NANO266 Lab 1 - Calculations on Molecules

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1 Introduction

We will begin our lab sessions with a gentle introduction into quantum mechanical modeling of molecules. For this purpose, we will be using computational chemistry techniques to study reaction energies, geometries, vibrational frequencies, etc. We will be using NWChem, an open source quantum chemistry code. Note that all calculations in this lab are fairly simple and on very small molecules. So you can run them on a modern desktop or laptop in serial mode, i.e., you do not actually need access to a supercomputing cluster to perform these calculations.

For this lab, we will be studying one of the most important reactions in the world - the formation of ammonia from nitrogen and hydrogen. Through the Haber-Bosch process, this is the main industrial reaction for the production of ammonia, which is then used in the production of fertilizers, etc. It is estimated that one-third of the Earth's population is sustained by fertilizer generated from ammonia produced by the Haber process.

In this lab, almost all analyses will be done using Unix-based command line tools as it is important for you to learn how to find data efficiently using these tools. Subsequent labs will provide you with the opportunity to use Python to automate and analyze data more effectively. You are of course welcome to write your own scripts if you have the know-how.

2 Initial setup

It is assumed that you have already followed the instructions in the README.md in the root labs folder and have access to nwchem, either on XSEDE or on your own computer or virtual machine. Do a git pull so that you are up to date with the repo. Also, read through the README.md file in the main labs folder and make sure that you have NWChem setup properly. Try typing `nwchem` in your terminal to make sure that everything is working. You will get an error message because there is no input file, but that's not a big deal.

Once you are done with the above, make sure you are in the lab1 folder by doing:

cd <path/to/repo>/labs/lab1

3 Q1 (10 points): Geometry optimization and energy of H2

We will start with one of the simplest molecules, diatomic hydrogen. In the directory, we have provided a sample `H2.nw` input file. First, open up the input file and understand its structure. Here's a replica of the input file with comments added.

```
memory total 1000 mb        # This specifies the memory for the job.

geometry units angstroms    # This section provides a summary of the input
 H 0 0 0                    # geometry of the molecule. You usually get this
 H 0 0 0.7414               # from an experimental source or some chemistry
end                         # rules

# This nwchem job comprises three steps - geometry optimization, a frequency
# calculation, and a final energy calculation at a larger basis set.

title "H2 dft optimize"     # This is just the title
charge 0                    # We are doing calculations on neutral H2.
basis                       # Specifies the basis set for each atomic species
 H library "6-31G"
end
dft
 mult 1                     # Spin multiplicity of 1, i.e., singlet state
 xc b3lyp                   # Exchange functional used is B3LYP.
end
task dft optimize           # Specify that we want to do a geometry optimization

title "H2 dft freq"
charge 0
basis
 H library "6-31G"          # The same basis set must be used for the frequency calculat
end
dft
 mult 1
 xc B3LYP                   # The same functional must be used for the frequency calcula
end
task dft freq               # Specify that we want to do a frequency calculation

title "H2 dft energy"
charge 0
```

```
basis
 H library "6-311G"         # A larger basis set is used to get better energies   end
dft
 mult 1
 xc b3lyp
end
task dft energy             # Specify that we want to do an energy calculation
```

Let us first create a separate directory to run the calculation. This makes it easier for us to cleanup after we are done.

```
mkdir scratch
cd scratch
```

Now, we copy the input files we want over, and run nwchem:

```
cp ../H2.nw .
nwchem H2.nw > H2.nwout
```

After a very short while, the calculation should complete and the results are in the `H2.nwout` file. To find the final coordinates, search for the final occurence of:

```
grep -A 8 '"geometry" -> ' H2.nwout
```

This command finds all instances that `"geometry" ->` occurs in `H2.nwout` and prints out 8 lines after each occurence.

To get the final total energy, we can use grep from the command line:

```
grep "Total DFT energy" H2.nwout
```

The last energy line gives the total energy in **Hartree**.

For this question, record down the final bond length of H2 in angstroms and the final total energy in eV. Keep all output files until the end of the lab.

