Programming Project 5 Exercises

1. Derive the Hartree-Fock energy expression

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

by expanding the Hartree-Fock determinant as

$$\Phi(1\cdots n) = \frac{1}{\sqrt{n!}} \sum_{i_1\cdots i_n}^n \varepsilon_{i_1\cdots i_n} \psi_{i_1}(1)\cdots\psi_{i_n}(n) \tag{2}$$

where $\varepsilon_{i_1\cdots i_n}$ is the Levi-Civita permutation tensor, given by

$$\varepsilon_{i_1\cdots i_n} = \begin{cases} +1 & \text{if } (i_1\cdots i_n) \text{ is an even permutation of } (1\cdots n) \\ -1 & \text{if } (i_1\cdots i_n) \text{ is an odd permutation of } (1\cdots n) \\ 0 & \text{otherwise.} \end{cases} \tag{3}$$

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

$$\overline{S}_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle \qquad \overline{T}_{\mu\nu} = -\tfrac{1}{2}\langle\chi_\mu|\nabla_1^2|\chi_\nu\rangle \qquad \overline{V}_{\mu\nu} = \sum_A \langle\chi_\mu|\frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|}|\chi_\nu\rangle \tag{4}$$

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 $\xi_{\mu+m} = \chi_\mu\beta$,

$$S_{\mu\nu} = \langle\xi_\mu|\xi_\nu\rangle \qquad T_{\mu\nu} = -\tfrac{1}{2}\langle\xi_\mu|\nabla_1^2|\xi_\nu\rangle \qquad V_{\mu\nu} = \sum_A \langle\xi_\mu|\frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|}|\xi_\nu\rangle \tag{5}$$

have the following block-diagonal structure.

$$\mathbf{S} = \begin{bmatrix} \overline{\mathbf{S}} & 0 \\ 0 & \overline{\mathbf{S}} \end{bmatrix} \qquad \mathbf{T} = \begin{bmatrix} \overline{\mathbf{T}} & 0 \\ 0 & \overline{\mathbf{T}} \end{bmatrix} \qquad \mathbf{V} = \begin{bmatrix} \overline{\mathbf{V}} & 0 \\ 0 & \overline{\mathbf{V}} \end{bmatrix} \tag{6}$$

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 $\overline{\mathbf{G}} = [\overline{\mathbf{G}}_{\mu\nu}]$ of matrices $\overline{\mathbf{G}}_{\mu\nu} = [(\chi_\mu\chi_\nu|\chi_\rho\chi_\sigma)]$. Explain why the spatial AO basis integral tensor $\overline{\mathbf{G}}$ is related to its spin-AO counterpart $\mathbf{G}$, where $\mathbf{G} = [\mathbf{G}_{\mu\nu}]$ and $\mathbf{G}_{\mu\nu} = [(\xi_\mu\xi_\nu|\xi_\rho\xi_\sigma)]$, via

$$\mathbf{G} = \begin{bmatrix} \overline{\mathbf{G}} & 0 \\ 0 & \overline{\mathbf{G}} \end{bmatrix} \qquad \mathbf{G}_{\mu\nu} = \begin{bmatrix} \overline{\mathbf{G}}_{\mu\nu} & 0 \\ 0 & \overline{\mathbf{G}}_{\mu\nu} \end{bmatrix} \tag{7}$$

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

$$\hat{f} = \hat{h} + \sum_{i=1}^{n} (\hat{J}_i - \hat{K}_i) \tag{8}$$

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

$$f_{pq} = h_{pq} + \sum_{i=1}^{n} \langle pi||qi\rangle \ . \tag{9}$$

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

$$\psi_p = \sum_{\mu} \xi_\mu C_{\mu p} \tag{10}$$

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

$$f_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma} \langle \mu\rho||\nu\sigma\rangle D_{\sigma\rho} \qquad\qquad D_{\mu\nu} = \sum_{i=1}^{n} C_{\mu i} C^*_{\nu i} \tag{11}$$

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.

$$\langle\Phi|\hat{H}_e|\Phi\rangle = \sum_{\mu\nu} h_{\mu\nu} D_{\nu\mu} + \frac{1}{2} \sum_{\mu\nu\rho\sigma} \langle\mu\rho||\nu\sigma\rangle D_{\nu\mu} D_{\sigma\rho} \tag{12}$$

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