CHEM 179 / 279 - Numerical Algorithms Applied to Computational Quantum Chemistry

Lecture 19: 3/1/2024

Outline

- Recap: Unrestricted Hartree-Fock (UHF) and bond-breaking

- How does HF chemistry compare to nature's chemistry?

- CNDO/2: An SCF method you can code yourself!

Berkeley
UNIVERSITY OF CALIFORNIA

Recap: Unrestricted Hartree-Fock (UHF)

- The UHF wavefunction uses different orbitals for the α and β electrons
  - $\phi_i^\alpha(\mathbf{r}) = \sum_\mu \omega_\mu(\mathbf{r}) C_{\mu i}^\alpha$ $\qquad$ $\phi_i^\beta(\mathbf{r}) = \sum_\mu \omega_\mu(\mathbf{r}) C_{\mu i}^\beta$
  - $P_{\mu\nu}^\alpha = \sum_i^p C_{\mu i}^\alpha C_{\nu i}^\alpha$ $\qquad$ $P_{\mu\nu}^\beta = \sum_i^q C_{\mu i}^\beta C_{\nu i}^\beta$ $\qquad$ $P_{\mu\nu}^{\text{tot}} = P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta$
- Different orbitals for different spins lets us treat radicals
  - Simulating reactive chemistry requires treating these unstable radicals
  - It also enables us to correctly describe bond-breaking
- Constrained minimization of E_{UHF} yields two sets of SCF equations:
  - $\mathbf{F}^\alpha \mathbf{C}^\alpha = \mathbf{S}\mathbf{C}^\alpha \boldsymbol{\varepsilon}^\alpha$ $\qquad\qquad$ $\mathbf{F}^\beta \mathbf{C}^\beta = \mathbf{S}\mathbf{C}^\beta \boldsymbol{\varepsilon}^\beta$
- UHF energy minimization defines the self-consistent field (SCF)
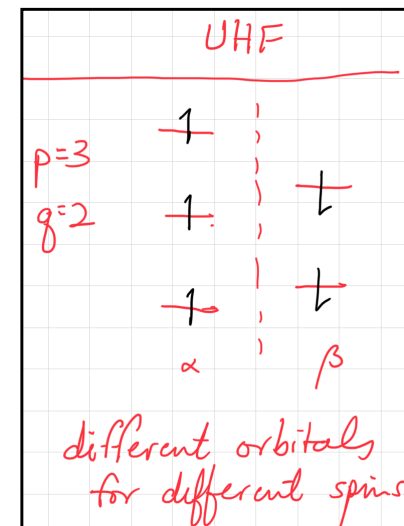
Recap: UHF is essential for bond-breaking

- RHF PES does not reach the limit of 2 H atoms!
  - Due to 50% ionic character
  - Correct answer is 100% covalent

- UHF PES reaches the correct limit of 2 H atoms at dissociation
  - separates from RHF at the Coulson-Fischer (CF) point
  - UHF is "spin-contaminated", becoming 50% singlet / 50% triplet at dissociation

