Problem set 1

Due March 12, 2025

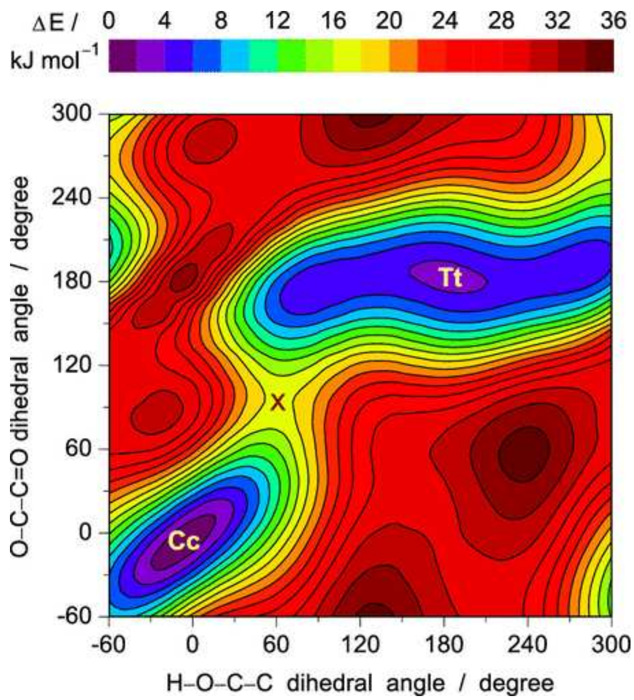
1. Write down the Z-matrices of the following two systems:

   - The hydrogen peroxide molecule (H_2O_2). The O-O bond length is 1.475 Å, both O-H bond lengths are 0.95 Å, both H-O-O bond angles are 111.5°, and the H-O-O-H dihedral angle is 90°. Make the oxygen atoms the first and the second one in the Z-matrix.
   - The ethene molecule (C_2H_4). The C=C bond length is 1.339 Å, all C-H bond lengths are 1.087 Å, the H-C-C bond angles are 121.3° and the molecule is planar. Make the carbon atoms the first and the second one in the Z-matrix.
   - The methane molecule (CH_4). All C-H bond lengths are 1.095 Å, all H-C-H bond angles are 109.47° and all improper H-C-H...H dihedral angles are ±120° (for the ideal tetrahedral geometry). Make the carbon atom the first one in the Z-matrix.

2. Sketch a picture of an ammonia (NH_3) molecule in two possible geometries, each one being the mirror image of its counterpart. Define the internal coordinate that distinguishes these two geometries and its approximate values for both of them.

3. How many coordinates are necessary to define the energy surface of a system consisting of two hydrogen fluoride (HF) molecules (a hydrogen fluoride dimer) *in vacuo*? Try to define these coordinates.

4. In the potential-energy map of glycolamide shown below (Lapinski et al., *J. Phys. Chem. A*, 2019, 123, 3831-3839) mark two energy minima, the saddle point that separates them and draw the approximate reaction path linking these minima.



5. The table below summarizes the energies and Hessian eigenvalues of critical points of a system undergoing a chemical reactions. Determine which points are minima (if any), maxima (if any), and saddle points (if any; define the order of the saddle points). Which of these critical points are on the reaction pathway and which are not and why?

Point	E	λ_1	λ_2	λ_3
(a)	-5	5	20	30
(b)	2	-4	7	10
(c)	5	-5	-5	1
(d)	-1	4	5	8