Modern Quantum Chemistry, Szabo & Ostlund
HW

王石嵘

October 2, 2019

Contents

3 The Hartree-Fock Approximation

3.1 The Hartree-Fock 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 Hartree-Fock 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