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 $\{\chi_\mu\}$.

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

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

$$\mathbf{S} = \begin{bmatrix} \overline{\mathbf{S}} & 0 \\ 0 & \overline{\mathbf{S}} \end{bmatrix} \qquad \mathbf{T} = \begin{bmatrix} \overline{\mathbf{T}} & 0 \\ 0 & \overline{\mathbf{T}} \end{bmatrix} \qquad \mathbf{V} = \begin{bmatrix} \overline{\mathbf{V}} & 0 \\ 0 & \overline{\mathbf{V}} \end{bmatrix} \tag{5}$$

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

3. 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

$$\mathbf{G} = \begin{bmatrix} \overline{\mathbf{G}} & 0 \\ 0 & \overline{\mathbf{G}} \end{bmatrix} \qquad (\mathbf{G})_{\mu\nu} = \begin{bmatrix} (\overline{\mathbf{G}})_{\mu\nu} & 0 \\ 0 & (\overline{\mathbf{G}})_{\mu\nu} \end{bmatrix} \tag{6}$$

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

$$\hat{f} = \hat{h} + \sum_{i=1}^{n} (\hat{J}_i - \hat{K}_i) \tag{7}$$

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

$$f_{pq} = h_{pq} + \sum_{i=1}^{n} \langle pi||qi\rangle \ . \tag{8}$$

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

$$\psi_p = \sum_{\mu} \xi_\mu C_{\mu p} \tag{9}$$

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

$$f_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma} \langle \mu\rho||\nu\sigma\rangle D_{\rho\sigma} \qquad\qquad D_{\mu\nu} = \sum_{i=1}^{n} C^*_{\mu i} C_{\nu i} \tag{10}$$

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.

$$\langle \Phi|\hat{H}_e|\Phi\rangle = \sum_{\mu\nu} h_{\mu\nu} D_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\rho\sigma} \langle \mu\rho||\nu\sigma\rangle D_{\mu\nu} D_{\rho\sigma} \tag{11}$$

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