

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

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

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

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

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

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

$$\tilde{\mathbf{f}}\tilde{\mathbf{C}} = \tilde{\mathbf{C}}\epsilon \quad \tilde{\mathbf{f}} = \mathbf{X}\mathbf{f}\mathbf{X} \quad \mathbf{C} = \mathbf{X}\tilde{\mathbf{C}} \quad \mathbf{X} = \mathbf{S}^{-\frac{1}{2}} \quad (5)$$

## Procedure

### Initialization.

1. Read in nuclear repulsion energy ( $V_{\text{Nu}}$ ) 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)

### Iteration to self-consistency.

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

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<sup>1</sup>This is the “core” guess, because  $f_{\mu\nu}$  becomes the core Hamiltonian  $h_{\mu\nu}$