22.6.3: ii. Exercises

Q1

By expanding the molecular orbitals $\{\phi\kappa\}$ 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:

$$F\phi_i - \epsilon_i\phi_j$$

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:

$$F_{\mu\nu} = \langle\chi_\mu|h|\chi_\nu\rangle + \sum_{\delta\kappa}\left[\gamma_{\delta\kappa}\langle\chi_\mu\chi_\delta|g|\chi_\nu\chi_\kappa\rangle - \gamma^{ex}_{\delta\kappa}\langle\chi_\mu\chi_\delta|g|\chi_\kappa\chi_\nu\rangle\right], \tag{22.6.3.1}$$

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

$$\text{and } \gamma^{ex}_{\delta\kappa} = \sum_{\substack{\text{occ and}\\ \text{same spin}}} C_{\delta i}C_{\kappa i}. \tag{22.6.3.3}$$

Note that the sum over i in $\gamma_{\delta\kappa}$ and $\gamma_{\delta\kappa}$ 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:

$$\text{E(SCF)} = 2\sum_k^{occ}\langle\phi_k|h|\phi_k\rangle + \sum_{kl}^{occ}\left[2\langle k1|gk1\rangle - \langle k1|g|1k\rangle\right] + \sum_{\mu>\nu}\frac{Z_\mu Z_\nu}{R_{\mu\nu}}.$$

Q3

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

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

where the ϵ_k refer to the HF orbital energies.