

# Modern Quantum Chemistry, Szabo & Ostlund

## HW

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### 3 The Hartree-Fock Approximation

#### 3.1 The HF Equations

##### 3.1.1 The Coulomb and Exchange Operators

##### 3.1.2 The Fock Operator

**Ex 3.1**

$$\begin{aligned}
 \langle \chi_i | \hat{f} | \chi_j \rangle &= \left\langle \chi_i(1) \left| h(1) + \sum_b [\mathcal{J}_b(1) - \mathcal{K}_b(1)] \right| \chi_j(1) \right\rangle \\
 &= [i|h|j] + \sum_{b \neq j} \left[ \left\langle \chi_i(1) \chi_b(2) \left| \frac{1}{r_{12}} \right| \chi_b(2) \chi_j(1) \right\rangle - \left\langle \chi_i(1) \chi_b(2) \left| \frac{1}{r_{12}} \right| \chi_b(1) \chi_j(2) \right\rangle \right] \\
 &= [i|h|j] + \sum_{b \neq j} ([ij|bb] - [ib|bj])
 \end{aligned} \tag{3.1.1}$$

Since

$$[ij|jj] - [ij|jj] = 0 \tag{3.1.2}$$

we have

$$\begin{aligned}
 \langle \chi_i | \hat{f} | \chi_j \rangle &= \langle i | h | j \rangle + \sum_b (\langle ib | jb \rangle - \langle ib | bj \rangle) \\
 &= \langle i | h | j \rangle + \sum_b \langle ib || jb \rangle
 \end{aligned} \tag{3.1.3}$$

#### 3.2 Derivation of the HF Equations

##### 3.2.1 Functional Variation

##### 3.2.2 Minimization of the Energy of a Single Determinant

**Ex 3.2** Take the complex conjugate of

$$\mathcal{L}[\{\chi_\alpha\}] = E_0[\{\chi_\alpha\}] - \sum_a^N \sum_b^N \varepsilon_{ba}([a|b] - \delta_{ab}) \tag{3.2.1}$$

we have

$$\mathcal{L}[\{\chi_\alpha\}]^* = E_0[\{\chi_\alpha\}]^* - \sum_a^N \sum_b^N \varepsilon_{ba}^*([a|b]^* - \delta_{ab}^*) \tag{3.2.2}$$

i.e.

$$\mathcal{L}[\{\chi_\alpha\}] = E_0[\{\chi_\alpha\}] - \sum_a^N \sum_b^N \varepsilon_{ba}^*([b|a] - \delta_{ab}) \tag{3.2.3}$$

thus

$$\sum_a^N \sum_b^N \varepsilon_{ba}([a|b] - \delta_{ab}) = \sum_a^N \sum_b^N \varepsilon_{ba}^*([b|a] - \delta_{ab}) = \sum_b^N \sum_a^N \varepsilon_{ab}^*([a|b] - \delta_{ba}) \tag{3.2.4}$$

$\therefore$

$$\varepsilon_{ba} = \varepsilon_{ab}^* \tag{3.2.5}$$

**Ex 3.3**  $\therefore$

$$[\delta \chi_a | h | \chi_a] = [\chi_a | h | \delta \chi_a]^* \tag{3.2.6}$$

$$[\chi_a \delta \chi_a | \chi_b \chi_b] = [\delta \chi_a \chi_a | \chi_b \chi_b]^* \tag{3.2.7}$$

$$[\chi_a \chi_a | \chi_b \delta \chi_b] = [\chi_a \chi_a | \delta \chi_b \chi_b]^* \tag{3.2.8}$$

$$[\chi_a \chi_b | \chi_b \delta \chi_a] = [\chi_b \delta \chi_a | \chi_a \chi_b] = [\delta \chi_a \chi_b | \chi_b \chi_a]^* \tag{3.2.9}$$

$$[\chi_a \chi_b | \delta \chi_b \chi_a] = [\delta \chi_b \chi_a | \chi_a \chi_b] = [\chi_a \delta \chi_b | \chi_b \chi_a]^* \tag{3.2.10}$$

