22.6.6: v. Exercise Solutions

Q1

$$F\phi_i = \varepsilon_i \phi_j = h\phi_i + \sum_j [J_j - K_j]\,\phi_i$$

Let the closed shell Fock potential bewritten as:

$$V_{ij} = \sum_k (2\langle ik|jk\rangle - \langle ik|kj\rangle)\text{, and the 1e}^-\text{component as:} \tag{22.6.6.1}$$

$$h_{ij} = \langle \phi_i - \frac{1}{2}\nabla^2 - \sum_A \frac{Z_A}{|r - R_A|}|\phi_j\rangle\text{, and the delta as:} \tag{22.6.6.2}$$

$$\delta_{ij} = \langle i|j\rangle\text{, so that: } h_{ij} + V_{ij} = \delta_{ij}\varepsilon_i \tag{22.6.6.3}$$

$$\text{using: } \phi_i = \sum_\mu C_{\mu i}\chi_\mu,\ \phi_j = \sum_\nu C_{\nu j}\chi_\nu\text{, and } \phi_k = \sum_\gamma C_{\gamma k}\chi_\gamma \tag{22.6.6.4}$$

, and transforming from the mo to ao basis we obtain:

$$V_{ij} = \sum_{k\mu\gamma\nu k} C_{\mu i}C_{\gamma k}C_{\nu j}C_{\kappa k}\,(2\langle\mu\gamma|\nu\kappa\rangle - \langle\mu\gamma|\kappa\nu\rangle) \tag{22.6.6.5}$$

$$= \sum_{k\mu\gamma\nu\kappa} (C_{\gamma k}C_{\kappa k})\,(C_{\mu i}C_{\nu j})\,(2\langle\mu\gamma|\nu\kappa\rangle - \langle\mu\gamma|\kappa\nu\rangle) \tag{22.6.6.6}$$

$$= \sum_{\mu\nu} (C_{\mu i}C_{\nu j})\,V_{\mu\nu}\text{ where,} \tag{22.6.6.7}$$

$$V_{\mu\nu} = \sum_{\gamma\kappa} P_{\gamma\kappa}\,(2\langle\mu\gamma|\nu\kappa\rangle - \langle\mu\gamma|\kappa\nu\rangle)\text{, and } P_{\gamma\kappa} = \sum_k (C_{\gamma k}C_{\kappa k})\text{,} \tag{22.6.6.8}$$

$$h_{ij} = \sum_{\mu\nu} (C_{\mu i}C_{\nu j})\,h_{\mu\nu}\text{ , where} \tag{22.6.6.9}$$

$$h_{\mu\nu} = \langle\chi_\mu| - \frac{1}{2}\nabla^2 - \sum_A \frac{Z_A}{|r - R_A|}|\chi_\nu\rangle\text{ , and} \tag{22.6.6.10}$$

$$\delta_{ij} = \langle i|j\rangle = \sum_{\mu\nu} (C_{\mu i}S_{\mu\nu}C_{\nu j})\,. \tag{22.6.6.11}$$

SO, $h_{ij} + V_{ij} = \delta_{ij}\varepsilon_j$ becomes:

$$\sum_{\mu\nu} (C_{\mu i}C_{\nu j})\,h_{\mu\nu} + \sum_{\mu\nu} (C_{\mu i}C_{\nu j})\,V_{\mu\nu} = \sum_{\mu\nu} (C_{\mu i}S_{\mu\nu}C_{\nu j})\,\varepsilon_j, \tag{22.6.6.12}$$

$$\sum_{\mu\nu} (C_{\mu i}S_{\mu\nu}C_{\nu j})\,\varepsilon_{-} \sum_{\mu\nu} (C_{\mu i}C_{\nu j})\,h_{\mu\nu} - \sum_{\mu\nu} (C_{\mu i}C_{\nu j})\,V_{\mu\nu} = 0\text{ for all i,j} \tag{22.6.6.13}$$

$$\sum_{\mu\nu} C_{\mu i}\,[\varepsilon_j S_{\mu\nu} - h_{\mu\nu} - V_{\mu\nu}]\,C_{\nu j} = 0\text{ for all i,j} \tag{22.6.6.14}$$

$$\text{Therefore,} \tag{22.6.6.15}$$

$$\sum_\nu [h_{\mu\nu} + V_{\mu\nu} - \varepsilon_j S_{\mu\nu}]\,C_{\nu j} = 0 \tag{22.6.6.16}$$

Tis is FC = SCE.

Q2

The Slater Condon rule for zero (spin orbital) difference with N electrons in N spin orbitals is:

$$E = \langle |H+G| \rangle = \sum_i^N \langle \phi_i | h | \phi_i \rangle + \sum_{i>j}^N \left(\langle \phi_i \phi_j | g | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | g | \phi_j \phi_i \rangle \right) \tag{22.6.6.17}$$

$$= \sum_i h_{ii} + \sum_{i>j} \left(g_{ijij} - g_{ijji} \right) \tag{22.6.6.18}$$

$$= \sum_i h_{ii} + \frac{1}{2} \sum_{ij} \left(g_{ijij} - g_{ijji} \right) \tag{22.6.6.19}$$

If all orbitals are doubly occupied and we carry out the spin integration we obtain:

$$E = 2 \sum_i^{occ} h_{ii} + \sum_{ij}^{occ} \left(2g_{ijij} - g_{ijji} \right),$$

where i and j now refer to orbitals (not spin-orbitals).

Q3

If the occupied orbitals obey $F\phi_k = \varepsilon_k \phi_k$, then the expression for E in problem 2 above can be rewritten as.

$$E = \sum_i^{occ} \left(h_{ii} + \sum_j^{occ} \left(2g_{ijij} - g_{ijji} \right) \right) + \sum_i^{occ} h_{ii}$$

We recognize the closed shell Fock operator expression and rewrite this as

$$E = \sum_i^{occ} F_{ii} + \sum_i^{occ} h_{ii} = \sum_i^{occ} \left(\varepsilon_i + h_{ii} \right)$$