Modern Quantum Chemistry, Szabo & Ostlund HW

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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

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

Since

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

we have

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

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 $\because$

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

$\therefore$

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

while

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

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

thus

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

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

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

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

thus the Fock operator is Hermitian.

Ex 3.5

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

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