Basis sets and HF

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Molecular **o**rbitals may be derived as **l**inear **c**ombinations of **a**tomic **o**rbitals (LCAO-MO) as a guess for a trial wavefunction (*note these are seldom orthonormal*):

$$\phi_i = \sum_{\mu=1}^{N} C_{i\mu} \chi_\mu$$

A note about notation! MO index is ***i,j***… and atomic orbital indices are $\mu, \nu, \lambda, \sigma$… HF solution will have orthonormal MOs, but AOs are usually not orthonormal.

Atomic functions are an efficient representation of MOs but they need not be centered on atoms or strictly tied to chemistry:
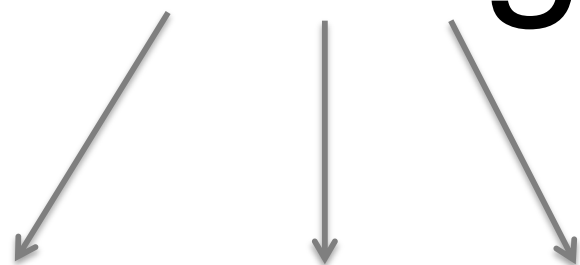
Non-atom-centered *s* functions
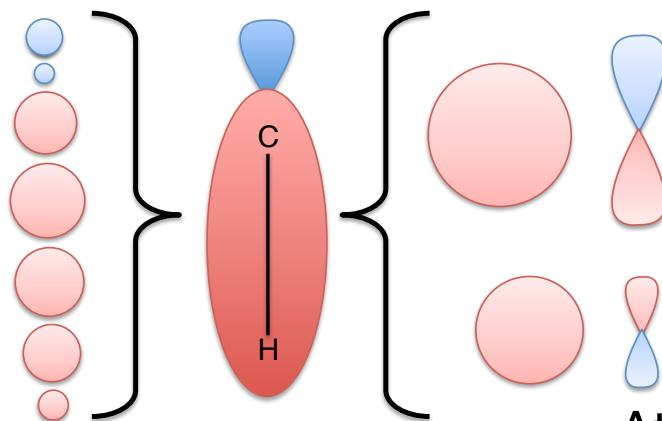
Atom-centered, p-polarized H

Decoding a basis set name

6-31g

Core orbitals: 6 PGTOs

Inner valence: 3 PGTOs

Outer valence: 1 PGTO

split-valence, double-zeta

add polarization:

6-31g* or 6-31g(d)

6-31g** or 6-31g(d,p)

larger valence:

6-311g

add diffuse functions:

6-31+g (diffuse s,p on Li-+)

6-31++g (also diffuse s on H,He)

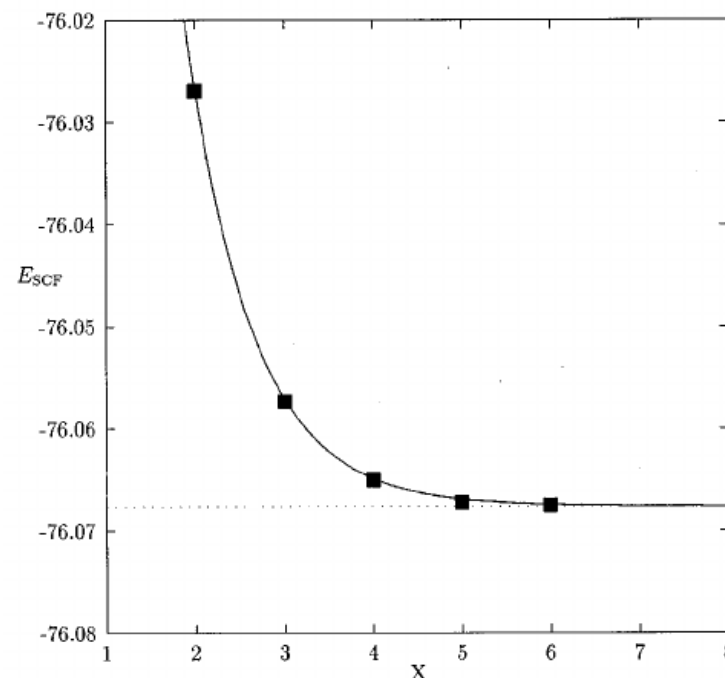**All of them together:**

6-311++g(d,p)

cc-pVDZ: double-zeta
cc-pVTZ: triple-zeta
cc-pVQZ:quadruple-zeta
cc-pV5Z: quintuple-zeta

These basis sets converge smoothly to the complete basis set limit following extrapolation formulae (usually want to discard the cc-pVDZ result):

$$E(n) = E(\infty) + Ae^{-\alpha n} \qquad E(\infty) = E(n-1) + \frac{E(n) - E(n-1)}{1 - (1 - 1/n)^3}$$

Three point formula (three unknowns)   *Alternate two point formula*

We can approximate the effect of each of these contributions independently:

$$E[\text{HF}/\text{6-311++G(d,p)}] \approx E[\text{HF}/\text{6-31G}]$$

Polarization functions $\quad +E[\text{HF}/\text{6-31G(d,p)}] - E[\text{HF}/\text{6-31G}]$

Larger valence $\quad +E[\text{HF}/\text{6-311G}] - E[\text{HF}/\text{6-31G}]$

Diffuse functions $\quad +E[\text{HF}/\text{6-31++G}] - E[\text{HF}/\text{6-31G}]$

Although we don't have a simple extrapolation formula for the Pople style basis sets (6-31G, etc), the idea is that the total time for these four smaller calculations should take less time than the larger one… (today we will test this)

How do basis sets influence structure?

