ME 5329 Homework 3

A Potential Energy Curve (PEC) With Butane Dihedral Angle

September 25, 2025

Dr. Aquino Fall 2025

Due: October 1, 2025

Objectives:

The purpose of a potential energy curve (PEC) is to illustrate how the potential energy of a molecule or system varies with respect to a specific coordinate, such as bond length, bond angle, or dihedral angle. PECs provide key insights into molecular stability, reaction pathways, vibrational modes, and conformational preferences-enhancing our understanding of molecular structure, reactivity, and dynamics. In this work, the following objectives will be emphasized:

a) how to generate multiple input geometries using `molecule_lib` and Python;

b) how to batch submit SLURM jobs;

c) how to post-process multiple calculations;

d) and how to create publication quality figures and graphs using matplotlib.pyplot.

Butane (C_4H_{10}) Dihedral PEC

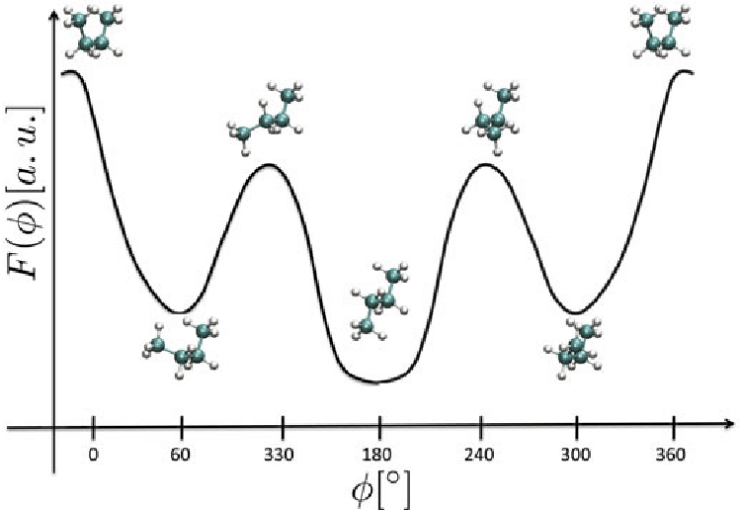

Figure 1: Example of the PEC for the Dihedral Angle in Butane

In this homework, **Steps 1-2** outline the calculation process, whereas **Steps 3-6** focus on the results and discussion.

1. Use Python and `molecule_lib` to rotate one half of the butane molecule (`butane.xyz` which is located in the Appendix) from $-180.0°$ to $+180.0°$ with a step of $5°$ and save each structure. The C-C-C-C dihedral angle observed in `butane.xyz` is $0°$. There should be 73 structures generated from these ranges. You may choose to use a finer step for butane dihedral angles. Please specify in the report if you choose to calculate a finer PEC.

   - 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]). This information is needed for the "index" argument in the XYZMolecule.manipulate() method.

2. Run an ORCA single point calculation for each geometry created in Step 1. Use the functional B3LYP and basis set TZVP. Also please include Grimme's D3 dispersion correction in the single point calculation. The charge and multiplicity of this system is 0 and 1, respectively. 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"`.
   - The **run_batch_jobs_orca.sh** SLURM script is located in `/home/jerschro/Share/` and will be explained further in class. This script executes all the generated butane structures from Step 1, which are stored in the "to_run_structures" directory, using the `orca.inp` template located in the parent directory. It is important to use this script to ensure efficient HPC usage and to avoid unnecessarily overloading the SLURM queue. In short, the script runs ORCA 73 times (once for each structure) within a single SLURM job submission, rather than submitting 73 separate SLURM jobs.
   - In the `orca.inp` template file, the xyz filename definition has a placeholder of "XYZ_FILENAME". This is automatically replaced by the unique structure filename by the **run_batch_jobs_orca.sh** SLURM script.

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"*. You can also add the "> FILENAME" after the grep command like this,

   ```
   grep "FINAL SINGLE POINT ENERGY" */orca.out > grep.txt
   ```

   and this will write the output of the grep command to the file named "grep.txt". You can read this "grep.txt" file to create the required graph described in the next step.

4. Create a graph showing the PEC 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). Show the fitted polynomial on the same graph 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 curve 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 PEC using the first derivative of the fitted polynomial found in the previous step. You may use `numpy.roots()` to do this. Report these critical points found from your fitted polynomial function. 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 in E_h. There should be 7 unique butane conformers shown in this step.

6. Discussion Questions:

    (a) Which of the structures reported in Step 5 would a geometry optimization converge to? If multiple minima exist, which conformer should be considered the ground-state (lowest-energy) structure?

    (b) Among the Step 5 structures, which are symmetry-equivalent or identical, and are any true enantiomers? If so, please identify them.

    (c) What is the terminology for molecules that share the same molecular formula but differ only in their conformation (3D-geometry)?

Submission Requirements:

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. Please consider this carefully.

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

Please submit it under the **'Homework 3'** assignment in Canvas.

Appendix:

butane.xyz

```
14
butane.xyz made for homework 3 - ME 5329 - Fall 2025
C      0.000000    0.000000    0.000000
C     -1.528951    0.000073   -0.000042
C      0.605451   -0.000019    1.395212
C     -2.134394   -0.000051    1.395172
H      0.373159   -0.866008   -0.559027
H      0.347936    0.894003   -0.531125
H     -1.902109    0.866140   -0.558978
H     -1.876891   -0.893872   -0.531260
H      1.694633    0.090529    1.331830
H      0.229682    0.840789    1.986742
H      0.380954   -0.927652    1.929780
H     -1.758627   -0.840922    1.986612
H     -1.909891    0.927524    1.929837
H     -3.223578   -0.090588    1.331786
```