The Potential Energy Surface of H_2

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1 Introduction

In this lab, you will look at how energy changes as the distance between the two H atoms in H_2 changes with three different theoretical methods.

2 Lab Instructions

1. Log in to PACE-ICE.

   ```
   ssh [username]@login-ice.pace.gatech.edu
   ```

2. Copy the templates for this lab into your personal directory.

   ```
   cp -r /storage/ice-shared/chem-workshop/tutorial_2/  pace-ice-home-data/tutorials/
   ```

3. Navigate to your personal tutorial 2 directory.

   ```
   cd pace-ice-home-data/tutorials/tutorial_2/
   ```

4. List the contents of the directory.

   ```
   ls
   ```

   You'll notice that there are three directories here: `/RHF/`, `/UHF/` and `/CCSD/`. We will be running essentially the same calculation, but with three different methods: Restricted Hartree-Fock (RHF), Unrestricted Hartree-Fock (UHF), and Coupled Cluster with Single and Double Excitations (CCSD). The file structure is shown in the flowchart below:
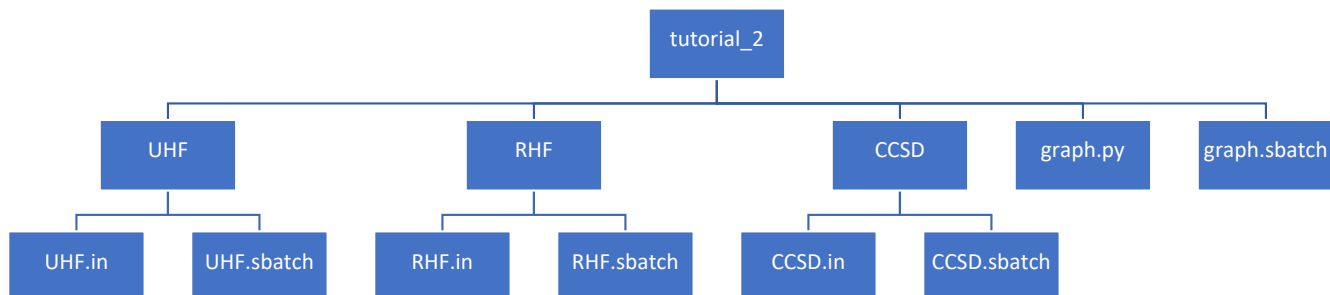
   The files that end in `.in` are Psi4 input files. The files that end in `.sbatch` are files which submit an input file to the computer cluster. `graph.py` will be used for analysis at the end of this tutorial.

5. Let's take a look at the input files. Navigate to the directory with `UHF.in` in it.

```
cd UHF/
```

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

```
vi UHF.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 H2 UHF energy
```

```
memory 10 GB
```
We declare how much memory is needed for this job.

```
molecule mol {
0 1
H
H 1 R
symmetry c1
}
```
Then we enter the molecule we would like to run calculations on. We include the atoms, connectivity, molecular symmetry, charge, etc.

```
Rvals = [.25,.5,.75,1,1.25,1.5,2,3,4]
```
Here are different atomic distances of the Hs in H_2.

```
table = Table(rows=["R"], cols=["E(UHF)"])
```
This sets up a table of energies for various H_2 molecules, each with a different HH bond length.

```
set {
  scf_type df
  mp2_type df
  cc_type df
  freeze_core true
  reference uhf
  guess_mix True
  guess gwh
}
```

```
for R in Rvals:
  mol.R = R
  euhf = energy()
  table[R] = [euhf]
```
This loops through the different bond lengths and calculates the energy of each molecule. The method used to calculate the energies will be entered in between the parentheses later in this tutorial.

```
print_out('Table of Results \n') print_out(str(table))
```
This prints out the table mentioned above, once the energies are obtained (purple box).

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 closing parenthesis of the following line

```
euhf = energy()
```

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 the level of theory 'hf/sto-3g' including the quotation marks.

(b) After you've typed this in, press the escape key. Your line should now look like

```
euhf = energy('hf/sto-3g')
```

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. Our input file is ready for submission, but before we run our calculation, take a look at the PBS script. Open it by typing

```
vi UHF.sbatch
```

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

```
#!/bin/bash
#SBATCH -J UHF
#SBATCH -N 1
#SBATCH -n 1
#SBATCH -t 30
#SBATCH -q pace-ice

export OMP_NUM_THREADS=1
export MKL_NUM_THREADS=1
cd $SLURM_SUBMIT_DIR
myscratch=${TMPDIR}

unset PSIDATADIR
unset PSI4DATADIR
PYTHONPATH=${PYTHONPATH:-""}
export PSI_SCRATCH=${TMPDIR}
```

```
module load psi4              PSI4, the quantum chemistry software, is loaded, then used to run the input file.
srun psi4 -i UHF.in -o UHF.out -n 1                          Results will go into the output file, UHF.out.
```

12. Close the vim editor.

```
:wq
```

13. Submit your job to the PACE-ICE queue.

```
sbatch UHF.sbatch
```

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

```
squeue -u [username]
```

In this table, you will see one of two status indicators:

- PD (pending) means your job is in the queue and waiting for an available CPU to run your job.
- R means your job is running.

