ME 5329 Assignment 3

ORCA Potential Energy Surfaces (PES)

September X, 2025

Dr. Aquino Fall 2025

Due: September X, 2025

Objectives:

- Learn how to generate multiple input geometries using `molecule_lib` and Python.
- Learn how to batch submit SLURM jobs to the HPCC.
- Learn how to post process multiple ORCA calculations.
- Learn how to create publication quality figures and graphs using `matplotlib.pyplot`.

Part 1: Butane (C_4H_{10}) Dihedral PES

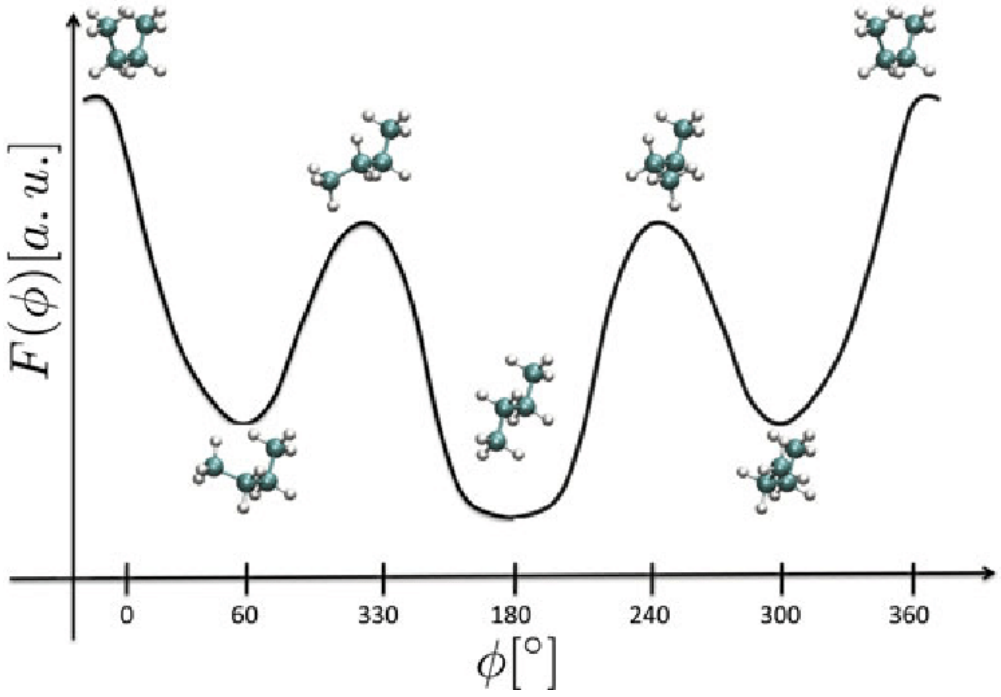

Figure 1: Example of the PES for the Dihedral Angle in Butane

1. Use Python and `molecule_lib` to rotate a half of the butane molecule (`butane.xyz` which will be distributed on Canvas) from $-180.0°$ to $+180.0°$ with a step of $5°$ and save each structure. The dihedral angle seen in `butane.xyz` is $0°$. There should be 73 structures generated from these ranges. You may choose to use a finer grid and/or sample a wider range of bond distances and bond angles. Please specify in the report if you choose to calculate a finer PES.

    - The method you need to use rotate specific atoms in `molecule_lib` is `XYZMolecule.manipulate()`. You then input the arguments for `XYZMolecule.rotate()` and ensure rotating about the centroid is disabled.
    - To select specific atoms in `molecule_lib` you can provide a list of atom numbers (list[int]), species (list[str]), or species+species number (list[str]).

2. Run an ORCA single point calculation for each geometry created in Step 1. Use the KS-DFT functional B3LYP and basis set 6-31G(d,p). Also please include Grimme's D3 dispersion correction in the single point calculation. The charge of this system is 0 and the multiplicity of this system is 1. You should use the **run_batch_jobs_orca.sh** SLURM script to be efficient with HPC usage.

