

10.675 LECTURE 13

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1. TODAY

- project description and literature search
- CI revisited
- partial CI, CID, CISD, MP
- Coupled-Cluster, CCD, CCSD, QCISD
- G1, G2, G3 and comparisons

2. CONCEPTS

CI

- Size Consistent
- Variationality

3. CI VS DFT

Extremely expensive and can only take into account a few atoms

DFT: Cost of a HF, but includes correlation

However, DFT has no systematic way of getting more accurate with computation resources. Meaning, there is no way to know if we are more or less accurate.

CI, recall that with a large enough basis set, gives the exact, non-relativistic energies.

$$\Phi_o = C_o \Psi_o + \sum_{ar} C_a^r \Psi_o^r + \sum_{a<b,r<s} C_{ab}^{rs} \Psi_{ab}^{rs} +$$

$\Psi \rightarrow$ Hartree-Fock determinants "single excitations" of HF determinants.

CI \rightarrow size consistent variational (method is equally accurate for systems with different number of electrons.

DFT/HF also has these properties

4. CI PROBLEMS

Scales with $N!$, where N is the # of basis sets.

Partial CI terminates the full CI series

CID \rightarrow configuration interaction doublets

$$\Phi_{CID} = \Phi_o + \sum_{a<b,r<s} C_{ab}^{rs} \Psi_{ab}^{rs}$$

Can include singlets, CISD, but they do not contribute much to the correlation.

GID, GISD are the key words.

5. CID

$H\Phi_{CID} = \epsilon_{CID}\Phi_{CID}$ subtract $E_o\Phi_{CID}$

E_o is the HF energy.

$$(H - E_o)\Phi_{CID} = (\epsilon_{CID} - E_o)\Phi_{CID} = E_{CID}^{Corr}\Phi_{CID}$$

Multiply by Φ and integrate.

$$\sum_{a < b, r < s} C_{ab}^{rs} \int \Phi_o H \Psi_{ab}^{rs} dr = E_{CID}^{Corr}$$

$$\text{Mult by } \Psi_{cd}^{tu} \text{ and integrate } \int \Psi_{cd}^{tu} H \Psi_o dr + \sum_{a < b, r < s} C_{ab}^{rs} \int \Psi_{cd}^{tu} (H - E_o) \Psi_{ab}^{rs} = C_{cd}^{tu} E_{cd}^{Corr}$$

Can use these equations to find E_{CID}^{Corr} (similarly w/CISD)

Variational and NOT size consistent

A and B in separate cells vs AB

Calculate as separation goes to ∞

$$|E_{A\infty B}^{Corr}| < |E_A^{Corr} + E_B^{Corr}|$$

A||B double excitations in both

A \leftrightarrow B double excitations of the entire system., but not double excitations of A

AND B together.

Extreme Case, XL system (infinite)

$$E_{CID}^{Corr} \text{ per atom} \rightarrow 0.$$

6. MP

\rightarrow are size consistent

\rightarrow Not variational

\rightarrow convergence slow with respect to terms in perturbation.

7. COUPLED CLUSTER METHOD APPROXIMATIONS

Ignore singlet/triplet/etc excitations from CI wavefunction

$$\Phi_o^{cc} = \Psi_o + \sum_{a < b, r < s} c_{ab}^{rs} \Psi_{ab}^{rs} + \sum_{a < b < c < d} c_{abcd}^{rstu} \Phi_{abcd}^{rstu}$$

One can show that higher order coefficients

$$C_{abcd}^{rstu} C_{ab}^{rs} * C_{cd}^{tu}$$

where * means the summation of the products of the doublets

$$\Phi^{cc} = \exp(\tau)\Phi_o, \tau = \sum_{a < b} c_{ab}^{rs} a_r^\dagger a_s^\dagger a_b a_a$$

Where the terms on the right are the creation/annihilation operators

CCD \rightarrow coupled clusters w/doublets

8. CCSD

There is a way to incorporate single excitations \Rightarrow

\rightarrow size consistent

\rightarrow not variational

QCISD is quadratic configuration, similar to coupled cluster methods

CCSD \rightarrow seen as the "gold standard" from the chemists community.

Tolerance of 1 Kcal/mole, which is the best we'll get.

9. G1, G2 METHODS

G1, G2 methods \rightarrow composite method for computing energies and enthalpies of molecules

NEED 1) Geometry Equilibrium 2) Total Electronic Energy 3) Harmonic Frequencies

Outline for G1

I Optimize geometry (restricted HF/6-31G*)

II Use equilibrium geometries from I, optimize again w/MP2/6-31G*

III Perform MP4 SDTQ, 6-31G** on valence electrons only

IV incorporate effects of better basis sets for diffuse sp functions

$$\Delta E(t) = E(MP4/6 - 311 + G^{**}) - E(MP4/6 - 311G^{**})$$

V Correct for additional polarization functions on non-H atoms

$$\Delta E(sdf) = E(MP4/6 - 311G^{**}(2df)) - E(MP4/6 - 311G^{**})$$

VI Correct for additional correlation effects

$$\Delta E(QCI) = E(QCISD(+))/6 - 31G^{**} - E(MP4/6 - 311G^{**})$$

VII E(combined) = E(MP4/6-311G**) + $\Delta E(t)$ + $\Delta E(2df)$ + $\Delta E(QCI)$

VIII HLC (higher order correlation)

$$\Delta E(HLC) = -5.95 N_{\beta} - 0.19 N_{\alpha}$$

$N_{\alpha} > N_{\beta}$ in milli-hartrees

Numbers were chosen, so that E_e is exact for H atom and H_2 .

$$E_c = E_{combined} + \Delta E(HLC)$$

IX Calc Frequencies at HF/6-31G* and scaled by 0.893 \Rightarrow ZPE zero point energy

X $E_o = E_e + \Delta(ZPE)$

also calculate ΔH_{rxn}^o , ΔH_f^o , etc

10. G2

I. Additional basis set correction

II. Correction to GI for a third d function to non-H, p function to H.

$$\Delta_2 E[MP2/6 - 311 + G(3df, 2d)] - E[MP2/6 - 311 + G(2df, p)]$$

III correction to atomization energies of 55 molecules w/well established experimental values.