CID Equations

1. Hamiltonian Matrix

We can shift the CID Hamiltonian by E_{HF} to consider only the correlation energy (see CIS notes for specifics).

$$\tilde{\mathbf{H}} = \begin{bmatrix} \cancel{\langle\Phi|\,\hat{H}_c\,|\Phi\rangle} & \langle\Phi|\,\hat{H}_c\,|\mathbf{\Phi}_{\mathrm{D}}\rangle \\ \langle\mathbf{\Phi}_{\mathrm{D}}|\,\hat{H}_c\,|\Phi\rangle & \langle\mathbf{\Phi}_{\mathrm{D}}|\,\hat{H}_c\,|\mathbf{\Phi}_{\mathrm{D}}\rangle \end{bmatrix}$$

where $|\mathbf{\Phi}_{\mathrm{D}}\rangle = \hat{C}_2\,|\Phi\rangle$ is a vector with elements $|\Phi_{ij}^{ab}\rangle$.

2. Hamiltonian Matrix Elements

W'll first evaluate the off-diagonal matrix elements $\langle\Phi|\,\hat{H}_c\,|\mathbf{\Phi}_{\mathrm{D}}\rangle = \langle\mathbf{\Phi}_{\mathrm{D}}|\,\hat{H}_c\,|\Phi\rangle^{\mathrm{T}}$, because $\hat{H}_c$ is Hermitian. Thus,

$$\begin{aligned} [\langle\mathbf{\Phi}_{\mathrm{D}}|\,\hat{H}_c\,|\Phi\rangle]_{ijab} &= \langle\Phi_{ij}^{ab}|\,\hat{H}_c\,|\Phi\rangle \\ [\langle\Phi|\,\hat{H}_c\,|\mathbf{\Phi}_{\mathrm{D}}\rangle]_{ijab} &= \langle\Phi|\,\hat{H}_c\,|\Phi_{ij}^{ab}\rangle \end{aligned}$$

Applying the Slater-Condon rules,

$$\begin{aligned} [\langle\mathbf{\Phi}_{\mathrm{D}}|\,\hat{H}_c\,|\Phi\rangle]_{ijab} &= \langle ij||ab\rangle \\ [\langle\Phi|\,\hat{H}_c\,|\mathbf{\Phi}_{\mathrm{D}}\rangle]_{ijab} &= \langle ab||ij\rangle \end{aligned}$$

Because the two-electron integral tensor is Hermitian, $\langle ij||ab\rangle = \langle ab||ij\rangle$.

Thus $\langle\mathbf{\Phi}_{\mathrm{D}}|\,\hat{H}_c\,|\Phi\rangle^{\dagger} = \langle\Phi|\,\hat{H}_c\,|\mathbf{\Phi}_{\mathrm{D}}\rangle$ are column vectors with entries $\langle ij||ab\rangle$.

Next consider $[\langle\mathbf{\Phi}_{\mathrm{D}}|\,\hat{H}_c\,|\mathbf{\Phi}_{\mathrm{D}}\rangle]_{ijab,klcd}$.

$$\begin{aligned} \langle\mathbf{\Phi}_{\mathrm{D}}|\,\hat{H}_c\,|\mathbf{\Phi}_{\mathrm{D}}\rangle]_{ijab,klcd} &= \langle\Phi|\,\tilde{a}_{ab}^{ij}\hat{H}_c\tilde{a}_{kl}^{cd}\,|\Phi\rangle \quad \text{(second quantization formalism).} \\ &= f_p^q\,\langle\Phi|\,\tilde{a}_{ab}^{ij}\tilde{a}_q^p\tilde{a}_{kl}^{cd}\,|\Phi\rangle + \frac{1}{4}\bar{g}_{pq}^{rs}\,\langle\Phi|\,\tilde{a}_{ab}^{ij}\tilde{a}_{rs}^{pq}\tilde{a}_{kl}^{cd}\,|\Phi\rangle \end{aligned}$$

We'll evaluate the necessary matrix elements separately.