- We use UHF when it lowers E

H$_2$: potential energy surface
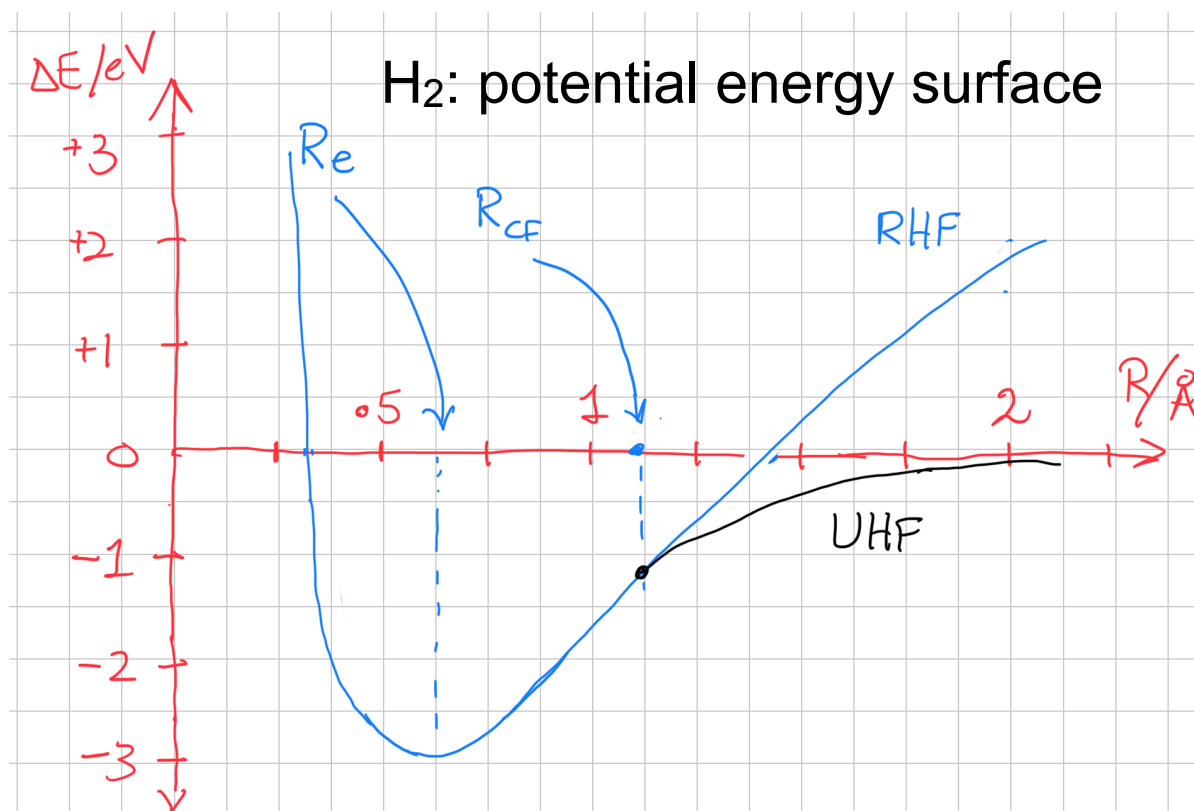
Hartree-Fock chemistry

- HF is the simplest "ab initio" (from 1st principles) MO theory
  - No experimental input. Only the geometry, charge, spin, and basis set.
  - RHF and UHF together permit description of almost any potential energy surface

- How should we choose the basis set?
  - Complete basis set (CBS) limit: approach that with a very large atomic orbital basis set
  - cc-pVQZ: 1g2f3d4p5s on C = 55 functions (at least 10 times larger than a 2s1p minimal basis)

- Can we predict structure of organic molecules?   YES
  - Bond lengths: typically too short by 0.02 Å. (That's very good: 1 - 2% error)
  - Bond angles: typically within about 2°   (Also very good!)

- What about the vibrational frequencies (infrared spectra)? YES
  - Systematically about 10% too high

- What about electron densities? YES
  - Dipole moments are typically 15% too large

Hartree-Fock chemistry

- Q: Why are so many of these error trends systematic?

- A: Because bonding orbitals are occupied and antibonding orbitals are empty
  - Consequence of the Aufbau principle and single determinant wavefunction
  - Think about mixing (configuration interaction) other (non-Aufbau) determinants to lower the energy
  - That would slightly de-occupy the occupied MOs
  - And slightly occupy the lower energy antibonding MOs

- As a consequence
  - Bond lengths: would get longer
  - Vibrational frequencies would get lower
  - Dipole moments would get smaller

- Is everything good? NO!
  - Bond energies in error by ~ 1eV per electron pair

- Isn't this a total disaster? No: **99% of true energy**
  - The bond energies are always too small. More on this later…..