4 Q2 (10 points): Geometry optimization and energy of N2

Repeat Q1, but this time with N2. For this question, copy `H2.nw` to `N2.nw` and then modify the file accordingly. The experimental N2 bond length is around 1.1 angstroms.

Again, record down the final bond length of H2 in angstroms and the final total energy in eV.

5 Q3 (25 points): Geometry optimization and energy of NH3

The geommetry of ammonia is somewhat more complex, so we have provided an `NH3.nw` file. Perform the same calculation as in Q1.

For NH3, record down the final N-H bond lengths, and also, calculate the angle between the bonds, i.e., the H-N-H bond. Compare the calculated values with the experimental ones. Cite the source of your experimental data (e.g., by providing a journal citation or a weblink.)

Now, modify the file to add polarization functions to the basis set. The easiest way is to change all "6–31G" to "6–31+G*" and all "6–311G" to "6–311+G*" (technically, this adds diffuse as well as polarization functions, but we are limited by the choice of basis sets available) Redo the calculation and determine the bond lengths and angles again. Comment on the difference in answer between the calculation with and without polarization functions.

Tip: One of the fastest ways to make changes to a file is using the unix command line tool called *sed*. For example, you can do the following:

```
sed 's/\(6-31[1]*\)G/\1+G*/' NH3.nw > NH3_polarized.nw
```

which will effectively replace all "6–31G" and "6–311G" with "6–31+G*" and "6–311+G*" in the file "NH3.nw". The first argument to *sed* is the regular expression. "s/" denotes that this is substitution. "\(6–31[1]*\)G" denotes that we want to match all instances of "6–31(1)G", where the second 1 is optional. The brackets denote that we want to store the match before the G in the first variable. The second half of the expressions "/\1+G*/" denotes that we want to replace all matches with the stored variable "\1" followed by "+G*". Finally, the last part of the command "> NH3_polarized.nw" means we want to pipe the output to a new file "NH3_polarized.nw".

Also record down the final energy of the NH3 molecule in eV.

6 Q4 (25 points): Formation enthalpy of NH3.

Calculate the formation enthalpy (per molecule) of NH3 in kJ/mol. To do this, you need to make sure that all calculations are done with the same basis set. So redo the calculations for Q1 and Q2 with the same basis set with polarization functions as in Q3.

Once you completed the calcualtions, you need to extract the thermal corrections to the enthalpy as well as the energies. For example,

```
grep "Thermal correction to Enthalpy" H2.nwout
```

Note the units stipulated by NWChem in the output.

The enthalpy H is then given by the energy + the correction. The formation energy of NH3 is given by the enthalpy change of the following:

0.5 N2 + 1.5 H2 -> NH3

Compare your calculated formation enthalpy with experimental values. The NIST Chemistry Webbook (http://webbook.nist.gov/chemistry/) is a good source of data for many common molecules.

7 Q5 (30 points)

In this question, you will investigate the effect that functional choice and basis set choice has on the formation enthalpy of NH3. Repeat Q1-Q4, but now modify your input files to experiment with the HFexch, PBE96 and B3LYP functionals. You can also modify the basis

set used between 6–31+g* and 6–311+g*. Note that you can either modify the functional or basis set for the geometry optimiation and frequency step, or the final energy calculation step, or both.

Discuss the effect of the functional and basis set on the geometries and final energies. What would be a general recommended strategy for other similar calculations if you want to perform the calculations as efficiently as possible while maintaining relatively good accuracy?

Note that this is an open-ended question, and there is no right or wrong answer. It is more important for you to understand the tradeoffs and come up with a good justification for your recommendation.

8 Bonus (10 points)

The formation enthalpy of ammonia is negative, but generally the reaction does not take place (or does so very slowly) under normal conditions. That is why the Haber process is performed under high pressures and temperatures with a catalyst. The main reason is that N2 is very unreactive. Can you give a rough estimate of the reaction barrier using a few simple calculations, assuming that one has to break the N2 triple bond for the reaction?