Electronic Structure Theory
TSTC Session 4

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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 $\alpha$ and $\beta$ spins, the $^1S$ state arising in this same $1s^22s^22p^2$ 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

\[ \vert \phi_1 \phi_2 \phi_3 \ldots \phi_N \vert \]

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

\[ \psi = \sum_L C_{L1,L2,\ldots,L_N} \vert \phi_{L1} \phi_{L2} \phi_{L3} \ldots \phi_{L_N} \vert. \]

This makes mathematical sense because the determinants

\[ \vert \phi_{L1} \phi_{L2} \phi_{L3} \ldots \phi_{L_N} \vert \]

form orthonormal complete sets \(<\vert \phi_{L1} \phi_{L2} \phi_{L3} \ldots \phi_{L_N} \rangle \vert \phi_{L1} \phi_{L2} \phi_{L3} \ldots \phi_{L_N} \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, H\(_2\), HF, and \(^1\)S 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:

\[
\Psi = C_1 \left| \ldots \phi \alpha \phi \beta \ldots \right| - C_2 \left| \ldots \phi' \alpha \phi' \beta \ldots \right|
\]

\[
= C_1/2 \left\{ \left| \ldots (\phi - x\phi')\alpha (\phi + x\phi')\beta \ldots \right| - \left| \ldots (\phi - x\phi')\beta (\phi + x\phi')\alpha \ldots \right| \right\}
\]

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

Two determinants that differ by a doubly occupied orbital \( \phi \) being replaced by a doubly occupied \( \phi' \) is equivalent to a 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 $\pi$ 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).

\[ \Psi = C_1 | ..\phi\alpha \phi\beta ..| - C_2 | ..\phi'\alpha \phi'\beta ..| \]
\[ = C_1/2 \{ | ..( \phi - x\phi')\alpha ( \phi + x\phi')\beta ..| - | ..( \phi - x\phi')\beta ( \phi + x\phi')\alpha ..| \}. \]

Sometimes the CI is essential— for example, to adequately describe breaking the \( \pi \) 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

\[ \Psi_{1S} = 3^{-1/2}[ |1s\alpha 1s\beta 2s\alpha 2s\beta 2p_z\alpha 2p_z\beta| - |1s\alpha 1s\beta 2s\alpha 2s\beta 2p_x\alpha 2p_x\beta| - |1s\alpha 1s\beta 2s\alpha 2s\beta 2p_y\alpha 2p_y\beta| ]. \]

\( CI \) 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 $\psi$ has cusps.

We replaced $V_{ee}$ by $V_{MF}$ to form $H^0$ which introduced orbitals $\phi_J$. 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 $\psi$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

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

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

\[
\psi = \Sigma_L C_{L_1,L_2,\ldots,L_N} |\phi_{L_1} \phi_{L_2} \phi_{L_3} \ldots \phi_{L_N}| (1 + \frac{1}{2} \sum_{k,l} r_{k,l})
\]

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

$$\psi = \sum_{L} C_{L_1,L_2,...,L_N} |\phi_{L_1} \phi_{L_2} \phi_{L_3} ... \phi_{L_N}|$$

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 $C_{L_1,L_2,...,L_N}$ coefficients, how they determine the spin-orbitals $\phi_{L_k}$, and how they determine the final energy $E$.

Let’s look a bit deeper at how one usually determines the spin-orbitals $\phi_J$ and the coefficients $C_{L_1,L_2,...,L_N}$, beginning with the spin-orbitals.