

# Modern Quantum Chemistry, Szabo & Ostlund

## HW

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## Contents

<b>3</b>	<b>The Hartree-Fock Approximation</b>	<b>2</b>
3.1	The HF Equations	2
3.1.1	The Coulomb and Exchange Operators	2
3.1.2	The Fock Operator	2
	Ex 3.1	2
3.2	Derivation of the HF Equations	2
3.2.1	Functional Variation	2
3.2.2	Minimization of the Energy of a Single Determinant	2
	Ex 3.2	2
	Ex 3.3	2
3.2.3	The Canonical HF Equations	3
3.3	Interpretation of Solutions to the HF Equations	3
3.3.1	Orbital Energies and Koopmans' Theorem	3
	Ex 3.4	3
	Ex 3.5	3
	Ex 3.6	4
3.3.2	Brillouin's Theorem	4
3.3.3	The HF Hamiltonian	4
	Ex 3.7	4
	Ex 3.8	4
3.4	Restricted Closed-shell HF: The Roothaan Equations	4
3.4.1	Closed-shell HF: Restricted Spin Orbitals	4
	Ex 3.9	4

### 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**

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

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

**Ex 3.6**

$$\begin{aligned}
{}^N E_0 - {}^{N+1} E^r &= \sum_a \langle a | h | a \rangle + \frac{1}{2} \sum_a \sum_b \langle ab || ab \rangle \\
&\quad - \left[ \sum_a \langle a | h | a \rangle + \langle r | h | r \rangle + \frac{1}{2} \sum_a \sum_b \langle ab || ab \rangle + \frac{1}{2} \sum_b \langle rb || rb \rangle + \frac{1}{2} \sum_a \langle ar || ar \rangle \right] \\
&= - \langle r | h | r \rangle - \frac{1}{2} \sum_b \langle rb || rb \rangle - \frac{1}{2} \sum_b \langle br || br \rangle \\
&= - \langle r | h | r \rangle - \sum_b \langle rb || rb \rangle
\end{aligned} \tag{3.3.4}$$

**3.3.2 Brillouin's Theorem**

**3.3.3 The HF Hamiltonian**

**Ex 3.7** Suppose  $\mathcal{H}_0$  commutes with  $\mathcal{P}_n$ ,

$$\begin{aligned}
\mathcal{H}_0 |\Psi_0\rangle &= \mathcal{H}_0 \frac{1}{\sqrt{N!}} \sum_n (-1)^{p_n} \mathcal{P}_n \left\{ \sum_i^N f(i) \chi_j(1) \cdots \chi_k(N) \right\} \\
&= \frac{1}{\sqrt{N!}} \sum_n (-1)^{p_n} \mathcal{P}_n \{ (\varepsilon_j + \cdots + \varepsilon_k) \chi_j(1) \cdots \chi_k(N) \} \\
&= \sum_a \varepsilon_a
\end{aligned} \tag{3.3.5}$$

Now we show  $\mathcal{H}_0$  commutes with  $\mathcal{P}_n$ , for example,  $\mathcal{P}_{ab}$

$$\mathcal{P}_{ab} \mathcal{H}_0 = \mathcal{P}_{ab} (\cdots + f(a) + \cdots + f(b) + \cdots) = (\cdots + f(b) + \cdots + f(a) + \cdots) \mathcal{P}_{ab} = \mathcal{H}_0 \mathcal{P}_{ab} \tag{3.3.6}$$

**Ex 3.8**

$$\mathcal{V} = \sum_i^N \sum_{j>i}^N \mathcal{O}_2 - \sum_i^N \sum_b^N [\mathcal{G}_b(i) - \mathcal{K}_b(i)] \tag{3.3.7}$$

thus

$$\begin{aligned}
\langle \Psi_0 | \mathcal{V} | \Psi_0 \rangle &= \sum_i^N \sum_{j>i}^N \langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle - \sum_i^N \sum_b^N [\langle \Psi_0 | \mathcal{G}_b(i) - \mathcal{K}_b(i) | \Psi_0 \rangle] \\
&= \frac{1}{2} \sum_a^N \sum_b^N \langle ab || ab \rangle - \sum_i^N \sum_b^N [\langle ib | ib \rangle - \langle ib | bi \rangle] \\
&= -\frac{1}{2} \sum_a^N \sum_b^N \langle ab || ab \rangle
\end{aligned} \tag{3.3.8}$$

**3.4 Restricted Closed-shell HF: The Roothaan Equations**

**3.4.1 Closed-shell HF: Restricted Spin Orbitals**

**Ex 3.9**

$$\begin{aligned}
\varepsilon_i &= (i|h|i) + \sum_b^N (\langle ib | ib \rangle - \langle ib | bi \rangle) \\
&= (i|h|i) + \sum_c^{N/2} (\langle ic | ic \rangle - \langle ic | ci \rangle) + \sum_{\bar{c}}^{N/2} (\langle i\bar{c} | i\bar{c} \rangle - \langle i\bar{c} | \bar{c}i \rangle)
\end{aligned} \tag{3.4.1}$$

Assume  $\chi_j$  has  $\alpha$  spin, since assuming  $\alpha$  or  $\beta$  is identical

$$\begin{aligned}
\varepsilon_i &= (i|h|i) + \sum_c^{N/2} [(ic|ic) \langle \alpha | \alpha \rangle \langle \alpha | \alpha \rangle - (ic|ci) \langle \alpha | \alpha \rangle \langle \alpha | \alpha \rangle] + \sum_c^{N/2} [(ic|ic) \langle \alpha | \alpha \rangle \langle \beta | \beta \rangle - (ic|ci) \langle \alpha | \beta \rangle \langle \beta | \alpha \rangle] \\
&= (i|h|i) + \sum_c^{N/2} [2(ic|ic) - (ic|ci)] \\
&= (i|h|i) + \sum_n^{N/2} (2J_{ib} - K_{ib})
\end{aligned} \tag{3.4.2}$$

### 3.4.2 Introduction of a Basis: The Roothaan Equations