

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

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

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

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 χ_j has α spin, since assuming α or β 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

Ex 3.10

$$\begin{aligned}
(\mathbf{C}^\dagger \mathbf{S} \mathbf{C})_{\mu\nu} &= \sum_i \sum_j C_{\mu i}^\dagger S_{ij} C_{j\nu} \\
&= \sum_i \sum_j C_{i\mu}^* \langle \phi_i | \phi_j \rangle C_{j\nu} \\
&= \langle \phi_\mu | \phi_\nu \rangle \\
&= \delta_{\mu\nu}
\end{aligned} \tag{3.4.3}$$

thus

$$\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{1} \tag{3.4.4}$$

3.4.3 The Charge Density

Ex 3.11

$$\begin{aligned}
\rho(\mathbf{r}) &= \langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle \\
&= \sum_i^N \frac{1}{N!} \sum_I^{N!} \sum_J^{N!} (-1)^{p_I} (-1)^{p_J} \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \hat{\mathcal{P}}_I \{ \chi_1(1) \cdots \chi_N(N) \}^* \delta(\mathbf{r}_i - \mathbf{r}) \hat{\mathcal{P}}_J \{ \chi_1(1) \cdots \chi_N(N) \}
\end{aligned} \tag{3.4.5}$$

Since $\{\chi_m\}$ are orthogonal,

$$\begin{aligned}
\rho(\mathbf{r}) &= \sum_i^N \frac{1}{N!} \sum_I^{N!} \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \hat{\mathcal{P}}_I \{ \chi_1(1) \cdots \chi_N(N) \}^* \delta(\mathbf{r}_i - \mathbf{r}) \hat{\mathcal{P}}_I \{ \chi_1(1) \cdots \chi_N(N) \} \\
&= \sum_i^N \frac{1}{N!} (N-1)! \sum_s^N \int d\mathbf{x}_i \chi_s^*(\mathbf{x}_i) \delta(\mathbf{r}_i - \mathbf{r}) \chi_s(\mathbf{x}_i) \\
&= \sum_i^N \frac{1}{N} \cdot 2 \sum_s^{N/2} \int d\mathbf{r}_i \phi_s(\mathbf{r}_i) \delta(\mathbf{r}_i - \mathbf{r}) \phi_s(\mathbf{r}_i) \\
&= \sum_i^N \frac{2}{N} \sum_s^{N/2} \phi_s(\mathbf{r}) \phi_s(\mathbf{r}) \\
&= N \frac{2}{N} \sum_s^{N/2} \phi_s(\mathbf{r}) \phi_s(\mathbf{r}) \\
&= 2 \sum_s^{N/2} \phi_s(\mathbf{r}) \phi_s(\mathbf{r})
\end{aligned} \tag{3.4.6}$$

Ex 3.12 From Ex 3.10, we have

$$\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{1} \tag{3.4.7}$$

i.e.

$$\sum_i^K \sum_j^K C_{i\mu}^* S_{ij} C_{j\nu} = \delta_{\mu\nu} \quad (3.4.8)$$

thus

$$\begin{aligned} (\mathbf{PSP})_{\mu\sigma} &= \sum_{\nu}^K \sum_{\lambda}^K P_{\mu\nu} S_{\nu\lambda} P_{\lambda\sigma} \\ &= 4 \sum_{\nu}^K \sum_{\lambda}^K \sum_a^{N/2} C_{\mu a} C_{\nu a}^* S_{\nu\lambda} \sum_b^{N/2} C_{\lambda b} C_{\sigma b}^* \\ &= 4 \sum_a^{N/2} \sum_b^{N/2} C_{\mu a} \left(\sum_{\nu}^K \sum_{\lambda}^K C_{\nu a}^* S_{\nu\lambda} C_{\lambda b} \right) C_{\sigma b}^* \\ &= 4 \sum_a^{N/2} \sum_b^{N/2} C_{\mu a} \delta_{ab} C_{\sigma b}^* \\ &= 4 \sum_a^{N/2} C_{\mu a} C_{\sigma a}^* \\ &= 2P_{\mu\sigma} \end{aligned} \quad (3.4.9)$$

