Hartree Fock theory in a finite basis.

In one sentence: Hartree-Fock approximates the wave function by a single determinant, and optimizes the orbitals in the determinant to minimize energy $\langle \phi_{HF} | \hat{H} | \phi_{HF} \rangle / \langle \phi_{HF} | \phi_{HF} \rangle$

If we denote the occupied spinorbitals in $|\phi_{HF}\rangle$ by labels a, b, then following the Slater rules

$$E_{HF} = \sum_{a}^{occ} \langle a | h | a \rangle + \frac{1}{2} \sum_{a,b} \langle ab || ab \rangle$$

To minimize this expression I assume the HF spin-orbitals can be expressed in a basis set of spinorbitals $|\mu\rangle$, (AO's) that will carry greek indices μ, ν, σ, τ.

At this moment I will do everything in terms of spin-orbitals.

The AO basis set (or better primitive) basis set is given, and does not change.

We need the following integrals

$$\langle \mu | \hat{h} | \nu \rangle = h_{\mu\nu} = \int \chi_\mu^*(1)\, \hat{h}(1)\, \chi_\nu(1)\, d1$$

$$\langle \mu\nu | \sigma\tau \rangle = \int \chi_\mu^*(1)\, \chi_\nu^*(2)\, \frac{1}{r_{12}}\, \chi_\sigma(1)\, \chi_\tau(2)\, d1\, d2$$

also $S_{\mu\nu} = \langle \mu | \nu \rangle = \int \chi_\mu^*(1)\, \chi_\nu(1)\, d1$

als. $\langle \mu\nu || \sigma\tau \rangle = \langle \mu\nu | \sigma\tau \rangle - \langle \mu\nu | \tau\sigma \rangle$

The overlap integrals are relevant because the primitive basis is non-orthogonal. (e.g. AO-basis)

The MO's can be expressed in the basis:

$$|a\rangle = \sum_\mu |\mu\rangle\, C_{\mu a}$$

The MO's are supposed to be orthonormal:

$$S_{ab} = \langle b | a \rangle = \sum_{\nu,\mu} C_{\nu b}^*\, \langle \nu | \mu \rangle\, C_{\mu a}$$

$$= \sum_{\nu,\mu} C_{\nu b}^*\, S_{\nu\mu}\, C_{\mu a}$$

$$= \sum_{\nu,\mu} (C^+)_{b\nu}\, S_{\nu\mu}\, C_{\mu a}$$

$$\Rightarrow \boxed{C^+ S C = \mathbb{1}}$$

Let us next consider the energy expression for a single determinant of orthonormal orb's.

$$E = \sum_a \langle a|h|a\rangle + \frac{1}{2}\sum_{a,b} \langle ab||ab\rangle$$

$$= \sum_{\substack{\mu,\nu \\ a,\,occ}} C^*_{\mu a}\, \langle \mu|h|\nu\rangle\, C_{\nu a}$$

$$+ \frac{1}{2}\sum_{\substack{a,b \\ occ}} \sum_{\mu\nu\sigma\tau} C^*_{\mu a}\, C^*_{\nu b}\, \langle \mu\nu||\sigma\tau\rangle\, C_{\sigma a}\, C_{\tau b}$$

Next define the (one-particle) density matrix:

$$D_{\nu\mu} = \sum_{a,\,occ} C_{\mu a}\, C^*_{\nu a}$$

use μ,σ labels.

$$= \sum_{a\,occ} C_{\nu a}\, (C^\dagger)_{a\mu}$$

$$= (C C^\dagger)_{\nu\mu}$$

Then the energy expression simplifies

$$E = \sum_{\mu,\nu} h_{\mu\nu}\, D_{\nu\mu} + \frac{1}{2}\sum_{\mu,\nu,\sigma,\tau} \langle \mu\nu||\sigma\tau\rangle\, D_{\sigma\mu}\, D_{\tau\nu}$$

$\Rightarrow$ The energy of a single determinant depends (quadratically) on the density matrix. $D_{\nu\mu}$

Let us now show a very fundamental property:

one can 'rotate' the occupied orbitals among themselves; this does not affect the density matrix:

$$|i'\rangle = \sum_{\mu} C_{\mu i} = \sum_{a} |a\rangle U_{ai}$$

$$C_{\mu i} = \sum_{a} C_{\mu a} U_{ai}$$

where $U^{+}U = UU^{+} = 1$

(i) (wrong order, no matter)

$$D_{\mu\nu} = \sum_{i} C_{\mu i} C^{*}_{\nu i}$$

$$= \sum_{a,b,i} \left(C_{\mu a} U_{ai} \right) \left(C^{*}_{\nu b} U^{*}_{bi} \right)$$

$$= \sum_{a,b} C_{\mu a} C^{*}_{\nu b} \left(\sum_{i} U_{ai} U^{*}_{bi} \right)$$

$$= \sum_{a,b} C_{\mu a} C^{*}_{\nu b} \delta_{ab} \qquad (UU^{+} = 1)$$

$$= \sum_{a} C_{\mu a} C^{*}_{\nu a}$$

(a)

$$\equiv D_{\mu\nu}$$

Hence the energy is invariant under rotation of occupied orbitals.

