Programming Project 8 Theory
Deriving CCD equations in Kutzelnigg-Mukherjee tensor notation

The electronic Hamiltonian can be expressed as follows.

$$H_e = E_{\mathrm{HF}} + H_c \qquad\qquad E_{\mathrm{HF}} = \langle\Phi|H_e|\Phi\rangle \qquad\qquad H_c = f_p^q \tilde{a}_q^p + \tfrac{1}{4}\overline{g}_{pq}^{rs}\tilde{a}_{rs}^{pq} \tag{1}$$

The CCD approximation parametrizes the wavefunction as $\Psi \approx e^{\hat{T}_2}\Phi$ where $\hat{T}_2 = \frac{1}{4}t_{ab}^{ij}a_{ij}^{ab}$. Substituting this ansatz into the Schrödinger equation and projecting by Φ and Φ_{ij}^{ab} gives the following system of equations.

$$E_c = \langle\Phi|H_c e^{\hat{T}_2}\Phi|\Phi\rangle \qquad \Longrightarrow \qquad E_c = \tfrac{1}{4}\langle\Phi|H_c|\Phi_{kl}^{cd}\rangle t_{cd}^{kl} \tag{2}$$

$$E_c t_{ab}^{ij} = \langle\Phi_{ij}^{ab}|H_c e^{\hat{T}_2}\Phi|\Phi\rangle \qquad \Longrightarrow \qquad E_c t_{ab}^{ij} = \langle\Phi_{ij}^{ab}|H_c|\Phi\rangle + \tfrac{1}{4}\langle\Phi_{ij}^{ab}|H_c|\Phi_{kl}^{cd}\rangle t_{cd}^{kl} + \tfrac{1}{2}\left(\tfrac{1}{4}\right)^2\langle\Phi_{ij}^{ab}|H_c|\Phi_{klmn}^{cdef}\rangle t_{cd}^{kl}t_{ef}^{mn} \tag{3}$$

The non-trivial terms to be evaluated are

$$\tfrac{1}{4}\langle\Phi_{ij}^{ab}|H_c|\Phi_{kl}^{cd}\rangle t_{cd}^{kl} = \tfrac{1}{4}f_p^q t_{cd}^{kl}(\tilde{a}_{ab}^{ij}\tilde{a}_q^p\tilde{a}_{kl}^{cd})_{\mathrm{f.c.}} + \left(\tfrac{1}{4}\right)^2\overline{g}_{pq}^{rs}t_{cd}^{kl}(\tilde{a}_{ab}^{ij}\tilde{a}_{rs}^{pq}\tilde{a}_{kl}^{cd})_{\mathrm{f.c.}} \tag{4}$$

$$\tfrac{1}{2}\left(\tfrac{1}{4}\right)^2\langle\Phi_{ij}^{ab}|H_c|\Phi_{klmn}^{cdef}\rangle t_{cd}^{kl}t_{ef}^{mn} = \tfrac{1}{2}\left(\tfrac{1}{4}\right)^3\overline{g}_{pq}^{rs}t_{cd}^{kl}t_{ef}^{mn}(\tilde{a}_{ab}^{ij}\tilde{a}_{rs}^{pq}\tilde{a}_{kl}^{cd}\tilde{a}_{mn}^{ef})_{\mathrm{f.c.}} \tag{5}$$

where $(\tilde{a}_{ab}^{ij}\tilde{a}_q^p\tilde{a}_{kl}^{cd})_{\mathrm{f.c.}}$ and $(\tilde{a}_{ab}^{ij}\tilde{a}_{rs}^{pq}\tilde{a}_{kl}^{cd})_{\mathrm{f.c.}}$ can be determined using Wick's theorem

