Electronic Structure Theory
TSTC Session 3

1. Born-Oppenheimer approx.- energy surfaces
2. Mean-field (Hartree-Fock) theory- orbitals
3. **Pros and cons of HF- RHF, UHF**
4. Beyond HF- why?
5. First, one usually does HF-how?
6. Basis sets and notations
7. MPn, MCSCF, CI, CC, DFT
8. Gradients and Hessians
9. Special topics: accuracy, metastable states

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Let's examine how important permutational antisymmetry and spin are by considering some Slater determinant wave functions for two electrons in π and π^* orbitals as in ethylene (or σ and σ^* orbitals in H_2 or σ and σ^* orbitals in HF) .

The purposes of these exercises are to practice forming singlet and triplet functions, to see how the different spin states have different physical content (i.e., charge distribution) even when the orbital occupancy is the same, and to introduce the idea that it is simply not possible, in certain circumstances, to use a single Slater determinant function as an approximation to $\psi_K(\mathbf{r}|\mathbf{R})$.

So, let's think of how the low-energy states of ethylene with two electrons in its π orbital framework should behave as we twist and break the π bond.

The full Slater determinants contain 16 spin-orbitals

$$\psi(r\,|\,R) = \frac{1}{\sqrt{16!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \phi_3(1) & & & & & \phi_{15}(1) & \phi_{16}(1) \\ \phi_1(2) & \phi_2(2) & \phi_3(2) & & & & & \phi_{15}(2) & \phi_{16}(2) \\ \phi_1(3) & \phi_2(3) & \phi_3(3) & & & & & \phi_{15}(3) & \phi_{16}(3) \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ \phi_1(16) & \phi_2(16) & \phi_3(16) & & & & & \phi_{15}(16) & \phi_{16}(16) \end{vmatrix} = |\phi_1(1)\phi_2(2)..\phi_{15}(15)\phi_{16}(16)|$$

However, the first 14 spin-orbitals are 7 doubly-occupied orbitals ($1s_C$,$1s_C$,CC σ bond, and 4CH σ bonds). We will "hide" the first 14 rows and columns and just write the last two that contain the π and π* orbitals.

Singlet π^2 $\quad |\pi\alpha(1)\ \pi\beta(2)| = 2^{-1/2}\ \pi(1)\pi(2)[\alpha1\beta2 - \beta1\alpha2]$

Singlet π^{*2} $\quad |\pi^*\alpha(1)\ \pi^*\beta(2)| = 2^{-1/2}\ \pi^*(1)\pi^*(2)[\alpha1\beta2 - \beta1\alpha2]$

Note the antisymmetric spin and symmetric spatial character of singlets.

Triplet $\pi\pi^*$ $\quad |\pi\alpha(1)\ \pi^*\alpha(2)| = 2^{-1/2}\ [\pi(1)\pi^*(2) - \pi(2)\pi^*(1)]\ \alpha1\alpha2$

$$|\pi\beta(1)\ \pi^*\beta(2)| = 2^{-1/2}\ [\pi(1)\pi^*(2) - \pi(2)\pi^*(1)]\ \beta1\beta2$$

Applying S_- to the $|\pi\alpha(1)\pi^*\alpha(2)|$ determinant, we generate the $M_S = 0$ triplet.

$$2^{-1/2}\ [|\pi\alpha(1)\ \pi^*\beta(2)| + |\pi\beta(1)\ \pi^*\alpha(2)] =$$

$$2^{-1}[\pi(1)\pi^*(2)\alpha1\beta2 + \pi(1)\pi^*(2)\beta1\alpha2$$

$$-\pi^*(1)\pi(2)\beta1\alpha2 - \pi^*(1)\pi(2)\alpha1\beta2]$$

Singlet $\pi\pi^*$ $\quad 2^{-1/2}\ [|\pi\alpha(1)\ \pi^*\beta(2)| - |\pi\beta(1)\ \pi^*\alpha(2)] =$

$$2^{-1}[\pi(1)\pi^*(2)\alpha1\beta2 - \pi(1)\pi^*(2)\beta1\alpha2$$

$$-\pi^*(1)\pi(2)\beta1\alpha2 + \pi^*(1)\pi(2)\alpha1\beta2]$$

Note: no single determinant can treat $M_S = 0$ triplet or singlet. Both were combinations of two determinants. In such cases, HF (or any other) theory based on a single determinant should not be used.

