Problem set 1

Due March 10, 2026

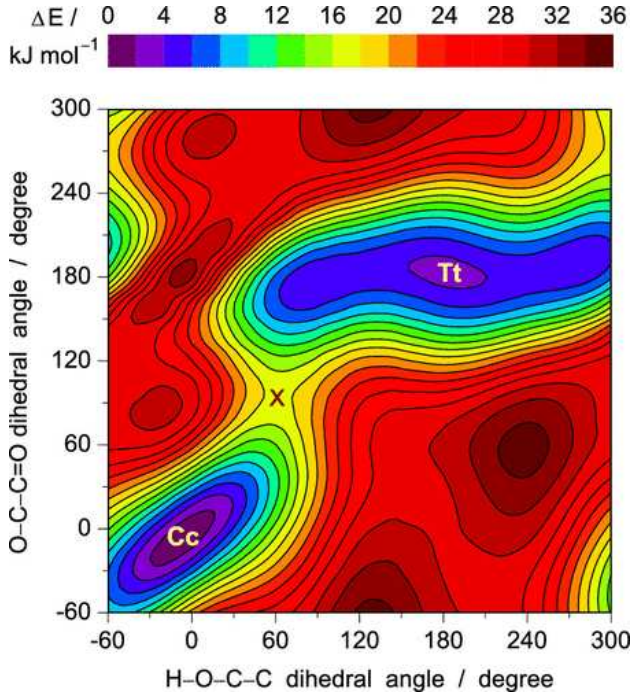
1. Sketch the following molecules, number/uniquely label their atoms (e.g., 1, 2, 3, ... or S1, S2, H3, ...) and write down their Z-matrices.

   - The dihydrogen disulfide molecule (H_2S_2). The S-S bond length is 2.06 Å, both S-H bond lengths are 1.35 Å, both H-S-S bond angles are 90.6°, and the H-S-S-H dihedral angle is −97°. Make the sulfur atoms the first and the second one in the Z-matrix.
   - The trans-1,2-dichloroethene molecule ($C_2H_2Cl_2$). The C=C bond length is 1.354 Å, both C-H bond lengths are 1.075 Å, both C-Cl bond lengths are 1.718 Å, both H-C=C bond angles are 124°, both Cl-C=C bond angles are 120.8° and the molecule is planar. Make the carbon atoms the first and the second one in the Z-matrix. Use only one regular dihedral (involving four atoms bonded consecutively; e.g. that defined by Cl-C=C-Cl) as an internal coordinate and improper dihedrals to complete the set of dihedral-angle internal coordinates. This selection ensures that the internal coordinates of an atom are defined relative to its closest neighbors (stability of the internal-coordinate set and no coordinate dependencies) and enables us to use only one regular dihedral angle to define the configuration of the molecule. Then modify the Z-matrix to change the molecule to the cis configuration.
   - The cyclic hexasulfur molecule (S_6). All bond lengths are 2.086 Å, all bond angles are 102.6° and all dihedral angles are 73.8° in absolute value (Steidel et al., *Z. Naturforsch. B*, **1978**, 33b, 1554-1555). To determine the signs of the dihedrals selected as internal coordinates use the information that this molecule has the structure resembling that of the chair conformation of cyclohexane (also, you can visit Wikipedia to see a picture of hexasulfur molecule).

2. Sketch a picture of a triphenylphosphine molecule, $P(C_6H_5)_3$ in two possible geometries, each one being the mirror image of its counterpart. Do not expand the phenyl groups, use the Ph symbol for the whole group instead. 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 hydrogen-bonded water dimer *in vacuo*? Try to define these coordinates. For the geometry of this dimer you can refer to `https://link.springer.com/article/10.1007/s00894-019-4274-2`.

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)	10	-40	-20	30
(b)	2	-80	30	50
(c)	-20	20	30	50
(d)	-1	10	20	20