Programming Project 7 Exercises

1. Identify the structure of the CI Hamiltonian matrix

$$\mathbf{H} = [\langle \Phi_P | \hat{H}_e | \Phi_Q \rangle], \quad \Phi_P \in \{\Phi, \Phi_i^a, \Phi_{ij}^{ab}, \Phi_{ijk}^{abc}, \ldots\} \tag{1}$$

   when the determinant basis is truncated at single-substitutions, $\{\Phi, \Phi_i^a\}$. Assuming a canonical Hartree-Fock reference determinant, how does Brillouin's theorem affect the structure of this matrix?

2. Explain why the Hartree-Fock energy $E_0 = \langle \Phi | \hat{H}_e | \Phi \rangle$ is an eigenvalue of the CIS Hamiltonian.

$$\mathbf{H}\mathbf{c}_0 = E_0 \mathbf{c}_0 \tag{2}$$

   What is $\mathbf{c}_0$?

3. Eigenvalues and eigenvectors of the CIS Hamiltonian

$$\mathbf{H}\mathbf{c}_K = E_K \mathbf{c}_K \tag{3}$$

   approximate the exact (full-CI) electronic excited states of a molecule. Specifically, by the *Hylleraas-Undheim theorem*,[1] each truncated CI eigenvalue provides a variational upper bound to a specific full-CI eigenvalue, approaching the latter as the basis of diagonalization is extended. Let $\tilde{\mathbf{H}}$ be the CIS Hamiltonian shifted by $-E_0$ times the identity, $\mathbf{I} = [\delta_{PQ}]$, with Φ removed from the determinant basis.

$$\tilde{\mathbf{H}} = [H_{PQ} - E_0 \delta_{PQ}] = [\langle \Phi_P | \hat{H}_e - E_0 | \Phi_Q \rangle], \quad \Phi_P \in \{\Phi_i^a\} \tag{4}$$

   Explain why the eigenvalues of this matrix

$$\tilde{\mathbf{H}}\mathbf{c}_K = \lambda_K \mathbf{c}_K \tag{5}$$

   are given by $\lambda_K = E_K - E_0$, where E_K is a CIS excited state energy. That is, diagonalizing $\tilde{\mathbf{H}}$ gives us the CIS excitation energies, $\Delta E_K = E_K - E_0$, directly.

4. Using Slater's rules, show that $\langle \Phi_i^a | \hat{H}_e | \Phi_j^b \rangle$ is equal to

   (a) $\langle aj || ib \rangle$ when $i \neq j$ and $a \neq b$

   (b) $f_{ab}\delta_{ij} + \langle aj || ib \rangle$ when $i = j$ and $a \neq b$

   (c) $-f_{ij}\delta_{ab} + \langle aj || ib \rangle$ when $i \neq j$ and $a = b$

   (d) $E_0 \delta_{ij}\delta_{ab} + f_{ab}\delta_{ij} - f_{ij}\delta_{ab} + \langle aj || ib \rangle$ when $i = j$ and $a = b$

5. Assuming a canonical Hartree-Fock reference, show that the matrix elements of $\tilde{\mathbf{H}}$ are given by the following expression.

$$\langle \Phi_i^a | \hat{H}_e - E_0 | \Phi_j^b \rangle = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle aj || ib \rangle \tag{6}$$

[1] See Helgaker, *Molecular Electronic-Structure Theory*, p.116