These single- or two-determinant wave functions are the minimal such functions having the specified orbital occupancy (e.g., π^2, $\pi\pi^*$, π^{*2}) and the correct spin. They are called configuration state functions (CSFs)

To see how the energies and characters of these singlet and triplet CSFs vary as we twist the ethylene, we express the π and π^* orbitals as even and odd combinations of Carbon 2p orbitals that we label left (L) and right (R)

$$\pi = 2^{-1/2}(R+L) \quad \pi^* = 2^{-1/2}(R-L).$$

Singlet π^2

$$|\pi\alpha(1)\ \pi\beta(2)| = 2^{-1}[|R\alpha(1)\ R\beta(2)| + |L\alpha(1)\ L\beta(2)| + |R\alpha(1)\ L\beta(2)| + |L\alpha(1)\ R\beta(2)|]$$

contains both ionic + diradical components

Triplet $\pi\pi^*$

$$|\pi\alpha(1)\ \pi^*\alpha(2)| = 2^{-1}[|L\alpha(1)\ R\alpha(2)| - |R\alpha(1)\ L\alpha(2)|] = |L\alpha(1)\ R\alpha(2)|$$

contains only diradical character

Singlet π^{*2}

$$|\pi^*\alpha(1)\ \pi^*\beta(2)| = 2^{-1}[|R\alpha(1)\ R\beta(2)| + |L\alpha(1)\ L\beta(2)| - |R\alpha(1)\ L\beta(2)| - |L\alpha(1)\ R\beta(2)|]$$

contains both ionic – diradical components

Singlet $\pi\pi^*$

$$2^{-1/2}\,[|\pi\alpha(1)\,\pi^*\beta(2)| - |\pi\beta(1)\,\pi^*\alpha(2)]$$

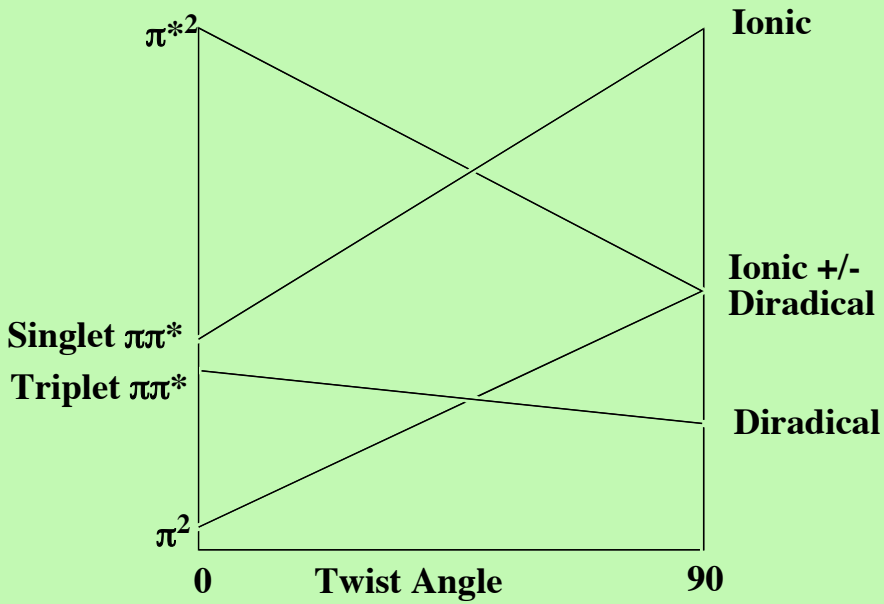
$$= 2^{-3/2}[\,|R\alpha(1)\,R\beta(2)| + |L\alpha(1)\,R\beta(2)| - |R\alpha(1)\,L\beta(2)| - |L\alpha(1)\,L\beta(2)|]$$

$$- 2^{-3/2}[|R\beta(1)\,R\alpha(2)| + |L\beta(1)\,R\alpha(2)| - |R\beta(1)\,L\alpha(2)| - |L\beta(1)\,L\alpha(2)|]$$

$$= 2^{-1/2}[\,|R\alpha(1)\,R\beta(2)| + |L\alpha(1)\,P\beta(2)|]$$

contains only ionic character

So, the spin state and orbital occupancy plus the antisymmetry have effects on the ionic/diradical character of the function. The single- or two-determinant CSF functions just analyzed would predict energy profiles as follows:

