Programming Project 5 Exercises

1. Let $\overline{\mathbf{S}}$, $\overline{\mathbf{T}}$, and $\overline{\mathbf{V}}$ be one-electron integrals with respect to the spatial AO basis $\{\chi_\mu\}$.

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

   Explain why their spin-orbital counterparts $\mathbf{S}$, $\mathbf{T}$, $\mathbf{V}$ have the following block-diagonal structure

$$\mathbf{S} = \begin{bmatrix} \overline{\mathbf{S}} & 0 \\ 0 & \overline{\mathbf{S}} \end{bmatrix} \qquad \mathbf{T} = \begin{bmatrix} \overline{\mathbf{T}} & 0 \\ 0 & \overline{\mathbf{T}} \end{bmatrix} \qquad \mathbf{V} = \begin{bmatrix} \overline{\mathbf{V}} & 0 \\ 0 & \overline{\mathbf{V}} \end{bmatrix} \tag{2}$$

   in the spin-AO basis $\{\chi_\mu\alpha\} \cup \{\chi_\mu\beta\}$.

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

$$\mathbf{G} = \begin{bmatrix} \overline{\mathbf{G}} & 0 \\ 0 & \overline{\mathbf{G}} \end{bmatrix} \qquad (\mathbf{G})_{\mu\nu} = \begin{bmatrix} (\overline{\mathbf{G}})_{\mu\nu} & 0 \\ 0 & (\overline{\mathbf{G}})_{\mu\nu} \end{bmatrix} \tag{3}$$

   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.

3. The spin-orbital Fock operator is given by

$$\hat{f} = \hat{h} + \sum_{i=1}^{n} (\hat{J}_i - \hat{K}_i) \tag{4}$$

   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

$$f_{pq} = h_{pq} + \sum_{i=1}^{n} \langle pi||qi\rangle \ . \tag{5}$$

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

$$\psi_p = \sum_\mu \xi_\mu C_{\mu p} \tag{6}$$

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

$$f_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma} \langle\mu\rho||\nu\sigma\rangle D_{\rho\sigma} \qquad D_{\mu\nu} = \sum_{i=1}^{n} C_{\mu i}^* C_{\nu i} \tag{7}$$

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

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

5. Show that the electronic part of the Hartree-Fock energy

$$\langle \Phi | \hat{H}_e | \Phi \rangle = \sum_{i}^{n} h_{ii} + \sum_{i<j}^{n} \langle ij||ij \rangle \tag{8}$$

can be expanded in terms of spin-AO basis integrals as follows.

$$\langle \Phi | \hat{H}_e | \Phi \rangle = \sum_{\mu\nu} h_{\mu\nu} D_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\rho\sigma} \langle \mu\rho||\nu\sigma \rangle D_{\mu\nu} D_{\rho\sigma} \tag{9}$$