General Equations

Our goal is to construct the best single determinant wave function for a system of *N* electrons. By best we mean the determinant having the lowest energy. We write our trial function as a determinant of N spin orbitals, one for each electron

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

where a spin orbital φ consist of a spatial function, $\chi(\vec{r})$ multiplied by a spin function, either α for up spin or β for down spin, i.e., $\varphi_i(\vec{r},\sigma)=\chi_i(\vec{r})\alpha$ *or* $\chi_i(\vec{r})\beta$ where σ is either α *or* β. We assume that the spin orbitals are orthonormal either because of spin or because the spatial functions $\chi_i(\vec{r})$ associated with a given spin are orthonormal. Consequently the spin orbitals are orthonormal

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

And so the determinant is normalized

$$\left\langle\psi\left(1,2,\cdots N\right)\middle|\psi\left(1,2,\cdots N\right)\right\rangle=1$$

$\hat{\mathcal{A}}$ is the antisymeterizing operator (*vide supra*)

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

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

is a minimum. Writing the Hamiltonian (in atomic units) as the sum of one and two body operators

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

Where $\hat{f}=-\frac{1}{2}\nabla^2-\sum_{k=1}^{nuclei}\frac{Z_k}{\left|\vec{r}-\vec{R}_k\right|}$ and $g\left(i,j\right)=\frac{1}{r_{ij}}$

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

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

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 recalculate the energy it should not change through terms of order $\delta\varphi_i$.

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

$$E\left(\varphi_1 + \delta\varphi_1, \varphi_2 + \delta\varphi_2, \cdots \varphi_N + \delta\varphi_N\right) = \sum_{i=1}^{N} \left\langle \varphi_i + \delta\varphi_i \middle| \hat{f} \middle| \varphi_i + \delta\varphi_i \right\rangle$$
$$+ \sum_{i>j}^{N} \left\langle \left(\varphi_i + \delta\varphi_i\right)\left(\varphi_j + \delta\varphi_j\right) \middle| g(1,2)\left(1 - \hat{P}_{12}\right) \middle| \left(\varphi_i + \delta\varphi_i\right)\left(\varphi_j + \delta\varphi_j\right) \right\rangle.$$

Note that we are keeping the spin associated with each spin orbital constant and are varying the spatial part of the orbital. 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

$$\sum_{i>j}^{N} \left\{ \left\langle \varphi_i(1)\varphi_j(2) \middle| \hat{G} \middle| \varphi_i(1)\varphi_j(2) \right\rangle + \left\langle \varphi_i(1)\delta\varphi_j(2) \middle| \hat{G} \middle| \varphi_i(1)\varphi_j(2) \right\rangle + \left\langle \delta\varphi_i(1)\varphi_j(2) \middle| \hat{G} \middle| \varphi_i(1)\varphi_j(2) \right\rangle \right.$$
$$\left. + \left\langle \varphi_i(1)\varphi_j(2) \middle| \hat{G} \middle| \varphi_i(1)\delta\varphi_j(2) \right\rangle + \left\langle \varphi_i(1)\varphi_j(2) \middle| \hat{G} \middle| \delta\varphi_i(1)\varphi_j(2) \right\rangle \right\} + 0\left(\delta^2\right),$$

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

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

Since *1* and *2 as well as i and j* are dummy indices, this term may be written as

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

and, of course,

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

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

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

Note that the differential volume element $d\tau = dr^3 d\sigma$ and the integration is over both spatial and spin coordinates. 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

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

and $\therefore$

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

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

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

Where we recognize that $\hat{F}$ is Hermitian.

Since the spin orbitals are orthonormal any variation must preserve this property and so we must not vary $\delta\varphi_i$ independently of $\delta\varphi_j$, since they are coupled by the constraints,

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

To comply with these constraints, we use the technique of Lagrangian multipliers which is discussed in the Mathematical Preliminaries section. Briefly, to vary the functional $F(\varphi(x))$ with respect to $\varphi(x)$ subject to $G(\varphi(x)) = 0,$ we first form the independent variations of *F* and *G*, i. e., δF and $\delta G,$ 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 *l* by requiring

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

l 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

$$\delta\langle\varphi_i|\varphi_j\rangle = \langle\varphi_i+\delta\varphi_i|\varphi_j+\delta\varphi_j\rangle - \langle\varphi_i|\varphi_j\rangle$$
$$= \langle\varphi_i|\delta\varphi_j\rangle + \langle\delta\varphi_i|\varphi_j\rangle + 0(\delta^2).$$

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

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

and so

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

We now require that this be true for arbitrary variations $\delta\varphi_i$, and thus 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 Hermitian 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,

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

where $\hat{F}\bar{\varphi} \equiv \left(\hat{F}\varphi_1 \hat{F}\varphi_2 \cdots \hat{F}\varphi_N\right)$

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

How one proceeds from this point on depends on the details of the Slater determinant. There are three broad classes of wavefunctions that one can consider. They are the unrestricted open shell, closed shell and the restricted open shell and we will discuss each. We will consider the unrestricted Hartree-Fock wavefunction first since the closed shell and restricted open shell are special cases of the unrestricted function..