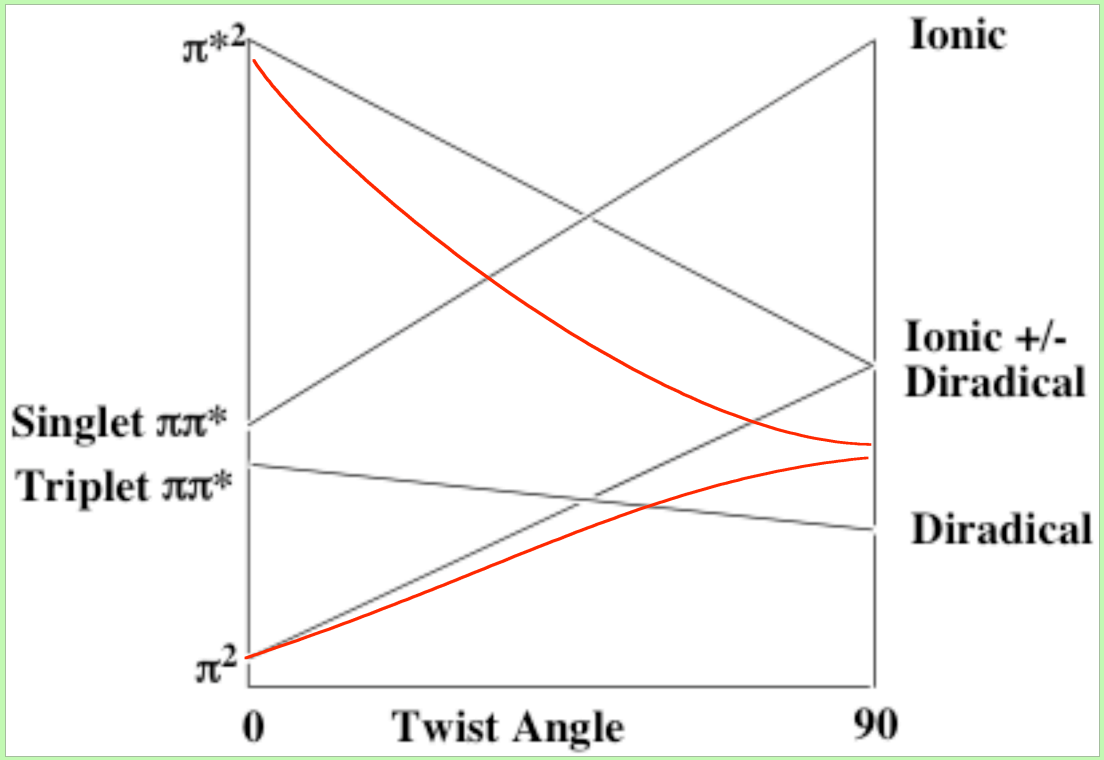


These profiles are wrong. The π^2 ground state does not evolve into a singlet diradical as it should.

These are diabatic energies in the sense that they have fixed orbital occupancy.

π^2 or $\pi\pi^*$ or π^{*2}. The correct adiabatic ground state must be allowed to mix any or all of these three orbital occupancies.

To more reasonably describe the (singlet) bond breaking, we need to mix the diabatic π^2 and π^{*2} **configuration state functions (CSF)** to achieve **adiabatic** functions whose energies we show in red.



How do we mix the π^2 and π^{*2} ; with what coefficients? Won't these coefficients depend on the twist angle?

