Electronic Structure Theory
TSTC Session 4

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?**
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Going beyond the single Slater determinant. When and Why?

Configuration State Functions (CSFs)

Some single-configuration functions can not be single determinants.

Although the determinant $|1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta\ 2p_z\alpha\ 2p_y\alpha|$ is an acceptable approximation to the carbon ^3P state if the 1s and 2s spin-orbitals are restricted to be equal for α and β spins, the ^1S state arising in this same $1s^2 2s^2 2p^2$ configuration can not be represented as a single determinant.

$$\psi(^1S)\ = 3^{-1/2}\,[1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta\ 2p_z\alpha\ 2p_z\beta|$$

$$-\ 1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta\ 2p_x\alpha\ 2p_x\beta|\ -\ 1s\alpha\ 1s\beta\ 2s\alpha\ 2s\beta\ 2p_y\alpha\ 2p_y\beta|\ ]$$

For proper singlet homolytic bond breaking, one may need more than one determinant:

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

The most common way to improve beyond the single determinant

$$|\phi_1 \ \phi_2 \ \phi_3 \ ...\phi_N|$$

is to use trial wave functions of the so-called *configuration interaction (CI)* form

$$\psi = \Sigma_L \ C_{L1,L2,...LN} \ |\phi_{L1} \ \phi_{L2} \ \phi_{L3} \ ...\phi_{LN}|.$$

This makes mathematical sense because the determinants

$$|\phi_{L1} \ \phi_{L2} \ \phi_{L3} \ ... \ \phi_{LN}|$$

form orthonormal complete sets $<|\phi_{L1} \ \phi_{L2} \ \phi_{L3} \ ... \ \phi_{LN}||\phi_{L1} \ \phi_{L2} \ \phi_{L3} \ ... \ \phi_{LN}|> = \delta_{K,L}$

You have already seen CI wave functions with 2 or 3 determinants (to handle the static (sometimes called essential) correlation in olefins, H_2, HF, and ^1S carbon.

But, when and why should one use more determinants, and physically, what does it mean?

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Here is a useful identity for two determinants that one can use to interpret such CI wave functions:

$$\Psi = C_1 |\,..\phi\alpha\ \phi\beta..| - C_2 |\,..\phi'\alpha\ \phi'\beta..|$$

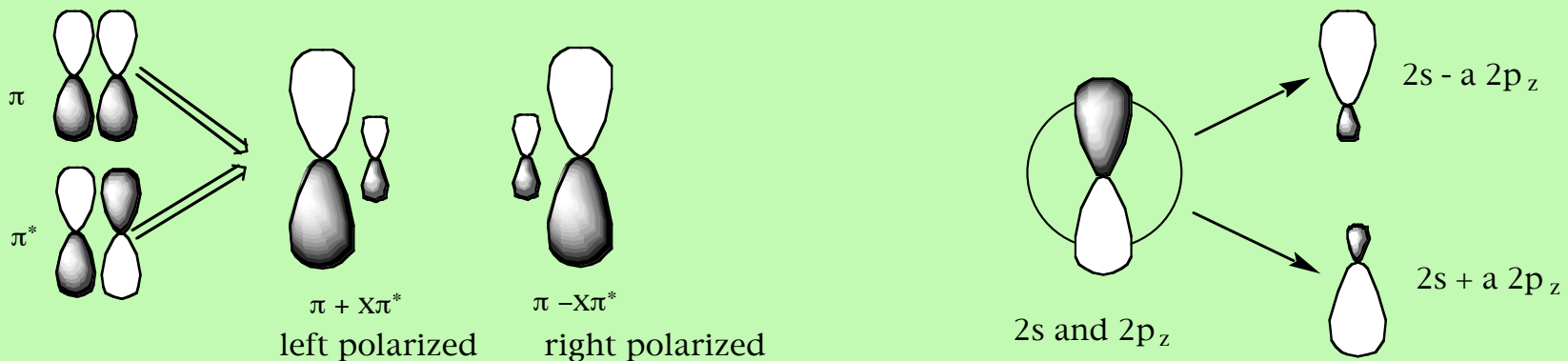$$= C_1/2\ \{\ |\,..(\phi - x\phi')\alpha\ (\phi + x\phi')\beta..| - |\,..(\phi - x\phi')\beta\ (\phi + x\phi')\alpha..|\ \}$$

