Programming Project 3: RHF
Restricted Hartree-Fock

Extra Files

file name	description
`project3_input.dat`	shows how to get Psi4's one- and two-electron integrals as `numpy.arrays`

Equations

Integrals. Let $\{\chi_1, \cdots, \chi_m\}$ be spatial AO basis functions.

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \quad T_{\mu\nu} = -\tfrac{1}{2}\langle \chi_\mu | \nabla_1^2 | \chi_\nu \rangle \quad V_{\mu\nu} = \sum_A \langle \chi_\mu | \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|} | \chi_\nu \rangle \tag{1}$$

$$(\chi_\mu \chi_\nu | \chi_\rho \chi_\sigma) = \langle \chi_\mu \chi_\rho | \chi_\nu \chi_\sigma \rangle = \langle \chi_\mu(1) \chi_\rho(2) | \frac{1}{r_{12}} | \chi_\nu(1) \chi_\sigma(2) \rangle \tag{2}$$

Working equations.

$$h_{\mu\nu} = T_{\mu\nu} + V_{\mu\nu} \qquad D_{\mu\nu} = 2\sum_{i=1}^{n_{\text{occ}}} C_{\mu i} C_{\nu i}^* \tag{3}$$

$$f_{\mu\nu} = h_{\mu\nu} + v_{\mu\nu} \qquad v_{\mu\nu} = \sum_{\rho\sigma} (\langle \chi_\mu \chi_\rho | \chi_\nu \chi_\sigma \rangle - \tfrac{1}{2}\langle \chi_\mu \chi_\rho | \chi_\sigma \chi_\nu \rangle) D_{\sigma\rho} \tag{4}$$

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

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

Procedure

Initialization.

1. Read in nuclear repulsion energy (V_{Nu}) from the `Molecule` object and integrals from `MintsHelper`
2. Form orthogonalizer $\mathbf{X}$ (eq. 6)
3. Set $D_{\mu\nu} = 0$ as starting guess[1]

Iteration to self-consistency.

1. Build Fock matrix (eq. 4)
2. Transform $\mathbf{f} \mapsto \tilde{\mathbf{f}}$ to orthogonalized AO basis (eq. 6)
3. Diagonalize $\tilde{\mathbf{f}}$, yielding orbital energies ϵ_p and MO coefficients $\tilde{C}_{\mu p}$ (eq. 6)
4. Backtransform $\tilde{\mathbf{C}} \mapsto \mathbf{C}$ to original AO basis (eq. 6)
5. Build density matrix $\mathbf{D}$ (eq. 3)
6. Evaluate energy (eq. 5).
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 $h_{\mu\nu}$