Programming Project 5: UHF
Unrestricted Hartree-Fock (spin-orbital)

See exercises to guide you through the derivation of equations 3–7.

Integrals. For spatial AO basis $\{\chi_1, \cdots, \chi_m\}$, the spin-AO basis is $\{\xi_1, \cdots, \xi_{2m}\}$, where $\xi_\mu = \chi_\mu \alpha$ and $\xi_{\mu+m} = \chi_\mu \beta$.

$$\overline{S}_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \quad \overline{T}_{\mu\nu} = -\tfrac{1}{2}\langle \chi_\mu | \nabla_1^2 | \chi_\nu \rangle \quad \overline{V}_{\mu\nu} = \sum_A \langle \chi_\mu | \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|} | \chi_\nu \rangle \quad (\chi_\mu \chi_\nu | \chi_\rho \chi_\sigma) = \langle \chi_\mu \chi_\rho | \frac{1}{r_{12}} | \chi_\nu \chi_\sigma \rangle \tag{1}$$

$$S_{\mu\nu} = \langle \xi_\mu | \xi_\nu \rangle \quad T_{\mu\nu} = -\tfrac{1}{2}\langle \xi_\mu | \nabla_1^2 | \xi_\nu \rangle \quad V_{\mu\nu} = \sum_A \langle \xi_\mu | \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|} | \xi_\nu \rangle \quad (\xi_\mu \xi_\nu | \xi_\rho \xi_\sigma) = \langle \xi_\mu \xi_\rho | \frac{1}{r_{12}} | \xi_\nu \xi_\sigma \rangle \tag{2}$$

$$\mathbf{S} = \begin{bmatrix} \overline{\mathbf{S}} & 0 \\ 0 & \overline{\mathbf{S}} \end{bmatrix} \quad \mathbf{T} = \begin{bmatrix} \overline{\mathbf{T}} & 0 \\ 0 & \overline{\mathbf{T}} \end{bmatrix} \quad \mathbf{V} = \begin{bmatrix} \overline{\mathbf{V}} & 0 \\ 0 & \overline{\mathbf{V}} \end{bmatrix} \quad \mathbf{G} = \begin{bmatrix} \overline{\mathbf{G}} & 0 \\ 0 & \overline{\mathbf{G}} \end{bmatrix} \quad \mathbf{G}_{\xi,\xi'} = \mathbf{G}_{\chi\omega,\chi'\omega'} = \delta_{\omega\omega'} \begin{bmatrix} \overline{\mathbf{G}}_{\chi\chi'} & 0 \\ 0 & \overline{\mathbf{G}}_{\chi\chi'} \end{bmatrix} \tag{3}$$

$$\text{where } \overline{\mathbf{G}} = [\overline{\mathbf{G}}_{\chi_\mu \chi_\nu}],\ \overline{\mathbf{G}}_{\chi_\mu \chi_\nu} = [(\chi_\mu \chi_\nu | \chi_\rho \chi_\sigma)] \text{ and } \mathbf{G} = [\mathbf{G}_{\xi_\mu \xi_\nu}],\ \mathbf{G}_{\xi_\mu \xi_\nu} = [(\xi_\mu \xi_\nu | \xi_\rho \xi_\sigma)] \tag{4}$$

Working equations.

$$f_{\mu\nu} = \quad h_{\mu\nu} + v_{\mu\nu} \qquad h_{\mu\nu} = T_{\mu\nu} + V_{\mu\nu} \qquad v_{\mu\nu} = \sum_{\rho\sigma} \langle \xi_\mu \xi_\rho || \xi_\nu \xi_\sigma \rangle D_{\sigma\rho} \qquad D_{\mu\nu} = \sum_{i=1}^{n_{\text{occ}}} C_{\mu i} C_{\nu i}^* \tag{5}$$

$$E = E_e + V_{\text{Nu}} \qquad E_e = \sum_{\mu\nu} (h_{\mu\nu} + \tfrac{1}{2} v_{\mu\nu}) D_{\nu\mu} \tag{6}$$

$$\tilde{\mathbf{f}}\tilde{\mathbf{C}} = \tilde{\mathbf{C}}\boldsymbol{\epsilon} \qquad \tilde{\mathbf{f}} = \mathbf{X}\mathbf{f}\mathbf{X} \qquad \mathbf{C} = \mathbf{X}\tilde{\mathbf{C}} \qquad \mathbf{X} = \mathbf{S}^{-\frac{1}{2}} \tag{7}$$

Procedure

Initialization.

1. Read in nuclear repulsion energy (V_{Nu}) from the Molecule object
2. Read in spatial AO basis integrals from LibMints (eq. 1)
3. Determine spin-AO basis integrals from spatial AO basis integrals (eq. 3 and 4)
4. Form orthogonalizer $\mathbf{X}$ (eq. 7)

Iteration to self-consistency.

1. Set $D_{\mu\nu} = 0$ as starting guess[1]
2. Build Fock matrix (eq. 5)
3. Transform $\mathbf{f} \mapsto \tilde{\mathbf{f}}$ to orthogonalized AO basis (eq. 7)
4. Diagonalize $\tilde{\mathbf{f}}$, yielding orbital energies ϵ_p and MO coefficients $\tilde{C}_{\mu p}$ (eq. 7)
5. Backtransform $\tilde{\mathbf{C}} \mapsto \mathbf{C}$ to original AO basis (eq. 7)
6. Build density matrix $\mathbf{D}$ (eq. 5)
7. Evaluate energy (eq. 6).
8. If the energy is not converged, return to step 2.

[1] This is the "core" guess, because $f_{\mu\nu}$ becomes the core Hamiltonian $h_{\mu\nu}$