$$\begin{aligned} \langle\Phi|\,\tilde{a}_{ab}^{ij}\,\tilde{a}_q^p\,\tilde{a}_{kl}^{cd}\,|\Phi\rangle &= \cancel{\langle\Phi|\,\vdots\tilde{a}_{ab}^{ij}\tilde{a}_q^p\tilde{a}_{kl}^{cd}\vdots\,|\Phi\rangle} + \langle\Phi|\,\vdots\overline{\tilde{a}_{ab}^{ij}\tilde{a}_q^p\tilde{a}_{kl}^{cd}}\vdots\,|\Phi\rangle \\ &= 0 + \vdots\overline{\tilde{a}_{ab}^{ij}\tilde{a}_q^p\tilde{a}_{kl}^{cd}}\vdots \\ &= \hat{P}_{(k/l)}^{(a/b\,|\,c/d)}\left[\vdots\tilde{a}_{a^{\circ1}b^{\circ2}}^{i^{\bullet1}j^{\bullet2}}\tilde{a}_{q^{\circ3}}^{p^{\circ1}}\tilde{a}_{k^{\bullet1}l^{\bullet2}}^{c^{\circ2}d^{\circ3}}\vdots\right] + \hat{P}_{(k/l)}^{(i/j|c/d)}\left[\vdots\tilde{a}_{a^{\circ1}b^{\circ2}}^{i^{\bullet1}j^{\bullet2}}\tilde{a}_{q^{\bullet1}}^{p^{\bullet3}}\tilde{a}_{k^{\bullet2}l^{\bullet3}}^{c^{\circ1}d^{\circ2}}\vdots\right] \\ &= \hat{P}_{(k/l)}^{(a/b|c/d)}\left[\vdots\tilde{a}_{a^{\circ1}b^{\circ2}q^{\circ3}k^{\bullet1}l^{\bullet2}}^{i^{\bullet1}j^{\bullet2}p^{\circ1}c^{\circ2}d^{\circ3}}\vdots\right] + \hat{P}_{(k/l)}^{(i/j\,|\,c/d)}\left[\vdots\tilde{a}_{a^{\circ1}b^{\circ2}q^{\bullet1}k^{\bullet2}l^{\bullet3}}^{i^{\bullet1}j^{\bullet2}p^{\bullet3}c^{\circ2}d^{\circ3}}\vdots\right] \\ &= \hat{P}_{(k/l)}^{(a/b|c/d)}\left[\vdots\tilde{a}_{k^{\bullet1}l^{\bullet2}a^{\circ1}b^{\circ2}q^{\circ3}}^{i^{\bullet1}j^{\bullet2}p^{\circ1}c^{\circ2}d^{\circ3}}\vdots\right] + \hat{P}_{(k/l)}^{(i/j|c/d)}\left[\vdots\tilde{a}_{q^{\bullet1}k^{\bullet2}l^{\bullet3}a^{\circ1}b^{\circ2}}^{i^{\bullet1}j^{\bullet2}p^{\bullet3}c^{\circ2}d^{\circ3}}\vdots\right] \\ &= -\hat{P}_{(k/l)}^{(a/b|c/d)}\left[\tilde{a}_{k^{\bullet1}l^{\bullet2}a^{\circ1}b^{\circ2}q^{\circ3}}^{i^{\bullet1}j^{\bullet2}p^{\circ1}d^{\circ2}c^{\circ3}}\right] - \hat{P}_{(k/l)}^{(i/j|c/d)}\left[\tilde{a}_{q^{\bullet1}l^{\bullet2}k^{\bullet3}a^{\circ1}b^{\circ2}}^{i^{\bullet1}j^{\bullet2}p^{\bullet3}c^{\circ2}d^{\circ3}}\right] \\ &= \hat{P}_{(k/l)}^{(a/b|c/d)}\left[\gamma_k^i\gamma_l^j\eta_a^p\eta_b^d\eta_q^c\right] - \hat{P}_{(k/l)}^{(i/j|c/d)}\left[\gamma_q^i\gamma_l^j\gamma_k^p\eta_a^c\eta_b^d\right] \end{aligned}$$