This table does not update automatically, so re-type the command above to see if your job has completed. A completed job will not show up on this list.

15. Once your job has completed, open the output file with Vim.

```
vi UHF.out
```

16. 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, see if you can figure out what went wrong. If you are stuck, ask someone for help!

17. This output file has a lot of information. Thankfully, the input file included scripting to make a table at the bottom of the output file. We will use this table later on. To close the file, type

```
:q
```

18. Continue this process with each input file by repeating steps 5 - 17 and the following notes.

- To go from /UHF/ to /RHF/, cd ../RHF/.
- For RHF.in, erhf=energy('hf/sto-3g'), and sbatch RHF.sbatch. *There are keywords already written which make this different from UHF.*
- For CCSD.in, eccsd=energy('ccsd/sto-3g'), and sbatch ccsd.sbatch.

19. Now that all jobs are completed, analyze the data by graphing it. A graphing script has already been written for you. Open graph.py through the following two (separate) commands.

```
cd ../
vi graph.py
```

This script reads the output files you created and grabs the energies from your tables, remembering which energies correspond to which method and bond length. It then graphs these energies as a function of bond length.

20. Close the file.

```
:wq
```

21. To create the graph, enter

```
sbatch graph.sbatch
```

22. Now the graph has been created, but it has been saved on a remote computer. To copy this file to your personal computer, **open a new terminal** and type (all in one line)

```
scp [username]@login-ice.pace.gatech.edu:/home/hice1/[username]/pace-ice-home-data/tutorials/tutorial_2/H2_PES.pdf

./Downloads/
```

This should copy the graph to your downloads folder on your personal computer. View the graph and continue to the analysis portion of this tutorial.

3 Analysis

3.1 Potential Energy Surface

You have now created a graph of electronic energy vs nuclear distances, a potential energy surface (PES). These play very important roles in computational and theoretical chemistry (more on that tomorrow). Let's focus on just the CCSD curve right now, as this is the most accurate curve.

1. To the right side of the well, the energy hits an asymptotic limit. When the atoms are far apart, they have no attractive or repulsive forces between them.

2. At some point, the atoms start to 'detect' each other, and form an attraction. Attractive forces decrease the energy, making a more stable molecule. Where on the curve are attractive forces dominant?

3. Eventually, the atoms are separated by what we call an 'equilibrium distance'. At this distance, the molecule has the lowest energy. At what point on the curve can we find the equilibrium distance?

4. The left wall of the well increases extremely quickly. What forces are dominant here? Attractive or repulsive?

The last page has the PES with important areas labeled so that you can check your understanding.

3.2   Bond Breaking: UHF vs RHF

You'll notice from your graph that RHF does not show the correct asymptotic behavior of H_2 dissociating, but UHF does. What is going on?

From a previous chemistry class, you may recall that the electron configuration for H is $1s^1$, meaning it has one electron in the 1s orbital. Many times, the atomic orbital is represented as:

↑

1s

When we have two hydrogens infinitely apart and, therefore, non-interacting, we can diagram this system similarly:

↑   ↑

1s   1s

If we were to model these orbitals, we would see a 1s orbital (spherical) on each hydrogen.

UHF puts one electron in one orbital, which results in the proper behavior of one electron on one H and the other electron on the other H.

Conversely, RHF allows electrons of opposite spins to occupy the same orbital. Therefore, there are four options for where the electrons go:

↑   ↓
1s   1s

↓   ↑
1s   1s

↑ ↓
1s   1s

                         ↑ ↓
1s   1s
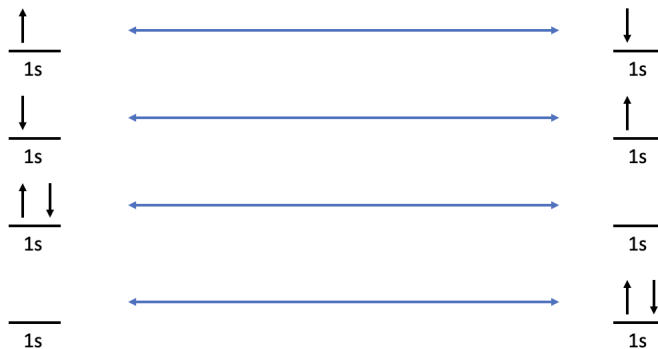
Do you see the problem? H_2 would never dissociate into H^+ and H^-!

4   Summary

You have determined the energy of H_2 at many different bond lengths and graphed a potential energy surface. You have also realized that it matters which method you choose, as some methods give you very wrong answers for your system.

Tomorrow, the lab will explore some other methods and how potential energy surfaces are a key part of computational chemistry.