Homework Assignment (60 Points)
ADF: Calculation Basics

CHEM 4631/5631, Spring 2022
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You may handwrite or type your responses to the questions in this assignment. You might find it helpful to refer to the ADF manual when answering some of these homework questions:
https://www.scm.com/doc/ADF/index.html

1 Geometry optimization tutorial (15 points)

1.1 Carefully work through the **Getting started: Geometry optimization of ethanol** tutorial on the SCM website:
`https://www.scm.com/doc/Tutorials/GettingStarted/GeometryOptimizationOfEthanol.html`

1.2 In a few sentences, describe what is being done when you use the "pre-optimize" button in the input window in Step 2 of the tutorial. Is a quantum mechanical calculation being performed?

1.3 State the *geometry convergence criteria* for energy convergence that was used by default when you ran your calculation in Step 4 of the tutorial. Open your logfile from the calculation and find where this convergence criteria is used. Take a screen shot of this section of your logfile or handwrite these line(s) and include it with your homework. In a few sentences, describe how the geometry convergence criteria information is used in your calculation.

1.4 State the *SCF convergence criteria* for energy convergence that was used by default when you ran your calculation in Step 4 of the tutorial. Open your logfile from the calculation and find where this convergence criteria is used. Take a screen shot of this section of your logfile or handwrite these lines and include it with your homework. In a few sentences, describe how the SCF convergence criteria information is used in your calculation. Include how this is different than the geometry convergence criteria in your explanation.

1.5 When you have the plot of energy, bond length, and bond angles created in the Movie window during Step 5 of the tutorial, discuss how you can tell that your geometry is converged using this information.

2 Geometry optimization on molecule of your choice (25 points)

Choose a molecule of interest to you that has at least eight non-hydrogen atoms.

2.1 Write the name of your molecule of choice, its molecular formula, and include an image of the molecular structure (sketch by hand, use ChemDraw, or get an image from the internet).

2.2 Build the molecule **manually** in an ADF Input window and run a SP calculation using the default settings except change relativity to None (unless you think relativity is necessary for your molecule, if so, state why), change basis set to TZP, and change frozen core to None. State the bonding energy of your molecule in kcal/mol after the calculation is complete (found at the bottom of your logfile or within your output file).

2.3 Using the same starting geometry and settings as in 2.2, run a GO on your molecule. State the bonding energy of your molecule in kcal/mol after the calculation is complete.

2.4 Watch the movie of your GO and, in a few sentences, describe how your molecule rearranged into its optimal geometry. Do you think you found a global minimum on the PES? Why or why not?

2.5 Compare the bonding energies from your SP and GO calculations. Which is lower? Does this make sense?

2.6 Search for your molecule in the search bar in a new ADF input window. Run a GO calculation using this as the starting geometry and the same settings as in 2.2. Compare the run time for the GO starting from the manually built molecule in 2.3 and using the pre-made structure (there are time stamps in your logfile). Did you get the same energy and geometry at the end using either starting geometry? If not, why not?
If you can not find a starting geometry for your molecule you should instead pre-optimize your structure from 2.3 and then run the GO calculation.

2.7 Starting from the same starting geometry as in 2.3, run another geometry optimization but with a looser geometry convergence criteria of Energy convergence = 0.01 E_h. Compare the bonding energy from this calculation to your results from 2.3 and 2.6. Do your results make sense?

3 Predicting Spectra (20 points)

Choose one of the following spectroscopy tutorials for this question:

`https://www.scm.com/doc/Tutorials/VibrationalSpectroscopy/IRSpectrumOfEthane.html#freq-ethane` (Vibrational frequencies and IR spectra of ethane)

`https://www.scm.com/doc/Tutorials/GettingStarted/ExcitationsAndUVVisOfEthene.html#excitation-ethene` (UV/Vis spectrum of ethene)

`https://www.scm.com/doc/Tutorials/NMR/H-NMRSpectrumSpin-SpinCoupling.html#adf-nmr-h` (H-NMR spectrum with spin-spin coupling)

After completion of the tutorial, write a 1-2 paragraph summary of what calculation(s) you performed, if the resulting spectra makes sense based on your previous knowledge and/or by comparing it to an experimental spectra you find, and consider when it might be useful to predict this kind of spectra in an experimental setting.