CIS Equations

For the Configuration Interaction method including only single excitations (CIS), we construct a Hamiltonian matrix in the basis of singly excited determinants to obtain a set of CIS energies.

1. Hamiltonian Matrix Structure

Recall that the electronic Hamiltonian in Φ-normal order is:

$$\hat{H}_e = E_{\mathrm{HF}} + f_p^q \tilde{a}_q^p + \tfrac{1}{4}\, \bar{g}_{pq}^{rs}\, \tilde{a}_{rs}^{pq}$$

The structure of the full configuration interaction (FCI) Hamiltonian matrix is:

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

In the CI Singles (CIS) approximation, we truncate the determinant basis at single excitations which gives the Hamiltonian matrix the following form:

$$\mathbf{H} = \begin{bmatrix} \langle \Phi | \hat{H}_e | \Phi \rangle & \langle \Phi | \hat{H}_e | \Phi_i^a \rangle \\ \langle \Phi_i^a | \hat{H}_e | \Phi \rangle & \langle \Phi_i^a | \hat{H}_e | \Phi_j^b \rangle \end{bmatrix}$$

Clearly $\langle \Phi | \hat{H}_e | \Phi \rangle = E_{\mathrm{HF}}$, the Hartree-Fock energy of the system.

$$\mathbf{H} = \begin{bmatrix} E_{\mathrm{HF}} & \langle \Phi | \hat{H}_e | \Phi_i^a \rangle \\ \langle \Phi_i^a | \hat{H}_e | \Phi \rangle & \langle \Phi_i^a | \hat{H}_e | \Phi_j^b \rangle \end{bmatrix}$$

Furthermore, we can apply Brillouin's theorem to show that $\langle \Phi_i^a | \hat{H}_e | \Phi \rangle = \langle \Phi_i^a | \hat{H}_e | \Phi \rangle = 0 \ \forall \ i, a$.

$$\mathbf{H} = \begin{bmatrix} E_{\mathrm{HF}} & \mathbf{0} \\ \mathbf{0} & \langle \Phi_i^a | \hat{H}_e | \Phi_j^b \rangle \end{bmatrix}$$

Now let's think about the matrix element $\langle \Phi_i^a | \hat{H}_e | \Phi_j^b \rangle$, which we can represent in the second quantization formalism.

$$\begin{aligned} \langle \Phi_i^a | \hat{H}_e | \Phi_j^b \rangle &= \langle \Phi | \tilde{a}_a^i \hat{H}_e \tilde{a}_j^b | \Phi \rangle \\ &= E_{\mathrm{HF}} \ \langle \Phi | \tilde{a}_a^i \tilde{a}_j^b | \Phi \rangle + \langle \Phi | \tilde{a}_a^i \left[f_p^q \tilde{a}_q^p + \tfrac{1}{4}\, \bar{g}_{pq}^{rs}\, \tilde{a}_{rs}^{pq} \right] \tilde{a}_j^b | \Phi \rangle \end{aligned}$$

By Slater's first rule,

$$= E_{\mathrm{HF}}\, \delta_{ij} \delta_{ab} + \langle \Phi | \tilde{a}_a^i \left[f_p^q \tilde{a}_q^p + \tfrac{1}{4}\, \bar{g}_{pq}^{rs}\, \tilde{a}_{rs}^{pq} \right] \tilde{a}_j^b | \Phi \rangle$$

If we define an eigenvalue-shifted correlation Hamiltonian $\hat{H}_c = f_p^q \tilde{a}_q^p + \frac{1}{4}\, \bar{g}_{pq}^{rs}\, \tilde{a}_{rs}^{pq}$,

$$= E_{\mathrm{HF}}\, \delta_{ij} \delta_{ab} + \langle \Phi | \tilde{a}_a^i \hat{H}_c \tilde{a}_j^b | \Phi \rangle$$

