Matrix Hartree-Fock Equations for a Closed Shell System

A single determinant wavefunction for a system containing an even number of electron (N) consists of N/2 spatial orbitals, each occupied with an α & β spin has the form

$$\psi(1,2,3,\cdots,N) = \hat{\mathcal{A}}\varphi_1(1)\alpha(1)\varphi_1(2)\beta(2)\varphi_2(3)\alpha(3)\varphi_2(4)\beta(4)\cdots\varphi_{N/2}(N-1)\alpha(N-1)\varphi_{N/2}(N)\beta(N)$$

The total electronic energy is

$$E = \langle\psi|\hat{H}|\psi\rangle = 2\sum_{i=1}^{N/2} f_i + \sum_{i,j}^{N/2}\left(2J_{ij} - K_{ij}\right)$$

Where the one electron terms are

$$f_i = \langle\varphi_i|-\frac{1}{2}\nabla^2 - \sum_{k=1}^{nuclei}\frac{Z_k}{|\vec{r}-\vec{R}_k|}|\varphi_i\rangle$$

and the coulomb, J_{ij} and exchange K_{ij} terms are

$$J_{ij} = \int \varphi_i^*(1)\varphi_i(1)g(1,2)\varphi_j^*(2)\varphi_j(2)dV(1)dV(2)$$

and

$$K_{ij} = \int \varphi_i^*(1)\varphi_j(1)g(1,2)\varphi_i^*(2)\varphi_j(2)dV(1)dV(2)$$

where $g(1,2) = \frac{1}{r_{12}}$.

The optimal orbitals obey the Hartree-Fock equations

$$\hat{F}\varphi_i = \varepsilon_i\varphi_i$$

where

$$\hat{F} = \hat{f} + \hat{U} = \hat{f} + \sum_{j=1}^{N/2}\left(2\hat{J}_j - \hat{K}_j\right)$$

where

$$\hat{f} = -\frac{1}{2}\nabla^2 - \sum_{k=1}^{nuclei} \frac{Z_k}{\left|\vec{r} - \vec{R}_k\right|}$$

$$\hat{J}_j = \int dV(2)\varphi_j(2)g(1,2)\varphi_j(2) = \int dV(2)\varphi_j^2(2)g(1,2)$$

and

$$\hat{K}_j = \int dV(2)\varphi_j(2)g(1,2)\hat{P}_{12}\varphi_j(2)$$

To solve the Hartree-Fock equations we introduce an basis of known functions $\left\{\chi_\mu\right\}_{\mu=1}^{M}$ which are usually atomic like orbitals hosted by the various nuclei in the system and write

$$\varphi_i = \sum_{\mu=1}^{M} \chi_\mu c_{\mu i} = \vec{\chi}\vec{c}_i$$

where we define the row and column vectors

$$\vec{\chi} = (\chi_1\chi_2\chi_3\cdots\chi_M) \quad \text{and} \quad \vec{c}_i = \begin{pmatrix} c_{1i} \\ c_{2i} \\ \vdots \\ c_{Mi} \end{pmatrix}$$

The Hartree-Fock equations become

$$\hat{F}\sum_{\mu=1}^{M} \chi_\mu c_{\mu i} = \varepsilon_i \sum_{\mu=1}^{M} \chi_\mu c_{\mu i}$$

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

$$\sum_{\mu=1}^{M} F_{\nu\mu} c_{\mu i} = \varepsilon_i \sum_{\mu=1}^{M} \Delta_{\mu\nu} c_{\mu i}$$

or

$$\boldsymbol{F}\vec{c}_i = \varepsilon_i \boldsymbol{\Delta}\vec{c}_i$$

where we define the Fock ($\boldsymbol{F}$) and overlap($\boldsymbol{\Delta}$) matrices as

$$F_{\mu\nu} = \left\langle \chi_\mu \middle| \hat{F} \middle| \chi_\nu \right\rangle = (\boldsymbol{F})_{\mu\nu}$$

and

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

Note that one can define a matrix $\boldsymbol{c} = \left(\vec{c}_1 \vec{c}_2 \vec{c}_3 \cdots \vec{c}_M\right)$ as a row vector of column vectors and write the eiegnvalue problem as

$$\boldsymbol{Fc = \Delta c\varepsilon}$$

where

$$\left(\boldsymbol{\varepsilon}\right)_{ij} = \delta_{ij}\varepsilon_i$$

The Fock matrix is composed of one and two electron terms

$$F_{\mu\nu} = \left\langle \chi_\mu \middle| \hat{f} + \hat{U} \middle| \chi_\nu \right\rangle = \left\langle \chi_\mu \middle| \hat{f} + \sum_{j=1}^{n/2} \left(2\hat{J}_j - \hat{K}_j\right) \middle| \chi_\nu \right\rangle$$

