Modern Quantum Chemistry, Szabo & Ostlund HW

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January 30, 2020

Contents

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

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

Since

$$[ij|jj] - [ij|jj] = 0 \qquad (3.1.2)$$

we have

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

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

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

we have

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

i.e.

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

thus

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

$\therefore$

$$\varepsilon_{ba} = \varepsilon_{ab}^* \qquad (3.2.5)$$

Ex 3.3 $\because$

$$\begin{aligned}
[\delta\chi_a|h|\chi_a] &= [\chi_a|h|\delta\chi_a]^* && (3.2.6) \\
[\chi_a\delta\chi_a|\chi_b\chi_b] &= [\delta\chi_a\chi_a|\chi_b\chi_b]^* && (3.2.7) \\
[\chi_a\chi_a|\chi_b\delta\chi_b] &= [\chi_a\chi_a|\delta\chi_b\chi_b]^* && (3.2.8) \\
[\chi_a\chi_b|\chi_b\delta\chi_a] &= [\chi_b\delta\chi_a|\chi_a\chi_b] = [\delta\chi_a\chi_b|\chi_b\chi_a]^* && (3.2.9) \\
[\chi_a\chi_b|\delta\chi_b\chi_a] &= [\delta\chi_b\chi_a|\chi_a\chi_b] = [\chi_a\delta\chi_b|\chi_b\chi_a]^* && (3.2.10)
\end{aligned}$$

$\therefore$

$$\delta E_0 = \sum_a^N [\delta\chi_a|h|\chi_a] + \frac{1}{2}\sum_a^N\sum_b^N \left([\delta\chi_a\chi_a|\chi_b\chi_b] + [\chi_a\chi_a|\delta\chi_b\chi_b]\right)$$
$$- \frac{1}{2}\sum_a^N\sum_b^N \left([\delta\chi_a\chi_b|\chi_b\chi_a] + [\chi_a\chi_b|\delta\chi_b\chi_a]\right) + \text{complex conjugates} \tag{3.2.11}$$

while

$$\sum_a^N\sum_b^N[\chi_a\chi_a|\delta\chi_b\chi_b] = \sum_b^N\sum_a^N[\chi_b\chi_b|\delta\chi_a\chi_a] = \sum_a^N\sum_b^N[\delta\chi_a\chi_a|\chi_b\chi_b] \tag{3.2.12}$$
$$\sum_a^N\sum_b^N[\chi_a\chi_b|\delta\chi_b\chi_a] = \sum_b^N\sum_a^N[\chi_b\chi_a|\delta\chi_a\chi_b] = \sum_a^N\sum_b^N[\delta\chi_a\chi_b|\chi_b\chi_a] \tag{3.2.13}$$

thus

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

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

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

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

thus the Fock operator is Hermitian.

Ex 3.5

$$\begin{aligned} \text{IP} &= {}^{N-2}E - E_0 \\ &= \sum_{a\neq c,d} \langle a \,|\, h \,|\, a \rangle + \frac{1}{2}\sum_{a\neq c,d}\sum_{b\neq c,d} \langle ab \,\|\, ab \rangle - \left[\sum_a \langle a \,|\, h \,|\, a \rangle + \frac{1}{2}\sum_a\sum_b \langle ab \,\|\, ab \rangle\right] \\ &= -\langle c \,|\, h \,|\, c \rangle - \langle d \,|\, h \,|\, d \rangle - \frac{1}{2}\sum_{a\neq c,d}\langle ac \,\|\, ac \rangle - \frac{1}{2}\sum_{a\neq c,d}\langle ad \,\|\, ad \rangle - \frac{1}{2}\sum_{b\neq c,d}\langle cb \,\|\, cb \rangle - \frac{1}{2}\sum_{b\neq c,d}\langle db \,\|\, db \rangle - \langle cd \,\|\, cd \rangle \\ &= -\langle c \,|\, h \,|\, c \rangle - \langle d \,|\, h \,|\, d \rangle - \sum_{a\neq c,d}\langle ac \,\|\, ac \rangle - \sum_{a\neq c,d}\langle ad \,\|\, ad \rangle - \langle cd \,\|\, cd \rangle \\ &= -\langle c \,|\, h \,|\, c \rangle - \langle d \,|\, h \,|\, d \rangle - \left(\sum_{a\neq c}\langle ac \,\|\, ac \rangle - \langle dc \,\|\, dc \rangle\right) - \left(\sum_{a\neq d}\langle ad \,\|\, ad \rangle - \langle cd \,\|\, cd \rangle\right) - \langle cd \,\|\, cd \rangle \\ &= -\varepsilon_c - \varepsilon_d + \langle cd \,|\, cd \rangle - \langle cd \,|\, dc \rangle \end{aligned} \tag{3.3.3}$$

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 $\mathscr{H}_0$ commutes with $\mathscr{P}_n$,

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

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

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

Ex 3.8

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

thus

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

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

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

3.4.2 Introduction of a Basis: The Roothaan Equations

Ex 3.10

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

thus

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

3.4.3 The Charge Density

Ex 3.11

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

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

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

Ex 3.12 From Ex 3.10, we have

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

i.e.

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

thus

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

thus

$$\mathbf{PSP} = 2\mathbf{P} \tag{3.4.10}$$

Ex 3.13 Eq. 3.122 shows

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

thus

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

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 $\because$

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \mathbf{s} \tag{3.4.13}$$

$\therefore$

$$\mathbf{S}\mathbf{U} = \mathbf{U}\mathbf{s} \tag{3.4.14}$$

i.e.

$$\sum_\nu S_{\mu\nu} U_{\nu i} = U_{\mu i} s_i \tag{3.4.15}$$

thus

$$\sum_\mu U^*_{\mu i} \sum_\nu S_{\mu\nu} U_{\nu i} = \sum_\mu U^*_{\mu i} U_{\mu i} s_i \tag{3.4.16}$$

$$\sum_\mu \sum_\nu U^*_{\mu i} \langle \phi_\mu \mid \phi_\nu \rangle U_{\nu i} = s_i \sum_\mu |U_{\mu i}|^2 \tag{3.4.17}$$

Suppose

$$\phi'_i = \sum_\nu U_{\nu i} \phi_\nu \tag{3.4.18}$$

thus

$$\langle \phi'_i \mid \phi'_i \rangle = s_i \sum_\mu |U_{\mu i}|^2 \tag{3.4.19}$$

$\because$

$$\langle \phi'_i \mid \phi'_i \rangle > 0 \qquad |U_{\mu i}|^2 > 0 \tag{3.4.20}$$

$\therefore$

$$s_i > 0 \tag{3.4.21}$$

Ex 3.16

- (3.174)

Since (ϕ, ϕ', ψ are row vectors)

$$\boldsymbol{\psi} = \boldsymbol{\phi}\mathbf{C} \tag{3.4.22}$$

$$\boldsymbol{\psi} = \boldsymbol{\phi}'\mathbf{C}' = \boldsymbol{\phi}\mathbf{X}\mathbf{C}' \tag{3.4.23}$$

we have

$$\mathbf{C} = \mathbf{X}\mathbf{C}' \tag{3.4.24}$$

i.e.

$$\mathbf{C}' = \mathbf{X}^{-1}\mathbf{C} \tag{3.4.25}$$

- (3.177)

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

i.e.

$$\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X} \tag{3.4.27}$$