Lecture 2: Scope and Goals of Computational Chemistry

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Scientific Computing

- Quantitatively evaluate theoretical hypotheses by comparison to experiment while being
  - as efficient (CPU time, carbon footprint, human effort) as possible,
  - obtaining desired results for the right reasons by the simplest possible means,
  - repeatable and reproducible,
  - transparent.

Computational Chemistry

Computational chemistry aims to

- predict experimental results, and partially replace them,
- explain known experimental results,
- allow a stringent test of theories and hypotheses by quantitative comparison to experiment

Making statements about quantities that cannot be measured is not the goal of computational or theoretical chemistry.

Computational Chemists' Essential Skill Set

Computational chemists

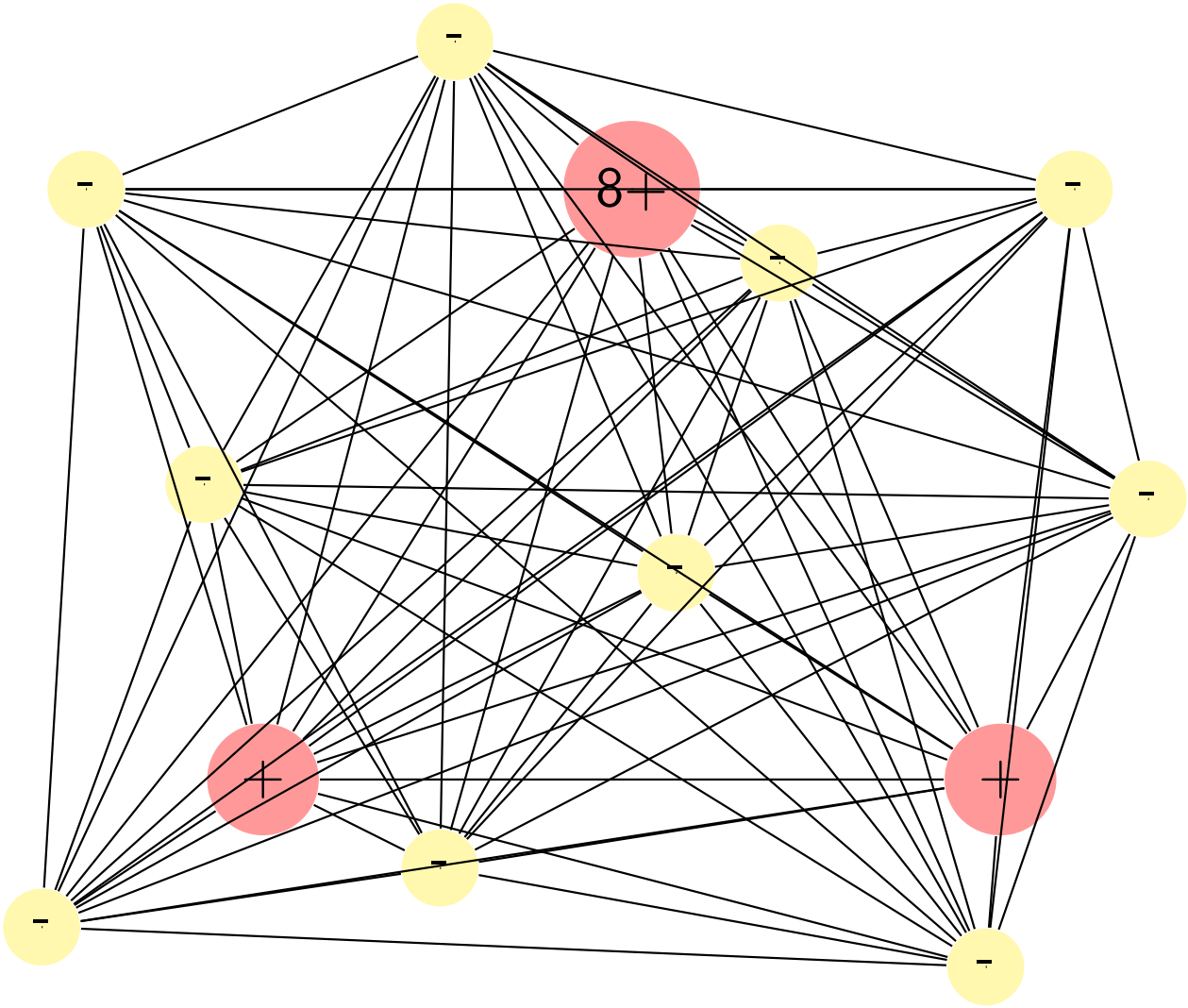
- know which questions to ask and why,
- are intimately familiar with experiment and theory,
- are able to communicate well using several "languages",
- understand how computers, computational methods, and algorithms work,
- know about methods and tools, understand where they are appropriate, and why,
- have an intuitive feeling for numbers and orders of magnitude.

What the Electrons Are Really Doing in Molecules[1]

I feel that chemical binding has not one nature, but many. Also, I do not wish to be necessarily committed to the familiar concept that molecules are composed of atoms, in other words, that atoms are still atoms when they have formed molecules.
(R. S. Mulliken, 1975)

[1] **mulliken**.

Water Molecule



Molecular Electronic Schrödinger Equation

$$\left\{ \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + V_{nn} \right\} \Psi(x_1, \ldots, x_N) = E\Psi(x_1, \ldots, x_N)$$

- Not separable
- No analyical solution
- Extremely high dimension
- Parametrically dependent on nuclear positions
- Eigenvalues: Born-Oppenheimer potential energy surfaces
- One of the hardest and most important challenges of theoretical science

Full Configuration Interaction

- Expand Ψ into a basis of Slater determinants
- Each Slater determinant corresponds to a possible occupation of N electrons over p orbitals, corresponding to an N-electron basis of dimension

$$D = \binom{N}{p}$$

- Example: Water, $N = 10$, $p = 18$ (SVP atomic orbital basis)
- Assume linear scaling of CPU time with D

	n	D	CPU time
H_2O	10	43 758	1h
$(H_2O)_2$	20	7 307 872 110	19 years
$(H_2O)_4$	40	???	???

