The Hartree-Fock Equations

Our goal is to construct the best single determinant wave function for a system of N electrons. We write our trial function as a determinant of spin orbitals

$$\psi(1,2,...N) = \mathcal{A}\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N),$$

where $\langle\varphi_i|\varphi_j\rangle = \delta_{ij}$, $\mathcal{A}$ is the antisymeterizing operator,

and we want to determine the orbitals $\{\varphi_i\}_{i=1}^N$, so that the energy E

$$E = \langle\psi(1,2,\cdots N)|\hat{H}|\psi(1,2,\cdots N)\rangle$$

is a minimum. Recall that the Hamiltonian is the sum of one and two body operators

$$\hat{H} = \sum_{i=1}^{N}\hat{f}(i) + \sum_{i<j}^{N} g(i,j)$$

Using the Slater-Condon rules the energy can be written in terms of integrals over the spin orbitals,

$$E = \langle\psi|\hat{H}|\psi\rangle = \sum_{i=1}^{N}\langle\varphi_i|\hat{f}|\varphi_i\rangle + \sum_{i>j}^{N}\langle\varphi_i(1)\varphi_j(2)|g(1,2)\left(1-\hat{P}_{12}\right)|\varphi_i(1)\varphi_j(2)\rangle$$

where $\hat{P}_{12}$ is a transposition operator that interchanges the coordinates 1 and 2. We want to find those orbitals for which the energy is stationary to first order. This means that if the orbitals we seek are $\{\varphi_i\}_{i=1}^N$, and we incremented each by an infinitesimal amount $\{\varphi_i + \delta\varphi_i\}_{i=1}^N$, and recalculated the energy it should not change.

Accordingly if we increment or vary each of the φ_i independently, we would write

$$E(\varphi_1+\delta\varphi_1, \varphi_2+\delta\varphi_2, \cdots\varphi_N+\delta\varphi_N) = \sum_{i=1}^{N}\langle\varphi_i+\delta\varphi_i|\hat{f}|\varphi_i+\delta\varphi_i\rangle$$

$$+\sum_{i>j}^{N}\langle(\varphi_i+\delta\varphi_i)(\varphi_j+\delta\varphi_j)|g(1,2)\left(1-\hat{P}_{12}\right)|(\varphi_i+\delta\varphi_i)(\chi_j+\delta\varphi_j)\rangle.$$

The one-electron contribution becomes

$$\sum_{i=1}^{N}\left\{\langle\varphi_i|\hat{f}|\varphi_i\rangle+\langle\delta\varphi_i|\hat{f}|\varphi_i\rangle+\langle\varphi_i|\hat{f}|\delta\varphi_i\rangle+\langle\delta\varphi_i|\hat{f}|\delta\varphi_i\rangle\right\}$$

or

$$\sum_{i=1}^{N}\left\{\langle\varphi_i|\hat{f}|\varphi_i\rangle+\langle\delta\varphi_i|\hat{f}|\varphi_i\rangle+\langle\varphi_i|\hat{f}|\delta\varphi_i\rangle\right\}+0\left(\delta^2\right).$$

In a similar way, we may expand the two-electron terms

$$\sum_{i>j}^{N}\left\{\langle\varphi_i\varphi_j|\hat{G}|\varphi_i\varphi_j\rangle+\langle\varphi_i\delta\varphi_j|\hat{G}|\varphi_i\varphi_j\rangle+\langle\delta\varphi_i\varphi_j|\hat{G}|\varphi_i\varphi_j\rangle\right.$$

$$\left.+\langle\varphi_i\varphi_j|\hat{G}|\varphi_i\delta\varphi_j\rangle+\langle\varphi_i\varphi_j|\hat{G}|\delta\varphi_i\varphi_j\rangle\right\}+0\left(\delta^2\right),$$

where $\hat{G}(1,2)=g(1,2)\left(1-\hat{P}_{12}\right)$.

We may write the restricted sum $\sum_{i>j}^{N}$ as the less restricted sum $\frac{1}{2}\sum_{i,j}^{N}{}'$

and so $$\sum_{i>j}^{N}\langle\varphi_i\delta\varphi_j|\hat{G}|\varphi_i\varphi_j\rangle=\frac{1}{2}\sum_{i,j}^{N}{}'\langle\varphi_i\delta\varphi_j|\hat{G}|\varphi_i\varphi_j\rangle,$$

where the prime on the sum means that $i \neq j$.