with $x = (C_2/C_1)^{1/2}$

Two determinants that differ by a doubly occupied orbital ϕ being replaced by a doubly occupied ϕ' is equivalent to **singlet $2^{-1/2}$ ($\alpha\beta - \beta\alpha$) coupled polarized orbital pairs**

$$\phi - x\phi'\ \text{and}\ \phi + x\phi'.$$

For example $\pi^2 \rightarrow \pi^{*2}$ CI in olefins or $2s^2 \rightarrow 2p^2$ CI in alkaline earth atoms produce the following polarized orbital pairs:


π

π^*

$\pi + X\pi^*$
left polarized

$\pi - X\pi^*$
right polarized

2s and 2p$_z$

2s - a 2p$_z$

2s + a 2p$_z$

This is how electrons try to "avoid" one another.

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In the case of the two π electrons in an olefin, the polarized
orbital pairs play qualitatively different roles at 0° and 90° twist
angles. At the fully twisted geometry, the two determinants had
to be mixed with equal amplitudes

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

to achieve the correct diradical bond cleavage products. In this
case, $x = 1$ and the two polarized orbitals $\phi - x\phi'$ and $\phi + x\phi'$
are $2^{-1/2}(\pi - \pi^*) = R$ and $2^{-1/2}(\pi + \pi^*) = L$.
Howerver, at 0 °, the two determinants still mix (but with much
smaller x) to produce polarized orbital
pairs that allow (to some extent) the
two electrons to avoid one another.

π

π^*

$\pi + X\pi^*$
left polarized

$\pi - X\pi^*$
right polarized

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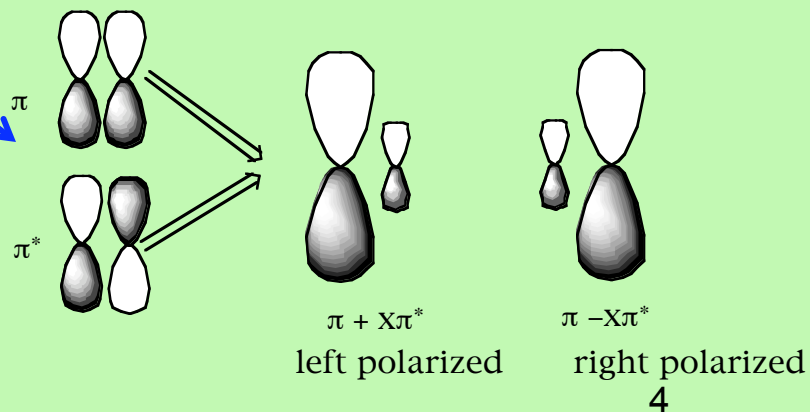
So, placing electron pairs into different polarized orbitals allows them to avoid one another and thus correlate their motions (memorize this).

$$\Psi = C_1 \mid ..\phi\alpha \ \phi\beta.. \mid - C_2 \mid ..\phi'\alpha \ \phi'\beta.. \mid$$

$$= C_1/2 \ \{ \mid ..(\phi - x\phi')\alpha \ (\phi + x\phi')\beta.. \mid - \mid ..(\phi - x\phi')\beta \ (\phi + x\phi')\alpha.. \mid \ \}.$$

Sometimes the CI is **essential**- for example, to adequately describe breaking the π bond in the singlet state of an olefin. One must combine

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

to obtain a diradical state. This is static or essential correlation.

Sometimes even one CSF requires more than one determinant

$$\Psi_{1_S} = 3^{-1/2} [1s\alpha \ 1s\beta \ 2s\alpha \ 2s\beta \ 2p_z\alpha \ 2p_z\beta \mid$$

$$- 1s\alpha \ 1s\beta \ 2s\alpha \ 2s\beta \ 2p_x\alpha \ 2p_x\beta \mid \ - 1s\alpha \ 1s\beta \ 2s\alpha \ 2s\beta \ 2p_y\alpha \ 2p_y\beta \mid \ ].$$

CI is always important if one wishes to include electron-electron avoidance that is

*called **dynamical correlation**.*

So, if a state cannot be represented by a single determinant, one should not use theoretical methods that are based on a single determinant.

