

# Exercise Ex3

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**Please use this template to submit your answers.**

If you had to modify code from the notebook, please include the modified code in your submission either as screenshot or in a

```
\begin{lstlisting}[language=Python]
\end{lstlisting}
```

environment.

You only need to include the code cells that you modified.

Note, that references to other parts of the documents aren't resolved in this template and will show as ??. Check the text of the exercises on website for the reference

## Exercise 1

Include a table of the the calculated energies using the three different basis sets

Table 1: Calculated energies  $H_2$  with different basis sets

Basis Set	Computed Energy (au)
6-31G	-1.126735094476615
6-311G	-1.127971247729403
aug-cc-pvtz	-1.1330222127939673

## Exercise 2

What is the meaning of the Delta E column? What is DIIS? (Hint: to get more details, it may help to check the HF page on psi4 manual)

The  $\Delta E$  column represents the change in total energy between consecutive SCF iterations. Indeed we have  $\Delta E = E_n - E_{n-1}$  where  $E_n$  is the energy at iteration  $n$ .

Concerning DIIS (Direct Inversion in the Iterative Subspace), it aims to accelerate SCF convergence by using previous Fock matrix iterates and an orbital gradient-based error criterion to estimate the next Fock matrix. In general, DIIS is almost always necessary for SCF convergence and is enabled by default in Psi4. But, in rare cases, DIIS may need modification or deactivation via specific options for difficult systems.

### Exercise 3

How does the basis set size influence the SCF convergence behaviour? Include in your report the plot of the energy convergence along SCF iterations.

We can first denote that **aug-cc-pvtz** which has 46 primary basis functions has a higher energy initial guess (first plot). But it also leads to a lower Hartree-Fock energy (closer to the Hartree-Fock basis set limit) due to more accurate electron distribution modeling compared to smaller basis set like **6-31G** (4 basis functions) and **6-311G** (6 basis functions). Therefore, we can say that the basis set size influences the behavior of the SCF convergence by providing greater variational flexibility in the molecular orbitals. We conclude that smaller basis sets converge faster but with less accuracy, indeed we have less flexibility (accuracy is worse) and less coefficients to optimize (converges faster).

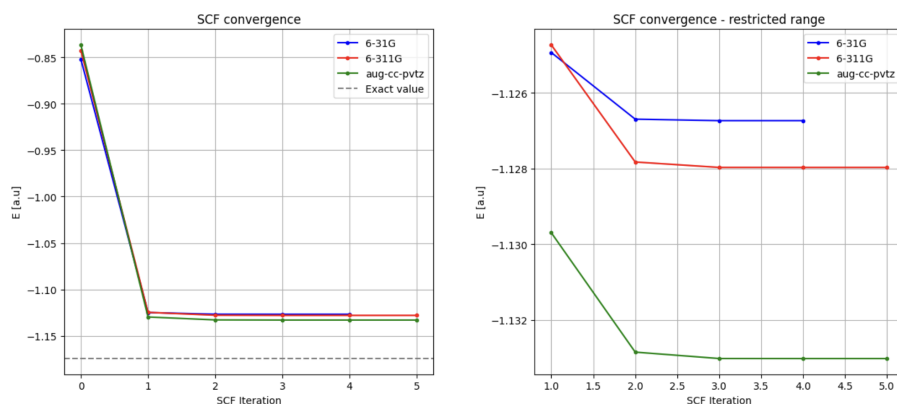


Figure 1: Plot of the energy convergence along SCF iterations

### Exercise 4

Explain the physical origin of the difference between the two dissociation curves. Discuss how important this difference is by comparing to the energy that is normally required to break a bond.