$$\begin{aligned}
(\tilde{a}_{ab}^{ij}\tilde{a}_q^p\tilde{a}_{kl}^{cd})_{\mathrm{f.c.}} &= \hat{P}_{(a/b|k/l)}^{(c/d)}\,\vdots\tilde{a}_{a^{\bullet 1}b^{\bullet 3}}^{i^{\circ 1}j^{\circ 2}}\tilde{a}_{q^{\bullet 2}}^{p^{\bullet 1}}\tilde{a}_{k^{\circ 1}l^{\circ 2}}^{c^{\bullet 2}d^{\bullet 3}}\vdots + \hat{P}_{(k/l)}^{(i/j|c/d)}\,\vdots\tilde{a}_{a^{\bullet 1}b^{\bullet 2}}^{i^{\circ 1}j^{\circ 3}}\tilde{a}_{q^{\circ 1}}^{p^{\circ 2}}\tilde{a}_{k^{\circ 2}l^{\circ 3}}^{c^{\bullet 1}d^{\bullet 2}}\vdots \\
&= \hat{P}_{(a/b|k/l)}^{(c/d)}\eta_a^p\eta_q^c\eta_b^d\gamma_k^i\gamma_l^j - \hat{P}_{(k/l)}^{(i/j|c/d)}\gamma_q^i\gamma_k^p\gamma_l^j\eta_a^c\eta_b^d \\
(\tilde{a}_{ab}^{ij}\tilde{a}_{rs}^{pq}\tilde{a}_{kl}^{cd})_{\mathrm{f.c.}} &= \hat{P}_{(a/b|k/l)}^{(c/d)}\,\vdots\tilde{a}_{a^{\bullet 1}b^{\bullet 2}}^{i^{\circ 1}j^{\circ 2}}\tilde{a}_{r^{\bullet 3}s^{\bullet 4}}^{p^{\bullet 1}q^{\bullet 2}}\tilde{a}_{k^{\circ 1}l^{\circ 2}}^{c^{\bullet 3}d^{\bullet 4}}\vdots + \hat{P}_{(k/l)}^{(i/j|c/d)}\,\vdots\tilde{a}_{a^{\bullet 1}b^{\bullet 2}}^{i^{\circ 1}j^{\circ 2}}\tilde{a}_{r^{\circ 1}s^{\circ 2}}^{p^{\circ 3}q^{\circ 4}}\tilde{a}_{k^{\circ 3}l^{\circ 4}}^{c^{\bullet 1}d^{\bullet 2}}\vdots \\
&\quad + \hat{P}_{(r/s|k/l|a/b)}^{(p/q|i/j|c/d)}\,\vdots\tilde{a}_{a^{\bullet 1}b^{\bullet 3}}^{i^{\circ 1}j^{\circ 3}}\tilde{a}_{r^{\circ 1}s^{\bullet 2}}^{p^{\circ 2}q^{\bullet 1}}\tilde{a}_{k^{\circ 2}l^{\circ 3}}^{c^{\bullet 2}d^{\bullet 3}}\vdots \\
&= \hat{P}_{(a/b|k/l)}^{(c/d)}\eta_a^p\eta_b^q\eta_r^c\eta_s^d\gamma_k^i\gamma_l^j + \hat{P}_{(k/l)}^{(i/j|c/d)}\gamma_r^i\gamma_s^j\gamma_k^p\gamma_l^q\eta_a^c\eta_b^d - \hat{P}_{(r/s|k/l|a/b)}^{(p/q|i/j|c/d)}\gamma_r^i\gamma_k^p\gamma_l^j\eta_a^q\eta_s^c\eta_b^d \\
(\tilde{a}_{ab}^{ij}\tilde{a}_{rs}^{pq}\tilde{a}_{kl}^{cd}\tilde{a}_{mn}^{ef})_{\mathrm{f.c.}} &= 2\hat{P}_{(k/l|m/n)}^{(c/d|e/f)}\,\vdots\tilde{a}_{a^{\bullet 1}b^{\bullet 2}}^{i^{\circ 1}j^{\circ 2}}\tilde{a}_{r^{\bullet 3}s^{\bullet 4}}^{p^{\circ 3}q^{\circ 4}}\tilde{a}_{k^{\circ 1}l^{\circ 2}}^{c^{\bullet 1}d^{\bullet 2}}\tilde{a}_{m^{\circ 3}n^{\circ 4}}^{e^{\bullet 3}f^{\bullet 4}}\vdots \\