∴

$$\begin{aligned}\delta E_0 &= \sum_a^N [\delta \chi_a | h | \chi_a] + \frac{1}{2} \sum_a^N \sum_b^N ([\delta \chi_a \chi_a | \chi_b \chi_b] + [\chi_a \chi_a | \delta \chi_b \chi_b]) \\ &\quad - \frac{1}{2} \sum_a^N \sum_b^N ([\delta \chi_a \chi_b | \chi_b \chi_a] + [\chi_a \chi_b | \delta \chi_b \chi_a]) + \text{complex conjugates}\end{aligned}\quad (3.2.11)$$

while

$$\sum_a^N \sum_b^N [\chi_a \chi_a | \delta \chi_b \chi_b] = \sum_b^N \sum_a^N [\chi_b \chi_b | \delta \chi_a \chi_a] = \sum_a^N \sum_b^N [\delta \chi_a \chi_a | \chi_b \chi_b] \quad (3.2.12)$$

$$\sum_a^N \sum_b^N [\chi_a \chi_b | \delta \chi_b \chi_a] = \sum_b^N \sum_a^N [\chi_b \chi_a | \delta \chi_a \chi_b] = \sum_a^N \sum_b^N [\delta \chi_a \chi_b | \chi_b \chi_a] \quad (3.2.13)$$

thus

$$\delta E_0 = \sum_a^N [\delta \chi_a | h | \chi_a] + \sum_a^N \sum_b^N ([\delta \chi_a \chi_a | \chi_b \chi_b] - [\delta \chi_a \chi_b | \chi_b \chi_a]) + \text{complex conjugates} \quad (3.2.14)$$

### 3.2.3 The Canonical HF Equations

## 3.3 Interpretation of Solutions to the HF Equations

### 3.3.1 Orbital Energies and Koopmans' Theorem

**Ex 3.4**

$$f_{ij} = \langle \chi_i | f | \chi_j \rangle = \langle i | h | j \rangle + \sum_b \langle ib || jb \rangle \quad (3.3.1)$$

$$\begin{aligned}f_{ji}^* &= \langle \chi_j | f | \chi_i \rangle^* = \langle j | h | i \rangle^* + \sum_b \langle jb || ib \rangle^* \\ &= \langle i | h | j \rangle + \sum_b \langle ib || jb \rangle \\ &= f_{ij}\end{aligned}\quad (3.3.2)$$

thus the Fock operator is Hermitian.

**Ex 3.5**

$$IP = {}^{N-2} E - E_0$$

$$\begin{aligned}&= \sum_{a \neq c, d} \langle a | h | a \rangle + \frac{1}{2} \sum_{a \neq c, d} \sum_{b \neq c, d} \langle ab || ab \rangle - \left[ \sum_a \langle a | h | a \rangle + \frac{1}{2} \sum_a \sum_b \langle ab || ab \rangle \right] \\ &= -\langle c | h | c \rangle - \langle d | h | d \rangle - \frac{1}{2} \sum_{a \neq c, d} \langle ac || ac \rangle - \frac{1}{2} \sum_{a \neq c, d} \langle ad || ad \rangle - \frac{1}{2} \sum_{b \neq c, d} \langle cb || cb \rangle - \frac{1}{2} \sum_{b \neq c, d} \langle db || db \rangle - \langle cd || cd \rangle \\ &= -\langle c | h | c \rangle - \langle d | h | d \rangle - \sum_{a \neq c, d} \langle ac || ac \rangle - \sum_{a \neq c, d} \langle ad || ad \rangle - \langle cd || cd \rangle \\ &= -\langle c | h | c \rangle - \langle d | h | d \rangle - \left( \sum_{a \neq c} \langle ac || ac \rangle - \langle dc || dc \rangle \right) - \left( \sum_{a \neq d} \langle ad || ad \rangle - \langle cd || cd \rangle \right) - \langle cd || cd \rangle \\ &= -\varepsilon_c - \varepsilon_d + \langle cd || cd \rangle - \langle cd || dc \rangle\end{aligned}\quad (3.3.3)$$