Using Multiconfiguration Methods to Treat Electron Correlation in PES Calculations
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Introduction

The fundamental method used in modern computational chemistry programs is the Hartree-Fock Self-Consistent Field method (HF-SCF), in which each electron is assumed to move in the average potential field of all the other electrons within a molecule. This assumption greatly reduces computational cost and generally produces good qualitative results and semi-quantitative results. However, the neglect of correlation among individual electrons is a serious limitation, and in certain situations such as bond dissociation, results from this method are not even qualitatively correct. Thus an awareness of the specific limitations of Hartree-Fock methods and of post-Hartree-Fock methods that can be used to recover electron correlation is very useful. My research this semester has dealt with these limitations and computational approaches to the recovery of electron correlation. This poster provides a brief description of electron correlation within the electronic Schrödinger equation, explains the lack of electron correlation within Hartree-Fock calculations, and discusses the use of post-HF methods in which multiple electron configurations describe the total electronic wavefunction of a molecule.

Electrons Are Inherently Uncorrelated in Hartree-Fock

Quantum chemical calculations involve the solution of a Schrödinger equation

$$\hat{H}\psi = E\psi$$  \hspace{1cm} (1)

The Hamiltonian operator $\hat{H}$ is

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_k \frac{\hbar^2}{2m_k} \nabla_k^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}}$$  \hspace{1cm} (2)

where $i$ and $j$ are electronic indices and $k$ and $l$ are nuclear indices. By setting the second term to zero and expressing the fifth term as an additive constant $V_N$, in accordance with the Born-Oppenheimer approximation, the above equation is reduced to the electronic Schrödinger equation

$$\left(\hat{H}_{el} + V_N\right)\psi(q_i;q_k) = E_{el} \psi(q_i;q_k)$$  \hspace{1cm} (3)

where electronic positions $q_i$ are independent variables, nuclear positions $q_k$ are parameters, and the electronic Hamiltonian $\hat{H}_{el}$ is

$$\hat{H}_{el} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}}$$  \hspace{1cm} (4)

Note that the first two terms on the right hand side of (4) can be calculated for each electron individually but the third requires information regarding all
electrons. To enable electrons to be treated individually in the iterative loop of a Self-Consistent Field calculation, Hartree-Fock calculations express this third term as a Coulombic interaction with the mean field of all other electrons instead of the sum of individual Coulombic interactions with the other electrons. Thus a specific orbital is calculated for each electron and the full electronic wavefunction is the antisymmetrized product of these 1-electron orbitals written as a Slater determinant. This simplifying assumption removes electron correlation and causes deviation of a Hartree-Fock calculation from an exact solution to the electronic Schrödinger equation.

**Dynamic and Static Electron Correlation**

Generally speaking, the electron correlation that is absent from the Hartree-Fock method can be separated into two categories, dynamic and static.

*Dynamic correlation* is short range and is a direct result of the $r_{ij}^{-1}$ term in the electronic Schrödinger equation. In a many-electron system, the position of each electron becomes the center of a region which other electrons will avoid due to Coulombic repulsion (a Coulomb hole). Within the Hartree-Fock method, however, the molecular wavefunction is a simple antisymmetrized product of all electronic orbitals, so the probability of finding two electrons within some small region is equal to the product of the uncorrelated probabilities that each is found within that region; i.e., there is no Coulomb hole.

Because of this lack of dynamic correlation, inter-electronic distances are underestimated. The increase in calculated repulsion energy based on these shorter distances leads to an increase in total energy. The energy difference introduced by the Hartree-Fock approximation is referred to as correlation energy, $E_{\text{corr}}$:

$$E_{\text{corr}} = E_{\text{HF}} - E_{\text{exact}}$$  \hspace{1cm} (5)

*Static correlation* is a term used to describe the mixing of degenerate or nearly-degenerate molecular wavefunctions. This type of correlation is long range and
becomes important when the electronic wavefunction of a molecule is not accurately described by a single Slater determinant, i.e., when the actual wavefunction is not dominated by any single electron configuration. Since Self-Consistent Field calculations produce wavefunctions that are antisymmetrized products of single-electron orbitals, these wavefunctions can always be written as single Slater determinants and thus will necessarily be insufficient when static correlation is important.