Since indices i, j, k, l correspond only to occupied orbitals and indices a, b, c, d correspond only to virtual orbitals,

$$= \hat{P}_{(k/l)}^{(a/b|c/d)}\left[\delta_{ki}\delta_{lj}\delta_{ap}\delta_{bd}\delta_{qc}\right] - \hat{P}_{(k/l)}^{(i/j|c/d)}\left[\delta_{qi}\delta_{lj}\delta_{kp}\delta_{ac}\delta_{bd}\right]$$

$$
\begin{aligned}
\langle\Phi|\, \tilde{a}^{ij}_{ab}\, \tilde{a}^{pq}_{rs}\, \tilde{a}^{cd}_{kl}\, |\Phi\rangle &= \cancel{\langle\Phi|\, \vdots\tilde{a}^{ij}_{ab}\tilde{a}^{pq}_{rs}\tilde{a}^{cd}_{kl}\vdots\, |\Phi\rangle} + \langle\Phi|\, \vdots\overline{\tilde{a}^{ij}_{ab}\tilde{a}^{pq}_{rs}\tilde{a}^{cd}_{kl}}\vdots\, |\Phi\rangle \\
&= 0 + \vdots\overline{\tilde{a}^{ij}_{ab}\tilde{a}^{pq}_{rs}\tilde{a}^{cd}_{kl}}\vdots \\
&= \hat{P}^{(i/j|c/d)}_{(k/l)} \left[\vdots\tilde{a}^{i^{\bullet 1}j^{\bullet 2}}_{a^{\circ 1}b^{\circ 2}}\tilde{a}^{p^{\bullet 3}q^{\bullet 4}}_{r^{\bullet 1}s^{\bullet 2}}\tilde{a}^{c^{\circ 1}d^{\circ 2}}_{k^{\bullet 3}l^{\bullet 4}}\vdots\right] + \hat{P}^{(a/b|c/d)}_{(k/l)} \left[\vdots\tilde{a}^{i^{\bullet 1}j^{\bullet 2}}_{a^{\circ 1}b^{\circ 2}}\tilde{a}^{p^{\circ 1}q^{\circ 2}}_{r^{\circ 3}s^{\circ 4}}\tilde{a}^{c^{\circ 3}d^{\circ 4}}_{k^{\bullet 1}l^{\bullet 2}}\vdots\right] \\
&+ \hat{P}^{(a/b|c/d|r/s)}_{(i/j|k/l|p/q)} \left[\vdots\tilde{a}^{i^{\bullet 1}j^{\bullet 2}}_{a^{\circ 1}b^{\circ 2}}\tilde{a}^{p^{\bullet 3}q^{\circ 1}}_{r^{\circ 3}s^{\bullet 1}}\tilde{a}^{c^{\circ 2}d^{\circ 3}}_{k^{\bullet 2}l^{\bullet 3}}\vdots\right] \\
