ME 5329 Project 2

Reaction Pathway of H_2CO Using Nudged Elastic Band (NEB) Transition State Algorithm

September 23, 2025

Dr. Aquino Fall 2025

Due: September 29, 2025

Objectives:

- Understand how to use the Nudged Elastic Band (NEB) algorithm to calculate a transition state (TS).
- Comprehend the role of the transition state (TS) in a reaction pathway.
- Recognize the significance of including zero-point energy (ZPE) correction in a reaction pathway calculation.

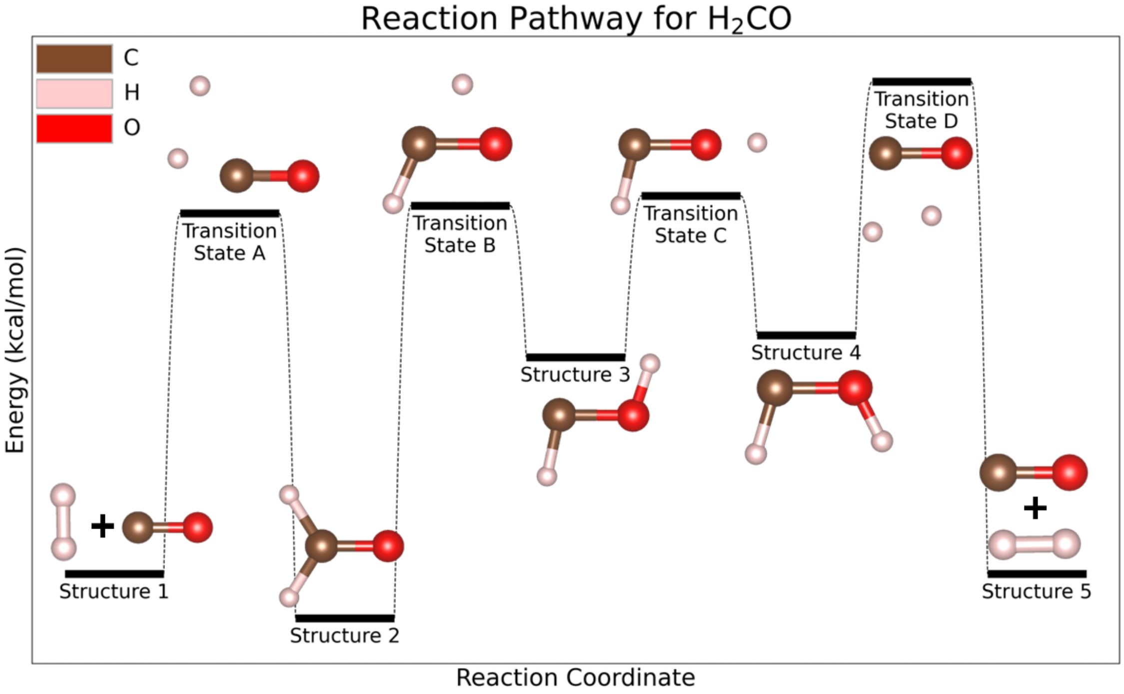

Figure 1: Stationary points on the H_2CO potential energy surface (PES).

Description of the Reaction Pathway for H_2CO:

1. By using ORCA we will characterize the reaction pathways shown in Figure 1. Each reaction to be characterized is described below:

- Reaction A: $H_2 + CO \longleftrightarrow H_2CO$
- Reaction B: $H_2CO \longleftrightarrow HCOH$ (anti)
- Reaction C: HCOH (anti) $\longleftrightarrow$ HCOH (syn)
- Reaction D: HCOH (syn) $\longleftrightarrow H_2 + CO$

2. Below are the names for each structure across the reaction pathway:

- Structure 1 and Structure 5: Hydrogen (H_2) and carbon monoxide (CO).
  - These Structures are also called the Reactants.
- Structure 2: Formaldehyde (H_2CO)
- Structure 3: Anti-hydroxycarbene (HCOH)
- Structure 4: Syn-hydroxycarbene (HCOH)
  - Hydroxycarbene is also traditionally called hydroxymethylene.

3. Some notes on chemistry terminology:

- The terms **anti** or **antiperiplanar** refers to when the H−C−O−H dihedral angle in hydroxycarbene is approximately $180\,^\circ$. Similarly, **syn** or **synperiplanar** refer to when this dihedral angle is approximately $0\,^\circ$. In other words, the anti conformer has the two hydrogens on opposite sides of the molecule, while the syn conformer has the hydrogens on the same side. This difference in dihedral angle is important because it can affect the molecule's reactivity.
- An **isomer** is a molecule that has the same molecular formula as another but differs in the connectivity or spatial arrangement of its atoms. Hydroxycarbene is an isomer of formaldehyde. We say it this way because formaldehyde is stable and hydroxycarbene is unstable.
- Hydroxycarbene is also called a **tautomer** of formaldehyde, which is a special type of isomer that differs in the position of a proton (H^+) and the location of a double bond between isomers.
- The specific isomer of a molecule can be very important in biology and medicine. A famous example is the drug **Thalidomide**, where one **enantiomer** (a mirror-image isomer) was used to treat morning sickness in pregnant women, while the other enantiomer caused severe birth defects in the 1950s and 1960s.

