The Geometry and Vibrational Frequencies of Water

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1 Introduction

In this lab, you will find the optimized bond lengths, bond angle, and vibrational frequencies of water with different levels of theory. After obtaining your theoretical results, you will compare those to experimental results.

2 Lab Instructions

1. Log in to HIVE-ICE.

2. Copy the templates for this lab into your personal directory. *Be sure to type the period at the end.*

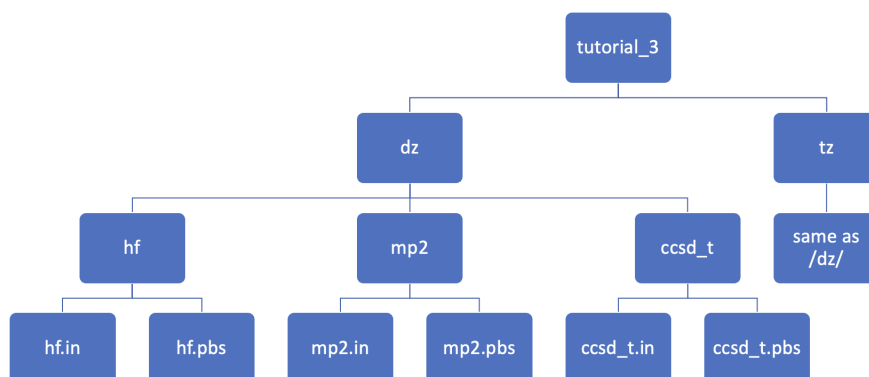   cp -r ../shared-classes/materials/chem-workshop/tutorial_3   tutorials/.

3. Navigate to your personal tutorial 3 directory.

    cd tutorials/tutorial_3

4. List the contents of the directory.

    ls

    You'll notice that there are two directories here: `/dz/` and `/tz/`. The file structure is shown in the flowchart below:

    Now, we will optimize the geometry of water and find it's vibrational frequencies by running the appropriate calculation. Begin by using a computationally inexpensive level of theory: HF with a cc-pVDZ basis set.

5. Navigate to the directory with input file in it.

```
cd dz/hf/
```

6. Open the input file with the terimal editor, Vim.

```
vi hf.in
```

7. You should now see what is printed below. Important parts of the input file have been highlighted. To orient yourself, locate the places I have highlighted below on your terminal.

```
#PSI4 file for HOH opt

memory 10 GB

molecule mol {
O 1
H
O 1 OH
H 2 OH 1 HOH

OH =                                    Here, you will enter the bond length between the oxygen and each hydrogen.
HOH =                                   Here, you will enter the bond angle.
}

set {
  scf_type df
  mp2_type df
  cc_type df
  freeze_core true
  basis cc-pvdz
}

optimize()          The methods for the geometry optimization and frequency calculation go here.
frequency(, dertype=1)   These should always be the same.
```

8. As you saw in the last step, some pieces of the input file are missing.

   (a) Use the arrow keys to move your cursor to the end of the line

```
OH =
```

   Now, press the letter a on your keyboard. This will tell vim that you would like to write something new in the file. After you press a, type in your guess for the bond length of H to O in water. (Hint: Something around 1 (Angstrom) should be appropriate.)

   (b) After you've typed in a number, press the escape key. Use your arrow keys to move to the end of the next line

```
HOH =
```

   Type in your best guess for the bond angle by pressing a, typing in your guess, and then pressing the escape key. (Hint: Use VSEPR theory to form this guess).

   (c) Use keystrokes in steps a and b to set the method for the geometry optimization and frequency calculation to Hartree-Fock. Your final lines should look like:

```
optimize('hf')
frequencies('hf', dertype=1)
```

9. Now that the input file is ready to go, save this edited version. Type

    ```
    :wq
    ```

    to write the file and quit the editor. You should now be back at the terminal command line.

