Lab1: Building molecules, Z-matrices, internal coordinates

Objective

- Z-matrices and Internal coordinates
- Building molecules using Avogadro
- Geometry optimization techniques
  - Broyden algorithm
  - Conjugate Gradient algorithm
  - Steepest Descent algorithm
  - Particle Swarm Optimization
  - BFGS

Z-matrix

- Z-matrix is a way of representing the geometry of a molecule, also known as internal coordinate representation.
- Cartesian Coordinates: geometry in terms of x, y, z coordinates
- Z-matrix: molecular geometry using bond lengths, bond angles, and dihedral angles.
- General format:
  - Element-label atom1 bond-length atom2 bond-angle atom3 dihedral-angle
  - Atom1, atom2, etc are line number of reference atom/atomic symbol
  - Element-label are either atomic number or symbol.

Full Z-matrix

Line1: First atom.

Line2: Second atom, reference atom, distance.

Line3: Third atom, reference atom A, distance between A and the third atom, reference atom B, angle defined by atoms A, B and the third atom.

Line4: Fourth atom, reference atom A, distance, reference atom B, angle, reference atom C, dihedral angle (A, B, C and the fourth atom).

Line5: All subsequent atoms follow the same basic form as Line4.

Avogadro tutorials

Water dimer

- Create a water dimer using Avogadro
- Do geometry optimization using the available force fields
- Measure hydrogen bond length and angle

Force field	Hbond length	Hbond angle
UFF		
GAFF		
MMFF94		

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Build molecules and energy minimization using MMFF94

- Carbonic Acid (H_2CO_3)
- Ethanol (CH_3CH_2OH)
- Ethylene (C_2H_4)
- Glucose or Fructose ($C_6H_{12}O_6$)
- Linear form of Ribose ($C_5H_{10}O_5$)
- Cyclic form of Ribose ($C_5H_{10}O_5$)
- Alanine ($C_3H_7NO_2$)
- Palmitic Acid ($CH_3(CH_2)_{14}COOH$)

Numerical optimization techniques

Efficiency of optimization depends on

- Initial geometry
- Choice of coordinate system
- Initial estimate for the Hessian
- Hessian update
- Controlling the step size and search direction

Numerical optimization techniques

- Broyden algorithm

1: Choose $x^{(0)}$
2: $B^{(0)} = B(x^{(0)})$
3: $d^{(0)} = -B_0^{-1} \nabla f(x^{(0)})$
4: $x^{(1)} = x^{(0)} + d^{(0)}$
5: $k = 0$
6: **while** not converged **do**
7: $\quad u^{(k)} = B_k^{-1} \nabla f(x^{(k+1)})$
8: $\quad c_k = d^{(k)} \cdot (d^{(k)} + u^{(k)})$
9: $\quad B_{k+1}^{-1} = B_k^{-1} - \frac{1}{c_k}[u^{(k)} \otimes d^{(k)}] B_k^{-1}$
10: $\quad k = k + 1$
11: $\quad d^{(k)} = -B_k^{-1} \nabla f(x^{(k)})$
12: $\quad x^{(k+1)} = x^{(k)} + d^{(k)}$
13: **end while**

Numerical optimization techniques

- Broyden algorithm
- Conjugate Gradient algorithm (Archisman, Saranagata)
- Steepest Descent algorithm (Ronit, Ronit)
- Particle Swarm Optimization (Kriti, Rituparna)
- BFGS (Sayantan, Samyabrata)

Use Broyden-skr.tex as a template file

References

1. https://avogadro.cc/
2. https://zipse.cup.uni-muenchen.de/teaching/computational-chemistry-1/topics/
3. Thomas A. Halgren, J. Comput. Chem., 17, 490-519 (1996).
4. Numerical optimization techniques,