Full CI For Water Tetramer

	n	D	CPU time
H_2O	10	43 758	1h
$(H_2O)_2$	20	7 307 872 110	19 years
$(H_2O)_4$	40	285 219 402 396 400 814 958	7×10^{11} yrs

- Age of the universe: $\sim 14 \times 10^9$ yrs
- Storage needed: $\sim 10^{10}$ TB, roughly world's total data storage capacity

The greatest free lunch ever: DFT

- 1964: Hohenberg and Kohn proved a theorem showing lowest energy can be found by search over electronic densities (much simpler than wavefunction)

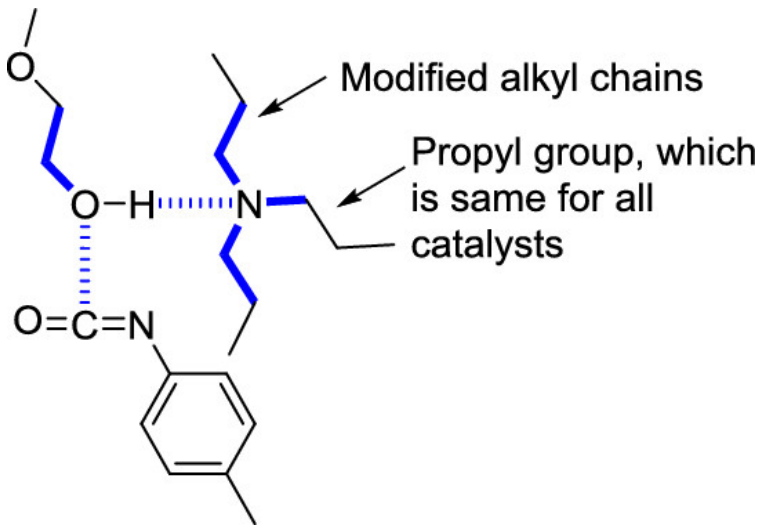
- 1965: Created Kohn-Sham (KS) equations of fake non-interacting electrons (not many-body anymore) which, when solved, yield lowest E and density alone.

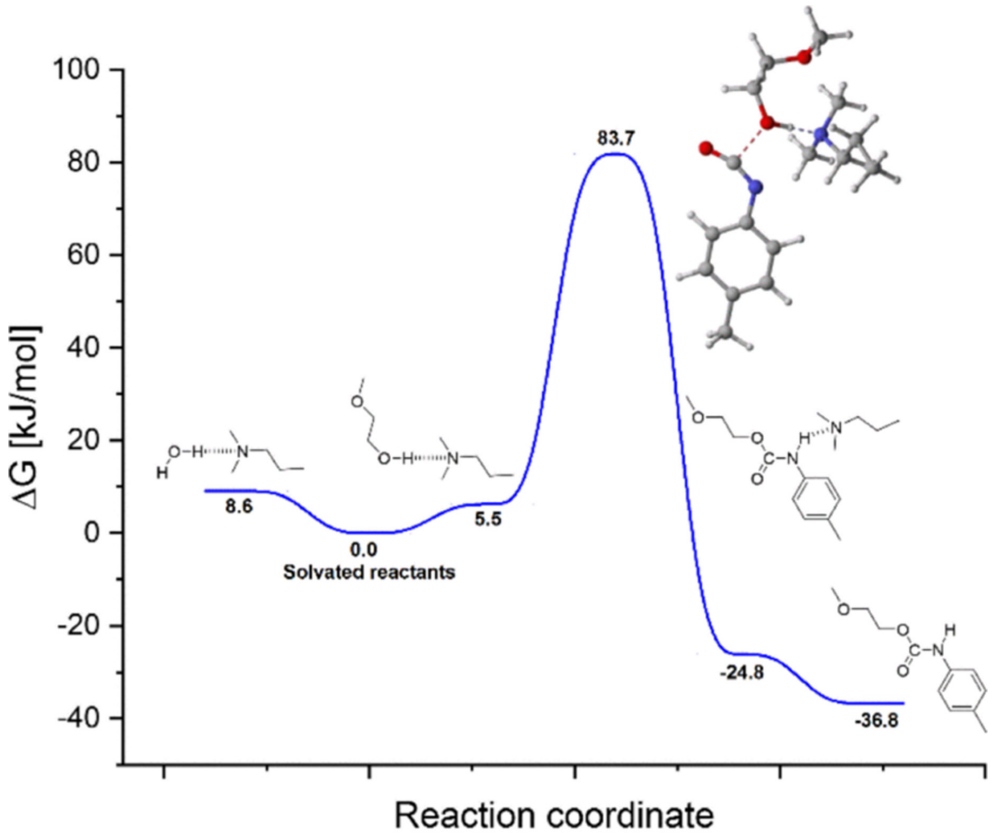
Electronic Structure Methods

- Mean-field methods: Hartree-Fock
- Single-reference correlated wavefunction methods: Coupled Cluster theory
- Multi-reference methods
- Density functional theory (DFT)
- Quantum Monte Carlo
- Semiempirical methods
- Empirical methods

Most useful approaches combine formal rigor with physical insight and computational efficiency. DFT is (by far) most common in chemistry and solid-state physics.

Example: Computational Catalysis





Rational design of polyurethane polymerization catalysts by electronic structure calculations[2].

[2] **Muuronen19**, **CEN19**.