Molecular Geometry and Rotational Constant Analysis

Dr. Yukio Yamaguchi

Center for Computational Quantum Chemistry, University of Georgia

with additions and modifications by T. Daniel Crawford, *Virginia Tech*

1. Read the molecular cartesian coordinates and atomic numbers from the given file.

2. Calculate all possible interatomic distances, R_{ij}.

$$R_{ij} = \sqrt{(X_i - X_j)^2 + (Y_i - Y_j)^2 + (Z_i - Z_j)^2} \tag{1}$$

3. Calculate all possible bond angles. For example, the angle, ϕ_{ijk}, between atoms $\mathbf{i}-\mathbf{j}-\mathbf{k}$, where $\mathbf{j}$ is the central atom is given by:

$$\cos\phi_{ijk} = \mathbf{e_{ji}} \cdot \mathbf{e_{jk}} \tag{2}$$

   where the $\mathbf{e_{ij}}$ are unit vectors between the atoms, e.g.,

$$e_{ij}^X = -\left(X_i - X_j\right)/R_{ij} \quad e_{ij}^Y = -\left(Y_i - Y_j\right)/R_{ij} \quad e_{ij}^Z = -\left(Z_i - Z_j\right)/R_{ij} \tag{3}$$

4. Calculate all possible out-of-plane angles. For example, the angle θ_{ijkl} for atom $\mathbf{i}$ out of the plane containing atoms $\mathbf{j}-\mathbf{k}-\mathbf{l}$ (with $\mathbf{k}$ as the central atom) is given by:

$$\sin\theta_{ijkl} = \frac{\mathbf{e_{kj}} \times \mathbf{e_{kl}}}{\sin\phi_{jkl}} \cdot \mathbf{e_{ki}}. \tag{4}$$

5. Calculate all possible torsional angles. For example, the torsional angle τ_{ijkl} for the atom connectivity $\mathbf{i}-\mathbf{j}-\mathbf{k}-\mathbf{l}$ is given by:

$$\cos\tau_{ijkl} = \frac{(\mathbf{e_{ij}} \times \mathbf{e_{jk}}) \cdot (\mathbf{e_{jk}} \times \mathbf{e_{kl}})}{\sin\phi_{ijk} \ \sin\phi_{jkl}} \tag{5}$$

   Can you also determine the sign of the torsional angle?

6. Find the center of mass of the molecule.

$$X_{c.m.} = \frac{\sum_i m_i X_i}{\sum_i m_i} \quad Y_{c.m.} = \frac{\sum_i m_i Y_i}{\sum_i m_i} \quad Z_{c.m.} = \frac{\sum_i m_i Z_i}{\sum_i m_i}, \tag{6}$$

   where m_i is the mass of atom i and the summation runs over all atoms in the molecule.

7. Calculate elements of the moment of inertia tensor.

$$I_{\alpha\alpha} = \sum_i m_i \left(\beta_i^2 + \gamma_i^2\right) \tag{7}$$

$$I_{\alpha\beta} = \sum_i m_i \alpha_i \beta_i, \tag{8}$$

   where α, β, and γ correspond to choices of x, y, and z (e.g., I_{xy} is one choice of $I_{\alpha\beta}$).

8. Diagonalize the inertia tensor to obtain the principal moments of inertia.

$$I_a \leq I_b \leq I_c \tag{9}$$

9. Determine the molecular type:

   - diatomic
   - linear polyatomic
   - asymmetric top
   - symmetric top (prolate or oblate)
   - spherical top

10. Determine the moments of inertia in amu.Å^2 and g.cm^2 and determine the rotational constants in cm^{-1} and MHz.

$$A \geq B \geq C \tag{10}$$

$$A = \frac{h}{8\pi^2 I_a} \qquad B = \frac{h}{8\pi^2 I_b} \qquad C = \frac{h}{8\pi^2 I_c} \tag{11}$$

For more information see E.B. Wilson, J.C. Decius, and P.C. Cross, '**Molecular Vibrations**', McGraw-Hill, 1955.