Since i and j are dummy indices, this term may be written as

$$\frac{1}{2}\sum_{i,j}^{N}{}'\langle\varphi_j\delta\varphi_i|\hat{G}|\varphi_j\varphi_i\rangle\equiv\frac{1}{2}\sum_{i,j}^{N}{}'\langle\delta\varphi_i\delta\varphi_j|\hat{G}|\varphi_i\varphi_j\rangle$$

and, of course,

$$\sum_{i>j}^{N}{}'\langle\varphi_i\varphi_j|\hat{G}|\varphi_i\delta\varphi_j\rangle=\frac{1}{2}\sum_{i,j}^{N}{}'\langle\varphi_i\varphi_j|\hat{G}|\delta\varphi_i\varphi_j\rangle.$$

So, if we form the difference

$$\delta E=E\left(\varphi_1+\delta\varphi_1,\varphi_2+\delta\varphi_2,\cdots\varphi_N+\delta\varphi_N\right)-E\left(\varphi_1,\varphi_2,\cdots\varphi_N\right)$$

we have the first order change in energy

$$\delta E = \sum_{i=1}^{N}\left\{\left\langle \delta\varphi_i \middle| \hat{f} \middle| \varphi_i \right\rangle + \left\langle \varphi_i \middle| \hat{f} \middle| \delta\varphi_i \right\rangle\right\}$$
$$+ \sum_{i,j}{}'\left\{\left\langle \delta\varphi_i\varphi_j \middle| \hat{G} \middle| \varphi_i\varphi_j \right\rangle + \left\langle \varphi_i\varphi_j \middle| \hat{G} \middle| \delta\varphi_i\varphi_j \right\rangle\right\}$$
$$\delta E = \sum_{i=1}^{N}\left\{\left\langle \delta\varphi_i(1)\middle| \hat{f} + \sum_{j=1}^{N}{}'\int \varphi_j^*(2)\hat{G}(1,2)\varphi_j(2)\,d\tau(2)\middle|\varphi_i(1)\right\rangle\right.$$
$$\left. + \left\langle \varphi_i(1)\middle| \hat{f} + \sum_{j=1}^{N}{}'\int \varphi_j^*(2)\hat{G}(1,2)\varphi_j(2)\,d\tau(2)\middle|\delta\varphi_i(1)\right\rangle\right\}.$$

Note that we may extend the summation $\sum_{j=1}^{N}{}'$ to $\sum_{j=1}^{N}$ because the term $i=j$ vanishes identically. For compactness, define the operator

$$\hat{V}(1) = \sum_{i=1}^{N}\int d\tau(2)\varphi_j^*(2)\,g(1,2)\left(1-\hat{P}_{12}\right)\varphi_j(2)$$

and $\therefore$

$$\delta E = \sum_{i=1}^{N}\left\{\left\langle \delta\varphi_i \middle| \hat{f} + \hat{V} \middle| \varphi_i \right\rangle + \left\langle \varphi_i \middle| \hat{f} + \hat{V} \middle| \delta\varphi_i \right\rangle\right\}.$$

$\hat{V}$ is called the Hartree-Fock Potential. We further define the Fock operator as $\hat{F} = \hat{f} + \hat{V}$ and write δE as

$$\delta E = \sum_{i=1}^{N}\left\{\left\langle \delta\varphi_i \middle| \hat{F} \middle| \varphi_i \right\rangle + \left\langle \varphi_i \middle| \hat{F} \middle| \delta\varphi_i \right\rangle\right\}.$$

We must not vary $\delta\varphi_i$ independently of $\delta\varphi_j$, since they are coupled by the constraints,

$$\left\langle \varphi_i \middle| \varphi_j \right\rangle = \delta_{ij}.$$

To comply with these constraints, we use the technique of Lagrangian multipliers.

Recall, to vary the functional $F\left(\varphi(x)\right)$ with respect to $\varphi(x)$ subject to $G\left(\varphi(x)\right) = 0$, we first form the independent variations of F and G, i. e., δF and δG, and then, add a multiple of the variation of the constraint to the variation of the functional to form $\delta F + \lambda\delta G$.

One then chooses $\varphi(x)$ such that this expression is zero, i. e., solve

$$\delta F + \lambda \delta G = 0.$$

We then obtain $\varphi(x,\lambda)$ and fix λ by requiring

$$G\left(\varphi(x,\lambda)\right) = 0.$$

λ is called a Lagrangian multiplier.