Before explaining how to handle the olefin configuration interaction (CI), we

note that this same kind of problem arises in
H_2 (σ_g^2) ➔ H(1s) + H(1s); here $\sigma_g = 2^{-1/2}[1s_R + 1s_L]$, $\sigma_u = 2^{-1/2}[1s_R - 1s_L]$
σ_g^2 and σ_u^2 dissociate into 50:50 mixtures of ionic and diradical. So, the σ_g^2 and σ_u^2 configurations have to be mixed to give a pure diradical.

It also arises in hetero-polar cases
HF(σ^2) ➔H(1s) + F($2p_\sigma$); σ = a 1s + b $2p_\sigma$, σ^* = b 1s - a $2p_\sigma$.
a and b change with bond length; at short R, b>a; at long R, b>>a.
σ^2 dissociates into $H^+ + F^-$; the singlet $\sigma\sigma^*$ CSF has to be mixed with the σ^2 to achieve a more realistic description.

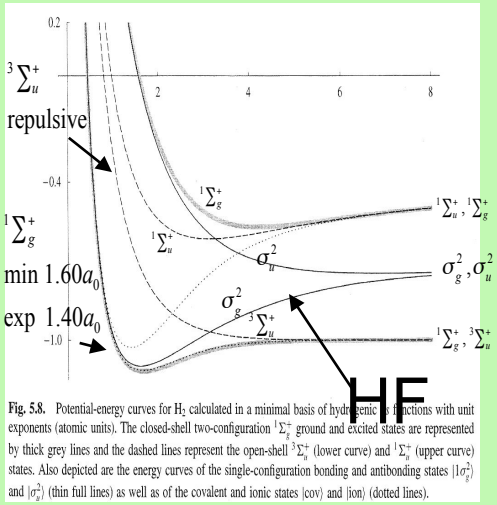
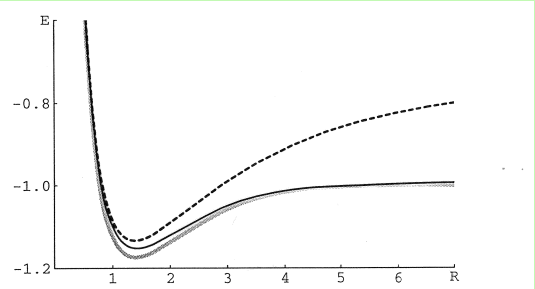
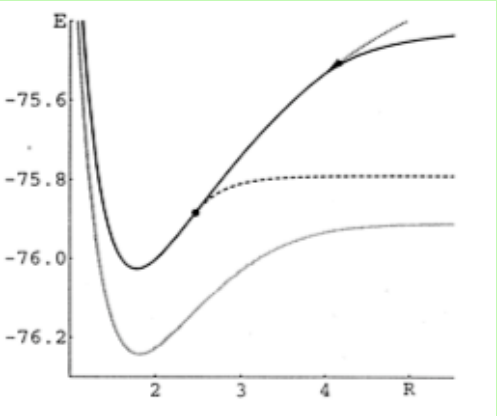


Fig. 5.8. Potential-energy curves for H_2 calculated in a minimal basis of hydrogenic AO functions with unit exponents (atomic units). The closed-shell two-configuration $^1\Sigma_g^+$ ground and excited states are represented by thick grey lines and the dashed lines represent the open-shell $^3\Sigma_u^+$ (lower curve) and $^1\Sigma_u^+$ (upper curve) states. Also depicted are the energy curves of the single-configuration bonding and antibonding states $|1\sigma_g^2\rangle$ and $|\sigma_u^2\rangle$ (thin full lines) as well as of the covalent and ionic states $|cov\rangle$ and $|ion\rangle$ (dotted lines).