10. Submit your job to the PACE-ICE queue

    ```
    qsub hf.pbs
    ```

11. Check to see that your job has been placed in a virtual queue.

    ```
    qstat -u [username]
    ```

    In this table, you will see one of three letters:

    - Q means your job is in the queue and waiting for an available CPU to run your job.
    - R means your job is running.
    - C means your job is complete.

    This table does not automatically update, so re-type the command above to see if your job has completed.

12. Now that your job is finished, open the output file with Vim.

    ```
    vi hf.out
    ```

13. Make sure your job as finished successfully by scrolling down to the bottom of your file, or equivalently typing `shift+G`. If your job finished successfully, you will see the line:

    ```
    Psi4 exiting successfully. Buy a developer a beer!
    ```

    If you do not see this message, see if you can figure out what went wrong. If you are stuck, ask someone for help!

14. This output file has a lot of information. To find what we need, we will make use of the grep command in the terminal. To close the file, type

    ```
    :q
    ```

15. To find the calculated equilibrium bond length and angle, type

    ```
    grep 'OH' hf.out
    ```

    You'll see a few Z matrices. These are the Z matrices from the iterations of the optimization. We want the structure from the end of the optimization. Record the last value for the equilibrium bond angle (HOH) and bond length (OH) in a table like the one below.

Level of Theory	Bond Length (Å)	Bond Angle (°)	$\omega_1(a_1)$ (cm^{-1})	$\omega_2(a_1)$ (cm^{-1})	$\omega_3(b_2)$ (cm^{-1})
HF/cc-pVDZ					
MP2/cc-pVDZ					
CCSD(T)/cc-pVDZ					
HF/cc-pVTZ					
MP2/cc-pVTZ					
CCSD(T)/cc-pVTZ					

16. To find the vibrational frequncies, type

    grep 'Freq' hf.out

    Record the wavenumbers of the three normal modes in the table.

    - You may recall from your chemistry class(es) that a molecule has 3N-6 vibrational modes, where N is the number of atoms. Does this agree with your output file? Does Psi4 calculate the correct number of vibrational modes?
    - Hopefully, Psi4 calculated frequencies for 3 vibrational modes, which correspond to

Normal modes

symmetric stretching   asymmetric stretching   bending
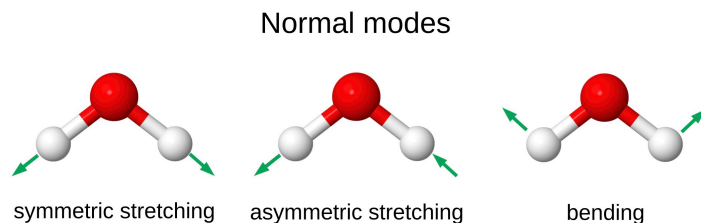
    If we had more time, we could actually visualize these vibrations with our Psi4 output file. Pretty cool!

17. Repeat steps 5-15 for the other levels of theory listed in the table.

3   Analysis

Now that you have calculated bond lengths, bond angles, and vibrational frequencices with Psi4, compare your results to experimental results from J. R. Thomas et al., J. Chem. Phys. 99, 403 (1993).

H_2O: $r_e(OH)$ = .957 Å, θ_e = 104.5°, $\omega_1(a_1)$ = 3832 cm^{-1}, $\omega_2(a_1)$ = 1649 cm^{-1}, $\omega_3(b_2)$ = 3943 cm^{-1}

1. For HF, are DZ or TZ results most accurate? What about for MP2? CCSD(T)?

2. Looking at only DZ data, what is the ordering of methods from least accurate to most accurate compared to experiment? What about for TZ?

4   Summary

You have now optimized the water molecule to find its equilibrium bond lengths and bond angle with six different levels of theory (method/basis set combinations). You have also found its vibrational frequencies with each level of theory and compared all of those values to experimental results.

Hopefully, you noticed a relative accuracy improvement from HF to MP2 to CCSD(T). You should have also noticed that TZ normally performs better than DZ basis sets, due to their increased size. TZ basis sets are a better approximation of atomic orbitals compared to DZ basis sets.