Programming Project 5 Exercises

1. Derive the Hartree-Fock energy expression:

$$\langle\Phi|\hat{H}_e|\Phi\rangle = \sum_i^n h_{ii} + \sum_{i<j}^n \langle ij||ij\rangle \tag{1}$$

2. Let $\overline{\mathbf{S}}$, $\overline{\mathbf{T}}$, and $\overline{\mathbf{V}}$ be one-electron integrals with respect to the spatial AO basis $\{\chi_1, \cdots, \chi_m\}$.

$$\overline{S}_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle \qquad \overline{T}_{\mu\nu} = -\tfrac{1}{2}\langle\chi_\mu|\nabla_1^2|\chi_\nu\rangle \qquad \overline{V}_{\mu\nu} = \sum_A \langle\chi_\mu|\frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|}|\chi_\nu\rangle \tag{2}$$

Explain why their counterparts $\mathbf{S}$, $\mathbf{T}$, $\mathbf{V}$ with respect to the spin-AO basis $\{\xi_1, \cdots, \xi_{2m}\}$, where $\xi_\mu = \chi_\mu\alpha$ and $\xi_{\mu+m} = \chi_\mu\beta$,

$$S_{\mu\nu} = \langle\xi_\mu|\xi_\nu\rangle \qquad T_{\mu\nu} = -\tfrac{1}{2}\langle\xi_\mu|\nabla_1^2|\xi_\nu\rangle \qquad V_{\mu\nu} = \sum_A \langle\xi_\mu|\frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|}|\xi_\nu\rangle \tag{3}$$

have the following block-diagonal structure.

$$\mathbf{S} = \begin{bmatrix} \overline{\mathbf{S}} & 0 \\ 0 & \overline{\mathbf{S}} \end{bmatrix} \qquad \mathbf{T} = \begin{bmatrix} \overline{\mathbf{T}} & 0 \\ 0 & \overline{\mathbf{T}} \end{bmatrix} \qquad \mathbf{V} = \begin{bmatrix} \overline{\mathbf{V}} & 0 \\ 0 & \overline{\mathbf{V}} \end{bmatrix} \tag{4}$$

3. The two-electron integrals $(\chi_\mu\chi_\nu|\chi_\rho\chi_\sigma)$ make up a 4-index tensor, which can be viewed as a matrix $\overline{\mathbf{G}} = [\overline{\mathbf{G}}_{\chi_\mu\chi_\nu}]$ of matrices $\overline{\mathbf{G}}_{\chi_\mu\chi_\nu} = [(\chi_\mu\chi_\nu|\chi_\rho\chi_\sigma)]$. Explain why the spatial AO basis integral tensor $\overline{\mathbf{G}}$ is related to its spin-AO counterpart $\mathbf{G}$, where $\mathbf{G} = [\mathbf{G}_{\xi_\mu\xi_\nu}]$ and $\mathbf{G}_{\xi_\mu\xi_\nu} = [(\xi_\mu\xi_\nu|\xi_\rho\xi_\sigma)]$, via

$$\mathbf{G} = \begin{bmatrix} \overline{\mathbf{G}} & 0 \\ 0 & \overline{\mathbf{G}} \end{bmatrix} \qquad \mathbf{G}_{\xi,\xi'} = \mathbf{G}_{\chi\omega,\chi'\omega'} = \delta_{\omega\omega'} \begin{bmatrix} \overline{\mathbf{G}}_{\chi\chi'} & 0 \\ 0 & \overline{\mathbf{G}}_{\chi\chi'} \end{bmatrix} \tag{5}$$

i.e. it has a block-diagonal structure with respect to each pair of indices. Note that this is one case where the index-ordering of chemist's notation has some advantages over physicist's notation.

4. The spin-orbital Fock operator is given by

$$\hat{f} = \hat{h} + \sum_{i=1}^n (\hat{J}_i - \hat{K}_i) \tag{6}$$

where $\hat{h}$ is the one-electron ("core") Hamiltonian and $\hat{J}_i$ and $\hat{K}_i$ are Coulomb and exchange operators. Show that its matrix elements with respect to the spin-orbital basis $\{\psi_p\}$ are given by

$$f_{pq} = h_{pq} + \sum_{i=1}^n \langle pi||qi\rangle \ . \tag{7}$$

5. Show that, if $C_{\mu p}$ are the expansion coefficients of ψ_p in the spin-AO basis $\{\xi_\mu\} = \{\chi_\mu\alpha\} \cup \{\chi_\mu\beta\}$

$$\psi_p = \sum_\mu \xi_\mu C_{\mu p} \tag{8}$$

then the spin-AO basis Fock matrix elements are given by

$$f_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma} \langle \xi_\mu \xi_\rho || \xi_\nu \xi_\sigma \rangle D_{\sigma\rho} \qquad\qquad D_{\mu\nu} = \sum_{i=1}^{n} C_{\mu i} C^*_{\nu i} \tag{9}$$

where $D_{\mu\nu}$ is called the Hartree-Fock density matrix.[1]

6. Show that the Hartree-Fock energy can be expanded in terms of spin-AO basis integrals as follows.

$$\langle \Phi | \hat{H}_e | \Phi \rangle = \sum_{\mu\nu} h_{\mu\nu} D_{\nu\mu} + \frac{1}{2} \sum_{\mu\nu\rho\sigma} \langle \xi_\mu \xi_\rho || \xi_\nu \xi_\sigma \rangle D_{\nu\mu} D_{\sigma\rho} \tag{10}$$

[1] This is the spin-AO-basis representation of the one-particle reduced density matrix of a Hartree-Fock determinant.