Project Instructions:

In this project, **Steps 1-4** outline the calculation process, whereas **Steps 5-8** focus on the results and discussion.

1. Create each structure found in the H_2CO reaction pathway (Figure 1). You may use SMILE strings or a Python script generating with a reasonable guess for species bond lengths and bond angles. For Structure 1 and Structure 5, create a reasonable structure containing CO and H_2 in one .xyz file with a distance of $\sim$ 5Å between the two gas molecules.

2. For each reaction pathway structure (Structure 1 to Structure 5), do an ORCA geometry optimization using functional B3LYP and basis set 6-31G*. After the optimization, calculate the vibrational frequencies of each structure. The charge and multiplicity of each system are 0 and 1, respectively.

3. For each reaction (Reaction A to Reaction D), use the nudged elastic band (NEB) algorithm in ORCA to locate the corresponding transition states (TS).

   - To do this, you take the initial optimized structure geometry (`initial_structure_opt.xyz`) and the final optimized structure geometry (`final_structure_opt.xyz`) and specify them in the ORCA input file. Below is how your `orca.inp` should look for the NEB calculations:

   ```
   ! FUNCTIONAL BASIS_SET NEB-TS FREQ

   %maxcore 4000

   %pal
   nprocs 12
   end

   %NEB NEB_END_XYZFILE "final_structure_opt.xyz"
   END

   * xyzfile 0 1 initial_structure_opt.xyz
   ```

   - You will want to ensure that the atom order matches between the initial and final .xyz file. Basically atom 1 in both files is C, atom 2 in both files is the same Hydrogen atom etc. If the atoms are not in the same order between .xyz files, NEB will fail. This is because NEB interpolates between the initial and the final .xyz file positions to find the transition state along that path.
   - When the NEB-TS ORCA calculation is finished, the transition state structure will be located in the file named ”`orca_NEB-TS_converged.xyz`”.

4. Take the transition state structure for each reaction (TS A to TS D) and do an ORCA single point frequency calculation using the same level of theory.

5. For each TS, report all of the vibrational frequencies calculated neatly in a table. Highlight what structures have an imaginary frequency (which is reported as a negative frequency in ORCA). You may also do the same analysis for each local minima structure but it is not required.

6. Use your prefered graphing code and create two reaction pathway schemes (your results of Figure 1). One graph will be without ZPE correction and the other graph will be with ZPE correction, both reported in kcal/mol. Ensure your energy values are normalized to ”Structure 1 (Reactants)”. You must add a label on the horizantal bars for each minima/maxima describing what structure it is (shown in Figure 1) and what relative energy (ΔE) it is located at. Note the x axis is an arbitrary axis and is called the ”Reaction Coordinate”. Be sure to provide your graphs with a unique title that includes your name or R#, ensuring it is clearly identifiable. You may also create a neat table showing your normalized energy results presented on the two graphs but it is not required.

- To find the normalized total energy, subtract the ”Structure 1 (Reactants)” energy from each data point in the dataset. This will shift the ”Structure 1 (Reactants)” energy to zero, so all other values are presented as relative difference to the ”Structure 1 (Reactants)” energy.

7. Visualize each TS in the visualization program of your choice. Then label the bond distances and any non-trivial bond angles directly on the screen shot or saved image of the visualized structure. You may use a visualization program or PowerPoint to organize and present these annotated visualized structures clearly. You may also do the same analysis on each optimized local minima structure but it is not required. Note: This task requires you to use the same analysis method that was applied in Homework 1 - Part 1 - Step 6.

8. Discussion Questions:

(a) How can you confirm that a computed TS structure is a true transition state of the reaction compared to just being a higher-energy local minimum?

(b) Why is Structure 2 (formaldehyde) called the ”global minimum” when compared to the other structures in this reaction pathway?

(c) Which reaction on the reaction pathway calculated has the highest activation barrier and which has the lowest? How do these differences affect the likelihood of observing these isomers experimentally?

(d) Why is the zero-point energy (ZPE) correction important to include when comparing computed structures found on a reaction pathway?

(e) Formaldehyde, anti-hydroxycarbene, and syn-hydroxycarbene all share the same molecular formula (H_2CO). What type of isomerism do they represent? Hint: Look at the definitions on Page 2.

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. If the information requested above is not provided, the instructor will assume plagaraism or collusion occured and respond accordingly.

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

Please submit it under the **'Project 2'** assignment in Canvas.

Citations:

- Dallos, M.; Lischka, H.; Ventura Do Monte, E.; Hirsch, M.; Quapp, W. Determination of Energy Structure and Saddle Structures Using Multireference Configuration Interaction Methods in Combination with Reduced Gradient Following: The S0 Surface of H2CO and the T1 and T2 Surfaces of Acetylene. Journal of computational chemistry 2002, 23 (5), 576-583. .