Also $|\varphi_a \varphi_b| = \text{sign} \cdot |\varphi_i \varphi_j|$ or phase

⇒ Only the density matrix matters, not the individual orbitals. Determinant matters, not orbitals.

(N.b: This answers the question what are orbitals for water?
delocalized, symmetry adapted or localized sp_3 hybrids ⇒ either)
[Summarize Self-consistent fields.]

<u>Derivation of Hartree-Fock equations.</u>

$$E = \sum_{\mu,\nu} h_{\mu\nu} D_{\nu\mu} + \frac{1}{2} \sum_{\mu,\nu,\sigma,\tau} \langle \mu\nu || \sigma\tau \rangle D_{\sigma\mu} D_{\tau\nu}$$

$$D_{\nu\mu} = \sum_{a, occ} C_{\mu a} C^{*}_{\nu a}$$

$$\sum_{\mu,\nu} C^{*}_{\mu a} S_{\mu\nu} C_{\nu b} = \delta_{ab} \quad \text{(orthonormality)}$$

Let us assume in the derivation that the orbitals, (and integrals) are real (they are for molecules).
[not for solids]
We want to optimize energy, i.e $C_{\mu a}$, while preserving orthonormality of orbitals.

Define functional

$$F = \sum_{\mu,\nu} h_{\mu\nu} D_{\nu\mu} + \frac{1}{2} \sum_{\substack{\mu\nu \\ \sigma\tau}} \langle \mu\nu \| \sigma\tau \rangle D_{\sigma\mu} D_{\nu\tau} - \sum_{a,b} \varepsilon_{ba} \left(\sum_{\mu,\nu} C_{\mu a} S_{\mu\nu} C_{\nu b} - \delta_{ab} \right)$$

The ε_{ab} are Lagrange multipliers, they allow us to do unconstraint variations of coefficients.
We want:

(1) $\frac{\partial F}{\partial C_{\lambda d}} = 0 \quad \forall \quad d, \lambda$

(2) $\frac{\partial F}{\partial \varepsilon_{ba}} = 0 \Rightarrow \sum_{\mu,\nu} C_{\mu a} S_{\mu\nu} C_{\nu b} = \delta_{ab}$

$\Rightarrow$ constraints.

at convergence $\Gamma = \bar{\Gamma}$ is optimal.

$$\frac{\partial F}{\partial C_{\lambda d}} = \sum_{\mu,\nu} h_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial C_{\lambda d}} \quad (A)$$

$$+ \frac{1}{2} \sum_{\substack{\mu,\nu \\ \sigma,\tau}} \langle \mu\nu \| \sigma\tau \rangle \frac{\partial D_{\sigma\mu}}{\partial C_{\lambda d}} D_{\nu\tau} \quad (B)$$

$$+ \frac{1}{2} \sum_{\substack{\mu,\nu \\ \sigma,\tau}} \langle \mu\nu \| \sigma\tau \rangle D_{\sigma\mu} \frac{\partial D_{\nu\tau}}{\partial C_{\lambda d}} \quad (C)$$

$$- \sum_{a,b} \varepsilon_{ba} \frac{\partial}{\partial C_{\lambda d}} \left(\sum_{\mu,\nu} C_{\mu a} S_{\mu\nu} C_{\nu b} - \delta_{ab} \right) \quad (D)$$

To simplify let me first note

(1) that (B) = (C)

e.g.: $\sum_{\mu\nu\sigma\tau} \langle \mu\nu \| \sigma\tau \rangle D_{\sigma\mu} \frac{\partial D_{\nu\tau}}{\partial C_{\lambda d}}$ (C)

$= \sum_{\substack{\mu'\nu' \\ \sigma'\tau'}} \langle \nu'\mu' \| \tau'\sigma' \rangle D_{\tau'\nu'} \frac{\partial D_{\sigma'\mu'}}{\partial C_{\lambda d}}$

$\begin{pmatrix} \mu \to \nu' & \sigma \to \tau' \\ \nu \to \mu' & \tau \to \sigma' \end{pmatrix}$

$= \sum_{\substack{\mu'\nu' \\ \sigma'\tau'}} \langle \mu'\nu' \| \sigma'\tau' \rangle \frac{\partial D_{\sigma'\mu'}}{\partial C_{\lambda d}} D_{\tau'\nu'}$

now drop the primes on indices (summation labels) and we have term (B).