An SCF theory suitable for problem set 4

- While HF theory is quite useful it is too hard to implement in a problem set
  - Need to code 2 new types of 1-electron integrals (KE, nuclear attraction) to make $h_{\mu\nu}$
  - Need to code the analytical electron repulsion integral (ERI) tensor, $(\mu\nu|\lambda\sigma)$
  - Need to implement the SCF method

- We will study approximate (semi-empirical) SCF methods and you will code one!
  - An excellent reference is Beveridge and Pople "Approximate Molecular Orbital Theory"
  - I will (maybe have?) upload an electronic version to bcourses
  - I highly recommend you read it! Better than Intro to Comp. Chem. For this purpose

- One important note about the Beveridge and Pople book!
  - They use exponential (Slater type) orbitals rather than the Gaussians that you will use

Berkeley
UNIVERSITY OF CALIFORNIA

Semi-empirical MO methods

- Roughly 60 years old and still under active development and in wide use today

- Strategy: Simplify as HF theory as much as possible with semi-empirical approximations that make it more efficient without losing too much accuracy.
  - Improve on extended Huckel by using the self-consistent field
  - Should better describe electron-electron repulsions

- Two-electron integrals, $(\mu\nu|\lambda\sigma)$, are the most important thing to simplify
  - $(\mu\nu|\lambda\sigma) = \int d\mathbf{r}\int d\mathbf{r}'\omega_\mu(\mathbf{r})\omega_\nu(\mathbf{r})|\mathbf{r}-\mathbf{r}'|^{-1}\omega_\lambda(\mathbf{r}')\omega_\sigma(\mathbf{r}')$
  - They fall off exponentially with inter-center distance between ω_μ and ω_ν (and likewise ω_λ and ω_σ)
  - And fall off only as R^{-1} with distance between $(\mu\nu)$ and $(\lambda\sigma)$

ω_μ

ω_ν

ω_λ

ω_σ

R^{-1}
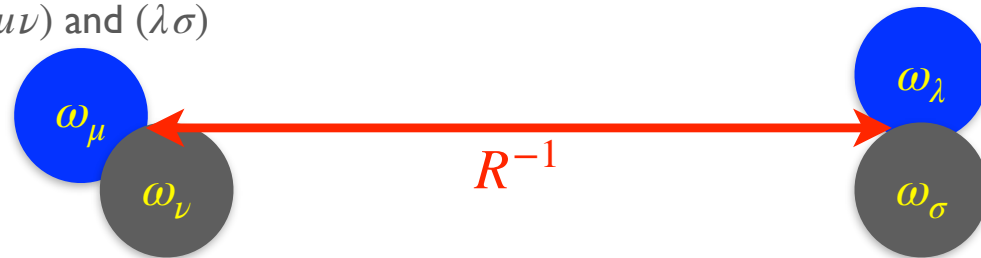
ZDO approximation

- Zero differential overlap (ZDO) approximation drastically simplifies the ERI tensor.
  - There is zero overlap between different AOs on the same site: $S_{\mu\nu} = \delta_{\mu\nu}$
  - For AO's on different sites, overlap may not be zero but $S_{\mu\nu} < 1$
  - Indeed $S_{\mu\nu}$ fall off exponentially with inter-center distance between ω_μ and ω_ν (& likewise ω_λ and ω_σ)
  - Motivates the ZDO approximation for ERIs: $(\mu\nu \mid \lambda\sigma) \approx (\mu\mu \mid \lambda\lambda)\delta_{\mu\nu}\delta_{\lambda\sigma}$

- The ZDO approximation is not applied to the core hamiltonian, $h_{\mu\nu}$.

- Rotational invariance is a key requirement for a good model
  - The true energy is unchanged when the (free) molecule is rotated
  - This will not happen if we use the "raw" ZDO approximation: $(\mu\nu \mid \lambda\sigma) \approx (\mu\mu \mid \lambda\lambda)\delta_{\mu\nu}\delta_{\lambda\sigma}$

Berkeley
UNIVERSITY OF CALIFORNIA

The CNDO/2 hamiltonian: A ZDO model

- Achieve rotational invariance by modeling the retained on-site integrals as spherically symmetric quantities:
  - $(\mu\nu|\lambda\sigma) \approx (\mu\mu|\lambda\lambda)\delta_{\mu\nu}\delta_{\lambda\sigma}$
  - $(\mu\mu|\lambda\lambda) \leftarrow \gamma_{AB}$

- The ERI problem is reduced to calculating $\mathcal{O}(A^2)$ ERIs (A is number of atoms). Great! What are they?