And the corresponding Hamiltonian matrix becomes

$$\begin{aligned} \mathbf{H} &= \begin{bmatrix} E_{\mathrm{HF}} & \mathbf{0} \\ \mathbf{0} & \langle \Phi_i^a | \hat{H}_c | \Phi_j^b \rangle + E_{\mathrm{HF}}\, \delta_{ij} \delta_{ab} \end{bmatrix} \\ &= \begin{bmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \langle \Phi_i^a | \hat{H}_c | \Phi_j^b \rangle \end{bmatrix} + E_{\mathrm{HF}}\, \mathbf{I} \\ &= \tilde{\mathbf{H}} + E_{\mathrm{HF}}\, \mathbf{I} \end{aligned}$$

We have constructed an eigenvalue-shifted $\tilde{\mathbf{H}} = \mathbf{H} - E_{\mathrm{HF}} \mathbf{I}$ which corresponds to the operator $\hat{H}_c = \hat{H}_e - E_{\mathrm{HF}}$. It has the same set of eigenstates as $\mathbf{H}$ but eigenvalues shifted down by E_{HF}. Since the first row and column are all zeros, we can clearly remove the first basis vector, which corresponds to the reference determinant Φ, from the basis and diagonalize $\tilde{\mathbf{H}}$ in the basis $\{\Phi_i^a\}$. Physically, this means that Φ is an eigenvector of $\hat{H}_c$ with eigenvalue 0, which means that the CIS correlation energy of the ground state Φ is 0. In other words, we will have to include higher excitations to observe correlation effects in the reference determinant.

2. Hamiltonian Matrix Elements

We'll write and solve for the matrix elements $\langle \Phi_i^a | \, \hat{H}_c \, | \Phi_j^b \rangle$ in the second quantization formalism.

$$\begin{aligned}
\tilde{\mathbf{H}}_{ijab} &= \langle \Phi | \, \tilde{a}_a^i \, \hat{H}_c \, \tilde{a}_j^b \, | \Phi \rangle \\
&= f_p^q \, \langle \Phi | \, \tilde{a}_a^i \, \tilde{a}_q^p \, \tilde{a}_j^b \, | \Phi \rangle + \tfrac{1}{4} \, \bar{g}_{pq}^{rs} \, \langle \Phi | \, \tilde{a}_a^i \, \tilde{a}_{rs}^{pq} \, \tilde{a}_j^b \, | \Phi \rangle
\end{aligned}$$

