Programming Project 7: CIS
Configuration interaction with singles (spin-orbital)

Let $\{\psi_p\}$ be canonical Hartree-Fock spin-orbitals with orbital energies $\{\epsilon_p\}$ and basis expansion coefficients $C_{\mu p}$, and let E_0 be the ground-state Hartree-Fock energy $E_0 = \langle\Phi|\hat{H}_e|\Phi\rangle$.

$$\langle\psi_p\psi_q|\psi_r\psi_s\rangle = \sum_{\mu\nu\rho\sigma} C^*_{\mu p} C^*_{\nu q} C_{\rho r} C_{\sigma s} \langle\xi_\mu\xi_\nu|\xi_\rho\xi_\sigma\rangle \tag{1}$$

$$\tilde{\mathbf{H}} = \mathbf{H} - E_0\mathbf{I} = [\langle\Phi_P|\hat{H}_e - E_0|\Phi_Q\rangle], \Phi_P \in \{\Phi_i^a\} \tag{2}$$

$$\langle\Phi_i^a|\hat{H}_e - E_0|\Phi_j^b\rangle = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj||ib\rangle \tag{3}$$

$$\tilde{\mathbf{H}}\mathbf{c}_K = \Delta E_K \mathbf{c}_K, \quad \Delta E_K = E_K - E_0 \tag{4}$$

Procedure

1. Run canonical spin-orbital Hartree-Fock code to obtain MO coefficients $\{C_{\mu p}\}$ and orbital energies $\{\epsilon_p\}$.
2. Transform two-electron integrals from the spin-AO basis $\{\xi_\mu\}$ to the spin-MO basis $\{\psi_p\}$ (equation 1).
3. Build the eigenvalue-shifted CIS Hamiltonian matrix (equation 2) using equation 3 to evaluate its matrix elements.
4. Diagonalize $\tilde{\mathbf{H}}$ to obtain CIS excitation energies $\{\Delta E_K\}$ and wavefunction expansion coefficients $\{\mathbf{c}_K\}$.