The difference between the RHF and UHF dissociation curves comes from the fact that RHF imposes a restriction of paired electron orbitals. When increasing the distance between the two  $H$  atoms, we face an unphysical energy due to neglected electron correlation and we don't converge towards the configuration of two isolated  $H$  atoms. On the other hand, UHF allows unpaired electrons, which accurately describes dissociation into separate atoms. This results in UHF stabilizing at  $\approx 0$  kcal/mol beyond 2.5 Å, whereas RHF increases to  $\approx 150$  kcal/mol at 6 Å. This difference is significant, as the typical H-H bond dissociation energy is  $\approx 104$  kcal/mol. Since  $E_{inter} \approx 150$  kcal/mol, we have that  $E_{RHF}$  is by far above 104 kcal/mol, showing that the system has an energy higher of the dissociative energy needed but still does reproduce the correct behaviour of two uncorrelated  $H$  atoms. This error highlights RHF's inadequacy for dissociation, while UHF is able to correctly reproduce the system at long distances.

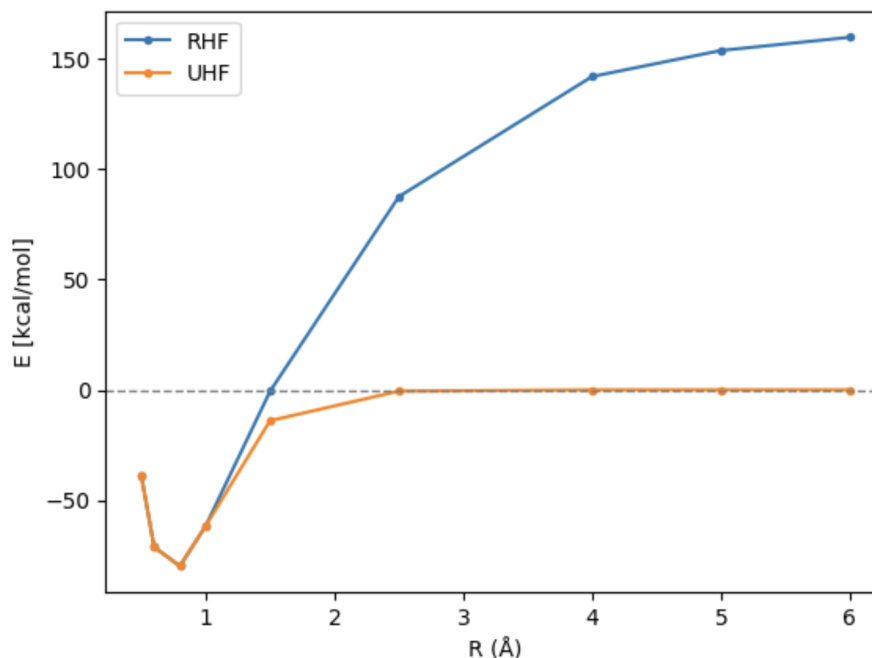


Figure 2: Dissociation curves of  $H_2$  with RHF vs UHF

#### Exercise 5 - Bonus

Try to find out why we are using `guess_mix:True` and `'guess':'gwh'`.

**Hint:** What happens if you use the same settings as for the RHF calculation?

You can also look at the Psi4 manual to find out about the different

options for the initial guess.

- The **guess\_mix**: **True** option in UHF mixes HOMO/LUMO orbitals to break alpha/beta spatial symmetry, enabling the description of open-shell character during  $H_2$  dissociation (where electrons become unpaired at long distances).
- The **guess**: **'gwh'** (Generalized Wolfsberg-Helmholtz) provides a suitable initial Hamiltonian approximation for open-shell systems, improving convergence over SAD.

As supposed, if we set the same settings for RHF we see that UHF follows the same shape :

