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Variational energy decomposition analysis of single chemical bonds

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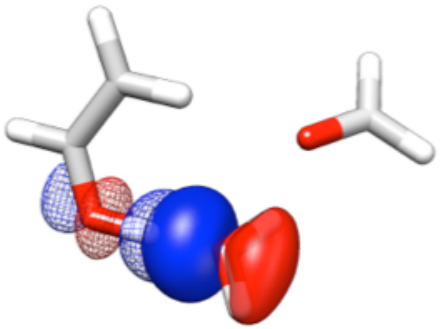
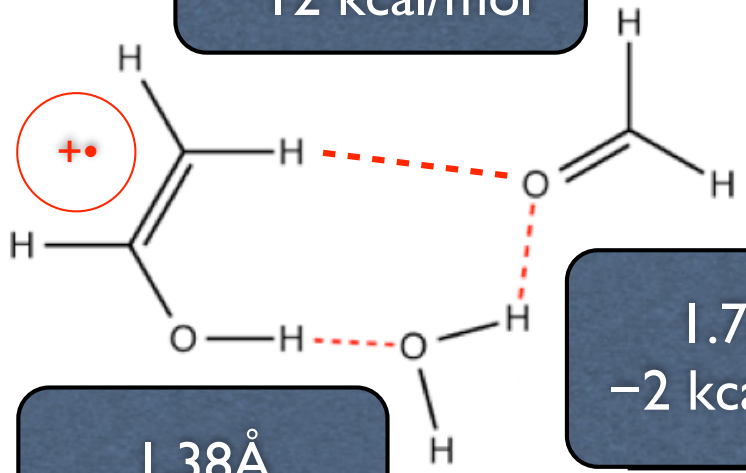
Variational DFT energy decomposition analysis (EDA)
"Absolutely localized MO's": ALMO-EDA Version 2

$$\Delta E = \Delta E_{\mathrm{FRZ}} + \Delta E_{\mathrm{POL}} + \Delta E_{\mathrm{CT}}$$

- FRZ: Frozen orbital interactions: electrostatics, sterics, VdW
- POL: Polarization treated via fragment-blocked SCF (ALMOs)
- CT: Donor-acceptor interactions: pairwise + higher order

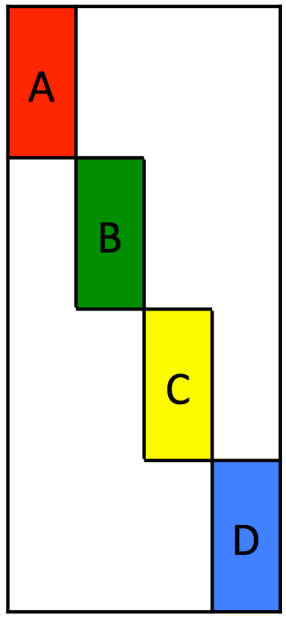




P.R. Horn, Y.Mao, MHG, PCCP 18, 23067 (2016)

ωB97M-V/def2-QZVPPD

An EDA for intermolecular interactions:
3 variational energies define 3 main interaction energies



- Frozen energy. $\Delta E_{\mathrm{FRZ}} = E_{\mathrm{FRZ}} - \sum_f E_f$
  - Find orbitals of isolated fragments ("frozen orbitals")
  - Variationally evaluate the energy with frozen orbitals
    - This frozen density obeys the Pauli Principle
- Polarization energy. $\Delta E_{\mathrm{POL}} = E_{\mathrm{POL}} - E_{\mathrm{FRZ}}$
  - Do fragment-blocked SCF in the frozen + FERF-DQ basis
  - FERFs are Fragment Electrical Response Functions
    - SVD response to a uniform electric (D) field
      - Gives 3 polarization functions per frozen orbital (x,y,z)
    - SVD response to a field gradient (Q)
      - Gives an extra 5 functions per frozen orbital
  - This is ALMO with a useful basis set limit!
- Total energy. $\Delta E_{\mathrm{CT}} = E_{\mathrm{TOT}} - E_{\mathrm{POL}}$

An EDA for single chemical bonds:
4 variational energies define 4 main interaction energies

- High spin frozen energy. $\Delta E_{\mathrm{FRZ}} = E_{\mathrm{FRZ}} - \sum_f E_f$
  - Find orbitals of isolated fragments ("frozen orbitals")
  - Variationally evaluate the triplet energy with frozen orbitals
- Spin-coupling energy. $\Delta E_{\mathrm{SC}} = E_{\mathrm{SC}} - E_{\mathrm{FRZ}}$
  - Couple the 2 open shell orbitals to a singlet (two configurations)
  - Evaluate this two-configuration energy with frozen orbitals
    - Isolates energy lowering due to spin-coupling (pairing)
- Polarization energy. $\Delta E_{\mathrm{POL}} = E_{\mathrm{POL}} - E_{\mathrm{FRZ}}$
  - Do fragment-blocked TCSCF in the frozen + FERF-DQ basis
  - Provides a useful basis set limit!
- Total energy. $\Delta E_{\mathrm{CT}} = E_{\mathrm{TOT}} - E_{\mathrm{POL}}$
  - Final result: CAS(2,2) or perfect pairing energy (~80% of binding)

Daniel Levine, Paul Horn, Yuezhi Mao, MHG, JCTC 12, 4812 (2016).

Let's look at some single bonds! (Daniel Levine)