Closed-Shell Hartree-Fock Equations

A system in which we have an even number of electrons, $N/2$ spatial orbitals and each spatial orbitals hosts both α and β spins is called a closed shell. Writing the spin orbitals as a product of a spatial orbital and a spin function $\phi_{i\alpha} = \phi_i\alpha$ and $\phi_{i\beta} = \phi_i\beta$ allows one to integrate the spin out of the Coulomb operators and express them in terms of spatial orbitals.

$$\hat{J}_\alpha = \sum_{i=1}^{N_\alpha} \int d\tau(2)\phi_{i\alpha}^*(2)g(1,2)\phi_{i\alpha}(2) = \sum_{i=1}^{N/2} \int dV(2)\phi_i^*(2)g(1,2)\phi_i(2) = \hat{J}_\beta$$

The subscripts are now irrelevant so we define $\hat{J} = \hat{J}_\alpha = \hat{J}_\beta$

$$\hat{F}^\alpha = \hat{f} + \hat{J}_\alpha + \hat{J}_\beta - \hat{K}_\alpha = \hat{f} + 2\hat{J} - \hat{K}_\alpha$$

Note that since $\hat{F}^\alpha$ operates on α spin functions we can integrate the spin out of $\hat{K}^\alpha$

$$\hat{K}^\alpha = \sum_{i=1}^{N/2} \int dV(2)\phi_i^*(2)g(1,2)\hat{P}_{12}\phi_i(2) = \hat{K}$$

and the eigenvalue problem for the spin orbitals $F^\alpha\phi_{i\alpha} = \phi_{i\alpha}\varepsilon_i^\alpha$; $i = 1,2,\cdots,N_\alpha$ becomes

$$\hat{F}\phi_i = \phi_i\varepsilon_i \text{ ; } i = 1,2,\cdots,N/2 \text{ where } \hat{F} = \hat{f} + 2\hat{J} - \hat{K}$$

As with the unrestricted functions we will discuss the solutions and their properties subsequently. Let's now look at the form of the equations that determine the restricted open shell solutions.