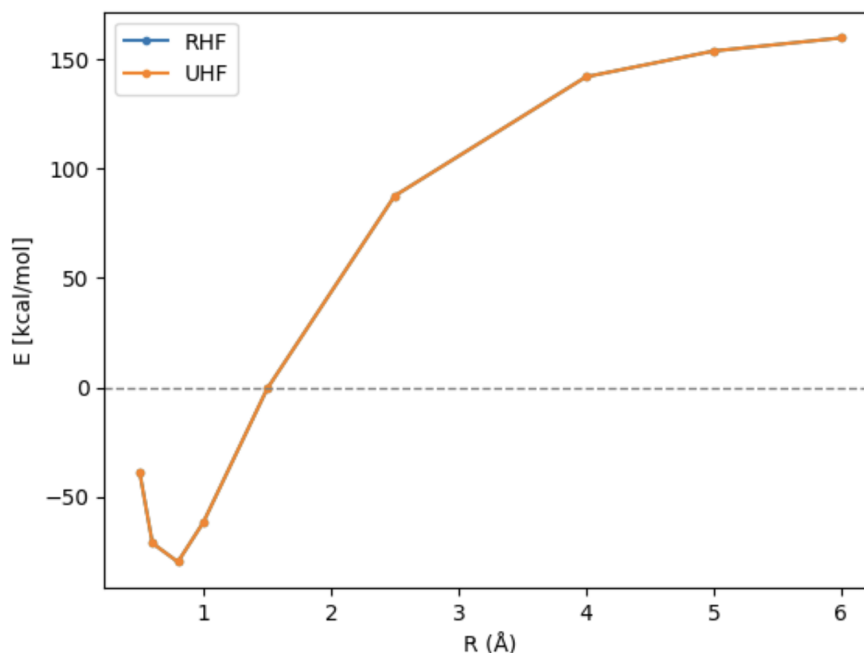


Figure 3: Dissociation curves of  $H_2$  with RHF vs UHF with same settings for both methods

### Exercise 6

Why are there multiple iterations of the SCF cycle?

For each iteration of a given geometry, we proceed similarly to the other exercises by solving HF equations and updating iteratively Fock matrix, the process repeats until convergence where the energy and density changes fall below a certain threshold. Therefore there is multiple SCF cycle since there is one per geometry which themselves are iteratively updated.

**Exercise 7**

Why does the optimization finish after several steps?

The optimization finishes after 7 steps, because convergence criteria (**Max Force** < 3.00e-04, **Max Disp** < 1.20e-03) are met at step 7. At this point, the energy becomes stable at -75.98534372 a.u., and forces and displacements reach their threshold. This indicates that the geometry and SCF procedure for this configuration have reached a minimum while this was not the case for the other 6 iterations (during which we also solved HF equations but led to above threshold results). The process stops when iterations yield negligible changes, confirming the optimal geometry for  $H_2O$  when the force gradient = **Max Force** is close to zero and to have a stable geometry (either the atoms hardly move anymore, or the energy is stable). Also note that optimization stops when **Max Force** and **Max Disp** have both reached their threshold, however delta E does not need to wait for its threshold in addition to the other two. This could be changed so that the optimization stops when the three conditions meet.

**Exercise 8**

Try to start from two (or more!) different suboptimal geometries of water and include the plots of the potential energy surface in the report, together with a screenshot of the starting and final geometry and/or the values of the O-H bond and H-O-H angle.

What do the points on the orange curve correspond to? Connect them to the flowchart at the beginning of this exercise?

See the 3 next pages for the answers.

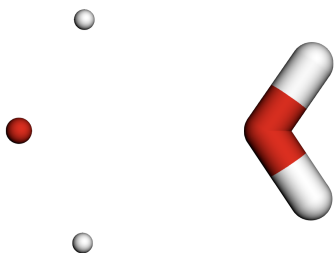


Figure 4: Suboptimal and Optimized Geometry of  $H_2O$  for  $r = 1.5$  and angle = 120 degrees

```
array([[ 113.26301073,    1.31815420,    1.31815420],
       [ 107.43234095,    0.94591197,    0.94591197],
       [ 113.19158490,    0.96853328,    0.96853328],
       [ 114.81408148,    0.93858201,    0.93858201],
       [ 111.74063416,    0.95051166,    0.95051166],
       [ 111.55969667,    0.94958191,    0.94958191]])
```

Figure 6: Angle values of  $H-O-H$  and distance of  $O-H$  bond Suboptimal through optimization process of  $H_2O$  for  $r = 1.5$  and angle = 120 degrees

