

Programming Project 5: UHF

Unrestricted Hartree-Fock

(spin-orbital)

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

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

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

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

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

Working equations.

$$F_{\mu\nu} = h_{\mu\nu} + v_{\mu\nu} \quad h_{\mu\nu} = T_{\mu\nu} + V_{\mu\nu} \quad v_{\mu\nu} = \sum_{\rho\sigma} \langle \mu\rho || \nu\sigma \rangle D_{\rho\sigma} \quad D_{\mu\nu} = \sum_{i=1}^{n_{\text{occ}}} C_{\mu i}^* C_{\nu i} \quad (4)$$

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

$$\mathbf{X} = \mathbf{S}^{-\frac{1}{2}} \quad \tilde{\mathbf{F}} = \mathbf{X} \mathbf{F} \mathbf{X} \quad \mathbf{C} = \mathbf{X} \tilde{\mathbf{C}} \quad (6)$$

Procedure

Initialization.

1. Read in nuclear repulsion energy (V_{Nu}) from the Molecule object
2. Read in AO basis integrals from LibMints (eq. 1)
3. Transform integrals from spatial AO basis to spin-AO basis (eq. 2 and 3)
4. Form orthogonalizer \mathbf{X} (eq. 6)

Iteration to self-consistency.

1. Set $D_{\mu\nu} = 0$ as starting guess¹
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 energy (eq. 5) not converged, return to step 2.

¹This is the “core” guess, because $F_{\mu\nu}$ becomes the core Hamiltonian $h_{\mu\nu}$