ME 5329 Assignment 1

Introduction to ORCA: Geometry Optimization and Frequency Calculations.

September X, 2025

Dr. Aquino Fall 2025

Objectives:

- Learn how to do an ORCA geometry optimization and frequency calculation.
- Understand the energy minimzation happening in a geometry optimization.
- Understand why the first vibrational frequencies are important.
- Understand what Mulliken/Löwdin population analysis is.
- Learn about and calculate theoretical IR Spectra for gas phase molecules.

Geometry Optimization and Frequency:

1. Generate initial structures for water (H_2O), oxygen (O_2), carbon dioxide (CO_2) and methanol (CH_3OH).

2. Do an ORCA geometry optimization using KS-DFT functional B3LYP and basis set 6-31G(d,p). For each system, the charge is 0 and the multiplicity is 1.

3. Calculate the vibrational frequencies of the optimized structure using ORCA.

- You can do Step 2 and Step 3 in one calculation. The ORCA input line should look like this: *"! B3LYP 6-31G(d,p) OPT FREQ"*

4. Report the total energy of each structure in E_h and kJ/mol in a table.

5. Report up to the first ten vibrational frequencies found for each structure in a table. If there are less than ten vibrational frequencies, state why this is the case.

- The first six frequencies should be near zero. If this is not the case, you should reoptimize the structure with a tighter convergence.

6. Visualize each optimized structure (found in the orca.xyz file) and report the bond distances and angles on the picture of the structure. You may use a visualization program or Powerpoint to do this in an organized manner.

- For CH_3OH, report all bond distances and the one H-O-C bond angles and the three H-C-O bond angles.

7. Choose the structure that has the most optimization cycles and create a line graph of the "Total Energy vs. Iterations" of the geometry optimization from reading the ORCA log file using Python.

8. Choose the same structure chosen in Step 7 and create a line graph of the "ΔE vs. Iterations" of the geometry optimization from reading the ORCA log file.

   - You can combine the previous two graphs into one graph like the example below if you choose.

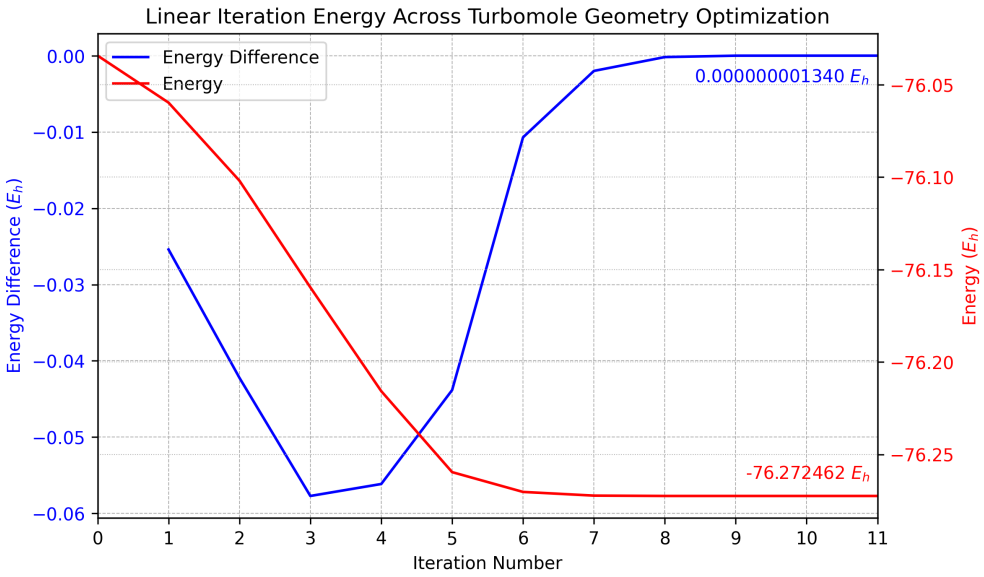

Figure 1: Example of total energy and ΔE across a DFT optimization graph.

9. If the curves you have plotted are jagged, theorize why this is the case and the calculation still converged.

Population Analysis Calculations:

1. Do a geometry optimization and frequency calculation for water (H_2O), hydrogen fluoride (HF), carbon monoxide (CO), nitrogen dioxide (NO_2^-), methane (CH_4), ammonia (NH_3) using KS-DFT functional PBE and basis set TZVP. The multiplicity of all structures is 1 and the charge of every structure excluding NO_2^- is 0. The charge of NO_2^- is -1.

2. Create a table and report the Mulliken and Löwdin (Loewdin) population analysis found in the ORCA output file for each atom in each molecule. Notice where the two techniques differ and where they agree. Are there any atoms that have a different reported charge than we would chemically expect them to have?

3. Report the total energy in E_h and kJ/mol for each molecule in a table.

IR Spectrum Calculations:

1. Do a geometry optimization and frequency calculation for formic acid (HCOOH), and methanol (CH_3OH) using KS-DFT functional PBE and basis set 6-31G**. For each system, the charge is 0 and the multiplicity is 1.

2. Report the IR Spectrum found in the ORCA output by creating a plot of Wavenumber/Frequency (cm^{-1}) vs. Absorbance Intensity (km/mol). The x-axis should consist of a range of Wavenumbers from 300 to 4000 cm^{-1} and need to be ordered in a descending fashion left to right.

    - To do this you may use the Jupyter notebook provided, *create_ir_spectrum_plot.ipynb*, which reads the orca.out file and creates the IR spectra graph.
    - It is also possible to use the ORCA utility **orca_mapspc**. This prints out a .dat file in which you will need to normalize and modify the data (as it prints out the Transmittance instead of Absorbance) in order to achieve the Absorbance plot.

3. Search on the NIST Chemistry WebBook for the Gas Phase IR Spectra for each molecule and compare the experimental IR Spectra to our theoretically calculated IR Spectra. State where our results differ to the experimental results.

4. Report the total energy in E_h and kJ/mol for each molecule in a table. Report the similarity or difference to the total energy found in Part 1 for methanol and explain why.

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 - Completion of all assigned tasks.	30
Part 2 - Completion of all assigned tasks.	30
Part 3 - Completion of all assigned tasks.	30
Formatting and submission of MS Word document.	5
Incusion of scripts and paths to calculations on HPC in Canvas Assignment submission.	5
Total	**100**