

Physical Interpretation of the Unrestricted Hartree-Fock equations.

Let's first consider the α electron orbitals for a UHF function. These are eigenfunctions of \hat{F}^α satisfying the differential equation

$$\hat{F}^\alpha \phi_{i\alpha} = (\hat{f} + \hat{J}_\alpha + \hat{J}_\beta - \hat{K}_\alpha) \phi_{i\alpha} = \epsilon_i^\alpha \phi_{i\alpha}$$

First we note that $\sum_{i=1}^{N_\alpha} \phi_{i\alpha}^*(2) \phi_{i\alpha}(2)$ is the density of electrons of α spin at point 2 and after

we integrate the spin coordinates $\rho_\alpha(2) = \int d\xi \sum_{i=1}^{N_\alpha} \phi_{i\alpha}^*(2) \phi_{i\alpha}(2)$ is the number density of electrons of α spin at point 2 so \hat{J}_α represents the electrostatic potential at point 1 due to the N_α α spins

$$\hat{J}_\alpha = \sum_{i=1}^{N_\alpha} \int d\tau(2) \phi_{i\alpha}^*(2) \frac{1}{r_{12}} \phi_{i\alpha}(2) = \int \frac{\rho_\alpha(2)}{r_{12}} dV(2) = V_\alpha(1)$$

With a similar interpretation for \hat{J}_β

$$\hat{J}_\beta = \sum_{i=1}^{N_\beta} \int d\tau(2) \phi_{i\beta}^*(2) \frac{1}{r_{12}} \phi_{i\beta}(2) = \int \frac{\rho_\beta(2)}{r_{12}} dV(2) = V_\beta(1)$$

There are two cases to consider according to whether or not the orbital $\phi_{i\alpha}$ is one of the orbitals used to form the potentials $V_\alpha(1)$ & $V_\beta(1)$ and exchange operator \hat{K}^α . If it is we say it's an occupied orbital and if it's not it's a virtual orbital. Let's first consider the case where $\phi_{i\alpha}$ is an occupied orbital.

Rewriting the Hartree-Fock equation we have

$$F^\alpha \phi_{i\alpha}(1) = \hat{f} \phi_{i\alpha}(1) + V_\alpha(1) \phi_{i\alpha}(1) + V_\beta(1) \phi_{i\alpha}(1) - \sum_{j=1}^{N_\alpha} \int d\tau(2) \phi_{j\alpha}^*(2) \frac{1}{r_{12}} \phi_{i\alpha}(2) \phi_{j\alpha}(1) = \epsilon_i^\alpha \phi_{i\alpha}(1)$$

This has the look of a Schrodinger equation for the one electron function $\phi_{i\alpha}$. \hat{f} is an operator representing the kinetic energy of the electron and its attraction to all of the nuclei in the system while V_β represents the interaction of the α spin electron in $\phi_{i\alpha}$ with the electrostatic potential due to the β electrons. V_α , however, represents the interaction of the α spin electron in $\phi_{i\alpha}$ with the electrostatic potential due to *all* α spin

orbitals including the one hosted by $\phi_{i\alpha}$. While it makes sense for the α spin electron to interact with all of the β spin electrons it should interact with one fewer α electrons, i.e., not with itself. Apparently the role of the exchange interaction, \hat{K}^α , which depends entirely on the α spin electrons, is to correct for this self-interaction. We can see more explicitly how this works by multiplying and dividing the exchange term by $\phi_{i\alpha}^* \phi_{i\alpha}$ giving

$$\sum_{j=1}^{N_\alpha} \int \phi_{j\alpha}^*(2) \frac{1}{r_{12}} \phi_{i\alpha}(2) d\tau(2) \phi_{j\alpha}(1) \frac{\phi_{i\alpha}^*(1) \phi_{i\alpha}(1)}{\phi_{i\alpha}^*(1) \phi_{i\alpha}(1)} = \int \gamma_i^\alpha(1,2) \frac{1}{r_{12}} d\tau(2) \phi_{i\alpha}(1)$$

Where $\gamma_i^\alpha(1,2)$ is given by

$$\gamma_i^\alpha(1,2) = \frac{\sum_{j=1}^{N_\alpha} \phi_{j\alpha}^*(2) \phi_{i\alpha}(2) \phi_{j\alpha}(1) \phi_{i\alpha}^*(1)}{\phi_{i\alpha}^*(1) \phi_{i\alpha}(1)}$$

We may regard $\int \gamma_i^\alpha(1,2) \frac{1}{r_{12}} d\tau(2)$ as representing the electrostatic potential at the

position of the electron in $\phi_{i\alpha}(1)$ due to the electron density $\gamma_i^\alpha(1,2)$ and since this density is related to the exchange term it is called the exchange charge density.

Let's look at the properties of this exchange density. First, by construction, it consists of electronic charge having the same spin as $\phi_{i\alpha}$. Second since the orbitals $\phi_{i\alpha}$ are orthonormal the number of electrons comprising this density is 1 as we see from

$$\int \gamma_i^\alpha(1,2) d\tau(2) = \int \sum_{j=1}^{N_\alpha} \frac{\phi_{j\alpha}^*(2) \phi_{i\alpha}(2) \phi_{j\alpha}(1) \phi_{i\alpha}^*(1)}{\phi_{i\alpha}^*(1) \phi_{i\alpha}(1)} d\tau(2) = 1$$

and third when point 1 equals point 2 the exchange charge density reduces to the total spin density of all electrons with the same spin as the electron at position 1.

$$\gamma_i^\alpha(1,1) = \sum_{j=1}^{N_\alpha} \frac{\phi_{j\alpha}^*(1) \phi_{i\alpha}(1) \phi_{j\alpha}(1) \phi_{i\alpha}^*(1)}{\phi_{i\alpha}^*(1) \phi_{i\alpha}(1)} = \sum_{j=1}^{N_\alpha} \phi_{j\alpha}^*(1) \phi_{j\alpha}(1) = \rho_\alpha(1)$$

The Coulombic interaction between the α spin density and an electron at coordinate 1 is then

$$\int \frac{(\rho_\alpha(2) - \gamma_i^\alpha(1,2))}{r_{12}} d\tau(2)$$

And since

$$\int (\rho_\alpha(2) - \gamma_i^\alpha(1,2)) d\tau(2) = N_\alpha - 1$$

We see that, as anticipated, the α electron at coordinate 1 does indeed interact with one fewer α electrons. Additionally since $\gamma_i^\alpha(1,1) = \rho_\alpha(1)$ the density of all of the α spin electrons at the location of coordinate 1, $\rho_\alpha(1) - \gamma_i^\alpha(1,1)$ is zero.

This is as if the electron described by $\phi_{i\alpha}$ carries with it a hole centered on its position such that electron density equal to one unit of charge of the same spin has been removed from this hole. This hole is called the Fermi hole and is a consequence of the exclusion principle that keeps electrons of the same spin away from one another.

Obviously the same conclusion would obtain if we analyzed a β orbital so the take home message is that the role of the exchange term is to reduce the electron-electron repulsion between electrons of the same spin. We will return to this interpretation when we discuss Density Functional Theory.