The Matrix Hartree-Fock equations

The most common method of solving the Hartree-Fock equations for the spatial orbitals is to expand them in terms of known functions, $\{\chi_\mu\}_{\mu=1}^{M}$ called the basis set. Let's first consider the spin-unrestricted case. We will expand both the $\alpha \,\&\, \beta$ spatial orbitals in terms of the same basis functions

$$\phi_i = \sum_{\mu=1}^{M} \chi_\mu C_{\mu i}^{\alpha} \;\; \& \;\; \gamma_i = \sum_{\mu=1}^{M} \chi_\mu C_{\mu i}^{\beta}$$

and then determine the expansion coefficients $C_{\mu i}^{\alpha} \,\&\, C_{\mu i}^{\beta}$. Note that these equalities hold only when the set $\{\chi_\mu\}_{\mu=1}^{M}$ is complete and this usually happens, if ever, when M is large and $\{\chi_\mu\}_{\mu=1}^{M}$ are carefully chosen. The quality of the solution depends critically on the extent to which the expansion basis is complete. We will return to this point subsequently.

Substituting the expansion of $\phi_i \,\&\, \gamma_i$ into the unrestricted Hartree-Fock equations results in

$$\hat{F}^{\alpha} \sum_{\mu=1}^{M} \chi_\mu C_{\mu i}^{\alpha} = \varepsilon_i^{\alpha} \sum_{\mu=1}^{M} \chi_\mu C_{\mu i}^{\alpha} \;\; \& \;\; \hat{F}^{\beta} \sum_{\mu=1}^{M} \chi_\mu C_{\mu i}^{\beta} = \varepsilon_i^{\beta} \sum_{\mu=1}^{M} \chi_\mu C_{\mu i}^{\beta}$$

and if one multiplies by χ_ν^* and integrates one obtains

$$\sum_{\mu=1}^{M} F_{\nu\mu}^{\alpha} C_{\mu i}^{\alpha} = \varepsilon_i^{\alpha} \sum_{\mu=1}^{M} \Delta_{\mu\nu} C_{\mu i}^{\alpha} \;\; \& \;\; \sum_{\mu=1}^{M} F_{\nu\mu}^{\beta} C_{\mu i}^{\beta} = \varepsilon_i^{\beta} \sum_{\mu=1}^{M} \Delta_{\mu\nu} C_{\mu i}^{\beta}$$

or

$$\boldsymbol{F}^{\alpha} \vec{C}_i^{\alpha} = \varepsilon_i^{\alpha} \boldsymbol{\Delta} \vec{C}_i^{\alpha} \;\; \& \;\; \boldsymbol{F}^{\beta} \vec{C}_i^{\beta} = \varepsilon_i^{\beta} \boldsymbol{\Delta} \vec{C}_i^{\beta}$$

where we define the Fock matrices for $\alpha \,\&\, \beta$ spins as

$$(\boldsymbol{F}^{\alpha})_{\nu\mu} = F_{\nu\mu}^{\alpha} = \langle \chi_\nu | \hat{F}^{\alpha} | \chi_\mu \rangle \;\; \& \;\; (\boldsymbol{F}^{\beta})_{\nu\mu} = F_{\nu\mu}^{\beta} = \langle \chi_\nu | \hat{F}^{\beta} | \chi_\mu \rangle$$

Δ is the overlap matrix in the expansion basis

$$\Delta_{\mu\nu} = \left\langle \chi_\mu \middle| \chi_\nu \right\rangle = (\Delta)_{\mu\nu}$$

and the column vectors containing the expansion coefficients

$$\vec{C}_i^{\alpha} = \begin{pmatrix} C_{1i}^{\alpha} \\ C_{2i}^{\alpha} \\ \vdots \\ C_{Mi}^{\alpha} \end{pmatrix} \;\&\; \vec{C}_i^{\beta} = \begin{pmatrix} C_{1i}^{\beta} \\ C_{2i}^{\beta} \\ \vdots \\ C_{Mi}^{\beta} \end{pmatrix}$$

Writing the Fock operators in terms of the expansion basis results in

$$F_{\nu\mu}^{\alpha} = \left\langle \chi_\nu \middle| \hat{f} + V_\alpha + V_\beta - \hat{K}^{\alpha} \middle| \chi_\mu \right\rangle = \left\langle \chi_\nu \middle| \hat{f} \middle| \chi_\mu \right\rangle + \sum_{\lambda\rho}^{M} \left(P_{\lambda\rho} \left\langle \nu\lambda \middle| \mu\rho \right\rangle - P_{\lambda\rho}^{\alpha} \left\langle \nu\lambda \middle| \rho\mu \right\rangle \right)$$

where

$$\left\langle \nu\lambda \middle| \mu\rho \right\rangle = \int \chi_\nu^*(1) \chi_\lambda^*(2) \frac{1}{r_{12}} \chi_\mu(1) \chi_\rho(2) dV(1) dV(2)$$

and

$$P_{\lambda\rho} = P_{\lambda\rho}^{\alpha} + P_{\lambda\rho}^{\beta}$$

with

$$P_{\lambda\rho}^{\alpha} = \sum_{i=1}^{N_\alpha} C_{\lambda i}^{\alpha} C_{\rho i}^{\alpha} \;\&\; P_{\lambda\rho}^{\beta} = \sum_{i=1}^{N_\beta} C_{\lambda i}^{\beta} C_{\rho i}^{\beta}$$

