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

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

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

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

we have

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

i.e.

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

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 $\because$

$$[\delta\chi_a|h|\chi_a] = [\chi_a|h|\delta\chi_a]^* \tag{3.2.6}$$
$$[\chi_a\delta\chi_a|\chi_b\chi_b] = [\delta\chi_a\chi_a|\chi_b\chi_b]^* \tag{3.2.7}$$
$$[\chi_a\chi_a|\chi_b\delta\chi_b] = [\chi_a\chi_a|\delta\chi_b\chi_b]^* \tag{3.2.8}$$
$$[\chi_a\chi_b|\chi_b\delta\chi_a] = [\chi_b\delta\chi_a|\chi_a\chi_b] = [\delta\chi_a\chi_b|\chi_b\chi_a]^* \tag{3.2.9}$$
$$[\chi_a\chi_b|\delta\chi_b\chi_a] = [\delta\chi_b\chi_a|\chi_a\chi_b] = [\chi_a\delta\chi_b|\chi_b\chi_a]^* \tag{3.2.10}$$

$\therefore$

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

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