thus

$$\mathbf{PSP} = 2\mathbf{P} \quad (3.4.10)$$

Ex 3.13 Eq. 3.122 shows

$$f(\mathbf{r}_1) = h(\mathbf{r}_1) + \sum_a^{N/2} \int d\mathbf{r}_2 \psi_a^*(\mathbf{r}_2) (2 - \hat{\mathcal{P}}_{12}) r_{12}^{-1} \psi_a(\mathbf{r}_2) \quad (3.4.11)$$

thus

$$\begin{aligned} f(\mathbf{r}_1) &= h(\mathbf{r}_1) + \sum_a^{N/2} \int d\mathbf{r}_2 \sum_{\sigma} C_{\sigma a}^* \phi_{\sigma}^*(\mathbf{r}_2) (2 - \hat{\mathcal{P}}_{12}) r_{12}^{-1} \sum_{\lambda} C_{\lambda a} \phi_{\lambda}(\mathbf{r}_2) \\ &= h(\mathbf{r}_1) + \sum_{\sigma} \sum_{\lambda} \left(\sum_a^{N/2} C_{\sigma a}^* C_{\lambda a} \right) \int d\mathbf{r}_2 \phi_{\sigma}^*(\mathbf{r}_2) (2 - \hat{\mathcal{P}}_{12}) r_{12}^{-1} \phi_{\lambda}(\mathbf{r}_2) \\ &= h(\mathbf{r}_1) + \frac{1}{2} \sum_{\sigma, \lambda} P_{\lambda\sigma} \int d\mathbf{r}_2 \phi_{\sigma}^*(\mathbf{r}_2) (2 - \hat{\mathcal{P}}_{12}) r_{12}^{-1} \phi_{\lambda}(\mathbf{r}_2) \end{aligned} \quad (3.4.12)$$

3.4.4 Expression for the Fock Matrix

Ex 3.14 In expression $(\mu\nu|\lambda\sigma)$, there are three interchangeable pairs, i.e. $\mu \leftrightarrow \nu$, $\lambda \leftrightarrow \sigma$, and $\mu\nu \leftrightarrow \lambda\sigma$. Thus $(\mu\nu|\lambda\sigma)$ has an 8-fold symmetry. Similarly, $(\mu\mu|\lambda\sigma)$, $(\mu\nu|\mu\lambda)$, $(\mu\nu|\mu\nu)$, $(\mu\mu|\sigma\sigma)$ has 2-fold symmetry, and $(\mu\mu|\mu\nu)$, $(\mu\mu|\mu\mu)$ has 1-fold symmetry.

Therefore, the number of unique 2e integrals is

expression	number	$K = 100$
$(\mu\nu \lambda\sigma)$	$K(K-1)(K-2)(K-3)/8$	11763675
$(\mu\mu \lambda\sigma)$	$K(K-1)(K-2)/2$	485100
$(\mu\nu \mu\lambda)$	$K(K-1)(K-2)/2$	485100
$(\mu\nu \mu\nu)$	$K(K-1)/2$	4950
$(\mu\mu \sigma\sigma)$	$K(K-1)/2$	4950
$(\mu\mu \mu\nu)$	$K(K-1)$	9900
$(\mu\mu \mu\mu)$	K	100

thus the total number is 12 753 775.

