Post-Hartree Fock Methods - I

1 The limitations of Hartree Fock approximation

The $2n-$electron single determinant Hartree Fock wave function is the variational best among all possible $2n-$electron single determinants constructed with a set of $n-$orthonormal paired spin orbitals. Even then it does not provide chemical accuracy. It can, at best, be the starting point of more refined calculations. What is the reason of the inadequacy of the Hartree Fock (HF) wave functions? One way to understand the source of inadequacy is to analyze the form of the probability density of finding the electrons in space, that the HF wave function produces. Let us take the case of a two electron system in its spin singlet ground state (^1S_o). The two orthonormal spin orbitals used in the HF description are $\phi_{o\alpha}(r)$ and $\phi_{o\beta}(r)$ and ψ_o^{HF} is given by the Stater determinant (α , β are orthonormal spin eigenfunctions)

$$\psi_o^{HF} = \frac{1}{\sqrt{2}} |\phi_{o\alpha}(r_1)\phi_{o\beta}(r_2)|$$

$$= \frac{1}{\sqrt{2}} \{\phi_{o\alpha}(r_1)\phi_{o\beta}(r_2) - \phi_{o\alpha}(r_2)\phi_{o\beta}(r_1)\} \tag{1}$$

$\phi_{o\alpha}$ and $\phi_{o\beta}$ have the same space part ($\phi_o(r)$), but different spin functions α and β i. e., $\phi_{o\alpha}^{(r_1)} = \phi_o(r_1)\alpha(s_1)$ and $\phi_{o\beta}(r_2) = \phi_o(r_2)\beta(s_2)$) where $r =$ spatial coordinate $s =$ spin coordinate. The two electron spin and spatial probability density $P(r_1, r_2, \alpha, \beta)$ is easily generated (assuming real spin orbital) as follows;

$$P(r_1, r_2, \alpha, \beta) = \psi_o^{HF} (\psi_o^{HF})^*$$

$$= \frac{1}{2}[(\phi_{o\alpha}(r_1)\phi_{o\beta}(r_2))^2 + (\phi_{o\alpha}(r_2)\phi_{o\beta}(r_1))^2 - \phi_{o\alpha}(r_1)\phi_{o\beta}(r_2)\phi_{o\alpha}(r_2)\phi_{o\beta}(r_1)$$

$$-\phi_{o\alpha}(r_2)\phi_{o\beta}(r_1)\phi_{o\alpha}(r_1)\phi_{o\beta}(r_2)] \tag{2}$$

If we integrate over the spin variables (s_1, s_2), we get the spatial probability density function $P(r_1, r_2)$ of the two electrons (i.e. the probability of finding one electron at r_1 and the other at r_2 whatever may the spin angular momenta of the electrons are)

$$P(r_1, r_2) = \{\phi_o(r_1)\}^2 \times \{\phi_o(r_2)\}^2 \tag{3}$$

To arrive at 10.3, we have used the usual orthonormality conditions for the spin functions, $\alpha(s)$ and $\beta(s)$.

Equation 10.3 immediately tells us that $P(r_1, r_2)$ is a product of two spatial probability density functions $P(r_1) = \{\phi_o(r_1)\}^2$ and $P(r_2) = \{\phi_o(r_2)\}^2$ which are mutually independent. That is, the probability of finding electron 1 at $r = r_1$ is uncorrelatedwith the probability of finding electron 2 at $r = r_2$. But that is clearly unphysical. Electrons are negatively charged and repel each other by Coulomb forces (repulsion energy= $\frac{e^2}{r_1 - r_2}$). They would naturally try to avoid each other and not be at the same point in space ($r_1 = r_2 = r$). They would exclude a certain volume of space around each of them (due to repulsion) where the probability of finding the other would be small. In other words the probability density would be correlated. The two-electron HF spatial probability density is, on the other hand, totally uncorrelated − a property that arises clearly from the single determinant approximation used in the HF description. We suspect therefore the neglect of electron correlation (more precisely Coulomb correlation) in the HF description is at the root of the inadequacy of HF wavefunction in describing the real atoms and molecules. We note here that ψ_o^{HF} vanishes when $r_1 = r_2 = r$ **and** $\alpha = \beta$ which means two electrons having the same spin cannot be at same point (r) in space. The HF description has Fermi or spin correlation built into the wave function, but Coulomb correlation is missing.

Post-Hartree Fock methods attempt to take care of the deficiency by switching over to many determinant description of the state being probed so that the (?hitherto) neglected (Coulomb) correlation appears in the spatial probability density function. We would now examine the issue thoroughly and find out what can be done to improve the quality of the wave function that the HF method provides.

