Derivation of Hartree - Fock Equations

Consider Hamiltonian of the form

$$H = \sum_{kl} \langle \psi_k | h | \psi_l \rangle a_k^+ a_l + \frac{1}{2} \sum_{klmn} \langle \psi_k \psi_l | g | \psi_m \psi_n \rangle a_k^+ a_l^+ a_m a_n$$

one-particle operator

two-particle operator

Expectation value with respect to anti-symmetric wave function:

$$E = \langle \Psi_{AS} | H | \Psi_{AS} \rangle$$

$$= \sum_{kl} \langle \psi_k | h | \psi_l \rangle \langle \Psi_{AS} | a_k^+ a_l | \Psi_{AS} \rangle$$

$$+ \frac{1}{2} \sum_{klmn} \langle \psi_k \psi_l | g | \psi_m \psi_n \rangle \langle \Psi_{AS} | a_k^+ a_l^+ a_m a_n | \Psi_{AS} \rangle$$

$$= \sum_{k} \langle \psi_k | h | \psi_k \rangle + \frac{1}{2} \sum_{kl} \Big[\langle \psi_k \psi_l | g | \psi_k \psi_l \rangle - \langle \psi_k \psi_l | g | \psi_l \psi_k \rangle \Big]$$

where we used the relations

$$\langle \Psi_{AS} | a_k^+ a_l | \Psi_{AS} \rangle = \delta_{kl}$$

$$\langle \Psi_{AS} | a_k^+ a_l^+ a_m a_n | \Psi_{AS} \rangle = (1 - \delta_{kl}) (\delta_{kn} \delta_{lm} - \delta_{ln} \delta_{km})$$

focus on second term; rewrite in real-space notation

second term =

$$\sum_{kl} \Big[\int dx\, dx' \, \psi_k^*(x) \psi_l^*(x') \, g(x,x') \, \psi_k(x) \psi_l(x')$$

$$- \int dx\, dx' \, \psi_k^*(x) \psi_l^*(x') g(x,x') \psi_l(x) \psi_k(x')$$

<u>Define</u>: $J_l(x)\, \psi_k(x) = \int dx' \, \psi_l^*(x') \, g(x,x') \, \psi_l(x') \, \psi_k(x)$

$$K_l(x) \; \psi_k(x) = \int dx' \, \psi_l^*(x') \, g(x,x') \, \psi_k(x') \; \psi_l(x)$$

$$J = \sum_l J_l$$

$$K = \sum_l K_l$$

then:

$$\text{second term} = \sum_k \int dx \; \psi_k^*(x) (J - K) \, \psi_k(x)$$

and

$$\boxed{E = \sum_k \langle \psi_k | h + \tfrac{1}{2}(J - K) | \psi_k \rangle}$$

the energy functional of a Slater determinant

<u>Important concept</u>:
Solving the Schrödinger equation
$H|\Psi\rangle = E|\Psi\rangle$ is the same as minimizing
$E[\Psi]$.

Thus, we want to minimize $E[\Psi_{1s}]$,
with the constraint that

$$\langle \psi_k | \psi_l \rangle = \delta_{kl} \quad \text{(orthonormality)}$$

This leads to:

$$\delta E - \sum_{kl} \underset{\substack{\uparrow \\ \text{Lagrange} \\ \text{multipliers}}}{\Lambda_{kl}} \left[\langle \delta\psi_k | \psi_l \rangle + \langle \psi_k | \delta\psi_l \rangle \right] = 0$$

Focus on δE:

$$\delta E = \sum_k \langle \delta\psi_k | h | \psi_k \rangle + \text{compl. conj.}$$

$$+ \frac{1}{2} \sum_{kl} \Big(\langle \delta\psi_k \psi_l | g | \psi_k \psi_l \rangle + \langle \psi_l \delta\psi_k | g | \psi_l \psi_k \rangle$$

$$- \langle \delta\psi_k \psi_l | g | \psi_l \psi_k \rangle - \langle \psi_l \delta\psi_k | g | \psi_k \psi_l \rangle \Big)$$

$$+ \text{complex conjugates}$$

use relation $\langle \psi_l \delta\psi_k | g | \psi_l \psi_k \rangle = \langle \delta\psi_k \psi_l | g | \psi_k \psi_l \rangle$

$$\delta E = \sum_k \langle \delta\psi_k | h | \psi_k \rangle + \sum_{kl} \left(\langle \delta\psi_k \psi_l | g | \psi_k \psi_l \rangle - \langle \delta\psi_k \psi_l | g | \psi_l \psi_k \rangle \right)$$

+ compl. conj.

$$= \sum_k \langle \delta\psi_k | \mathcal{F} | \psi_k \rangle + \langle \psi_k | \mathcal{F} | \delta\psi_k \rangle$$

with $\mathcal{F} = h + J - K$

This leads to :

$$0 = \langle \delta\psi_k | \mathcal{F} | \psi_k \rangle + \langle \psi_k | \mathcal{F} | \delta\psi_k \rangle - \sum_l \Lambda_{kl} \left(\langle \delta\psi_k | \psi_l \rangle + \langle \psi_l | \delta\psi_k \rangle \right)$$

Since $\delta\psi$ is small, but arbitrary, this implies

$$\mathcal{F} | \psi_k \rangle = \sum_l \Lambda_{kl} \psi_l$$

The Lagrange multiplies must be chosen such that ψ_k form an orthonormal set. An obvious solution is obtained by taking the ψ_k as eigenvectors of Fock operator $\mathcal{F}$, with eigenvalues ε_k, and

$$\Lambda_{kl} = \varepsilon_k \delta_{kl}$$

$$\rightarrow \boxed{\mathcal{F} | \psi_k \rangle = \varepsilon_k | \psi_k \rangle}$$ the Hartree-Fock equation