Where $P_{\lambda\rho}^{\alpha}$ & $P_{\lambda\rho}^{\beta}$ are elements of the Coulson density matrix for $\alpha \,\&\, \beta$ spins.
While the two electron integrals in the expansion basis are often written as $\left\langle \nu\lambda \middle| \mu\rho \right\rangle$ with the assumed electron order 1212 one also sees the notation $\left(\nu\mu \middle| \lambda\pi\right)$ with the electron order 1122, i.e.,

$$\int dV(1,2) \chi_\nu^*(1) \chi_\lambda^*(2) \frac{1}{r_{12}} \chi_\mu(1) \chi_\rho(2) = \left\langle \nu\lambda \middle| \mu\rho \right\rangle \equiv \left(\nu\mu \middle| \lambda\rho\right)$$

We will use both notations, distinguishing them by either the bra-ket notation (order 1212) or the parenthesis notation (order 1122).

By symmetry the Fock matrix for β spins has the form

$$F_{\nu\mu}^{\beta} = \langle \chi_\nu | \hat{f} + V_\alpha + V_\beta - \hat{K}^\beta | \chi_\mu \rangle = \langle \chi_\nu | \hat{f} | \chi_\mu \rangle + \sum_{\lambda\rho}^{M} \left(P_{\lambda\rho} \langle \nu\lambda | \mu\rho \rangle - P_{\lambda\rho}^{\beta} \langle \nu\lambda | \rho\mu \rangle \right)$$

If we define the matrices $\boldsymbol{G}^{\alpha}$ & $\boldsymbol{G}^{\beta}$

$$G_{\nu\mu}^{\alpha} = \sum_{\lambda\rho}^{M} \left(P_{\lambda\rho} \langle \nu\lambda | \mu\rho \rangle - P_{\lambda\rho}^{\alpha} \langle \nu\lambda | \rho\mu \rangle \right) \;\&\; G_{\nu\mu}^{\beta} = \sum_{\lambda\rho}^{M} \left(P_{\lambda\rho} \langle \nu\lambda | \mu\rho \rangle - P_{\lambda\rho}^{\beta} \langle \nu\lambda | \rho\mu \rangle \right)$$

We may write the Fock matrices as

$$F_{\nu\mu}^{\alpha} = f_{\nu\mu} + G_{\nu\mu}^{\alpha} \;\&\; F_{\nu\mu}^{\beta} = f_{\nu\mu} + G_{\nu\mu}^{\beta}$$

Knowing the basis functions the one electron term, $f_{\mu\nu}$, is easily calculated whereas the two electron terms, $G_{\nu\mu}^{\alpha}$ & $G_{\nu\mu}^{\beta}$ are more complicated as they depend on the expansion coefficients $\vec{C}_i^{\alpha}$ & $\vec{C}_i^{\beta}$ (through the Coulson density matrices) which are to be determined. To determine the expansion coefficients we first calculate all of the required one and two electron integrals in the expansion basis. Then

1. Estimate the density matrices for each spin. This is not as difficult as it might seem. One could use Huckel orbitals to form an approximate $\boldsymbol{P}$ or even set the initial estimate to zero.

2. Form the matrices

$$G_{\nu\mu}^{\alpha} = \sum_{\lambda\rho}^{M} \left(P_{\lambda\rho} \langle \nu\lambda | \mu\rho \rangle - P_{\lambda\rho}^{\alpha} \langle \nu\lambda | \rho\mu \rangle \right) \;\&\; G_{\nu\mu}^{\beta} = \sum_{\lambda\rho}^{M} \left(P_{\lambda\rho} \langle \nu\lambda | \mu\rho \rangle - P_{\lambda\rho}^{\beta} \langle \nu\lambda | \rho\mu \rangle \right)$$

3. Assemble the Fock and overlap matrices

4. Solve the generalized eigenvalue problem $\boldsymbol{F}^{\alpha}\vec{C}_i^{\alpha} = \varepsilon_i^{\alpha}\Delta\vec{C}_i^{\alpha}$ & $\boldsymbol{F}^{\beta}\vec{C}_i^{\beta} = \varepsilon_i^{\beta}\Delta\vec{C}_i^{\beta}$ for $\vec{C}_i^{\alpha}$ & $\vec{C}_i^{\beta}$ and ε_i^{α} & ε_i^{β}

5. Construct the Coulson density matrices, $\boldsymbol{P}^{\alpha}$ & $\boldsymbol{P}^{\beta}$ and compare with the previous estimate. If they agree within a given tolerance we are finished. If they do not, return to step 2 and form the matrices with the current vectors. Repeat the process until the input and output density matrices are equal within the set tolerance. This tolerance often depends on the subsequent use of the orbitals.