Let us assume that we have generated all the HF orbitals $\{\phi_i\}_i$, occupied or unoccupied, for the two-electron systems. The exact two electron wave function for the singlet ground state of our two-electron system ($\psi(x_1, x_2)$) can be written as a product of $\psi(r_1, r_2)$ (space part of ψ) and $\eta(s_1, s_2, S=0)$ (spin part of the wave function) so that

$$\psi(x_1, x_2) = \psi_{space}(r_1, r_2) \times \eta_{spin}(s_1, s_2, S=0) \tag{4}$$

$\eta_{spin}(s_1, s_2, S=0)$ is given by the combination eigenfunctions of the s_z operator as

$$\eta_{spin}(s_1, s_2, S=0) = \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \tag{5}$$

To arrive at a complete description of $\psi_{space}(r_1, r_2)$ we start by assuming that we have kept r_2 fixed at $\overline{r_2}$ so that $\psi_{space}(r_1, \overline{r_2})$ can be expanded in the complete set of orthonormal HF orbitals $\{\phi_i(r_1)\}$:

$$\psi_{space}(r_1, \overline{r_2}) = \sum_{i=1} c_i(\overline{r_2})\phi_i(r_1) \tag{6}$$

where $c_i(\overline{r_2})$ parametrically depends on $\overline{r_2}$. Now we assume that $\overline{r_2}$ has been unfrozen, so that $c_i(r_2)$ can be regarded as s function of r_2 (as a coordinate) which can therefore be expanded in the complete orthonormal set $\{\phi_j(r_2)\}$ yielding,

$$c_i(r_2) = \sum_{j=1} c_{ij}\phi_j(r_2) \tag{7}$$

Using 10.8 in 10.7 , we have, for the space part of the two-electron wave function

$$\psi_{space}(r_1, r_2) = \sum_i \sum_j c_{ij}\phi_i(r_1)\phi_j(r_2) \tag{8}$$

and the total wave function as

$$\psi(x_1, x_2) = \{\sum_i \sum_j c_{ij}\phi_i(r_1)\phi_j(r_2)\} \times \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \tag{9}$$

$\psi(x_1, x_2)$ as represented in equation 10.10 suffers from one shortcoming, − it does not satisfy Pauli exclusion principle; i.e. it is not antisymmetric with respect to interchange of space-spin coordinates of the two electrons. An inspection of the right hand side of equation 10.10 immediately tells us that $\eta_{spin}(s_1, s_2, S=0)$ is antisymmetric with respect to the interchange of the spin coordinates (s_1, s_2) so that $\psi_{space}(r_1, r_2)$ must be symmetric with respect to the interchange of spatial coordinates (r_1, r_2) of the two electrons. That means we must symmetrize the product $\phi_i(r_1)\phi_j(r_2)$ and replace it by $\{\phi_i(r_1)\phi_j(r_2)+\phi_i(r_2)\phi_j(r_1)\}$. With the imposition of the symmetry constraint, we now have

$$\psi(x_1,x_2)=\sum_i\sum_j c_{ij}\{\phi_i(r_1)\phi_j(r_2)+\phi_i(r_2)\phi_j(r_1)\}\times\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\} \tag{10}$$

Introducing spin orbitals $\phi_{i\alpha},\phi_{i\beta}$ etc. we have

$$\psi(x_1,x_2)=\sum_{ij}c_{ij}[\frac{1}{\sqrt{2}}\{\phi_{i\alpha}(1)\phi_{j\beta}(2)-\phi_{j\alpha}(1)\phi_{i\beta}(2)\}] \tag{11}$$

where $\phi_{i\alpha}(1)=\phi_i(r_1)\alpha(1)$

$$\phi_{j\beta}(1)=\phi_j(r_1)\beta(1) \tag{12}$$

are spin orbitals, and similar definition holds for $\phi_{j\alpha}(1),\phi_{i\beta}(1)$.

$\frac{1}{\sqrt{2}}|\phi_{i\alpha}(1)\phi_{j\beta}(2)|,\frac{1}{\sqrt{2}}|\phi_{j\alpha}(1)\phi_{i\beta}(2)|$ represent single Slater determinant wave functions, constructed from the orthonormal spin orbitals $\phi_{i\alpha}(r),\phi_{j\beta}(r)$. Since the spin orbitals are already known (from HF calculation), the only unknowns in equation 10.12 are the coefficients $c_{ij}s$. We can try to determine them variationally by invoking the linear variation principle. But the problem is that it will lead to an infinite number of secular equations ($c_{ij}s$ are infinite in number). To keep the problem tractable, one is forced to use a finite number of spin orbitals ($i,j=1,N, say$) in the expansion 10.12 generated from the n_{occ} number of doubly occupied HF orbitals and $n=(N-n_{occ})$ number of unoccupied or virtual orbitals, and solve a finite number of secular equations arising out of the linear variational principle. The most important point about the expansion 10.12 is that the probability density $P(r_1,r_2)$ can no longer be factorized into $P(r_1,r_2)=P(r_1)\times P(r_2)$ as was possible in the HF description (equation 10.3). The many determinant wave function of equation 10.12 is therefore said to have electron-correlation built into it. All Post-Hartree Fock methods try to incorporate the effects of the additional determinants either variationally (configuration interaction (CI), MCSCF) or perturbatively (many body perturbation theory) or by non-perturbative non-variational (such as coupled cluster) methods. Let us first consider the variational option.