The one electron term, $\left\langle \chi_\mu \middle| \hat{f} \middle| \chi_\nu \right\rangle$, is easily calculated whereas the two electron terms, $\left\langle \chi_\mu \middle| \hat{U} \middle| \chi_\nu \right\rangle$ are more complicated as they depend on the expansion coefficients $\vec{c}_i$ which are to be determined. Introducing the basis function expansion into $\hat{J}_j$ & $\hat{K}_j$ gives

$$\hat{J}_j = \int dV(2) g(1,2) \varphi_j^2(2) = \sum_{\lambda=1}^{M}\sum_{\rho=1}^{M} c_{\lambda j} c_{\rho j} \int dV(2) \chi_\lambda(2) g(1,2) \chi_\rho(2)$$

and

$$\hat{K}_j = \int dV(2) \varphi_j(2) g(1,2) \hat{P}_{12} \varphi_j(2) = \sum_{\lambda=1}^{M}\sum_{\rho=1}^{M} c_{\lambda j} c_{\rho j} \int dV(2) \chi_\lambda(2) g(1,2) \hat{P}_{12} \chi_\rho(2)$$

and so

$$2\hat{J}_j - \hat{K}_j = \sum_{\lambda=1}^{M}\sum_{\rho=1}^{M} c_{\lambda j} c_{\rho j} \int dV(2) \chi_\lambda(2) g(1,2) \left(2 - \hat{P}_{12}\right) \chi_\rho(2)$$

The two electron term becomes

$$\left\langle \chi_\mu \left| \hat{U} \right| \chi_\nu \right\rangle = \sum_{j=1}^{n/2} \sum_{\lambda=1}^{M} \sum_{\rho=1}^{M} c_{\lambda j} c_{\rho j} \int dV(2) \chi_\mu(1) \chi_\lambda(2) g(1,2) \left(2 - \hat{P}_{12}\right) \chi_\nu(1) \chi_\rho(2)$$

Since the only term in the sum that depends on j is the product of the expansion coefficents we can interchange the order of the summations and write

$$\left\langle \chi_\mu \left| \hat{U} \right| \chi_\nu \right\rangle = \sum_{\lambda=1}^{M} \sum_{\rho=1}^{M} P_{\lambda\rho} \int dV(2) \chi_\mu(1) \chi_\lambda(2) g(1,2) \left(2 - \hat{P}_{12}\right) \chi_\nu(1) \chi_\rho(2)$$

where the matrix $\boldsymbol{P}$ has the elements

$$\left(\boldsymbol{P}\right)_{\lambda\rho} = P_{\lambda\rho} = \sum_{j=1}^{n/2} c_{\lambda j} c_{\rho j}$$

and is called the Density matrix. The integral is often written in a more compact form as

$$\left\langle \mu\lambda \left| g(1,2)(2 - \hat{P}_{12}) \right| \nu\rho \right\rangle = \int dV(2) \chi_\mu(1) \chi_\lambda(2) g(1,2) \left(2 - \hat{P}_{12}\right) \chi_\nu(1) \chi_\rho(2) = \left\langle \mu\lambda \right|\left| \nu\rho \right\rangle$$

$$\left\langle \chi_\mu \left| \hat{U} \right| \chi_\nu \right\rangle = \sum_{\lambda=1}^{M} \sum_{\rho=1}^{M} P_{\lambda\rho} \left\langle \mu\lambda \right|\left| \nu\rho \right\rangle$$