3.4.5 Orthogonalization of the Basis

Ex 3.15 \therefore

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \mathbf{s} \quad (3.4.13)$$

\therefore

$$\mathbf{S} \mathbf{U} = \mathbf{U} \mathbf{s} \quad (3.4.14)$$

i.e.

$$\sum_{\nu} S_{\mu\nu} U_{\nu i} = U_{\mu i} s_i \quad (3.4.15)$$

thus

$$\sum_{\mu} U_{\mu i}^* \sum_{\nu} S_{\mu\nu} U_{\nu i} = \sum_{\mu} U_{\mu i}^* U_{\mu i} s_i \quad (3.4.16)$$

$$\sum_{\mu} \sum_{\nu} U_{\mu i}^* \langle \phi_{\mu} | \phi_{\nu} \rangle U_{\nu i} = s_i \sum_{\mu} |U_{\mu i}|^2 \quad (3.4.17)$$

Suppose

$$\phi'_i = \sum_{\nu} U_{\nu i} \phi_{\nu} \quad (3.4.18)$$

thus

$$\langle \phi'_i | \phi'_i \rangle = s_i \sum_{\mu} |U_{\mu i}|^2 \quad (3.4.19)$$

\therefore

$$\langle \phi'_i | \phi'_i \rangle > 0 \quad |U_{\mu i}|^2 > 0 \quad (3.4.20)$$

\therefore

$$s_i > 0 \quad (3.4.21)$$

Ex 3.16

- (3.174)

Since (ϕ, ϕ', ψ) are row vectors

$$\psi = \phi \mathbf{C} \quad (3.4.22)$$

$$\psi = \phi' \mathbf{C}' = \phi \mathbf{X} \mathbf{C}' \quad (3.4.23)$$

we have

$$\mathbf{C} = \mathbf{X} \mathbf{C}' \quad (3.4.24)$$

i.e.

$$\mathbf{C}' = \mathbf{X}^{-1} \mathbf{C} \quad (3.4.25)$$

- (3.177)

$$\begin{aligned} F'_{\mu\nu} &= \langle \phi'_{\mu} | f | \phi'_{\nu} \rangle \\ &= \left\langle \sum_i \phi_i X_{i\mu} \left| f \right| \sum_j \phi_j X_{j\nu} \right\rangle \\ &= \sum_i \sum_j X_{i\mu}^* X_{j\nu} \langle \phi_i | f | \phi_j \rangle \\ &= \sum_i \sum_j X_{i\mu}^* F_{ij} X_{j\nu} \end{aligned} \quad (3.4.26)$$

i.e.

$$\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X} \quad (3.4.27)$$

3.4.6 The SCF Procedure

3.4.7 Expectation Values and Population Analysis

Ex 3.17 From (3.148) in the textbook, we get

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + G_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_a^{N/2} [2(\mu\nu|aa) - (\mu a|a\nu)] \quad (3.4.28)$$

thus

$$\begin{aligned} E_0 &= \sum_a^{N/2} [2h_{aa} + \sum_b^{N/2} (2J_{ab} - K_{ab})] \\ &= 2 \sum_a^{N/2} (a|h|a) + \sum_a^{N/2} \sum_b^{N/2} [2(aa|bb) - (ab|ba)] \\ &= 2 \sum_a^{N/2} \sum_\mu \sum_\nu C_{\mu a}^* C_{\nu a} (\mu|h|\nu) + \sum_a^{N/2} \sum_b^{N/2} \left[2 \sum_\mu \sum_\nu C_{\mu a}^* C_{\nu a} (\mu\nu|bb) - \sum_\mu \sum_\nu C_{\mu a}^* C_{\nu a} (\mu b|b\nu) \right] \\ &= 2 \sum_\mu \sum_\nu P_{\mu\nu} H_{\mu\nu}^{\text{core}} + \sum_b^{N/2} \sum_\mu \sum_\nu [2P_{\mu\nu}(\mu\nu|bb) - P_{\mu\nu}(\mu b|b\nu)] \\ &= \sum_\mu \sum_\nu P_{\mu\nu} [2H_{\mu\nu}^{\text{core}} + G_{\mu\nu}] \\ &= \sum_\mu \sum_\nu P_{\mu\nu} [H_{\mu\nu}^{\text{core}} + F_{\mu\nu}] \end{aligned} \quad (3.4.29)$$