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

See exercises to guide you through the derivation of equations 2–5.

Integrals. For spatial AO basis $\{\chi_1, \cdots, \chi_m\}$, let $\{\xi_1, \cdots, \xi_{2m}\}$ represent the spin-AO basis, with $\xi_\mu = \chi_\mu\alpha$ and $\xi_{\mu+m} = \chi_\mu\beta$. Let $\overline{\mathbf{S}}$, $\overline{\mathbf{T}}$, $\overline{\mathbf{V}}$, and $\overline{\mathbf{G}}$ be represent molecular integrals over the spatial AO basis. Then the spin-AO integrals are given by

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

$$\mathbf{S} = \begin{bmatrix}\overline{\mathbf{S}} & 0\\ 0 & \overline{\mathbf{S}}\end{bmatrix} \quad \mathbf{T} = \begin{bmatrix}\overline{\mathbf{T}} & 0\\ 0 & \overline{\mathbf{T}}\end{bmatrix} \quad \mathbf{V} = \begin{bmatrix}\overline{\mathbf{V}} & 0\\ 0 & \overline{\mathbf{V}}\end{bmatrix} \quad \mathbf{G} = \begin{bmatrix}\overline{\mathbf{G}} & 0\\ 0 & \overline{\mathbf{G}}\end{bmatrix} \quad \mathbf{G}_{\xi,\xi'} = \mathbf{G}_{\chi\omega,\chi'\omega'} = \delta_{\omega\omega'}\begin{bmatrix}\overline{\mathbf{G}}_{\chi\chi'} & 0\\ 0 & \overline{\mathbf{G}}_{\chi\chi'}\end{bmatrix} \tag{2}$$

where $\overline{\mathbf{G}} \equiv [\overline{\mathbf{G}}_{\chi_\mu\chi_\nu}]$, $\overline{\mathbf{G}}_{\chi_\mu\chi_\nu} \equiv [(\chi_\mu\chi_\nu|\chi_\rho\chi_\sigma)]$ and $\mathbf{G} \equiv [\mathbf{G}_{\xi_\mu\xi_\nu}]$, $\mathbf{G}_{\xi_\mu\xi_\nu} \equiv [(\xi_\mu\xi_\nu|\xi_\rho\xi_\sigma)]$.

Working equations.

$$f_{\mu\nu} = \quad h_{\mu\nu} + v_{\mu\nu} \qquad h_{\mu\nu} = T_{\mu\nu} + V_{\mu\nu} \qquad v_{\mu\nu} = \sum_{\rho\sigma}\langle\xi_\mu\xi_\rho||\xi_\nu\xi_\sigma\rangle D_{\sigma\rho} \qquad D_{\mu\nu} = \sum_{i=1}^{n_{\text{occ}}} C_{\mu i}C_{\nu i}^* \tag{3}$$

$$E = E_e + V_{\text{Nu}} \qquad E_e = \sum_{\mu\nu}(h_{\mu\nu} + \tfrac{1}{2}v_{\mu\nu})D_{\nu\mu} \tag{4}$$

$$\tilde{\mathbf{f}}\tilde{\mathbf{C}} = \tilde{\mathbf{C}}\boldsymbol{\epsilon} \qquad \tilde{\mathbf{f}} = \mathbf{X}\mathbf{f}\mathbf{X} \qquad \mathbf{C} = \mathbf{X}\tilde{\mathbf{C}} \qquad \mathbf{X} = \mathbf{S}^{-\frac{1}{2}} \tag{5}$$

Procedure

Initialization.

1. Read in nuclear repulsion energy (V_{Nu}) from the Molecule object
2. Read in spatial AO basis integrals from LibMints
3. Determine spin-AO basis integrals from spatial AO basis integrals (eq. 2)
4. Form orthogonalizer $\mathbf{X}$ (eq. 5)
5. Set $D_{\mu\nu} = 0$ as starting guess[1]

Iteration to self-consistency.

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

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