The elements of the Fock matrix are then

$$F_{\mu\nu} = f_{\mu\nu} + \sum_{\lambda=1}^{M} \sum_{\rho=1}^{M} P_{\lambda\rho} \left\langle \mu\lambda \right|\left| \nu\rho \right\rangle$$

To solve for $\boldsymbol{c} \,\&\, \boldsymbol{\varepsilon}$ one first calculates all of the required integrals, $\Delta_{\mu\nu}, f_{\mu\nu}, \& \left\langle \mu\lambda \right|\left| \nu\rho \right\rangle$ and then form an estimate of $\boldsymbol{P}$. One then forms the Fock matrix and solves the equations $\boldsymbol{Fc = \Delta c\varepsilon}$. The calculated vectors in $\boldsymbol{c}$ are then used to calculate a new $\boldsymbol{P}$ which is compared to the initial estimate. They are almost always different so one forms a new Fock matrix with the new $\boldsymbol{P}$, calculates an updated $\boldsymbol{P}$ with the resulting vectors in $\boldsymbol{c}$ and compares the two. If they differ one repeats the iterations until the input and output $\boldsymbol{P}$ are identical to some agreed on accuracy. The final $\boldsymbol{c} \,\&\, \boldsymbol{\varepsilon}$ are the molecular orbital coefficients and one electron energies.

Once one has the molecular orbital coefficients one can calculate the total energy as an expectation value of the Hamiltonian $\hat{H}$ augmented with the nuclear repulsion energy V_{NN}

$$E = \langle \psi | \hat{H} | \psi \rangle + V_{NN} = 2\sum_{i=1}^{N/2} f_i + \sum_{i,j}^{N/2} \left(2J_{ij} - K_{ij} \right) + \sum_{K<L}^{Nuc} \frac{Z_K Z_L}{R_{KL}}$$

This may be simplified considerably by noting that

$$\sum_{i=1}^{N/2} f_i = \sum_{i=1}^{N/2} \langle \varphi_i | \hat{f} | \varphi_i \rangle = \sum_{i=1}^{N/2} \sum_{\mu=1}^{M} \sum_{\nu=1}^{M} c_{\mu i} c_{\nu i} \langle \mu | \hat{f} | \nu \rangle = \sum_{\mu=1}^{M} \sum_{\nu=1}^{M} P_{\mu\nu} f_{\mu\nu} = trace\boldsymbol{Pf}$$

In a similar fashion we find

$$\sum_{i,j}^{N/2} \left(2J_{ij} - K_{ij} \right) = \sum_{\mu=1}^{M} \sum_{\lambda=1}^{M} \sum_{\rho=1}^{M} \sum_{\nu=1}^{M} P_{\mu\nu} P_{\lambda\rho} \langle \mu\lambda || \nu\rho \rangle$$

The electronic energy becomes

$$2\sum_{\mu=1}^{M} \sum_{\nu=1}^{M} P_{\mu\nu} f_{\mu\nu} + \sum_{\mu=1}^{M} \sum_{\lambda=1}^{M} \sum_{\rho=1}^{M} \sum_{\nu=1}^{M} P_{\mu\nu} P_{\lambda\rho} \langle \mu\lambda || \nu\rho \rangle = \sum_{\mu=1}^{M} \sum_{\nu=1}^{M} P_{\mu\nu} \left(2f_{\mu\nu} + \sum_{\lambda=1}^{M} \sum_{\rho=1}^{M} P_{\lambda\rho} \langle \mu\lambda || \nu\rho \rangle \right)$$

Which from the definition of the Fock matrix given above we recognize as

$$\sum_{\mu=1}^{M} \sum_{\nu=1}^{M} P_{\mu\nu} \left(f_{\mu\nu} + F_{\mu\nu} \right) = trace\boldsymbol{P}\left(\boldsymbol{f} + \boldsymbol{F} \right)$$

So to obtain the electronic energy we take the converged Fock matrix, add the one electron operator matrix, multiply the sum by the converged density matrix and form the trace. The total energy is then

$$E = \langle \psi | \hat{H} | \psi \rangle + V_{NN} = trace\boldsymbol{P}\left(\boldsymbol{f} + \boldsymbol{F} \right) + \sum_{K<L}^{Nuc} \frac{Z_K Z_L}{R_{KL}}$$