    - To run a single point calculation in ORCA, all that is needed in the input line is `"! DFT_FUNCTIONAL BASIS_SET"`.

3. Collect the ORCA total energy results for each single point calculation using Bash (`grep` command) or Python. The string to search for in the *orca.out* file that contains the total energy in E_h is *"FINAL SINGLE POINT ENERGY"*.

4. Create a graph showing the PES using `matplotlib.pyplot.scatter()` (or your preferred graphing code) with the x axis being dihedral angle and the y axis being relative total energy in kcal/mol. Use `numpy.polyfit()` and `numpy.poly1d()` to fit the points on the graph to a polynomial of a chosen high order (≥ 20). Graph the fitted polynomial and report the polynomial function. Make sure to include a legend.

    - You may use the Python library `pandas` to help with data post processing.
    - To find the relative total energy, subtract the lowest energy in the dataset from each data point. This shifts the minimum energy to zero, so all other values are presented as positive differences relative to the minimum. This allows you to visualize the potential energy surface in terms of relative energy, rather than absolute values.

5. Identify the local minima and maxima and global minima and maxima that you found on your PES using the first derivative of the fitted polynomial found in the previous step. Show the structures nearest to the critical points of the fitted polynomial using a visualization program such as VESTA or Avogadro and report their relative energy in kcal/mol and total energy E_h.

Part 2: Water (H_2O) O–H Bond Distance vs. H–O–H Bond Angle PES

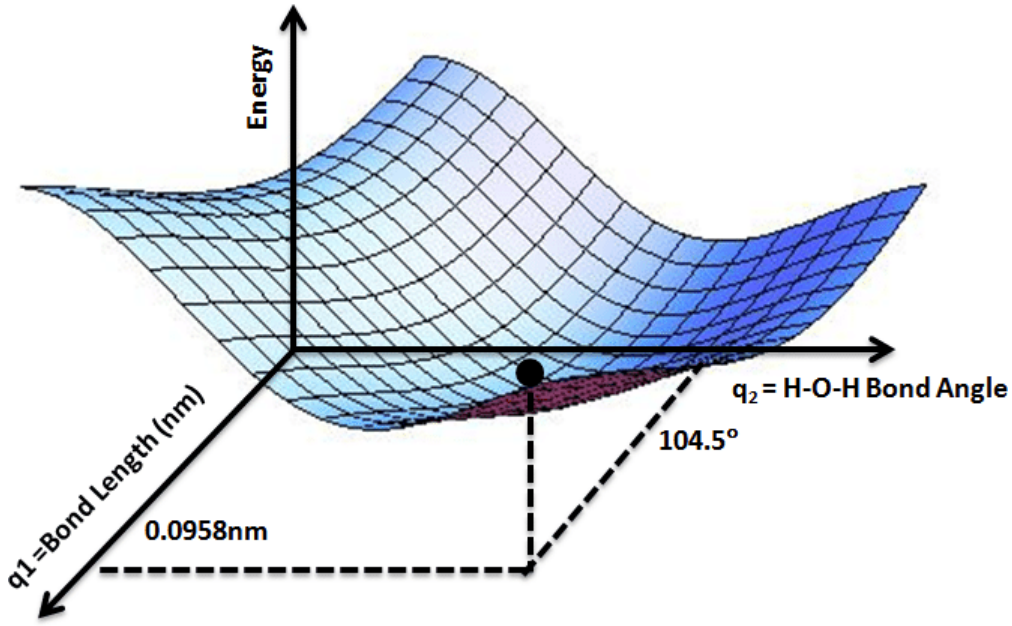

Figure 2: Example of the PES for Water

1. Use Python (or your preferred programming language) and create .xyz files for water with the O-H bond distance varied from 0.8Å-1.2Å with a step of 0.1Å and the H-O-H bond angle varied from 90°-130° with a step of 1°. There should be 205 structures generated from these ranges. You may choose to use a finer grid and/or sample a wider range of bond distances and bond angles. Please specify in the report if you choose to calculate a finer PES.