(2) $\frac{\partial D_{\mu\nu}}{\partial C_{\lambda d}} = \frac{\partial}{\partial C_{\lambda d}} \sum_a \left(C_{\mu a} C_{\nu a} \right)$

$= \sum_a \left(\delta_{\mu\lambda} \delta_{ad} C_{\nu a} + C_{\mu a} \delta_{\nu\lambda} \delta_{ad} \right)$

$= \delta_{\mu\lambda} C_{\nu d} + \delta_{\nu\lambda} C_{\mu d}$

(3) $\frac{\partial}{\partial C_{\lambda d}} \left(\sum_{a,b} \sum_{\mu\nu} C_{\mu a} S_{\mu\nu} C_{\nu b} \right) =$

$\sum_{\mu,\nu} \sum_{a,b} \varepsilon_{ba} \left(\delta_{\mu\lambda} \delta_{ad} S_{\mu\nu} C_{\nu b} + C_{\mu a} S_{\mu\nu} \delta_{\nu\lambda} \delta_{bd} \right)$

$= \sum_{\nu,b} S_{\lambda\nu} C_{\nu b} \varepsilon_{bd} + \sum_{\mu,a} C_{\mu a} S_{\mu\lambda} \varepsilon_{da}$

This leads to :

$$\sum_{\mu\nu} h_{\mu\nu}\,\delta_{\mu\lambda}\,C_{\nu d} + \sum_{\mu,\nu} h_{\mu\nu}\,\delta_{\lambda\nu}\,C_{\mu d}$$

$$+ \sum_{\substack{\mu\nu \\ \sigma\tau}} \langle \mu\nu \| \sigma\tau \rangle\, D_{\nu\tau} \left(\delta_{\mu\lambda} C_{\sigma d} + \delta_{\sigma\lambda} C_{\mu d} \right)$$

$$- S_{\lambda\nu}\, C_{\nu b}\, \varepsilon_{db} - S_{\lambda\nu}\, C_{\lambda a}\, \varepsilon_{ad} = 0$$

or :

$$\left[\sum_{\nu} h_{\lambda\nu}\, C_{\nu d} + \sum_{\sigma\tau} \langle \lambda\nu \| \sigma\tau \rangle\, D_{\nu\tau}\, C_{\sigma d} - S_{\lambda\nu}\, C_{\nu b}\, \varepsilon^{*}_{bd} \right]$$

$$+ \sum_{\mu} \left(C_{\mu d}\, h_{\mu\lambda} + \sum_{\nu,\tau} C_{\mu d} \langle \mu\nu \| \lambda\tau \rangle\, D_{\nu\tau} - \varepsilon^{*}_{da}\, C_{\lambda a}\, S_{\lambda\nu} \right) = 0$$

If we now define the so-called Fock Matrix

$$f_{\mu\sigma} = \sum_{\nu\tau} \langle \mu\nu \| \sigma\tau \rangle\, D_{\nu\tau} + h_{\mu\nu}$$

we can write :

$$\sum_{\nu} f_{\lambda\nu} C_{\nu d} - \sum_{\nu,b} S_{\lambda\nu} C_{\nu b} \varepsilon_{bd}$$

$$+ \sum_{\mu} C_{\mu d} f_{\mu\lambda} - \sum_{a,\lambda} \varepsilon_{da} C_{\lambda a} S_{\lambda\nu} = 0$$

or

$$(fC - SC\varepsilon) + (C^{+}f - \varepsilon C^{+}S) = 0$$

or

$$(fC - SC\varepsilon) + (fC - SC\varepsilon^{+})^{+} = 0$$

If we assume (can be shown) that $\varepsilon = \varepsilon^{+}$ then we are left to

$$fC - SC\varepsilon = 0 \quad + \text{h.c.}$$

Here ε is a matrix of Lagrangian multipliers.
if $\varepsilon = \varepsilon^{+}$, it can be diagonalized

$$\varepsilon = U \lambda U^{+}$$
$$\varepsilon U = U \lambda \qquad \lambda: \text{diagonal}$$

$$\Rightarrow fCU - SCU\lambda$$

or $$fC' = SC'\lambda$$

C' are the so-called canonical orbitals

They satisfy the generalized eigenvalue equation

$$\mathbf{f}\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\lambda}$$

$$= \mathbf{S}\mathbf{C}\boldsymbol{\varepsilon}, \text{ where now } \boldsymbol{\varepsilon} \text{ is diagonal.}$$

As we have shown before, the density matrix is invariant under transformation of occupied orbitals.
The orbitals that we obtain from Hartree Fock, are usually canonical orbitals, together with @ Hartree-Fock orbital energies.

The derivation of Hartree-Fock equations is difficult.
We are also obtaining equations that are not so easy to interpret.
Let me try to clarify in a next set of notes.