In this problem we have N^2 constraints of the form $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$ and each has the variation

$$\begin{aligned}\delta \langle \varphi_i | \varphi_j \rangle &= \langle \varphi_i + \delta\varphi_i | \varphi_j + \delta\varphi_j \rangle - \langle \varphi_i | \varphi_j \rangle \\ &= \langle \varphi_i | \delta\varphi_j \rangle + \langle \delta\varphi_i | \varphi_j \rangle + 0\left(\delta^2\right).\end{aligned}$$

Introduce the Lagrangian multipliers λ_{ij} and subtract all the constraint variations to δE, resulting in

$$\begin{aligned}&\delta \mathrm{E} - \sum_{i,j}^{N} \left\{ \lambda_{ij} \left(\langle \varphi_i | \delta\varphi_j \rangle + \langle \delta\varphi_i | \varphi_j \rangle \right) \right\} \\ &= \delta E - \sum_{i,j}^{N} \left(\lambda_{ji} \langle \varphi_j | \delta\varphi_i \rangle + \lambda_{ij} \langle \delta\varphi_i | \varphi_j \rangle \right).\end{aligned}$$

Now, using the fact the Fock operator is Hermetian we can write δE as

$$\delta E = \sum_{i-1}^{N} \left\{ \langle \delta\varphi_i | \hat{F} | \varphi_i \rangle + \langle \delta\varphi_i | \hat{F} | \varphi_i \rangle^* \right\}.$$

We may also rearrange the constraint variations as

$$\sum_{i,j} \lambda_{ij} \delta \langle \varphi_i | \varphi_j \rangle = \sum_{i,j} \left\{ \lambda_{ij} \langle \delta\varphi_i | \varphi_j \rangle + \left(\lambda_{ji}^* \langle \delta\varphi_i | \varphi_j \rangle \right)^* \right\}.$$

allowing us to write

$$\delta E + \sum_{i,j} \lambda_{ij} \delta \left\langle \varphi_i \middle| \varphi_j \right\rangle =$$

$$\sum_{i=1}^{N} \int \delta\varphi_i^*(1) \left\{ \hat{F}(1)\varphi_i(1) - \sum_{j=1}^{N} \lambda_{ij}\varphi_j(1) \right\} d\tau(1) \sum_{i=1}^{N} \left(\int \delta\varphi_i^*(1) \left\{ \hat{F}(1)\varphi_i(1) - \sum_{j=1}^{N} \lambda_{ji}^*\varphi_j(1) \right\} \right)^* d\tau(1)$$

If we require that this be zero, we recover the equations

$$\hat{F}\varphi_i - \sum_{j=1}^{N} \lambda_{ij}\varphi_j = 0 \text{ and } \hat{F}\varphi_i - \sum_{j=1}^{N} \lambda_{ji}^*\varphi_j = 0,$$

from which we deduce $\lambda_{ij} = \lambda_{ji}^*$; i. e., λ_{ij} is an element of an Hermetian matrix. Since the two sets of equations are equivalent, we consider only one, i. e.,

$$\hat{F}\varphi_i = \sum_{j=1}^{N} \lambda_{ij}\varphi_j$$

Now, define a row vector $\vec{\varphi} = (\varphi_1 \varphi_2 \cdots \varphi_N)$, and note that we may write the above set of equations in a very compact matrix notation,

$$\hat{F}\vec{\boldsymbol{\varphi}} = \vec{\boldsymbol{\varphi}}\boldsymbol{\lambda},$$

where $\hat{F}\vec{\boldsymbol{\varphi}} \equiv \left(\hat{F}\boldsymbol{\varphi}_1 \hat{F}\boldsymbol{\varphi}_2 \cdots \hat{F}\boldsymbol{\varphi}_N \right)$

and $\boldsymbol{\lambda}$ is the Hermetian matrix with elements λ_{ij}.

To continue, we make use of the invariance of a Slater determinant to a unitary transformation of the constituent spin orbitals; i. e., since the normalized Slater determinant

$$\Psi(1,2,\cdots N) = \mathcal{A}\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N)$$

has associated with it a matrix, $\boldsymbol{\varphi}$, i. e.,

$$\varphi = \begin{pmatrix} \varphi_1(1) & \varphi_1(2) & \cdots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \cdots & \varphi_2(N) \\ \vdots & \vdots & & \vdots \\ \varphi_N(1) & \varphi_N(2) & \cdots & \varphi_N(N) \end{pmatrix}$$

then,

$$\Psi(1,2,\cdots N) = \frac{1}{\sqrt{N!}} \|\boldsymbol{\varphi}\|$$

where $\|\boldsymbol{\varphi}\|$ is the determinant of $\boldsymbol{\varphi}$.