If more than one configuration is needed, for example, to homolytically cleave a bond, *CI is essential/static*.

To allow for electron "avoidance", CI can be used and is then called *dynamical*.

How big an effect is dynamical electron correlation?

We know V_{ee} makes the SE non-separable and that ψ has cusps.

We replaced V_{ee} by V_{MF} to form H^0 which introduced orbitals ϕ_J. We used CI to correlate electron pairs, but does this adequately allow for the e-e cusps and how big an effect is the electron correlation?
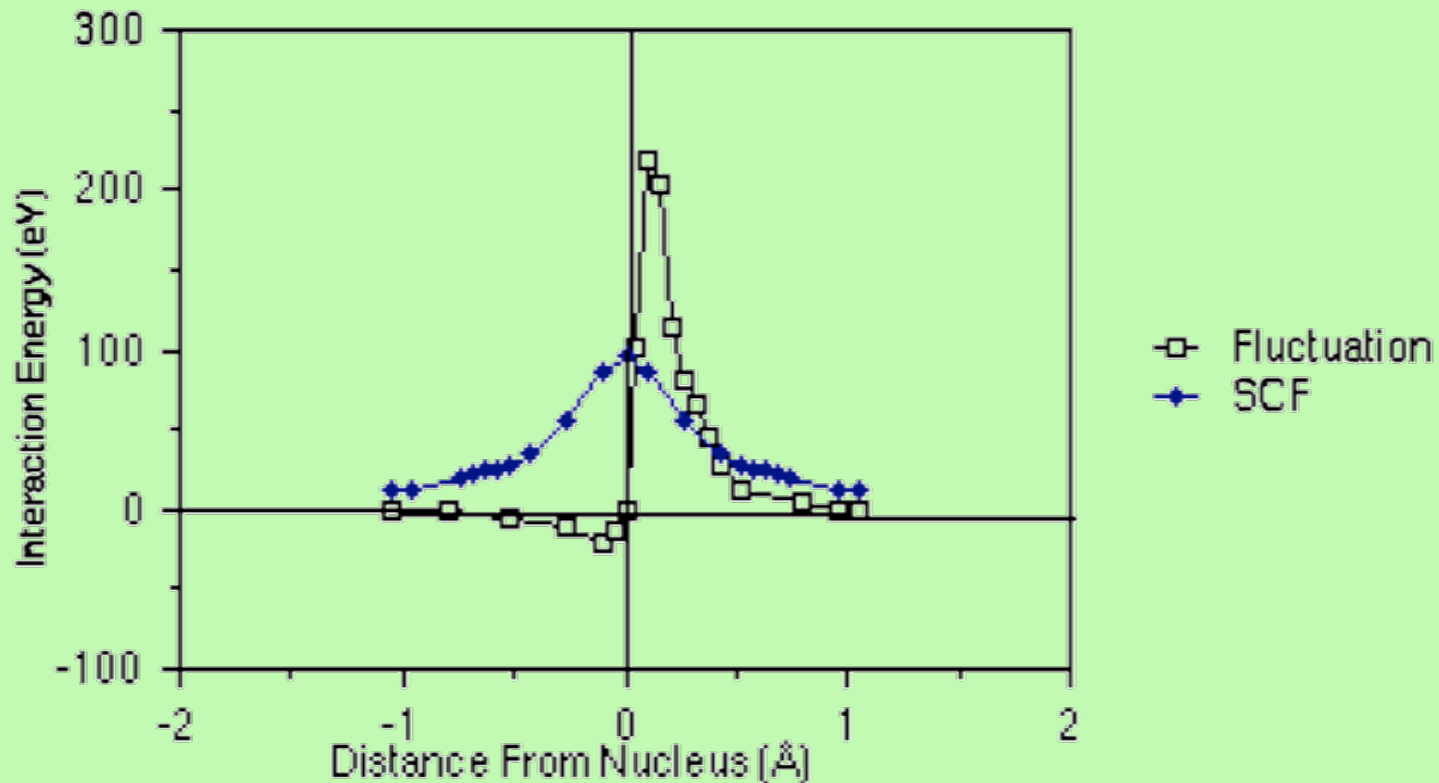

For a Be atom, this is $J_{1s}(r)$, and this is $e^2/r_{1.2} - J_{1s}(r)$ with one electron held at 0.13 Å. The fluctuation potential V_{ee}-V_{MF} is *shorter-range* than V_{ee}, but is still very "strong".