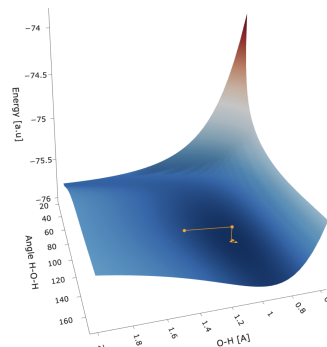


Figure 5: Energy curve as a function of Angle  $H-O-H$  and distance  $O-H$  along with gradient descent procedure (orange points for  $r = 1.5$  and angle = 120 degrees)

```
[-75.75646101262812,
-75.85024662483806,
-75.98480857161212,
-75.98447999591548,
-75.98489427708284,
-75.98534064888659,
-75.98534376014419]
```

Figure 7: DF-UHF Final Energy of  $H_2O$  for  $r = 1.5$  and angle = 120 degrees

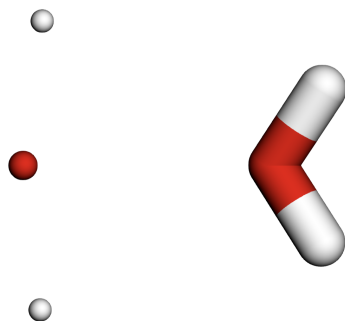


Figure 8: Suboptimal and Optimized Geometry of  $H_2O$  for  $r = 1.5$  and angle = 165 degrees

```
array([[ 154.82585378, 1.32510360, 1.32510360],
       [ 133.37599604, 0.97812980, 0.97812980],
       [ 111.46566050, 0.79080609, 0.79080609],
       [ 112.07345681, 0.88427031, 0.88427031],
       [ 112.80932981, 0.95152390, 0.95152390],
       [ 111.02057551, 0.94943779, 0.94943779],
       [ 111.70377682, 0.94990544, 0.94990544],
       [ 111.55084872, 0.94975327, 0.94975327]])
```

Figure 10: Angle values of  $H - O - H$  and distance of  $O - H$  bond Sub-optimal through optimization process of  $H_2O$  for  $r = 1.5$  and angle = 165 degrees

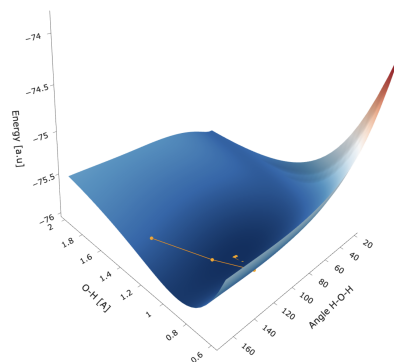


Figure 9: Energy curve as a function of Angle  $H - O - H$  and distance  $O - H$  along with gradient descent procedure (orange points for  $r = 1.5$  and angle = 165 degrees)

```
[-75.7671380085819,
 -75.85604058724778,
 -75.98238127878481,
 -75.98328017462997,
 -75.98412348871801,
 -75.98533553328173,
 -75.98534371690391]
```

Figure 11: DF-UHF Final Energy of  $H_2O$  for  $r = 1.5$  and angle = 165 degrees

The orange points correspond to the water potential energy of our current configuration in term of angle value of  $H-O-H$  and distance of the  $O-H$  bond. Since we are using gradient descent, we see that the orange curve and points follow the steepest gradient in order to converge to a minimum of the energy, meaning a force equals to 0 so that our system is stable. This can be related to the flowchart when we evaluate the force at this configuration and see that the force is non zero, we didn't reach the minimum and have to reiterate as shown with the yellow highlighter.

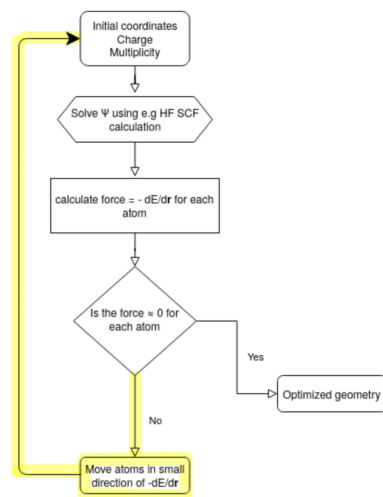


Fig. 3.1 Procedure of a geometry optimization. #

Figure 12: Flowchart illustrating the gradient descent process for optimizing the  $H_2O$  configuration.