Problem 1. Show that the two-electron density $P(r_1, r_2)$ function is not factorizable in general.

Linear Variational Principle

Let the system be represented by the Hamiltonian 'H'. Let us suppose that we have carried out a linear variational calculation with two orthonormal basis function ϕ_1 and ϕ_2 and let the two roots of the secular equation be $E_0^{(1)}$ and $E_0^{(2)}$ with $E_1^{(2)} \le E_2^{(2)}$. The subscript '1' stands for the ground state, '2' for the first excited state while the superscript (2) stand for the two-dimensional nature of the basis-space. Let the corresponding wavefunctions be $\psi_1^{(2)}$ and $\psi_2^{(2)}$. We now add a third basis function ϕ_3 (orthogonal to $\psi_1^{(2)}$ and $\psi_2^{(2)}$, and normalized). The function $\psi_1^{(2)}$, $\psi_2^{(2)}$ and ϕ_3 form an orthonormal set. In this 3-dimensional basis space the secular determinant reads

$$\Delta^{(3)}(\varepsilon) = \begin{bmatrix} (E_1^{(2)} - \varepsilon) & 0 & h_1 \\ 0 & (E_1^{(2)} - \varepsilon) & h_2 \\ h_1^* & h_2^* & H_{33} - \varepsilon \end{bmatrix} \tag{21}$$

where $E_1^{(2)} = < \psi_1^{(2)} \left| H \right| \psi_1^{(2)} >$, $E_2^{(2)} = < \psi_2^{(2)} \left| H \right| \psi_2^{(2)} >$

$H_{33} = < \phi_3 \left| H \right| \phi_3 >$

$h_1 = < \psi_1^{(2)} \left| H \right| \phi_3 >$, $h_2 = < \psi_2^{(2)} \left| H \right| \phi_3 >$

ε is the variational approximation to energy which can be obtained by setting $\Delta^{(3)}(\varepsilon) = 0$. By expanding $\Delta^{(3)}(\varepsilon)$ we have

$$(E_1^{(2)} - \varepsilon) \begin{vmatrix} (E_2^{(2)} - \varepsilon) & h_2 \\ h_2^* & (H_{33} - \varepsilon) \end{vmatrix} + h_1 \begin{vmatrix} 0 & (E_2^{(2)} - \varepsilon) \\ h_1^* & h_2^* \end{vmatrix} = 0$$

i.e. $$(E_1^{(2)} - \varepsilon)(E_2^{(2)} - \varepsilon)(H_{33} - \varepsilon) - \left| h_1 \right|^2 (E_2^{(2)} - \varepsilon) - \left| h_2 \right|^2 (E_1^{(2)} - \varepsilon) = 0 \tag{22}$$

A-2 is a cubic polynomial equation in ε. We can try to locate the range in which the possible roots can lie by applyingthe rule of sign change of the polynomial as ε is varied.

Let us first note that as $\varepsilon \to -\infty$, $\Delta^3(\varepsilon) > 0$ as the 'sign' will be controlled by the first term on the LHS of eqn. 22.

At $\varepsilon = E_1^{(2)}$, the first and the 3rd terms are zero, while the 2nd term < 0 (note $E_2^{(2)} > E_1^{(2)}$). Therefore $\Delta^{(3)}(\varepsilon)$ changes sign between $\varepsilon = -\infty$ and $E_1^{(2)}$. So the lowest root of 3×3 secular equation (Let us call it $E_1^{(3)}$) lies on the energy axis to the left of $E_1^{(2)}$.

At $\varepsilon = E_2^{(2)}$, the first term is once again zero while the 2nd term also vanishes. If we note that $E_1^{(2)} < E_2^{(2)}$, we immediately see, that the 3rd term on the LHS of eqn. 22 is greater than 0 so that we get another sign change of $\Delta^3(\varepsilon)$ between $\varepsilon = E_1^{(2)}$ and $E_2^{(2)}$. The 2^{nd} root $E_2^{(3)}$ would then be lower than $E_2^{(2)}$.

Similarly by letting $\varepsilon \to +\infty$, we can show that the 3rd root $E_3^{(3)}$ would lie to the right of $E_2^{(2)}$.

Now you can consider passage from three dimensional orthonormal basic space four-dimensional space in the same vain to show that $E_3^{(4)} \leq E_3^{(3)}$, $E_2^{(4)} \leq E_2^{(3)}$ and $E_1^{(4)} \leq E_1^{(3)}$ and finally generalize the result for increasing the basis space from n to $n+1$ dimension (See Mcdonald).