&= \hat{P}^{(i/j|c/d)}_{(k/l)} \left[\tilde{a}^{i^{\bullet 1}j^{\bullet 2}p^{\bullet 3}q^{\bullet 4}c^{\circ 1}d^{\circ 2}}_{a^{\circ 1}b^{\circ 2}r^{\bullet 1}s^{\bullet 2}k^{\bullet 3}l^{\bullet 4}}\right] + \hat{P}^{(a/b|c/d)}_{(k/l)} \left[\tilde{a}^{i^{\bullet 1}j^{\bullet 2}p^{\circ 1}q^{\circ 2}c^{\circ 3}d^{\circ 4}}_{a^{\circ 1}b^{\circ 2}r^{\circ 3}s^{\circ 4}k^{\bullet 1}l^{\bullet 2}}\right] + \hat{P}^{(a/b|c/d|r/s)}_{(i/j|k/l|p/q)} \left[\tilde{a}^{i^{\bullet 1}j^{\bullet 2}p^{\bullet 3}q^{\circ 1}c^{\circ 2}d^{\circ 3}}_{a^{\circ 1}b^{\circ 2}r^{\circ 3}s^{\bullet 1}k^{\bullet 2}l^{\bullet 3}}\right] \\
&= \hat{P}^{(i/j|c/d)}_{(k/l)} \left[\tilde{a}^{i^{\bullet 1}j^{\bullet 2}p^{\bullet 3}q^{\bullet 4}c^{\circ 1}d^{\circ 2}}_{r^{\bullet 1}s^{\bullet 2}k^{\bullet 3}l^{\bullet 4}a^{\circ 1}b^{\circ 2}}\right] + \hat{P}^{(a/b|c/d)}_{(k/l)} \left[\tilde{a}^{i^{\bullet 1}j^{\bullet 2}p^{\circ 1}q^{\circ 2}c^{\circ 3}d^{\circ 4}}_{k^{\bullet 1}l^{\bullet 2}a^{\circ 1}b^{\circ 2}r^{\circ 3}s^{\circ 4}}\right] - \hat{P}^{(a/b|c/d|r/s)}_{(i/j|k/l|p/q)} \left[\tilde{a}^{i^{\bullet 1}j^{\bullet 2}p^{\bullet 3}q^{\circ 1}c^{\circ 2}d^{\circ 3}}_{s^{\bullet 1}k^{\bullet 2}l^{\bullet 3}a^{\circ 1}b^{\circ 2}r^{\circ 3}}\right] \\
&= \hat{P}^{(i/j|c/d)}_{(k/l)} \left[\gamma^i_r\gamma^j_s\gamma^p_k\gamma^q_l\eta^c_a\eta^d_b\right] + \hat{P}^{(a/b|c/d)}_{(k/l)} \left[\gamma^i_k\gamma^j_l\eta^p_a\eta^q_b\eta^c_r\eta^d_s\right] + \hat{P}^{(a/b|c/d|r/s)}_{(i/j|k/l|p/q)} \left[\gamma^i_s\gamma^j_k\gamma^p_l\eta^q_a\eta^c_b\eta^d_r\right] \\
&= \hat{P}^{(i/j|c/d)}_{(k/l)} \left[\delta^i_r\delta^j_s\delta^p_k\delta^q_l\delta^c_a\delta^d_b\right] + \hat{P}^{(a/b|c/d)}_{(k/l)} \left[\delta^i_k\delta^j_l\delta^p_a\delta^q_b\delta^c_r\delta^d_s\right] + \hat{P}^{(a/b|c/d|r/s)}_{(i/j|k/l|p/q)} \left[\delta^i_s\delta^j_k\delta^p_l\delta^q_a\delta^c_b\delta^d_r\right]
\end{aligned}
$$

