

CH 362 Winter 2021

COMPUTATIONAL MODELING IN CHEMISTRY



Oregon State
University

Goal: What are energy, structure, properties?

- Two main approaches:
- Molecular Mechanics (fully empirical)
- Electronic structure (based on Schrödinger Equation)

Molecular Mechanics

- Each atom has a “preferred” geometry; anything different adds strain or destabilization of some sort.
 - Bond lengths: Hooke’s law $k(d-d_0)^2$
 - Bond angles: Hooke’s law $k(\theta-\theta_0)^2$
 - Dihedral angles: $\sum K(1+\cos(n\phi-\delta_n))$
 - Van der Waals: $4\epsilon[(\sigma/r)^{12}-((\sigma/r)^6)]$
 - Electrostatic: $q_i q_j / (4\pi\epsilon_0 r_{ij})$
- Sum over every atom and measurement, then change structure to minimize. Good for big systems (biomolecules).

Electronic Structure

- Based on Schrödinger's Equation: $\hat{H}\Psi = E\Psi$
- Hamiltonian: $\{(-\hbar^2/2m)\nabla^2 + V(r)\}\Psi = E\Psi$
- $\Psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 + \dots$ (linear combination of atomic orbitals: LCAO)
- $E = \hat{H}\Psi/\Psi$ (or $\Psi^*\hat{H}\Psi/\Psi^*\Psi$ to remove factors in i)
- Take the derivative of E with respect to each of c_n ; set equal to zero and solve for each of c_n . Then change structure to get a minimized energy.

Electronic Structure: Problems & Solutions

- Easy parts of \hat{H} : Nucleus-Nucleus repulsion (nuclei move slowly with respect to electrons; treat as “fixed”). Born-Oppenheimer approximation.
- Nucleus-electron attraction: Harder, but basically the same multiplied by many electrons. Some challenges with heavy elements (relativistic effects).
- Electron-electron repulsion: Impossible to solve analytically.

Electron Correlation Problem

- Use more basis set functions
- STO-3G: essentially the H-atom 1-electron functions you derive in P-Chem. (Challenge: shifting from polar coordinated to Cartesian)
- 3-21G, 6-31G, 6-311G, etc. Different functional form ($\varphi = x^l y^m z^n e^{-\zeta r^2}$), and each atom has multiple functions for each atomic orbital. Gives electrons more mathematical freedom to find a lower energy. Helps but does not solve the problem. Also costs computational time!

Semiempirical methods

- Different approach. We know a simple STO-3G or 3-21G basis set gives a “wrong” answer, but often the error is consistent.
- Use a parameterized Hamiltonian:
- $\{(-\hbar^2/2m)\nabla^2 + V(r) + C\}$ C is a “fudge factor”—or several—to correct for electron correlation. Many of these factors are based on experimental (empirical) data. Major savings in computational time.
- AM1 (1985): used 19 parameters, optimized for a collection of 167 organic molecules. Focused on structure, ΔH_f° , ionization potential, electron affinity.
- PM3 (1989): Successor approach; >2000 molecules in optimization. Better overall. PM6: 4492 compounds (2007).

Quick demo: the WebMO/Gaussian program

- Build a starting geometry; different conformers will be different local minima.
- Choose a method; optimize geometry and calculate energy. PM6 will return a ΔH_f° ; ab initio, DFT methods will give total energies (vs. isolated nuclei/electrons). Harder to translate to thermochemical values but can be done. (Guest access to WebMO limited to 30 s CPU time.)
- Core questions: most stable form of each ester (conformations), and difference in enthalpy between the lowest two.
- Calculate the IR and animate most important bands (demo)
- Look at LUMO to find interactions between C=O and other electrons.