

22.6.3: ii. Exercises

Q1

By expanding the molecular orbitals $\{\phi_k\}$ as linear combinations of atomic orbitals $\{\chi_\mu\}$,

$$\phi_k = \sum_{\mu} c_{\mu k} \chi_{\mu}$$

show how the canonical Hartree-Fock (HF) equations:

$$F\phi_i = \epsilon_i \phi_i$$

reduce to the matrix eigenvalue-type equation of the form given in the text:

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i}$$

where:

$$F_{\mu\nu} = \langle \chi_{\mu} | h | \chi_{\nu} \rangle + \sum_{\delta\kappa} [\gamma_{\delta\kappa} \langle \chi_{\mu} \chi_{\delta} | g | \chi_{\nu} \chi_{\kappa} \rangle - \gamma_{\delta\kappa}^{ex} \langle \chi_{\mu} \chi_{\delta} | g | \chi_{\kappa} \chi_{\nu} \rangle], \quad (22.6.3.1)$$

$$S_{\mu\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle, \gamma_{\delta\kappa} = \sum_{i=occ} C_{\delta i} C_{\kappa i}, \quad (22.6.3.2)$$

$$\text{and } \gamma_{\delta\kappa}^{ex} = \sum_{\substack{i=occ \\ \text{and} \\ \text{same spin}}} C_{\delta i} C_{\kappa i}. \quad (22.6.3.3)$$

Note that the sum over i in $\gamma_{\delta\kappa}$ and $\gamma_{\delta\kappa}^{ex}$ is a sum over spin orbitals. In addition, show that this Fock matrix can be further reduced for the closed shell case to:

$$F_{\mu\nu} = \langle \chi_{\mu} | h | \chi_{\nu} \rangle + \sum_{\delta\kappa} P_{\delta\kappa} \left[\langle \chi_{\mu} \chi_{\delta} | g | \chi_{\nu} \chi_{\kappa} \rangle - \frac{1}{2} \langle \chi_{\mu} \chi_{\delta} | g | \chi_{\kappa} \chi_{\nu} \rangle \right],$$

where the charge bond order matrix, P, is defined to be:

$$P_{\delta\kappa} = \sum_{i=occ} 2C_{\delta i} C_{\kappa i},$$

where the sum over i here is a sum over orbitals not spin orbitals.

Q2

Show that the HF total energy for a closed-shell system may be written in terms of integrals over the orthonormal HF orbitals as:

$$E(\text{SCF}) = 2 \sum_k^{occ} \langle \phi_k | h | \phi_k \rangle + \sum_{kl}^{occ} [2 \langle k1 | g k1 \rangle - \langle k1 | g | 1k \rangle] + \sum_{\mu>\nu} \frac{Z_{\mu} Z_{\nu}}{R_{\mu\nu}}.$$

Q3

Show that the HF total energy may alternatively be expressed as:

$$E(\text{SCF}) = \sum_k^{occ} (\epsilon_k + \langle \phi_k | h | \phi_k \rangle) + \sum_{\mu>\nu} \frac{Z_{\mu} Z_{\nu}}{R_{\mu\nu}}$$

where the ϵ_k refer to the HF orbital energies.

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