Now we can apply the expressions for these matrix elements to our expression for elements of the Hamiltonian.

$$
\begin{aligned}
\langle\Phi^{ab}_{ij}|\, \hat{H}_c\, |\Phi^{cd}_{kl}\rangle &= \hat{P}^{(a/b|c/d)}_{(k/l)} \left[f^q_p\delta^i_k\delta^j_l\delta^p_a\delta^d_b\delta^c_q\right] - \hat{P}^{(i/j|c/d)}_{(k/l)} \left[f^q_p\delta^i_q\delta^j_l\delta^p_k\delta^c_a\delta^d_b\right] \\
&+ \tfrac{1}{4}\left(\hat{P}^{(i/j|c/d)}_{(k/l)} \left[\bar{g}^{rs}_{pq}\delta^i_r\delta^j_s\delta^p_k\delta^q_l\delta^c_a\delta^d_b\right] + \hat{P}^{(a/b|c/d)}_{(k/l)} \left[\bar{g}^{rs}_{pq}\delta^i_k\delta^j_l\delta^p_a\delta^q_b\delta^c_r\delta^d_s\right] + \hat{P}^{(a/b|c/d|r/s)}_{(i/j|k/l|p/q)} \left[\bar{g}^{rs}_{pq}\delta^i_s\delta^j_k\delta^p_l\delta^q_a\delta^c_b\delta^d_r\right]\right) \\
&= \hat{P}^{(a/b|c/d)}_{(k/l)} \left[f^c_a\delta^i_k\delta^j_l\delta^d_b\right] - \hat{P}^{(i/j|c/d)}_{(k/l)} \left[f^i_k\delta^j_l\delta^c_a\delta^d_b\right] \\
&+ \tfrac{1}{4}\left(\hat{P}^{(i/j|c/d)}_{(k/l)} \left[\bar{g}^{ij}_{kl}\delta^c_a\delta^d_b\right] + \hat{P}^{(a/b|c/d)}_{(k/l)} \left[\bar{g}^{cd}_{ab}\delta^i_k\delta^j_l\right] + 4\hat{P}^{(a/b|c/d)}_{(i/j|k/l)} \left[\bar{g}^{di}_{la}\delta^j_k\delta^c_b\right]\right) \\
&= \hat{P}^{(a/b|c/d)}_{(k/l)} \left[f^c_a\delta^i_k\delta^j_l\delta^d_b\right] - \hat{P}^{(i/j|c/d)}_{(k/l)} \left[f^i_k\delta^j_l\delta^c_a\delta^d_b\right] \\
&+ \tfrac{1}{4}\left(4\hat{P}^{(c/d)} \left[\bar{g}^{ij}_{kl}\delta^c_a\delta^d_b\right] + 4\hat{P}^{(k/l)} \left[\bar{g}^{cd}_{ab}\delta^i_k\delta^j_l\right] + 4\hat{P}^{(a/b|c/d)}_{(i/j|k/l)} \left[\bar{g}^{di}_{la}\delta^j_k\delta^c_b\right]\right) \\
&= \hat{P}^{(a/b|c/d)}_{(k/l)} \left[f^c_a\delta^i_k\delta^j_l\delta^d_b\right] - \hat{P}^{(i/j|c/d)}_{(k/l)} \left[f^i_k\delta^j_l\delta^c_a\delta^d_b\right] + \hat{P}^{(c/d)} \left[\bar{g}^{ij}_{kl}\delta^c_a\delta^d_b\right] + \hat{P}^{(k/l)} \left[\bar{g}^{cd}_{ab}\delta^i_k\delta^j_l\right] + \hat{P}^{(a/b|c/d)}_{(i/j|k/l)} \left[\bar{g}^{di}_{la}\delta^j_k\delta^c_b\right]
\end{aligned}
$$

Now we having everything necessary to build the CID matrix. However, it is almost always too expensive to diagonalize, even for small systems. Furthermore, a matrix diagonalization gives us a lot of unnecessary information. We are really only interested in the ground state eigenvalue, which is a good approximation to the ground state correlation energy. The other eigenvalues of the CID Hamiltonian – corresponding to excited state correlation energies – are not very good. Thus, it makes sense to approach this problem from a different direction.

3. Iterative CID

The main idea that most modern CI codes is to write an expression for the correlation energy in terms of doubly excited coefficients and derive a set of amplitude equations which can be used to solve iteratively for those doubly excited coefficients and that's how we obtain a correlation energy.

i. Energy Expression

Start with the Schrödinger equation:

$$\hat{H}_c\, |\Psi_{\mathrm{CID}}\rangle = E_c\, |\Psi_{\mathrm{CID}}\rangle$$

Impose the intermediate normalization condition, $\langle\Phi|\Psi_{\mathrm{CID}}\rangle = 1$, and left- project with $\langle\Phi|$.

$$
\begin{aligned}
\langle\Phi|\, \hat{H}_c\, |\Psi_{\mathrm{CID}}\rangle &= E_c\, \langle\Phi|\Psi_{\mathrm{CID}}\rangle \\
&= E_c
\end{aligned}
$$

Now using $|\Psi_{\text{CID}}\rangle = (1 + \hat{C}_2)|\Phi\rangle$,

$$
\begin{aligned}
E_c &= \cancel{\langle\Phi|\hat{H}_c|\Phi\rangle} + \langle\Phi|\hat{H}_c\hat{C}_2|\Phi\rangle \\
&= \tfrac{1}{4}c^{ij}_{ab}\langle\Phi|\hat{H}_c\tilde{a}^{ab}_{ij}|\Phi\rangle
\end{aligned}
$$

