Homework Assignment (60 Points)
ADF: Basis Sets, Functionals, and PES Scans

CHEM 4631/5631, Spring 2022
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You may handwrite or type your responses to the questions 1 and 2 in this assignment. You must type the essay for question 3. 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 Comparison of Basis Sets and Levels of Theory (15 points)

In this question you will compare the accuracy of various basis sets and functionals for determining the energy and geometry of an ammonia molecule.

1.1 Build an ammonia molecule in an ADF input window by placing one nitrogen atom in the window and then using the "add hydrogens" tool (Atoms → Add Hydrogens) to automatically add three hydrogen atoms to the molecule in reasonable starting geometries.

1.2 Create a table of results for the following combinations of geometry optimization (GO) calculations and results. Use all of the default ADF parameters other than changing the level of theory and basis set for each calculation. After each geometry optimization, run a SP calculation at the TPSS/TZ2P level from your optimized geometry. You can set up each calculation manually (making sure to save each calculation with a new file name) or look up how to use the ADF "Prepare" feature. You may also want to look up the "Report" feature in ADF to consolidate your results.

- Use the following headers for your columns: Level of Theory/Basis Set, # Steps required for GO, Bonding Energy, H-N-H angle, H-N bond length, SP energy at TPSS/TZ2P.
- For your first column (level of theory/basis set) test the following 8 combinations: LDA/SZ, LDA/DZ, LDA/DZP, LDA/TZP, B3LYP/SZ, B3LYP/DZ, B3LYP/DZP, B3LYP/TZP

Notes: For the H-N-H angle and H-N bond length, choose any one of these three angles/bond lengths from your final structure. They should all be the same due to the symmetry of your molecule. To check this, make sure your calculation is using the symmetry C_{3V} in your calculation, which will be listed near the top of your logfile. To count the nubmer of optimization steps, either look at the last GO Step # listed in your logfile or watch the movie of your GO and check what the last step is in the movie.

1.3 In a few sentences, discuss how the bond angles and bond distances in ammonia converge with the level of theory and basis set.

1.4 In a few sentences, discuss how the energy of ammonia converges with the level of theory and basis set, including the values from your SP calculations. Also considering the number steps required for each GO, what would the fastest scheme be to achieve an accurate energy value?

2 Potential Energy Surface (PES) of SN_2 Reaction (15 points)

1. Build a chloromethane molecule in ADF input and optimize the geometry using the following settings, Functional: LDA, Relativity: None, Basis set: TZP, Frozen core: none.
2. After the chloromethane is optimized, add a bromide ion on the backside of the methane compound so that it can act as an nucleophile that will have an SN2 reaction with the chloromethane. Change the distance between the carbon and bromide ion to 500 pm (5 Å). Make sure you change the total charge to -1 in the input window to account for the anion. Change the Task to "PES Scan"
3. Go to the "Geometry Constraints and PES Scan" tab. Highlight the bromide ion and the carbon atom and then click on the + button that appears next to Br-C distance.
4. Next highlight the chlorine atom and the carbon atom and again click on the + button that appears next to Cl-C distance.
5. Now we will adjust the distance start/end points so that these bond lengths will change to scan the PES. For the C-Br distance, leave the first distance alone, but change the second distance (the ending point) to 1.93 Å (an average C-Br bond length). For the C-Cl distance, leave the first distance alone but change the second distance to 5.000 Å.
6. Make sure both Scan coordinates for these parameters are listed as "1". Note that the default settings on the screen show that you will take 10 steps between these distance constraints.
7. Save and run the PES scan. You can watch a movie of the logfile to see the progress of your calculation in real time. *Note: This calculation will take some time. It took 7 minutes on my laptop*
8. When your calculation is finished, open the ADF Movie and go to View → Accepted geometries only.

2.1 In Step 8, describe what your graph is showing before and after changing the view to accepted geometries only.

2.2 How could you use this graph to determine a rate of a reaction? Based on your results from Question 1, discuss if you think the level of theory and basis set for your PES scan would give you an accurate reaction rate.

2.3 Based on your graph, which reaction do you think is more favorable, $CH_3Cl + Br^- \rightarrow CH_3Br + Cl^-$ or $CH_3Br + Cl^- \rightarrow CH_3Cl + Br^-$. Explain how you determined this from your graph. Does this match your knowledge from organic chemistry courses?

3 Journal Article Critique (30 points)

Find and read the following article on ligand-exchange reactions of methylmercury, J Comput Chem. 2020;41:2045–2054. Answer the following questions in a one to two page, single-spaced, typed essay. Make sure to be cricital of the work and think about how this approach could be used in your research. Please use 1 inch margins and 12 point font size.

1. What question(s) does the paper address?
2. What are the main conclusions(s) of the paper?
3. What evidence do the authors provide to support the conclusion(s)?
4. Why are the conclusion(s) important?
5. Is the approach they used sufficient/correct for the problem?
6. How could you apply what you learned in this paper to your research (or research questions of interest to you if you are not currently performing chemistry research)?