Unrestricted Open-Shell Hartree-Fock

When we describe a system having a different number of α and β spins with a single Slater determinant we are dealing with an open shell wavefunction and the function is unrestricted when the orbitals hosting α and β spin electrons are different.
If we have N_α spin orbitals with α spin and N_β with β spin the two electron terms in the Fock operator may be partitioned into two parts and the operator written as

$$\hat{F} = \hat{f} + \sum_{j=1}^{N_\alpha} \int d\tau(2) \varphi_{j\alpha}^*(2) g(1,2)\left(1-\hat{P}_{12}\right)\varphi_{j\alpha}(2) + \sum_{j=1}^{N_\beta} \int d\tau(2) \varphi_{j\beta}^*(2) g(1,2)\left(1-\hat{P}_{12}\right)\varphi_{j\beta}(2)$$

Where $\varphi_{j\alpha}$ & $\varphi_{j\beta}$ are α and β spin orbitals. This may be written more compactly in terms of Coulomb and exchange operators

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

Where the Coulomb operators are

$$\hat{J}_\alpha = \sum_{j=1}^{N_\alpha} \int d\tau(2) \varphi_{j\alpha}^*(2) g(1,2) \varphi_{j\alpha}(2) \text{ and } \hat{J}_\beta = \sum_{j=1}^{N_\beta} \int d\tau(2) \varphi_{j\beta}^*(2) g(1,2) \varphi_{j\beta}(2)$$

and the exchange operators are

$$\hat{K}_\alpha = \sum_{j=1}^{N_\alpha} \int d\tau(2) \varphi_{j\alpha}^*(2) g(1,2) \hat{P}_{12} \varphi_{j\alpha}(2) \text{ and } \hat{K}_\beta = \sum_{j=1}^{N_\beta} \int d\tau(2) \varphi_{j\beta}^*(2) g(1,2) \hat{P}_{12} \varphi_{j\beta}(2)$$

Note that $\hat{K}_\alpha \varphi_{j\beta} = 0$ and $\hat{K}_\beta \varphi_{j\alpha} = 0$ because of spin orthogonality, so there is a Fock operator for α spin orbitals and a separate one for β spin orbitals.

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

Since the α and β spin orbitals are automatically orthogonal the Lagrangian multiplier matrix is block diagonal and the Fock operator will not mix spins and we may write

$$\hat{F}^\alpha \varphi_{i\alpha} = \sum_{j=1}^{N_\alpha} \varphi_{j\alpha} \lambda_{ji}^\alpha \; ; i = 1,2,\cdots,N_\alpha$$

and

$$\hat{F}^{\beta}\varphi_{i\beta} = \sum_{j=1}^{N_\beta}\varphi_{j\beta}\lambda_{ji}^{\beta} \ ; i = 1,\cdots,N_\beta$$

Or more compactly as

$$\hat{F}^{\alpha}\vec{\varphi}_{\alpha} = \vec{\varphi}_{\alpha}\boldsymbol{\lambda}^{\alpha} \text{ and } \hat{F}^{\beta}\vec{\varphi}_{\beta} = \vec{\varphi}_{\beta}\boldsymbol{\lambda}^{\beta}$$

Where $\vec{\varphi}_{\alpha}\ \&\ \vec{\varphi}_{\beta}$ are row vectors, $\vec{\varphi}_{\alpha} = \left(\varphi_{1\alpha}\varphi_{2\alpha}\cdots\varphi_{N_\alpha\alpha}\right)$ & $\vec{\varphi}_{\beta} = \left(\varphi_{1\beta}\varphi_{2\beta}\cdots\varphi_{N_\beta\beta}\right)$ and $\left(\boldsymbol{\lambda}^{\alpha}\right)_{ij} = \lambda_{ji}^{\alpha}$ and $\left(\boldsymbol{\lambda}^{\beta}\right)_{ij} = \lambda_{ji}^{\beta}$

We will use the invariance of the Slater determinant to a unitary transformation of the orbitals to eliminate the off diagonal elements of the Lagrangian matrix. Because we choose to not mix $\alpha\ \&\ \beta$ spins (the spin orbitals have either $\alpha\ or\ \beta$ spins) we can transform the two sets independently. Accordingly we replace the original spin orbitals with

$$\phi_{i\alpha} = \sum_{j=1}^{N_\alpha}\varphi_{j\alpha}D_{ji}^{\alpha} \text{ and } \phi_{i\beta} = \sum_{j=1}^{N_\beta}\varphi_{j\beta}D_{ji}^{\beta}$$

or

$$\varphi_{i\alpha} = \sum_{j=1}^{N_\alpha}\phi_{j\alpha}C_{ji}^{\alpha} \text{ and } \varphi_{i\beta} = \sum_{j=1}^{N_\beta}\phi_{j\beta}C_{ji}^{\beta}$$

where $C_{ij}^{\alpha}\ \&\ C_{ij}^{\beta}$ are elements of two independent unitary matrices to be determined. In terms of the row vectors $\vec{\varphi}_{\alpha} = \left(\varphi_{1\alpha}\varphi_{2\alpha}\cdots\varphi_{N_\alpha\alpha}\right)$ & $\vec{\varphi}_{\beta} = \left(\varphi_{1\beta}\varphi_{2\beta}\cdots\varphi_{N_\beta\beta}\right)$ these equations become

$$\vec{\varphi}_{\alpha} = \vec{\phi}_{\alpha}\boldsymbol{C}^{\alpha} \ \ \&\ \ \vec{\varphi}_{\beta} = \vec{\phi}_{\beta}\boldsymbol{C}^{\beta}.$$