Define a new set of functions ξ_i, by the unitary transformation

$$\xi_i(k) = \sum_{j=1}^{N} U_{ij}\varphi_j(k) \qquad i = 1,\cdots N;\ k = 1,\cdots N$$

or in matrix notation

$$\boldsymbol{\xi} = U\boldsymbol{\varphi}$$

and

$$\boldsymbol{\varphi} = U^T\boldsymbol{\xi}$$

Note that if we choose not to consider the electron index as a label we may write the transformation as

$$\xi_i = \sum_{j=1}^{N} U_{ij}\varphi_j = \sum_{j=1}^{N} \varphi_j U^T_{ji} \quad i = 1,\cdots N$$

and the row vectors $\vec{\xi}$ and $\vec{\varphi}$ are related by

$$\vec{\boldsymbol{\xi}} = \vec{\boldsymbol{\varphi}}\ \boldsymbol{U^T}$$

or

$$\vec{\boldsymbol{\varphi}} = \vec{\boldsymbol{\xi}}\ \boldsymbol{U}$$

The wavefunction in terms of the transformed orbitals becomes

$$\Psi(1,2,\cdots \boldsymbol{N}) = \frac{1}{\sqrt{\boldsymbol{N}!}}\|\boldsymbol{\varphi}\| = \frac{1}{\sqrt{\boldsymbol{N}!}}\left\|\boldsymbol{U^T\xi}\right\| = \frac{1}{\sqrt{\boldsymbol{N}!}}\left\|\boldsymbol{U^T}\right\|\|\boldsymbol{\xi}\| = \frac{1}{\sqrt{\boldsymbol{N}!}}\|\boldsymbol{\xi}\|$$

and so, the determinant formed from a unitary transformation of the $\{\varphi\}$ functions is equal to the original determinant. Given this invariance, how are the Hartree-Fock Equations in the φ basis related to those in the ξ basis? To find out we substitute $\vec{\varphi} = \vec{\xi}\ U$ into the Hartree-Fock equations.

Since

$$\hat{F}(\vec{\boldsymbol{\varphi}})\vec{\boldsymbol{\varphi}} = \vec{\boldsymbol{\varphi}}\boldsymbol{\lambda}$$

we have

$$\hat{\boldsymbol{F}}\left(\vec{\boldsymbol{\xi}}\boldsymbol{U}\right)\vec{\boldsymbol{\xi}}\boldsymbol{U} = \vec{\boldsymbol{\xi}}\boldsymbol{U}\boldsymbol{\lambda}$$

and so

$$\hat{\boldsymbol{F}}\left(\vec{\boldsymbol{\xi}}\boldsymbol{U}\right)\vec{\boldsymbol{\xi}} = \vec{\boldsymbol{\xi}}\boldsymbol{U}\boldsymbol{\lambda}\boldsymbol{U}^{\boldsymbol{T}}$$

Now, U is an arbitrary unitary matrix and λ is Hermetian. Since a Hermetian matrix may always be diagonalized by a unitary matrix we have

$$\boldsymbol{U}^{\boldsymbol{T}}\boldsymbol{\lambda}\boldsymbol{U} = \boldsymbol{\varepsilon}$$

where $\boldsymbol{\varepsilon}$ is a diagonal matrix containing the eigenvalues of λ. Then,

$$\hat{\boldsymbol{F}}\left(\vec{\boldsymbol{\xi}}\boldsymbol{U}\right)\vec{\boldsymbol{\xi}} = \vec{\boldsymbol{\xi}}\boldsymbol{\varepsilon}$$

To find $\hat{\boldsymbol{F}}\left(\vec{\boldsymbol{\xi}}\boldsymbol{U}\right)$, we note:

$$\begin{aligned}\hat{F}(\vec{\varphi}) &= \hat{f}(1) + \sum_{j=1}^{N}\int \varphi_j^*(2)\hat{G}(1,2)\varphi_j(2)\,d\tau(2) \\ &= \hat{f}(1) + \text{trace}\left\langle \vec{\varphi}^{\mathrm{T}}(2)\middle|\hat{G}(1,2)\middle|\vec{\varphi}(2)\right\rangle_2 \\ &= \hat{f}(1) + \text{trace}\ \boldsymbol{G}_{\varphi}(1).\end{aligned}$$

