

# Programming Project 5 Exercises

1. Derive the Hartree-Fock energy expression

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

by expanding the Hartree-Fock determinant as

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

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

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

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

$$\bar{S}_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \quad \bar{T}_{\mu\nu} = -\frac{1}{2} \langle \chi_\mu | \nabla_1^2 | \chi_\nu \rangle \quad \bar{V}_{\mu\nu} = \sum_A \langle \chi_\mu | \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|} | \chi_\nu \rangle \quad (4)$$

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

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

have the following block-diagonal structure.

$$\mathbf{S} = \begin{bmatrix} \bar{\mathbf{S}} & 0 \\ 0 & \bar{\mathbf{S}} \end{bmatrix} \quad \mathbf{T} = \begin{bmatrix} \bar{\mathbf{T}} & 0 \\ 0 & \bar{\mathbf{T}} \end{bmatrix} \quad \mathbf{V} = \begin{bmatrix} \bar{\mathbf{V}} & 0 \\ 0 & \bar{\mathbf{V}} \end{bmatrix} \quad (6)$$

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  $\bar{\mathbf{G}} = [\bar{\mathbf{G}}_{\mu\nu}]$  of matrices  $\bar{\mathbf{G}}_{\mu\nu} = [(\chi_\mu \chi_\nu | \chi_\rho \chi_\sigma)]$ . Explain why the spatial AO basis integral tensor  $\bar{\mathbf{G}}$  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

$$\mathbf{G} = \begin{bmatrix} \bar{\mathbf{G}} & 0 \\ 0 & \bar{\mathbf{G}} \end{bmatrix} \quad (\mathbf{G})_{\mu\nu} = \begin{bmatrix} (\bar{\mathbf{G}})_{\mu\nu} & 0 \\ 0 & (\bar{\mathbf{G}})_{\mu\nu} \end{bmatrix} \quad (7)$$

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

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

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

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

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

$$\psi_p = \sum_{\mu} \xi_{\mu} C_{\mu p} \quad (10)$$

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

$$f_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma} \langle \mu\rho || \nu\sigma \rangle D_{\sigma\rho} \quad D_{\mu\nu} = \sum_{i=1}^n C_{\mu i} C_{\nu i}^* \quad (11)$$

where  $D_{\mu\nu}$  is called the Hartree-Fock density matrix.<sup>1</sup>

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

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

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<sup>1</sup>This is the spin-AO-basis representation of the one-particle reduced density matrix of a Hartree-Fock determinant.