Assignment I

CH603

Molecular Geometry and Rotational Constant Analysis

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

Hint 1: Opening and closing the file
Hint 2: Reading the number of atoms
Hint 3: Storing the z-values and the coordinates

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

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

Hint 1: Memory allocation
Hint 2: Loop structure
Hint 3: Printing the results

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

$$\cos\phi_{ijk} = e_{ji}.e_{jk}$$

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

$$e_{ij}^{X} = -\frac{\left(X_i - X_j\right)}{R_{ij}} \qquad e_{ij}^{Y} = -\frac{\left(Y_i - Y_j\right)}{R_{ij}} \qquad e_{ij}^{Z} = -\frac{\left(Z_i - Z_j\right)}{R_{ij}}$$

Hint 1: Memory allocation
Hint 2: Avoiding a divide-by-zero
Hint 3: Memory allocation for the bond angles
Hint 4: Printing only unique non-zero angle

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

$$sin\theta_{ijkl} = \frac{\left(\tilde{e}_{kj} \times \tilde{e}_{kl}\right)}{\sin\phi_{jkl}} \cdot \tilde{e}_{ki}$$

Hint 1: Decide do we need to store it.
Hint 2: Calculation of Cross products
Hint 3: Take care of the numerical precision to make sure that sin functions can only have values from -1.0 to +1.0
Hint 4. need to exclude ijkl combinations involving coincidences among the indices as well as distant atom pairs:

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

$$cos\tau_{ijkl} = \frac{\left(\tilde{e}_{ij} \times \tilde{e}_{jk}\right) \cdot \left(\tilde{e}_{jk} \times \tilde{e}_{kl}\right)}{\sin\phi_{ijk} \sin\phi_{jkl}}$$

Can you also determine the sign of the torsional angle?

Hint 1: Decide do we need to store it.
Hint 2: Take care of the numerical precision to make sure that sin functions can only have values from -1.0 to +1.0
Hint 3. Print only the unique dihedral angles and limit the printing only to atom pairs that are close together.

6. **Find the center of mass of the molecule**

$$X_{c.m.} = \frac{\sum_i m_i X_i}{\sum_i m_i} \qquad Y_{c.m.} = \frac{\sum_i m_i Y_i}{\sum_i m_i} \qquad Z_{c.m.} = \frac{\sum_i m_i Z_i}{\sum_i m_i}$$

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

Hint 1: An excellent source for atomic masses and other physical constants is the National Institute of Standard and Technology (NIST) website.

Hint 2: Use the masses of the most abundant isotope of each element

7. **Calculate elements of the moment of inertia tensor.**

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

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

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.**

$$I_a \leq I_b \leq I_c$$

Hint 1: Use numpy for diagonalization

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.**

$$A \geq B \geq C$$

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

test input and sample output can be found in the input and output directory. For more information see E.B. Wilson, J.C. Decius, and P.C. Cross, 'Molecular Vibrations', McGraw-Hill, 1955.
(Adapted from https://crawford.chem.vt.edu)