HF (top), exact (bottom) for H_2



HF (top), exact (bottom) for H_2O

These problems occur whenever homolytic cleavage is lowest in energy. To adequately describe the (singlet) π bond breaking to give the singlet diradical, we need to mix the π^2 and π^{*2} **configuration state functions (CSF)**.

$$|\pi\alpha(1)\ \pi\beta(2)| = 2^{-1}[|R\alpha(1)\ R\beta(2)| + |L\alpha(1)\ L\beta(2)|$$

$$+ |R\alpha(1)\ L\beta(2)| + |L\alpha(1)\ R\beta(2)|]$$

ionic + diradical

$$|\pi^*\alpha(1)\ \pi^*\beta(2)| = 2^{-1}[|R\alpha(1)\ R\beta(2)| + |L\alpha(1)\ L\beta(2)|$$

$$-|R\alpha(1)\ L\beta(2)| - |L\alpha(1)\ R\beta(2)|]$$

ionic + diradical

So, at the 90° twisted geometry, one must combine them 50:50

$$2^{-1/2}\{|\pi\alpha(1)\ \pi\beta(2)| - |\pi^*\alpha(1)\ \pi^*\beta(2)|\}$$

to obtain a diradical state and 50:50

$$2^{-1/2}\{|\pi\alpha(1)\ \pi\beta(2)| + |\pi^*\alpha(1)\ \pi^*\beta(2)|\}$$

to obtain an ionic state.

A single determinant function won't work! So, one should not use any method based on a single determinant in such a case.

Analogous "trouble" occurs if one uses a single determinant wave function to describe a bond that one wants to break homolytically:

$$H_2\,(\sigma_g^2) \rightarrow H(1s_A) + H(1s_B)$$

$$H_3C\text{-}CH_3\,(\sigma^2) \rightarrow H_3C\bullet + \bullet CH_3$$

$$HF(\sigma^2) \rightarrow H(1s) + F(2p_\sigma)$$

The $|\sigma\alpha(1)\sigma\beta(2)|$ determinant has diradical and ionic or only ionic terms at large-R.

Whenever we have to combine two or more determinants to achieve a qualitatively correct description, the resultant wave function is said to include static correlation. This is different from the dynamical correlation needed to treat the Coulomb hole.

Other than combining two or more determinants to describe homolytic bond cleavage (as we recently discussed), is there anything else we can do?

Yes. It is possible to use a single determinant of the form $|\phi\alpha(1)\phi'\beta(2)|$ and to allow the spacial parts of ϕ and ϕ' to evolve from being σ and σ near the equilibrium bond length into being L and R functions (e.g., $1s_A$ and $1s_B$ or 1s and $2p_\sigma$) at large bond lengths.

However, the function $|L\alpha(1)R\beta(2)|$ is not a singlet; it is a mixture of singlet and triplet. Moreover, how do you let ϕ and ϕ' evolve?

This is the approach used in so-called unrestricted Hartree-Fock theory (UHF)

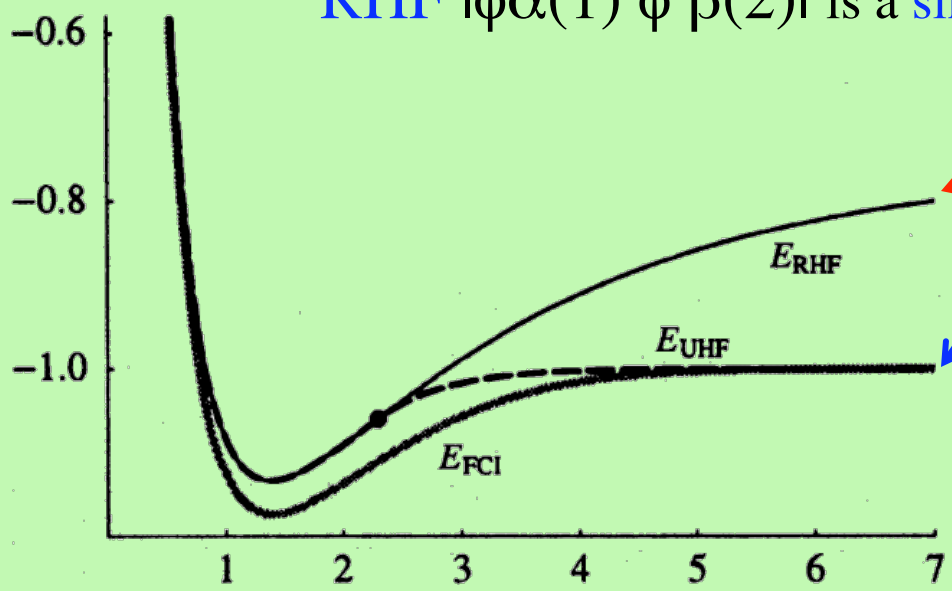
The UHF function $|\phi\alpha(1)\ \phi'\beta(2)|$ is neither a singlet nor a triplet, but a mixture:

of singlet $2^{-1/2}[\ |\phi\alpha(1)\ \phi'\ \beta(2)| - |\phi\beta(1)\ \phi'\ \alpha(2)|]$ and

triplet $2^{-1/2}[\ |\phi\alpha(1)\ \phi'\ \beta(2)| + |\phi\beta(1)\ \phi'\ \alpha(2)|]$

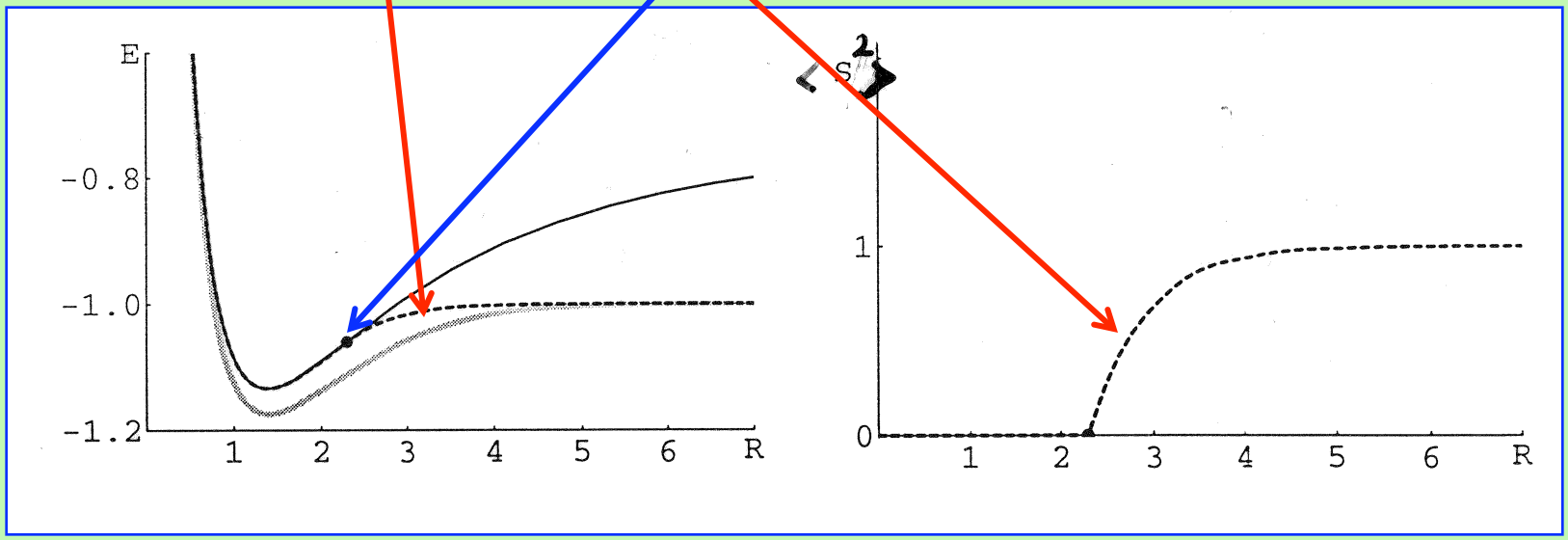
On the other hand, UHF $|\phi\alpha(1)\ \phi'\beta(2)|$ dissociates to diradicals.