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So, the electron-electron interactions are large quantities and the errors made in describing them in terms of the HF mean-field picture are also large.

This makes it difficult for a perturbative (MPn) or a variational (CI) approach that assumes HF to be a dominant factor to give accurate energies or ψs.
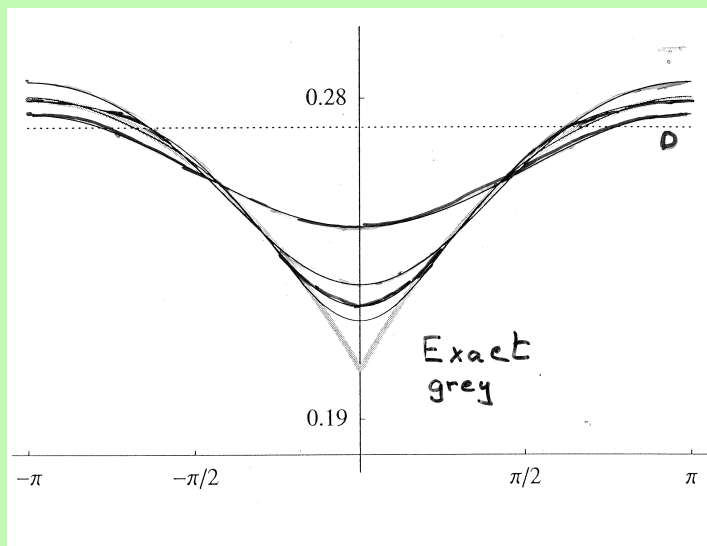
The coulomb hole for He in cc-pVXZ (X=D,T,Q,5) basis set with one electron fixed at 0.5 a_0 carried out at full CI

A single determinant function has no electron-electron cusps, so it can not describe electron "avoidance" (dynamical correlation). CI attempts to include cusps, but does so only crudely.

Sometimes we incorporate cusps into trial functions (explicitly correlated wave functions are used in so-called **r-12 methods**), but this results in very difficult theories to implement and very computer-intensive calculations.

Earlier, we saw the e-e cusp condition

$$\partial / \partial r_{k,l} \, \psi = 1/2 \, m_e e^2 / \hbar^2 \psi \, (\text{as } r_{k,l} \rightarrow 0)$$

The most straightforward way to introduce this condition into CI is to take a trial function of the form (in au's so the m_e, e, and h' go away)

$$\psi = \Sigma_L \, C_{L1,L2,...LN} \, |\phi_{L1} \, \phi_{L2} \, \phi_{L3} \, ...\phi_{LN}| \, (1 + 1/2 \, \Sigma_{k,l} \, r_{k,l})$$

Using such a trial function in

$$< \psi |H| \psi >$$

gives rise to integrals of the form:

$$\int \phi_L(r_1) \, \phi_K(r_2) \, r_{1,3} \, r_{2,4} \, (1/r_{2,3}) \, \phi_M(r_3) \, \phi_N(r_4) \, d1 \, d2 \, d3 \, d4$$

which are *16-dimensional 4-electron integrals!*

This makes the computational implementation of such theories very difficult.

So, the most common and practical ways to introduce electron correlation is to use functions of the CI form

$$\psi = \Sigma_L \ C_{L1,L2,...LN} \ |\phi_{L1} \ \phi_{L2} \ \phi_{L3} \ ...\phi_{LN}|$$

The various methods (e.g., Møller-Plesset perturbation theory (MPn), the configuration interaction method (CI), multi-configuration self-consistent field (MCSCF), etc.) differ in how they determine the $C_{L1,L2,...LN}$ coefficients, how the determine the spin-orbitals ϕ_{Lk}, and how they determine the final energy E.

Let's look a bit deeper at how one usually determines the spin-orbitals ϕ_J and the coefficients $C_{L1,L2, ...LN}$, beginning with the spin-orbitals.