have suggestions or comments on material in this tutorial please contact us at the SCS Computer Center. We are looking forward to hearing from you.

8. Appendix: Running *Gaussian* in queue on triton (Linux cluster)

Please make sure to understand each line of the shell script below. Edit it to match your file names.

Submit the queue script to the queue:

```
> qsub g09_qjob
```

Note: The following is probably not needed for the fast test job.

Check the status of your job:

```
> qstat
```

Delete the job if need:

```
> qdel
```

Study the shell script for queue submission open g09_gjob:

```
#!/bin/tcsh
#$ -cwd
#$ -pe default 1
#$ -q general
source /share/apps/gaussian/g09_login.csh
g09 input.com
```

References

[1] Christopher J. Cramer. *Essentials of computational chemistry: theories and models*. Wiley, Hoboken, NJ, second edition, 2004.

[2] James B. Foresman and Aellen Frisch. *Exploring chemistry with electronic structure methods*. Gaussian, Inc, Pittsburg, PA, second edition, 1996.

[3] Jeffey P. Merrick, Damian Moran, and Leo Radom. An evaluation of harmonic vibrational frequency scale factors. *J. Phys. Chem.*, 111:11683–11700, 2007.

[4] Taras V. Pogorelov and Mike Hallock. Quantum chemistry with gaussian : A very brief introduction. https://netfiles.uiuc.edu/pogorelo/www/Tutorials, February 2010. Tutorial.

[5] Taras V. Pogorelov and Mike Hallock. Unix/linux primer. https://netfiles.uiuc.edu/pogorelo/www/Tutorials, February 2010. Tutorial.