

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.

$$\begin{aligned} \psi(^1S) = & 3^{-1/2} [1s\alpha \ 1s\beta \ 2s\alpha \ 2s\beta \ 2p_z\alpha \ 2p_z\beta | \\ & - 1s\alpha \ 1s\beta \ 2s\alpha \ 2s\beta \ 2p_x\alpha \ 2p_x\beta | - 1s\alpha \ 1s\beta \ 2s\alpha \ 2s\beta \ 2p_y\alpha \ 2p_y\beta |] \end{aligned}$$

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

$$|\phi_1 \phi_2 \phi_3 \dots \phi_N|$$

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

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

This makes mathematical sense because the determinants

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

form orthonormal complete sets $\langle |\phi_{L1} \phi_{L2} \phi_{L3} \dots \phi_{LN}| | \phi_{K1} \phi_{K2} \phi_{K3} \dots \phi_{KN}| \rangle = \delta_{K,L}$

You have already seen CI wave functions with 2 or 3 determinants (to handle the static (sometimes called essential) correlation in olefins, H₂, HF, and ¹S carbon.

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

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

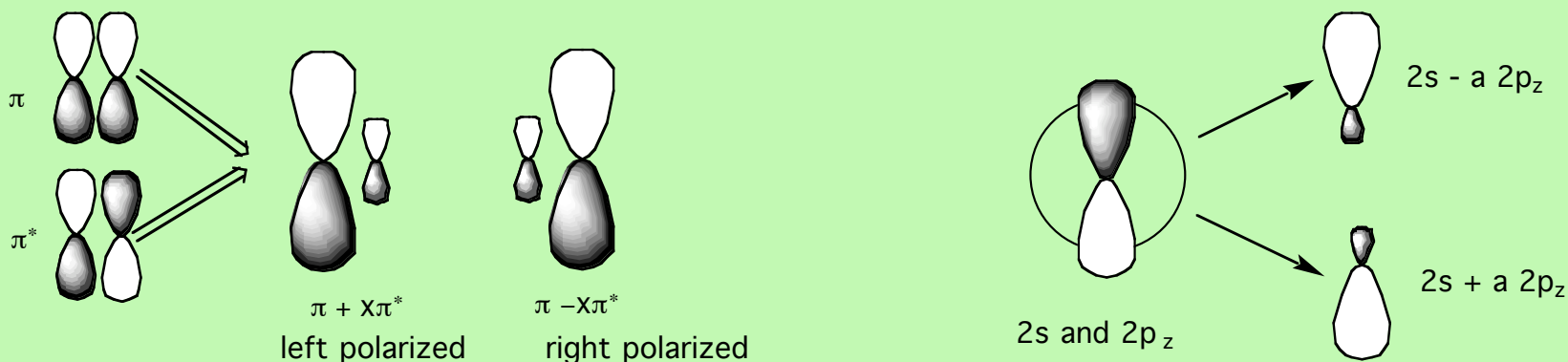
$$\begin{aligned}\Psi &= C_1 | \dots \phi \alpha \phi \beta \dots | - C_2 | \dots \phi' \alpha \phi' \beta \dots | \\ &= C_1/2 \{ | \dots (\phi - x\phi') \alpha (\phi + x\phi') \beta \dots | - | \dots (\phi - x\phi') \beta (\phi + x\phi') \alpha \dots | \}\end{aligned}$$

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:



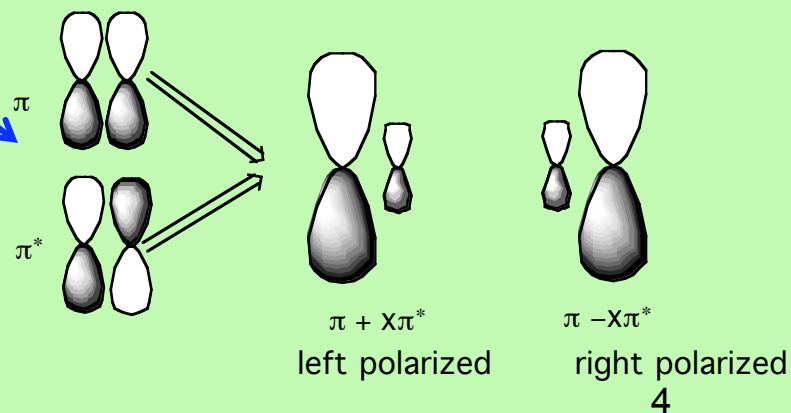
This is how electrons try to “avoid” one another.

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

However, **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.



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

$$\begin{aligned}\Psi &= C_1 | \dots \phi \alpha \phi \beta \dots | - C_2 | \dots \phi' \alpha \phi' \beta \dots | \\ &= C_1/2 \{ | \dots (\phi - x\phi') \alpha (\phi + x\phi') \beta \dots | - | \dots (\phi - x\phi') \beta (\phi + x\phi') \alpha \dots | \}.\end{aligned}$$

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

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

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

Sometimes even one **CSF requires more than one determinant**

$$\begin{aligned}\Psi_{1_S} &= 3^{-1/2} [1s\alpha \ 1s\beta \ 2s\alpha \ 2s\beta \ 2p_z\alpha \ 2p_z\beta | \\ &\quad - 1s\alpha \ 1s\beta \ 2s\alpha \ 2s\beta \ 2p_x\alpha \ 2p_x\beta | - 1s\alpha \ 1s\beta \ 2s\alpha \ 2s\beta \ 2p_y\alpha \ 2p_y\beta |].\end{aligned}$$

*CI is always important if one wishes to include electron-electron avoidance that is called **dynamical correlation**.* Polarized orbital pairs is how CI tries to treat the e-e cusp.

