MATH 728A, BIOMOLECULAR GEOMETRY, HOMEWORK #2

Problem 1 (Impropers). Suppose a molecule contains four distinct atoms A_1, A_2, A_3, A_4, and the bonds $b_1 = \{A_1, A_2\}, b_2 = \{A_2, A_3\}, b_3 = \{A_2, A_4\}$ are in the atom/bond tree $\Gamma^{(0)}$. Let $a_1 = \{b_1, b_2\}, a_2 = \{b_3, b_2\}$ be angles in the bond/angle tree $\Gamma^{(1)}$ and $d = \{a_1, a_2\}$ is an improper in the angle/dihedral tree $\tilde{\Gamma}^{(2)}$. Let $\mathcal{X}(A)$ denote the position in space of an atom A. As discussed in class define:

$$\begin{aligned}
\mathbf{u} &= \frac{\mathcal{X}(A_3) - \mathcal{X}(A_2)}{\|\mathcal{X}(A_3) - \mathcal{X}(A_2)\|} \\
\mathbf{v}_1 &= \frac{\mathcal{X}(A_1) - \mathcal{X}(A_2) - \mathbf{u}\{\mathbf{u} \cdot [\mathcal{X}(A_1) - \mathcal{X}(A_2)]\}}{\|\mathcal{X}(A_1) - \mathcal{X}(A_2) - \mathbf{u}\{\mathbf{u} \cdot [\mathcal{X}(A_1) - \mathcal{X}(A_2)]\}\|} \\
\mathbf{v}_2 &= \frac{\mathcal{X}(A_4) - \mathcal{X}(A_2) - \mathbf{u}\{\mathbf{u} \cdot [\mathcal{X}(A_4) - \mathcal{X}(A_2)]\}}{\|\mathcal{X}(A_4) - \mathcal{X}(A_2) - \mathbf{u}\{\mathbf{u} \cdot [\mathcal{X}(A_4) - \mathcal{X}(A_2)]\}\|}.
\end{aligned}$$

Show that if the angles a_1 and a_2 are not collinear then the above expressions make sense. Show that if we replace A_2 in the expressions for $\mathbf{v}_1$ and $\mathbf{v}_2$ by A_3 then the vectors $\mathbf{v}_1$ and $\mathbf{v}_2$ are unchanged. If we orient d from a_1 to a_2 then the dihedral angle ϕ is uniquely determined (up to addition of an integer multiple of 2π) by the relation

$$e^{i\phi} = \cos\phi + i\sin\phi = \mathbf{v}_1 \cdot \mathbf{v}_2 + i(\mathbf{v}_1 \times \mathbf{v}_2) \cdot \mathbf{u}.$$

Show that if d is oriented in the opposite manner then the dihedral angle should be replaced by $-\phi$.

Problem 2 (Stereoisomers of Methane). Print a picture of a RASMOL stereo view of the molecule of methane from homework 1.1. In IMIMOL change the signs of all the impropers and again export another Z-matrix (with a different name). Print out a RASMOL stereo view of this molecule. Describe the relationship between these two versions of methane.

Problem 3 (Free Rotation). Look back at your trees for the ethane molecule (homework 1.2). Suppose you wanted to rotate the group $C_1H_1H_2H_3$ with respect to the group $C_2H_4H_5H_6$ about an axis along the C_1C_2 bond. How many internal coordinates do you have to change to accomplish this? (You had better check by drawing pictures with RASMOL). If necessary change your angle/wedge tree so that this can be done by changing only one wedge angle. Draw (and print) stereo pictures of three different conformations of ethane with different degrees of rotation.