So,

$$\hat{F}(\xi U) = \hat{f}(1) + \text{ trace } \left\langle (\xi U)^T \middle| \hat{G} \middle| \xi U \right\rangle$$
$$= \hat{f}(1) + \text{ trace } \left\{ U^T \left\langle \vec{\xi}^T \middle| \hat{G} \middle| \vec{\xi} \right\rangle U \right\}$$
$$= \hat{f}(1) + \text{ trace } \left\{ U^T \boldsymbol{G}_\xi U \right\} = \hat{f}(1) + \text{ trace } \left\{ \boldsymbol{G}_\xi \right\}$$

and so $\hat{\boldsymbol{F}}(\vec{\boldsymbol{\xi}}\boldsymbol{U}) = \hat{\boldsymbol{F}}(\vec{\boldsymbol{\xi}})$

or $\hat{F}\xi_i = \varepsilon_i \xi_i$.

These are the canonical Hartree-Fock Equations. The ξ_i are the molecular (atomic) orbitals and the ε_i are called the Hartree-Fock eigenvalues or the one-electron eigenvalues.

Total Energy

Once one has the HF orbitals, one may calculate the total energy, as follows:

$$E = \left\langle \Psi(1,2,\cdots N) \middle| \hat{H} \middle| \Psi(1,2,\cdots N) \right\rangle$$
$$= \left\langle \mathcal{A}\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N) \middle| \hat{H} \middle| \mathcal{A}\varphi_1(1)\varphi_2(2)\cdots\varphi_N(N) \right\rangle$$
$$= \sum_{i=1}^{N} \left\langle \varphi_i \middle| \hat{f} \middle| \varphi_i \right\rangle + \sum_{i>j}^{N} \left\langle \varphi_i(1)\varphi_j(2) \middle| \hat{G}(1,2) \middle| \varphi_i(1)\varphi_j(2) \right\rangle + \text{nuclear repulsion}$$

Recall the Hartree-Fock potential $\hat{V}(1)$ is given by

$$\hat{V}(1) = \sum_{j=1}^{N} \int d\tau(2) \varphi_j^*(2) \hat{G}(1,2) \varphi_j(2),$$

and so,

$$E = \sum_{i=1}^{N} \left\langle \varphi_i \middle| \hat{f} + \frac{1}{2}\hat{V} \middle| \varphi_i \right\rangle + \sum_{K<L}^{\text{nuclei}} Z_K Z_L / R_{KL},$$

since $\hat{F} = \hat{f} + \hat{V}$ at least two choices present themselves:

i) $$\hat{f}+\frac{1}{2}\hat{V}=\frac{1}{2}\hat{f}+\frac{1}{2}\left(\hat{f}+\hat{V}\right)=\frac{1}{2}\left(\hat{f}+\hat{F}\right),$$

The energy may be written in terms of the Hartree-Fock eigenvalues (the orbital energies) the one electron matrix elements f_i, and the nuclear repulsion energy.

$$E \;=\frac{1}{2}\sum_{i=1}^{N}\left\langle\varphi_i\left|\hat{f}+\hat{F}\right|\varphi_i\right\rangle=\frac{1}{2}\sum_{i=1}^{N}\left(\varepsilon_i+\hat{f}_i\right)+\sum_{K<L}^{Nuclei} Z_K Z_L \Big/ R_{KL}$$

ii) Alternatively we may write the energy in terms of the Hartee-Fock eigenvalues, the two electron matrix elements (coulomb and exchange integrals) and the nuclear repulsion energy.

$$\hat{f}+\frac{1}{2}\hat{V}=\left(f+\hat{V}\right)-\frac{1}{2}\hat{V}=\hat{F}-\frac{1}{2}\hat{V},$$

then

$$E=\sum_{i=1}^{N}\left\langle\varphi_i\left|\hat{F}-\frac{1}{2}\hat{V}\right|\varphi_i\right\rangle=\sum_{i=1}^{N}\varepsilon_i-\frac{1}{2}\sum_{i=1}^{N}\left\langle\varphi_i\left|\hat{V}\right|\varphi_i\right\rangle+\sum_{K<L}^{Nuclei} Z_K Z_L \Big/ R_{KL}$$

$$=\sum_{i=1}^{N}\varepsilon_i-\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\int\varphi_i^*(1)\varphi_j^*(2)\hat{G}(1,2)\varphi_i(1)\varphi_j(2)\,d\tau(1,2)+\sum_{K<L}^{Nuclei} Z_K Z_L \Big/ R_{KL}$$