2. Run an ORCA single point calculation for each geometry created in Step 1. Use the KS-DFT functional B3LYP and basis set 6-31G**. The charge of this system is 0 and the multiplicity of this system is 1. You should use the **run_batch_jobs_orca.sh** SLURM script to be efficient with HPC usage.

    - To run a single point calculation in ORCA, all that is needed in the input line is `"! DFT_FUNCTIONAL BASIS_SET"`.

3. Collect the ORCA total energy results for each single point calculation using Bash or python. The string to search for in the *orca.out* file that contains the total energy in E_h is *"FINAL SINGLE POINT ENERGY"*.

4. Create a 2D heat map showing the PES found using `matplotlib.pyplot.contourf()` (or your preferred graphing code) with the x axis being O-H bond distance, the y axis being the H-O-H bond angle and the color (or z axis) being the relative total energy in kcal/mol. Please use a colormap such as matplotlib's "jet" or a sequential colormap where you can clearly see minimum values and maximum values. Please also identify the lowest point on the graph (it should be 0.0 kcal/mol) with a plotted point that will stand out on the heatmap. The provided Jupyter notebook, **create_water_pes_heatmap.ipynb** provides guidance and gives example code of how to create this graph.

    - You may use the Python library `pandas` to help with data post processing.
    - To find the relative total energy, subtract the lowest energy in the dataset from each data point. This shifts the minimum energy to zero, so all other values are presented as positive differences relative to the minimum. This allows you to visualize the potential energy surface in terms of relative energy, rather than absolute values.
    - Below is an example of how the heatmap should look like:

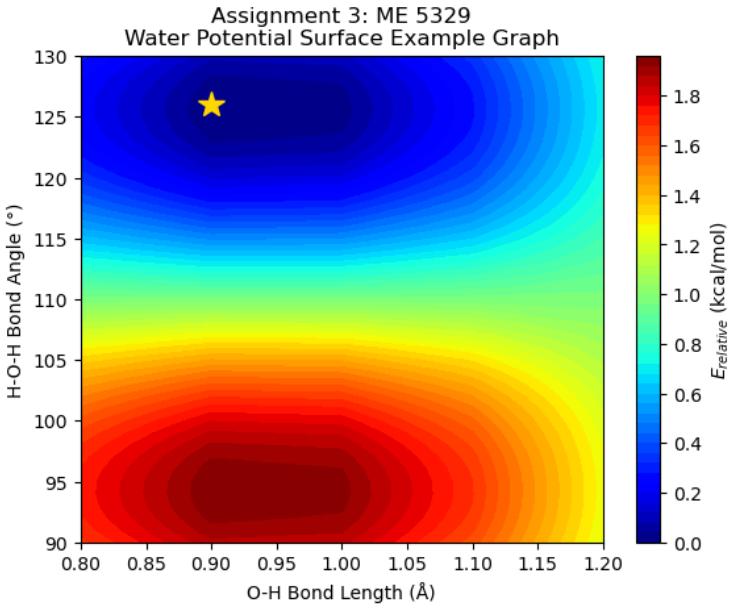

Figure 3: Example Heatmap of the Water PES

5. Visualize the lowest energy structure found on the PES and specify the bond distances and bond angles in an image. Report the relative energy in kcal/mol and total energy E_h.

6. Visualize the highest energy structure found on the PES and specify the bond distances and bond angles in an image. Report the relative energy in kcal/mol and total energy E_h. Hypothesize why this structure has a higher energy than the lowest energy structure.

Grading Rubric

Please include the scripts you used to generate the structures or information on where the structures were found, paths to where the calculations were ran on the HPC (a parent directory for this specific project works also) and your post processing scripts that generated the graphs and results in the Canvas Assignment submission. Including this information is the student's way of showing work in this class. If the information requested above is not provided, the instructor will assume plagaraism or collusion occured and respond accordingly.

The only accepted submission for the report is a MS Word document.

Criteria	**Points**
Part 1 - Butane PES	45
Part 2 - Water PES	45
Formatting and Submission of Word Document	5
Incusion of scripts and paths to calculations on HPC	5
Total	**100**