Is NH_3 bent or planar?

*Cramer
Chap. 6*
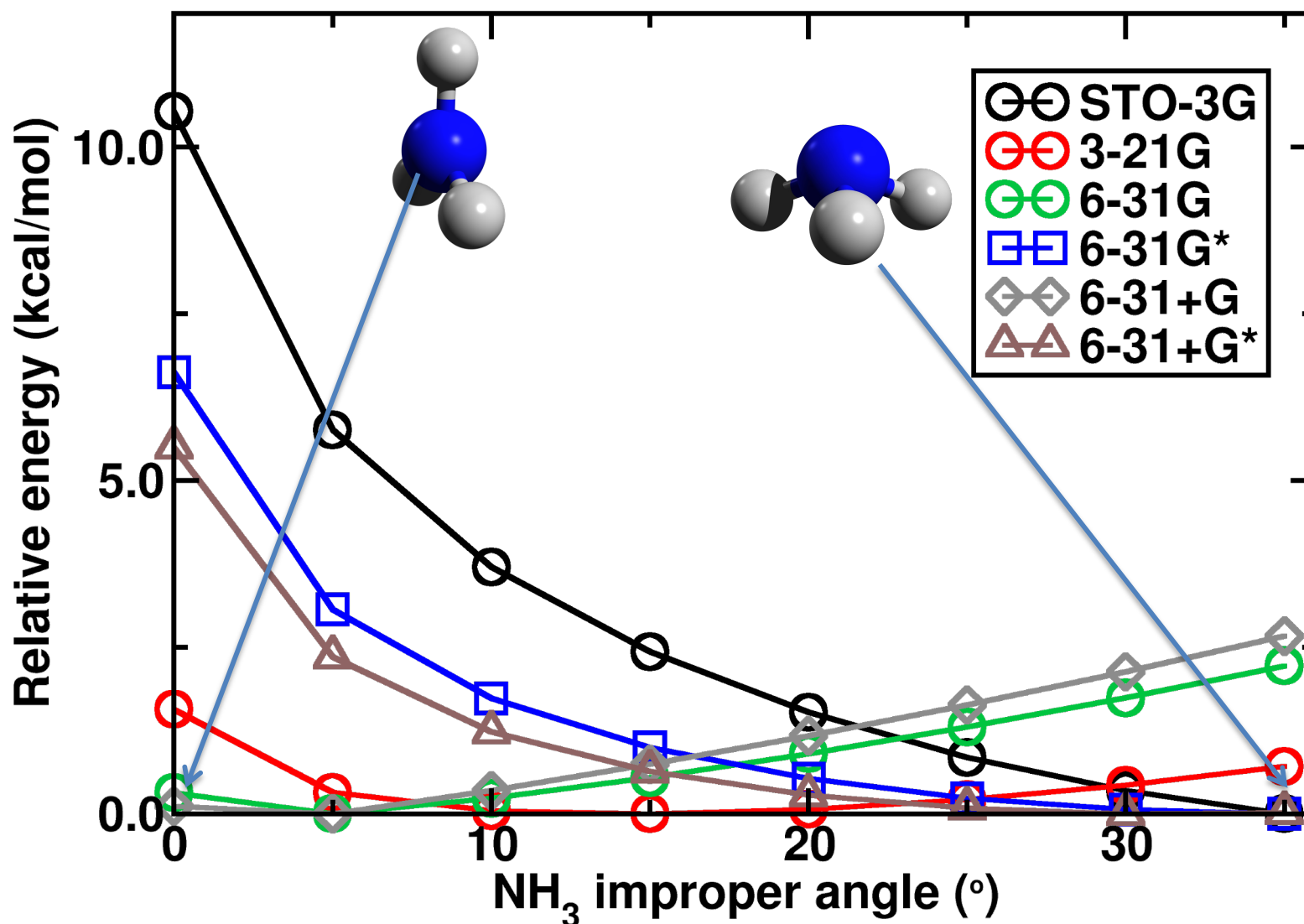
This week's lab

We will use Q-Chem today to run Hartree-Fock calculations.

- Part A: Basis set extrapolation for energies in C_2H_4.
  - Test correlation consistent basis sets on the ethylene molecule we optimized in Topic 4.
- Part B: Effect of minimal basis sets on NH_3
  - Geometry optimize NH_3 with a range of basis sets to determine when the relative energy and structure of different minima can be accurately predicted.
- Part C: Orthogonal basis set contributions in tetracene
  - Carry out the additivity approach on a tetracene molecule to estimate the time and the effect on the energy of including polarization, diffuse, and larger valence basis functions.