

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

$$\mathbf{G} = \begin{bmatrix} \bar{\mathbf{G}} & 0 \\ 0 & \bar{\mathbf{G}} \end{bmatrix} \quad \mathbf{G}_{\xi, \xi'} = \mathbf{G}_{\chi\omega, \chi'\omega'} = \delta_{\omega\omega'} \begin{bmatrix} \bar{\mathbf{G}}_{\chi\chi'} & 0 \\ 0 & \bar{\mathbf{G}}_{\chi\chi'} \end{bmatrix} \quad (7)$$

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 ψ_p in the spin-AO basis $\{\xi_\mu\} = \{\chi_\mu\alpha\} \cup \{\chi_\mu\beta\}$

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

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

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

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

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

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

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