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

See exercises to guide you through the derivation of equations 1–6.

Spatial AO basis $\{\chi_\mu\}$ integrals.

$$\overline{S}_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle \qquad \overline{T}_{\mu\nu} = -\tfrac{1}{2}\langle\chi_\mu|\nabla_1^2|\chi_\nu\rangle \qquad \overline{V}_{\mu\nu} = \sum_A \langle\chi_\mu|\frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|}|\chi_\nu\rangle \qquad (\mu\nu|\rho\sigma) = \langle\chi_\mu\chi_\rho|\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}|\chi_\nu\chi_\sigma\rangle \tag{1}$$

Spin-AO basis $\{\chi_\mu\alpha\} \cup \{\chi_\mu\beta\}$ integrals.

$$\mathbf{S} = \begin{bmatrix} \overline{\mathbf{S}} & 0 \\ 0 & \overline{\mathbf{S}} \end{bmatrix} \qquad \mathbf{T} = \begin{bmatrix} \overline{\mathbf{T}} & 0 \\ 0 & \overline{\mathbf{T}} \end{bmatrix} \qquad \mathbf{V} = \begin{bmatrix} \overline{\mathbf{V}} & 0 \\ 0 & \overline{\mathbf{V}} \end{bmatrix} \qquad \mathbf{G} = \begin{bmatrix} \overline{\mathbf{G}} & 0 \\ 0 & \overline{\mathbf{G}} \end{bmatrix} \qquad (\mathbf{G})_{\mu\nu} = \begin{bmatrix} (\overline{\mathbf{G}})_{\mu\nu} & 0 \\ 0 & (\overline{\mathbf{G}})_{\mu\nu} \end{bmatrix} \tag{2}$$

where $\overline{\mathbf{G}}$ represents $(\mu\nu|\rho\sigma)$ viewed as a matrix of matrices: $\overline{\mathbf{G}} = \left[(\overline{\mathbf{G}})_{\mu\nu}\right]$, $(\overline{\mathbf{G}})_{\mu\nu} = [((\overline{\mathbf{G}})_{\mu\nu})_{\rho\sigma}] = [(\mu\nu|\rho\sigma)]$ (3)

Working equations.

$$f_{\mu\nu} = h_{\mu\nu} + v_{\mu\nu} \qquad h_{\mu\nu} = T_{\mu\nu} + V_{\mu\nu} \qquad v_{\mu\nu} = \sum_{\rho\sigma}\langle\mu\rho||\nu\sigma\rangle D_{\rho\sigma} \qquad D_{\mu\nu} = \sum_{i=1}^{n_{\text{occ}}} C^*_{\mu i} C_{\nu i} \tag{4}$$

$$E = E_e + V_{\text{Nu}} \qquad E_e = \sum_{\mu\nu}(h_{\mu\nu} + \tfrac{1}{2}v_{\mu\nu})D_{\mu\nu} \tag{5}$$

$$\mathbf{X} = \mathbf{S}^{-\frac{1}{2}} \qquad \tilde{\mathbf{f}} = \mathbf{X}\mathbf{f}\mathbf{X} \qquad \mathbf{C} = \mathbf{X}\tilde{\mathbf{C}} \tag{6}$$

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. 2 and 3)
4. Form orthogonalizer $\mathbf{X}$ (eq. 6)

Iteration to self-consistency.

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

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