**RHF Fails When Static Correlation Effects Are Important**

An instructive example is the very simple case of H$_2$ dissociation within the spin-restricted Hartree-Fock (RHF) method. Here, the electronic wavefunction for the H$_2$ ground state $X^1\Sigma^+_g$ is

$$\psi_X = \hat{A}\sigma^a_g (1)\sigma^b_g$$  \hspace{1cm} (6)

In (6) above, $\hat{A}$ is an antisymmetrizing operator, $\alpha$ and $\beta$ are spin functions, and $\sigma^a_g$ is a bonding orbital for the $\alpha$-spin electron given by $\sigma^a_g = Z_{\sigma_g} (\chi_A^\alpha + \chi_B^\alpha)$, where $Z_{\sigma_g}$ is a normalization constant and $\chi_A$ and $\chi_B$ are $s$-like orbitals centered on nuclei $A$ and $B$. In the limit of infinite separation, $\chi_A$ and $\chi_B$ are $1s_A$ and $1s_B$ orbitals, and the normalization constant is $Z_{\sigma_g} = \frac{1}{\sqrt{2}}$. Thus at complete dissociation,

$$\psi_X = \frac{1}{2} \hat{A} \left( (1s_A^\alpha + 1s_B^\alpha)(1s_A^\beta + 1s_B^\beta) \right)$$

$$\psi_X = \frac{1}{2} \hat{A} \left( 1s_A^\alpha 1s_B^\beta + 1s_B^\alpha 1s_A^\beta + 1s_A^\alpha 1s_A^\beta + 1s_B^\alpha 1s_B^\beta \right)$$  \hspace{1cm} (7)

Notice that the first and second terms in (7) each describe a pair of neutral hydrogen atoms, where $\alpha$- and $\beta$-spin orbitals are centered on separate nuclei, while the third and fourth terms each describe two hydrogen ions, where both orbitals are centered on the same nucleus. Thus the RHF wavefunction includes equal contributions from neutral and ionic products. Physically, however, only neutral hydrogen atoms should be expected, since the electron-electron repulsion on an H$^-$ ion would cause the total energy of ionic products to be higher than the total energy of neutral products. Since the neutral and ionic terms make equal contributions to the wavefunction, the calculated energy is halfway between the energy of two hydrogen atoms (H...H) and the energy of two hydrogen ions (H$^+$...H$^-$), and RHF overestimates bond dissociation energy, as shown in the PES below.
The presence of ionic terms in the RHF wavefunction at dissociation is the result of the uncorrelated motion of the two electrons in H$_2$. Each has an equal probability of being located near either of the nuclei, regardless of the position of the other electron, so the probability that both electrons are near the same nucleus is equal to the probability that they are near opposite nuclei. The PES above clearly shows that static correlation error at long distance in the RHF method leads to the overbinding of H$_2$ and thus to underestimated bond lengths and overestimated vibrational frequencies.

**UHF Gives Better Results But Is Spin-Contaminated**

One way to avoid this unphysical result is to remove the spin symmetry requirement by using spin-unrestricted Hartree-Fock (UHF). This method allows each electron to have a unique wavefunction. Near equilibrium, UHF results will be identical to RHF results, but as the molecule dissociates, the electrons will be able to localize on specific nuclei, according to one of two degenerate wavefunctions, $\psi_x = \hat{A} 1s_A^{\alpha} 1s_B^{\beta}$ or $\psi_x = \hat{A} 1s_A^{\alpha} 1s_A^{\beta}$. These wavefunctions do not contain the unphysical ionic terms found in the RHF wavefunction and therefore give more accurate energy values, as shown in the PES above. Unfortunately, UHF results suffer from a property known as spin contamination which causes them to be unreliable as starting points for more advanced methods used to recover correlation.

For a UHF calculation to produce better results than an RHF calculation as shown above, non-symmetric initial guess wavefunctions must be used. These are achieved with the nosym and rotate commands in Molpro or the guess=mix keyword in Gaussian. Symmetric initial guess wavefunctions will lead to the same results as would be produced by RHF, which is a subset of UHF.
Multiple Configurations Treat Static Correlation

Fortunately, it is possible to accurately describe bond dissociation in Hartree-Fock with spin symmetry still intact. In fact, for \( \text{H}_2 \) the method is quite simple. Consider the excited \( ^1\Sigma^+_g \) state of \( \text{H}_2 \), which has an RHF wavefunction

\[
\psi_E = \hat{A} \sigma^\alpha_u (1) \sigma^\beta_u (2)
\]

This is identical to (6) above, except that \( \sigma^\alpha_u (1) = Z_{\sigma_u} \left( \chi^\alpha_A - \chi^\alpha_B \right) \) is an antibonding orbital for the \( \alpha \)-spin electron. At dissociation this wavefunction becomes

\[
\psi_E = Z_{\sigma_u}^2 \hat{A} \left( \chi^\alpha_A - \chi^\alpha_B \right) \left( \chi^\beta_A - \chi^\beta_B \right)
\]

\[
\psi_E = \frac{1}{2} \hat{A} \left( \chi^\alpha_A \chi^\beta_B - \chi^\beta_A \chi^\alpha_B + 1 \chi^\alpha_A \chi^\beta_B - 1 \chi^\beta_A \chi^\alpha_B \right)
\]

