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

$$\left\langle \chi_i \left| \hat{f} \right| \chi_j \right\rangle = \left\langle \chi_i(1) \left| h(1) + \sum_b [\mathscr{J}_b(1) - \mathscr{K}_b(1)] \right| \chi_j(1) \right\rangle$$

$$= [i|h|j] + \sum_{b \neq j} \left[\left\langle \chi_i(1)\chi_b(2) \left| \frac{1}{r_{12}} \right| \chi_b(2)\chi_j(1) \right\rangle - \left\langle \chi_i(1)\chi_b(2) \left| \frac{1}{r_{12}} \right| \chi_b(1)\chi_j(2) \right\rangle \right]$$

$$= [i|h|j] + \sum_{b \neq j} ([ij|bb] - [ib|bj]) \tag{3.1.1}$$

Since

$$[ij|jj] - [ij|jj] = 0 \tag{3.1.2}$$

we have

$$\left\langle \chi_i \left| \hat{f} \right| \chi_j \right\rangle = \langle i \,|\, h \,|\, j \rangle + \sum_b (\langle ib \,|\, jb \rangle - \langle ib \,|\, bj \rangle)$$

$$= \langle i \,|\, h \,|\, j \rangle + \sum_b \langle ib \,\|\, jb \rangle \tag{3.1.3}$$

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

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

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 $\because$

$$[\delta\chi_a|h|\chi_a] = [\chi_a|h|\delta\chi_a]^* \tag{3.2.6}$$

$$[\chi_a\delta\chi_a|\chi_b\chi_b] = [\delta\chi_a\chi_a|\chi_b\chi_b]^* \tag{3.2.7}$$

$$[\chi_a\chi_a|\chi_b\delta\chi_b] = [\chi_a\chi_a|\delta\chi_b\chi_b]^* \tag{3.2.8}$$

$$[\chi_a\chi_b|\chi_b\delta\chi_a] = [\chi_b\delta\chi_a|\chi_a\chi_b] = [\delta\chi_a\chi_b|\chi_b\chi_a]^* \tag{3.2.9}$$

$$[\chi_a\chi_b|\delta\chi_b\chi_a] = [\delta\chi_b\chi_a|\chi_a\chi_b] = [\chi_a\delta\chi_b|\chi_b\chi_a]^* \tag{3.2.10}$$

$\therefore$

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

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

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

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

$$f_{ji}^* = \langle \chi_j | f | \chi_i \rangle^* = \langle j | h | i \rangle^* + \sum_b \langle jb \| ib \rangle^*$$

$$= \langle i | h | j \rangle + \sum_b \langle ib \| jb \rangle$$

$$= f_{ij} \qquad (3.3.2)$$

thus the Fock operator is Hermitian.