- $\gamma_{AB} = \int d\mathbf{r} \int d\mathbf{r}'[s_A(\mathbf{r})]^2 |\mathbf{r} - \mathbf{r}'|^{-1} [s_B(\mathbf{r}')]^2$

- In summary, we have kept the largest ERIs and made a rotationally invariant approximation for them.

s_B^2

R^{-1}

s_A^2
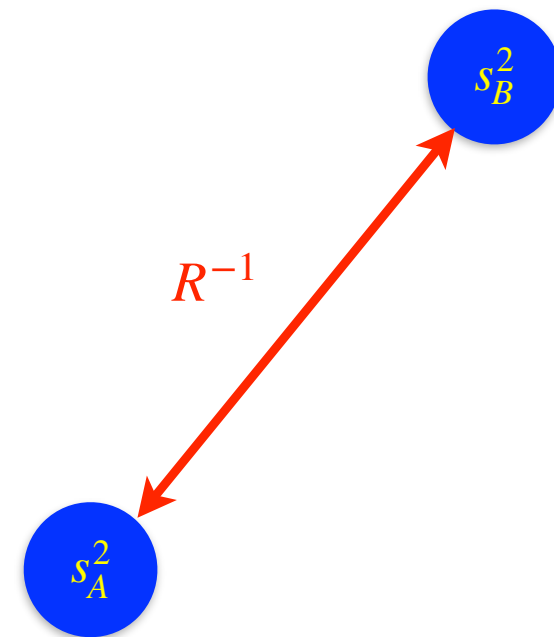
The CNDO/2 Fock matrix

- $\gamma_{AB} = \int d\mathbf{r} \int d\mathbf{r}'[s_A(\mathbf{r})]^2 |\mathbf{r} - \mathbf{r}'|^{-1}[s_B(\mathbf{r}')]^2$
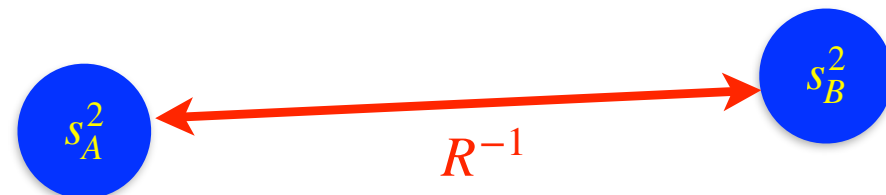
- Diagonal Fock matrix elements with ZDO
  - Figure out where each term of the ab initio Hamiltonian is accounted for…..
  - $f_{\mu\mu}^{\alpha} = -\frac{1}{2}\left(I_\mu + A_\mu\right) + \left[\left(p_{AA}^{\text{tot}} - Z_A\right) - \left(p_{\mu\mu}^{\alpha} - \frac{1}{2}\right)\right]\gamma_{AA} + \sum_{B \neq A}\left(p_{BB}^{\text{tot}} - Z_B\right)\gamma_{AB}$

    Tabulated IP and EA   On-site electrostatics   On-site Exchange   Off-site electrostatics

- Off-diagonal Fock matrix elements with ZDO
  - $f_{\mu\nu}^{\alpha} = \frac{1}{2}\left(\beta_A + \beta_B\right)s_{\mu\nu} - p_{\mu\nu}^{\alpha}\gamma_{AB}$

    Tabulated site-site h+J   site-site exchange

quantity	H	C	N	O	F
$\frac{1}{2}(I_s + A_s)$	7.176	14.051	19.316	25.390	32.272
$\frac{1}{2}(I_p + A_p)$		5.572	7.275	9.111	11.080
$-\beta$	9	21	25	31	39

(eV)