MATH 728A, BIOMOLECULAR GEOMETRY, HOMEWORK #11

Problem 1 (Z-system to Z-matrix). Consider the Z-system you wrote down for the molecule ethane in Homework 1.2. If necessary go back and correct it. Select a root in each of the atom/bond, bond/angle, and triangle/wedge trees, where the three roots (A, b, t) satisfy $A \in b \subset t$. By picking leaves in the triangle/wedge tree that are as far from the root as possible, give an ordering of the triangles (with the root triangle first). Since each leaf triangle determines a leaf bond, which determines a leaf atom, display the corresponding orderings of the bonds and of the atoms. Compute an unlabelled Z-matrix for ethane corresponding to your Z-system with the chosen root and leaf picking order. Then give a labelled Z-matrix for ethane (label your unlabelled Z-matrix). Take care that the signs of your Z-matrix wedge angles are correctly related to the wedge angles in your Z-system.

Problem 2 (Proline ring conformations). Build a Z-system for the proline ring (leave out the ring hydrogens) where the bond $\{N, C^\delta\}$ is omitted from the atom/bond tree. (See the CHARM22-all hydrogen-topology file at https://rxsecure.umaryland.edu/research/amackere/research.html for the standard atom names and the bonding pattern; note that atoms $C^\alpha, C^\beta, C^\gamma, C^\delta$ are written as CA, CB, CG, CD.) In comparison with our discussion in class of five-membered rings, let $A_0 = N, A_1 = C^\alpha, A_2 = C^\beta, A_3 = C^\gamma, A_4 = C^\delta$. Assign the all the bond lengths and the bond angles τ_1, τ_2, τ_3 from the CHARM22-all hydrogen-parameter file. Assign $\nu_1 = -22^\circ, \nu_2 = 33^\circ$. (These values are from the 3rd chemistry paper in my bibliography on five-membered rings.) Enter this data in IMIMOL and export an xyz file. Using the data from this xyz file answer the following:

(1) Compute the actual bond length of $\{N, C^\delta\}$ in this conformation and compare it with the equilibrium bond length from the parameter file.
(2) Compute the standard pose of the Marzec-Day coordinate system.
(3) Compute the Cremer-Pople puckering amplitude q and phase P.
(4) Compute the Marzec-Day elongation amplitude S and phase Γ.
(5) Using these four parameters q, P, S, Γ and the five bond lengths (from the parameter files), recompute the bond angles τ_1, τ_2, τ_3 and the wedge angles ν_1, ν_2. (Use the MAPLE procedures from my website.)

Do you think the new (recomputed) internal coordinates are satisfactory? Enter them in IMIMOL, export a MOPAC Z-Matrix, and make a labelled picture using RASMOL. Print it out.

Problem 3 (Exocyclic bond and wedge angles). Use spherical trigonometry to prove the formulae

$$\cos\theta(\tau) = \frac{-2}{1 + \sqrt{1 + \frac{16}{1+\cos\tau}}}, \qquad \phi(\tau) = \pi - \frac{1}{2}\cos^{-1}\left(\frac{\cos\theta(\tau)}{1+\cos\theta(\tau)}\right),$$

for the exocyclic bond angle $\theta(\tau)$, and the exocyclic wedge angle $\phi(\tau)$, from the plane of the endocyclic (strained) bond angle τ to the plane containing one of the two substituent atoms to the ring atom, and an endocyclic bond extending from the ring atom. Show that when $\tau = \cos^{-1}(-1/3)$ then $\theta(\tau) = \tau$ and $\phi(\tau) = 2\pi/3 = 120^\circ$.

Problem 4 (Complete proline conformations). Use the formulae from problem 3 to compute the exocyclic bond and wedge angles for all the ring hydrogens in proline. (Show how to plug into the formulae in the case of all the substituents of C^β, and use the MAPLE procedures for the rest.) Build a complete Z-system for proline and print out a RASMOL stereo picture.