Where we have used Einstein notation, implying that repeated indices are implicitly summed over. We can simplify this expression further using Wick's theorem to obtain

$$
E_c = \tfrac{1}{4}c^{ij}_{ab}\,\bar{g}^{ab}_{ij}
$$

This is a surprisingly simple expression, and it is not an approximation within the specified basis set. If we were able to solve for the coefficients c^{ij}_{ab}, this expression would give us the exact FCI energy. But now we need to think about how to obtain these double excitation coefficients.

ii. Amplitude Equations

We'll start again with the Schrödinger equation but left-project a doubly-excited determinant, Φ^{ab}_{ij} this time.

$$
\begin{aligned}
\langle\Phi^{ab}_{ij}|\hat{H}_c|\Psi_{\text{CID}}\rangle &= E_c\langle\Phi^{ab}_{ij}|\Psi_{\text{CID}}\rangle \\
\langle\Phi^{ab}_{ij}|\hat{H}_c(1+\hat{C}_2)|\Phi\rangle &= E_c\langle\Phi^{ab}_{ij}|(1+\hat{C}_2)\Phi\rangle
\end{aligned}
$$

Simplifying the right-hand side,

$$
\begin{aligned}
E_c\langle\Phi^{ab}_{ij}|(1+\hat{C}_2)\Phi\rangle &= E_c\cancel{\langle\Phi^{ab}_{ij}|\Phi\rangle} + E_c\langle\Phi^{ab}_{ij}|\hat{C}_2\Phi\rangle \\
&= E_c\tfrac{1}{4}\sum_{klcd}c^{kl}_{cd}\langle\Phi^{ab}_{ij}|\Phi^{cd}_{kl}\rangle \\
&= E_c\tfrac{1}{4}\sum_{klcd}c^{kl}_{cd}\hat{P}^{(i/j)}_{(a/b)}(\delta_{ac}\delta_{bd}\delta_{ik}\delta_{jl}) \\
&= E_c c^{ij}_{ab}
\end{aligned}
$$

Now consider the left-hand side (in Einstein notation):

$$
\langle\Phi^{ab}_{ij}|\hat{H}_c(1+\hat{C}_2)|\Phi\rangle = \langle\Phi^{ab}_{ij}|\hat{H}_c|\Phi\rangle + \tfrac{1}{4}c^{kl}_{cd}\langle\Phi^{ab}_{ij}|\hat{H}_c|\Phi\rangle
$$

Now we set the sides equal to each other in order to obtain the amplitude equation for the excitation $ij \to ab$.

$$
E_c c^{ij}_{ab} = \langle\Phi^{ab}_{ij}|\hat{H}_c|\Phi\rangle + \tfrac{1}{4}c^{kl}_{cd}\langle\Phi^{ab}_{ij}|\hat{H}_c|\Phi^{cd}_{kl}\rangle
$$

These are the formal CID amplitude equations, which we can simplify by plugging in our previously obtained results for these matrix elements:

$$
\begin{aligned}
E_c c^{ij}_{ab} &= \langle ij||ab\rangle \\
&\quad + \tfrac{1}{4}c^{kl}_{cd}\left(\hat{P}^{(a/b|c/d)}_{(k/l)}\left[f^c_a\delta^i_k\delta^j_l\delta^d_b\right] - \hat{P}^{(i/j|c/d)}_{(k/l)}\left[f^i_k\delta^j_l\delta^c_a\delta^d_b\right] + \hat{P}^{(c/d)}\left[\bar{g}^{ij}_{kl}\delta^c_a\delta^d_b\right] + \hat{P}^{(k/l)}\left[\bar{g}^{cd}_{ab}\delta^i_k\delta^j_l\right] + \hat{P}^{(a/b|c/d)}_{(i/j|k/l)}\left[\bar{g}^{di}_{la}\delta^j_k\delta^c_b\right]\right)
\end{aligned}
$$