Because the $\boldsymbol{C}^{\alpha}\ \&\ \boldsymbol{C}^{\beta}$ matrices are unitary, we have the equalities

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

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

$$\hat{K}_{\alpha} = \sum_{i=1}^{N_{\alpha}} \int d\tau(2)\varphi_{i\alpha}^{*}(2)g(1,2)\hat{P}_{12}\varphi_{i\alpha}(2) = \sum_{i=1}^{N_{\alpha}} \int d\tau(2)\phi_{i\alpha}^{*}(2)g(1,2)\hat{P}_{12}\phi_{i\alpha}(2)$$

and

$$\hat{K}_{\beta} = \sum_{i=1}^{N_{\beta}} \int d\tau(2)\varphi_{i\beta}^{*}(2)g(1,2)\hat{P}_{12}\varphi_{i\beta}(2) = \sum_{i=1}^{N_{\beta}} \int d\tau(2)\phi_{i\beta}^{*}(2)g(1,2)\hat{P}_{12}\phi_{i\beta}(2)$$

And so the Fock operators are identical in either basis and the Hartree-Fock equations in terms of the $\vec{\phi}_{\alpha}$ and $\vec{\phi}_{\beta}$ orbitals becomes

$\hat{F}^{\alpha}\vec{\phi}_{\alpha}\boldsymbol{C}^{\alpha} = \vec{\phi}_{\alpha}\boldsymbol{C}^{\alpha}\boldsymbol{\lambda}^{\alpha}$ and $\hat{F}^{\alpha}\vec{\phi}_{\alpha}\boldsymbol{C}^{\alpha} = \vec{\phi}_{\alpha}\boldsymbol{C}^{\alpha}\boldsymbol{\lambda}^{\alpha}$ or

$\hat{F}^{\alpha}\vec{\phi}_{\alpha} = \vec{\phi}_{\alpha}\boldsymbol{C}^{\alpha}\boldsymbol{\lambda}^{\alpha}\boldsymbol{C}^{\alpha+}$ and $\hat{F}^{\beta}\vec{\phi}_{\beta} = \vec{\phi}_{\beta}\boldsymbol{C}^{\beta}\boldsymbol{\lambda}^{\beta}\boldsymbol{C}^{\beta+}$

Since $\boldsymbol{\lambda}^{\alpha}$ and $\boldsymbol{\lambda}^{\beta}$ are Hermitian we may choose the matrices $\boldsymbol{C}^{\alpha}$ and $\boldsymbol{C}^{\beta}$ to diagonalize them and so

$\hat{F}^{\alpha}\vec{\phi}_{\alpha} = \vec{\phi}_{\alpha}\boldsymbol{\varepsilon}^{\alpha}$ or $\hat{F}^{\alpha}\phi_{i\alpha} = \phi_{i\alpha}\varepsilon_{i}^{\alpha}$; $i = 1,2,\cdots,N_{\alpha}$

where $\boldsymbol{\varepsilon}^{\alpha} = \boldsymbol{C}^{\alpha}\boldsymbol{\lambda}^{\alpha}\boldsymbol{C}^{\alpha+}$ is a N_{α} *by* N_{α} diagonal matrix with the elements ε_{i}^{α} The resulting orbitals are called the canonical unrestricted α spin orbitals. A similar scenario obtains for the β spin orbitals, i.e.

$\hat{F}^{\beta}\vec{\phi}_{\beta} = \vec{\phi}_{\beta}\boldsymbol{\varepsilon}^{\beta}$ with $\boldsymbol{\varepsilon}^{\beta} = \boldsymbol{C}^{\beta}\boldsymbol{\lambda}^{\beta}\boldsymbol{C}^{\beta+}$ and

$\hat{F}^{\beta}\phi_{i\beta} = \phi_{i\beta}\varepsilon_{i}^{\beta}$; $i = 1,2,\cdots,N_{\beta}$

So for an unrestricted Hartree Fock wavefunction we determine the α spin orbitals by solving $\hat{F}^{\alpha}\phi_{i\alpha} = \phi_{i\alpha}\varepsilon_{i}^{\alpha}$; $i = 1,2,\cdots,N_{\alpha}$ and the β spin orbitals from $\hat{F}^{\beta}\phi_{i\beta} = \phi_{i\beta}\varepsilon_{i}^{\beta}$; $i = 1,2,\cdots,N_{\beta}$. We will discus the solution to these equations , their properties and physical interpretation subsequently. Now let’s look at the closed shell Hartree-Fock equations.