Once we have the converged Hartree-Fock orbitals $\{\phi_i\}_{i=1}^{N_\alpha}$ & $\{\gamma_i\}_{i=1}^{N_\beta}$ and eigenvalues $\left\{\varepsilon_i^{\alpha}\right\}_{i=1}^{N_\alpha}$ & $\left\{\varepsilon_i^{\beta}\right\}_{i=1}^{N_\beta}$ the electronic energy may be written as

$$E=\langle\psi|\hat{H}|\psi\rangle=\sum_{i=1}^{N_\alpha}\langle\phi_i|\hat{f}+\frac{1}{2}\left(\hat{J}^{\alpha}+\hat{J}^{\beta}-\hat{K}^{\alpha}\right)|\phi_i\rangle+\sum_{i=1}^{N_\beta}\langle\gamma_i|\hat{f}+\frac{1}{2}\left(\hat{J}^{\alpha}+\hat{J}^{\beta}-\hat{K}^{\beta}\right)|\gamma_i\rangle$$

And recognizing as above that $\hat{F}^{\alpha}=\hat{f}+\hat{J}^{\alpha}+\hat{J}^{\beta}-\hat{K}^{\alpha}$ and $\hat{F}^{\beta}=\hat{f}+\hat{J}^{\alpha}+\hat{J}^{\beta}-\hat{K}^{\beta}$

we have

$$E=\frac{1}{2}\sum_{i=1}^{N_\alpha}\langle\phi_i|\hat{f}+\hat{F}^{\alpha}|\phi_i\rangle+\frac{1}{2}\sum_{i=1}^{N_\beta}\langle\gamma_i|\hat{f}+\hat{F}^{\beta}|\gamma_i\rangle$$

or

$$E=\frac{1}{2}\sum_{i=1}^{N_\alpha}\left(\langle\phi_i|\hat{f}|\phi_i\rangle+\varepsilon_i^{\alpha}\right)+\frac{1}{2}\sum_{i=1}^{N_\beta}\left(\langle\gamma_i|\hat{f}|\gamma_i\rangle+\varepsilon_i^{\beta}\right)$$

Which in terms of the basis functions and the one electron integrals becomes

$$E=\frac{1}{2}\sum_{\nu\mu}^{M}P_{\nu\mu}f_{\nu\mu}+\frac{1}{2}\left(\sum_{i=1}^{N_\alpha}\varepsilon_i^{\alpha}+\sum_{i=1}^{N_\beta}\varepsilon_i^{\beta}\right)$$

Another convenient form involving the two electron integrals is easily derived

$$E=\frac{1}{2}trace\boldsymbol{P}^{\alpha}\boldsymbol{\Gamma}^{\alpha}+\frac{1}{2}trace\boldsymbol{P}^{\beta}\boldsymbol{\Gamma}^{\beta}$$

Where

$$\left(\boldsymbol{\Gamma}^{\alpha}\right)_{\nu\mu}=\Gamma_{\nu\mu}^{\alpha}=2f_{\nu\mu}+G_{\nu\mu}^{\alpha}\ \ \&\ \ \left(\boldsymbol{\Gamma}^{\beta}\right)_{\nu\mu}=\Gamma_{\nu\mu}^{\beta}=2f_{\nu\mu}+G_{\nu\mu}^{\beta}$$

Closed Shell Systems

The matrix Hartree-Fock equations for a closed shell system are a special case of the unrestricted equations that obtain when $N_\alpha = N_\beta = N/2$ and the spatial part of the α and β spin orbitals are identical, ie, $\phi_i = \gamma_i$. One solves $\boldsymbol{F}\vec{C}_i = \varepsilon_i \boldsymbol{\Delta}\vec{C}_i$ where

$F_{\nu\mu} = f_{\nu\mu} + G_{\nu\mu}$ and $G_{\nu\mu} = \frac{1}{2}\sum_{\lambda\rho}^{M}\left(P_{\lambda\rho}\left(2\langle\nu\lambda|\mu\rho\rangle - \langle\nu\lambda|\rho\mu\rangle\right)\right)$ with $P_{\lambda\rho} = 2\sum_{i=1}^{N/2} C_{\lambda i}C_{\rho i}$.

Once one has the orbitals and eigenvalues the electronic energy may be obtained from

$$E = \frac{1}{2}\sum_{\nu\mu}^{M} P_{\nu\mu}f_{\nu\mu} + \sum_{i=1}^{N/2}\varepsilon_i$$

or

$$E = trace\boldsymbol{P\Gamma}$$

Where

$$(\boldsymbol{\Gamma})_{\nu\mu} = \Gamma_{\nu\mu} = f_{\nu\mu} + \frac{1}{2}G_{\nu\mu}$$