RHF $|\phi\alpha(1)\ \phi\ \beta(2)|$ is a singlet, but dissociates incorrectly



Energy of H_2 (Hartrees) vs. bond length (Bohrs)

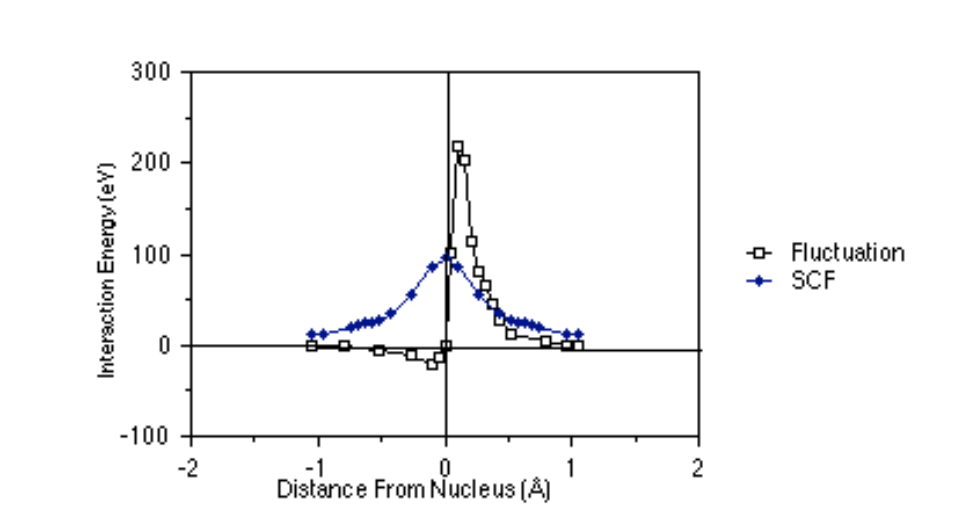
When doing, UHF, one experiences jerks (not in the energy, but in its derivatives) as well as spin impurity when the RHF and UHF curves connect ($S^2 = S(S+1)$ should be zero, is 2 for triplet).



RHF: doubly occupied orbitals restricted to have identical spatial character.
Problems- not all states can be described by a single determinant;
gives qualitatively incorrect description of homolytic cleavage.

UHF: each spin-orbital allowed to have its own spatial character.
Problems- not all states can be described by a single determinant;
does not preserve spin purity.
Does give *qualitatively* correct description of energy profile for homolytic cleavage.

HF: uses a single determinant, chooses orbitals to minimize the energy. Gives V_{MF} approximation to $\Sigma_{j<k} 1/r_{j,k}$. How good is this?

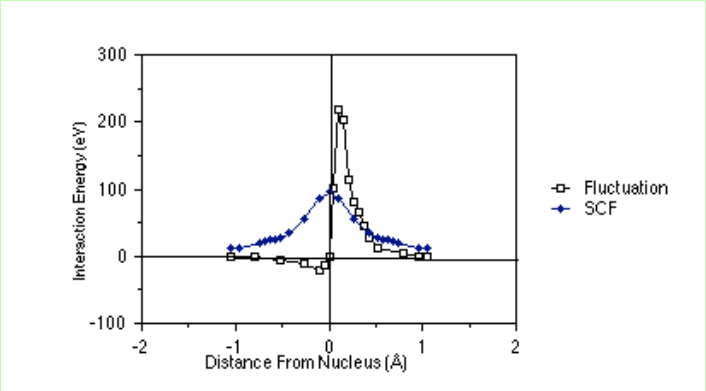


He's two 1s electrons HF Coulomb interaction $J_{1s,1s}$ compared to the exact interaction with one electron held fixed at its most likely place in the HF 1s orbital. The fluctuation potential is LARGE!

What is needed now?

1. A HF theory/method that allows the approximate wave function to be a small number of Slater determinants (e.g., to make a proper singlet $\pi\pi^*$ or $\sigma\sigma^*$ or s^1p^1 state). We have this. It is called restricted open-shell Hartree-Fock (ROHF).

2. A way too go beyond the HF single determinant approximation. This is crucial because the fluctuation potential $\sum_{j<k=1,N} \frac{1}{r_{j,k}} - \sum_i [J_i - K_i]$ is quite large.

Example- carbon atom's total electronic energy is – 1030.080 eV and $J_{2px,2py}$ = 13 eV, so the J's (and K's) are large quantities on a "chemical" scale of 1 kcal/mol.

The Be 1s/1s fluctuation potential.