Modern Quantum Chemistry, Szabo & Ostlund

HW

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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

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

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