So, if a state cannot be represented by a single determinant, one should not use theoretical methods that are based on a single determinant (RHF, UHF, MPn, CC).

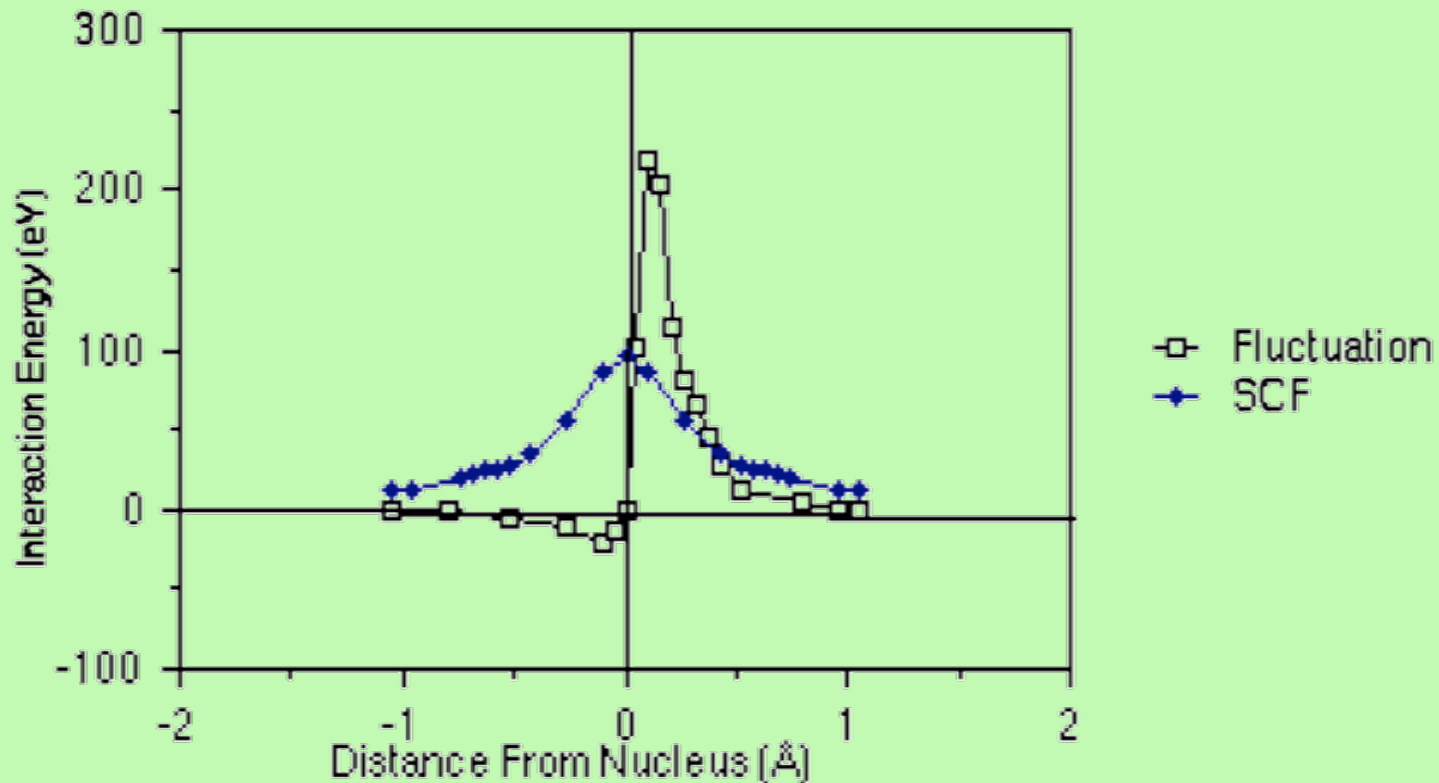
If more than one configuration is needed, for example, to homolytically cleave a bond, *CI is essential/static*.

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.

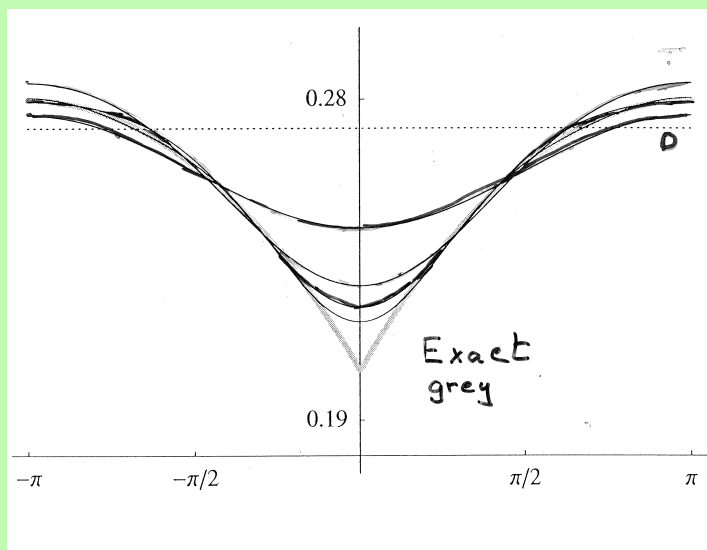
We replaced V_{ee} by V_{MF} to form H^0 which introduced orbitals ϕ_J . We used CI to correlate electron pairs, but does this adequately allow for the e-e **cusps** and how big an effect is the electron correlation?



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**”.

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 ψ s.



*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 \hbar go away)

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

Using such a trial function in

$$\langle \psi | H | \psi \rangle$$

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

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

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 they 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.