(8)

The same unphysical mixture of neutral and ionic terms is present in this wavefunction as was present in (7) above, but notice that the sum

\[
\psi_X + \psi_E = \sigma^2_x + \sigma^2_u
\]

contains no ionic terms. This is a simple example of configuration interaction (CI), where a wavefunction is represented as a linear combination of ground and excited state configurations, i.e., Slater determinants. In this example, the CI wavefunction for \( \text{H}_2 \) is

\[
\psi = c_X \psi_X + c_E \psi_E
\]

where coefficients \( c_X \) and \( c_E \) vary with bond length. Near equilibrium, one would expect \( c_X \approx 1 \) and \( c_E \approx 0 \), while at dissociation one would expect \( c_X \approx \frac{1}{\sqrt{2}} \) and \( c_E \approx -\frac{1}{\sqrt{2}} \).

This particular use of CI is an example of a more general type of post-HF treatments of electron correlation, called *multi-configurational* methods, where the molecular wavefunction is approximated as some linear combination of Slater determinants,

\[
\Psi_{\text{multi-config}} = \sum_k c_k \psi_k
\]

(9)

The motivation for this type of wavefunction construction is simple: since every Slater determinant wavefunction \( \psi_k \) is an eigenfunction of the Hartree-Fock Hamiltonian, and since the Hamiltonian is a Hermitian operator, the set of all Slater determinants \( \{ \psi_k \} \) is complete and orthonormal. This set forms the basis of an abstract vector space which contains a vector describing the exact wavefunction, so in principle the exact wavefunction can be found if the expansion in (9) contains all possible Slater determinants.

\[
\Psi_{\text{exact}} = \sum_{k=1}^\infty c_k \psi_k
\]

(10)

The expansion in (10) is called *Full CI* and is computationally unattainable for all but the simplest of cases.
Recovering Electron Correlation
As mentioned earlier, dynamic correlation error within the Hartree-Fock method leads to overestimated bond lengths and underestimated binding. Conversely, static correlation error leads to underestimated bond lengths and overbinding of molecules due to the spin restrictions of RHF. Thus the effects of these two types of correlation are partially cancelled in RHF, despite its simplicity. However, this partial cancellation is not a solution to the problem of electron correlation, and post-HF methods are necessary to recover electron correlation.

When static correlation effects are small, as is the case for most molecules near equilibrium geometry, the Hartree-Fock determinant is a satisfactory starting point for post-HF methods. Post-HF methods using this approach are called single-reference methods. By far the most common classes of single-reference post-HF methods are configuration interaction (CIS, CISD, etc.), perturbation theory (MP2, MP4, etc.), and coupled cluster theory (CCSD, CCSD(T), etc.).

When static correlation is significant, as is the case in bond dissociations and in molecules with near electron degeneracy, the single Hartree-Fock reference determinant is not a very good starting point for post-HF methods, because other degenerate or nearly-degenerate determinants also contribute to the actual wavefunction. In these cases, it is better to start with multiple reference determinants, i.e., to use multi-reference methods. One such method is the multi-configurational self-consistent field (MCSCF) method, where both the coefficients and the wavefunctions in (9) are optimized to minimize the calculated energy at each geometry.

Since dynamic and static correlation errors arise for different reasons, a good treatment for one will not necessarily be a good treatment for the other. Single-reference CI, PT, and CC methods recover dynamic correlation quickly but are slow (or unable) to recover static correlation; multi-reference methods recover static correlation quickly but are slow to recover dynamic correlation. In the limit of infinite expansion, both approach the actual wavefunction, but this approach is slow and impractical. Therefore a better approach is to use a method that treats both static and dynamic correlation simultaneously, such as MRCI or CASPT2.

H₂ Bond Dissociation Revisited
A few final remarks can be made about the H₂ bond dissociation example used above. First, the reason that UHF gives a better initial description of bond dissociation in H₂ than RHF does is that the α- and β-spin electrons can each contribute a unique determinant in UHF. In other words, the real advantage of UHF over RHF in this example is that UHF becomes a multi-reference method while RHF does not. Second, the CI method used to treat static correlation was technically single reference (it involved only the ground state HF determinant ψᵣ and a second determinant ψₑ excited from that reference), but it also functioned as a multi-reference method because this excited determinant happened to be the degenerate electron configuration near dissociation.
Bibliography
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