Applying Wick's theorem for Φ-normal ordered operators,

$$\begin{aligned}
&= f_p^q \left(\cancel{\langle \Phi | \, \colon\!\tilde{a}_a^i \, \tilde{a}_q^p \, \tilde{a}_j^b \colon\!| \Phi \rangle} + \langle \Phi | \, \colon\!\overline{\tilde{a}_a^i \, \tilde{a}_q^p} \, \tilde{a}_j^b \colon\!| \Phi \rangle \right) + \tfrac{1}{4} \, \bar{g}_{pq}^{rs} \left(\cancel{\langle \Phi | \, \colon\!\tilde{a}_a^i \, \tilde{a}_{rs}^{pq} \, \tilde{a}_j^b \colon\!| \Phi \rangle} + \langle \Phi | \, \colon\!\overline{\tilde{a}_a^i \, \tilde{a}_{rs}^{pq}} \, \tilde{a}_j^b \colon\!| \Phi \rangle \right) \\
&= f_p^q \left(0 + \colon\!\overline{\tilde{a}_a^i \, \tilde{a}_q^p} \, \tilde{a}_j^b \colon\! \right) + \tfrac{1}{4} \, \bar{g}_{pq}^{rs} \left(0 + \colon\!\overline{\tilde{a}_a^i \, \tilde{a}_{rs}^{pq}} \, \tilde{a}_j^b \colon\! \right) \\
&= f_p^q \left[\colon\!\tilde{a}_{a\circ}^{i\bullet} \tilde{a}_{q\bullet}^{p\bullet\bullet} \tilde{a}_{j\bullet\bullet}^{b\circ} \colon\! + \colon\!\tilde{a}_{a\circ}^{i\bullet} \tilde{a}_{q\circ\circ}^{p\circ} \tilde{a}_{j\bullet}^{b\circ\circ} \colon\! \right] + \tfrac{1}{4} \, \bar{g}_{pq}^{rs} \left[\hat{P}_{(r/s)}^{(p/q)} (\colon\!\tilde{a}_{a\circ}^{i\bullet} \tilde{a}_{r\circ\circ s\bullet}^{p\bullet\bullet q\circ} \, \tilde{a}_{j\bullet\bullet}^{b\circ\circ} \colon\!) \right] \\
&= f_p^q \left[\tilde{a}_{a\circ q\bullet j\bullet\bullet}^{i\bullet p\bullet\bullet b\circ} + \tilde{a}_{a\circ q\circ\circ j\bullet}^{i\bullet p\circ b\circ\circ} \right] + \tfrac{1}{4} \, \bar{g}_{pq}^{rs} \left[\hat{P}_{(r/s)}^{(p/q)} (\tilde{a}_{a\circ r\circ\circ s\bullet j\bullet\bullet}^{i\bullet p\bullet\bullet q\circ b\circ\circ}) \right] \\
&= f_p^q \left[\tilde{a}_{q\bullet j\bullet\bullet a\circ}^{i\bullet p\bullet\bullet b\circ} + \tilde{a}_{j\bullet a\circ q\circ\circ}^{i\bullet p\circ b\circ\circ} \right] + \tfrac{1}{4} \, \bar{g}_{pq}^{rs} \left[\hat{P}_{(r/s)}^{(p/q)} (\tilde{a}_{s\bullet j\bullet\bullet a\circ r\circ\circ}^{i\bullet p\bullet\bullet q\circ b\circ\circ}) \right] \\
&= f_p^q \left[\gamma_j^i \eta_a^p \eta_q^b - \gamma_q^i \gamma_j^p \eta_a^b \right] + \tfrac{1}{4} \, \bar{g}_{pq}^{rs} \left[\hat{P}_{(r/s)}^{(p/q)} [\, \gamma_s^i \gamma_j^p \eta_a^q \eta_r^b \,] \right] \\
&= f_p^q \left[\gamma_j^i \eta_a^p \eta_q^b - \gamma_q^i \gamma_j^p \eta_a^b \right] + \tfrac{1}{4} \, \bar{g}_{pq}^{rs} \left[\gamma_s^i \gamma_j^p \eta_q^a \eta_r^b - \gamma_s^i \gamma_j^q \eta_p^a \eta_r^b + \gamma_r^i \gamma_j^q \eta_p^a \eta_s^b - \gamma_r^i \gamma_j^p \eta_q^a \eta_s^b \right] \\
&= f_a^b \gamma_j^i - f_j^i \eta_a^b + \tfrac{1}{4} \left[\bar{g}_{ja}^{bi} - \bar{g}_{aj}^{bi} + \bar{g}_{aj}^{ib} - \bar{g}_{ja}^{ib} \right] \\
&= f_a^b \gamma_j^i - f_j^i \eta_a^b + \bar{g}_{ja}^{bi}
\end{aligned}$$

Recall that the SCF procedure constructs a diagonal Fock matrix whose diagonal elements are orbital energies:

$$f_a^b = f_a^a \delta_a^b = e_a \delta_a^b$$

Furthermore, if indices i, j loop over occupied and a, b loop over virtual orbitals, then $\gamma_i^j = \delta_i^j$ and $\eta_a^b = \delta_a^b$. So

$$\langle \Phi_i^a | \, \hat{H}_c \, | \Phi_j^b \rangle = (e_a - e_i) \delta_a^b \delta_j^i + \bar{g}_{ja}^{bi}$$

And these are the standard CIS equations.