&\quad + 2\hat{P}_{(a/b|r/s|k/l|m/n)}^{(c/d|e/f)}\,\vdots\tilde{a}_{a^{\bullet 1}b^{\bullet 2}}^{i^{\circ 1}j^{\circ 2}}\tilde{a}_{r^{\bullet 3}s^{\bullet 4}}^{p^{\circ 3}q^{\circ 4}}\tilde{a}_{k^{\circ 1}l^{\circ 2}}^{c^{\bullet 1}d^{\bullet 3}}\tilde{a}_{m^{\circ 3}n^{\circ 4}}^{e^{\bullet 2}f^{\bullet 4}}\vdots \\
&\quad + 2\hat{P}_{(k/l|m/n)}^{(i/j|p/q|c/d|e/f)}\,\vdots\tilde{a}_{a^{\bullet 1}b^{\bullet 2}}^{i^{\circ 1}j^{\circ 2}}\tilde{a}_{r^{\bullet 3}s^{\bullet 4}}^{p^{\circ 3}q^{\circ 4}}\tilde{a}_{k^{\circ 1}l^{\circ 3}}^{c^{\bullet 1}d^{\bullet 2}}\tilde{a}_{m^{\circ 2}n^{\circ 4}}^{e^{\bullet 3}f^{\bullet 4}}\vdots \\
&\quad + 2\hat{P}_{(k/l|m/n)}^{(c/d|e/f)}\,\vdots\tilde{a}_{a^{\bullet 1}b^{\bullet 2}}^{i^{\circ 1}j^{\circ 2}}\tilde{a}_{r^{\bullet 3}s^{\bullet 4}}^{p^{\circ 3}q^{\circ 4}}\tilde{a}_{k^{\circ 1}l^{\circ 2}}^{c^{\bullet 3}d^{\bullet 4}}\tilde{a}_{m^{\circ 3}n^{\circ 4}}^{e^{\bullet 1}f^{\bullet 2}}\vdots \\
&\quad + \hat{P}_{(a/b|r/s|k/l|m/n)}^{(i/j|p/q|c/d|e/f)}\,\vdots\tilde{a}_{a^{\bullet 1}b^{\bullet 2}}^{i^{\circ 1}j^{\circ 2}}\tilde{a}_{r^{\bullet 3}s^{\bullet 4}}^{p^{\circ 3}q^{\circ 4}}\tilde{a}_{k^{\circ 1}l^{\circ 3}}^{c^{\bullet 1}d^{\bullet 3}}\tilde{a}_{m^{\circ 2}n^{\circ 4}}^{e^{\bullet 2}f^{\bullet 4}}\vdots \\
&= 2\hat{P}_{(k/l|m/n)}^{(c/d|e/f)}\gamma_k^i\gamma_l^j\gamma_m^p\gamma_n^q\eta_a^c\eta_b^d\eta_r^e\eta_s^f \\
&\quad - 2\hat{P}_{(a/b|r/s|k/l|m/n)}^{(c/d|e/f)}\gamma_k^i\gamma_l^j\gamma_m^p\gamma_n^q\eta_a^c\eta_b^e\eta_r^d\eta_s^f \\
&\quad - 2\hat{P}_{(k/l|m/n)}^{(i/j|p/q|c/d|e/f)}\gamma_k^i\gamma_m^j\gamma_l^p\gamma_n^q\eta_a^c\eta_b^d\eta_r^e\eta_s^f \\
&\quad + 2\hat{P}_{(k/l|m/n)}^{(c/d|e/f)}\gamma_k^i\gamma_l^j\gamma_m^p\gamma_n^q\eta_a^e\eta_b^f\eta_r^c\eta_s^d \\
&\quad + \hat{P}_{(a/b|r/s|k/l|m/n)}^{(i/j|p/q|c/d|e/f)}\gamma_k^i\gamma_m^j\gamma_l^p\gamma_n^q\eta_a^c\eta_b^e\eta_r^d\eta_s^f
\end{aligned}$$

giving the following.

$$
\begin{aligned}
\tfrac{1}{4} f_p^q t_{cd}^{kl} (\tilde{a}_{ab}^{ij} \tilde{a}_q^p \tilde{a}_{kl}^{cd})_{\text{f.c.}} &= f_p^q t_{cd}^{kl} \hat{P}_{(a/b)} \eta_a^p \eta_q^c \eta_b^d \gamma_k^i \gamma_l^j - f_p^q t_{cd}^{kl} \hat{P}^{(i/j)} \gamma_q^i \gamma_k^p \gamma_l^j \eta_a^c \eta_b^d \\
&= \hat{P}_{(a/b)} f_a^c t_{cb}^{ij} - \hat{P}^{(i/j)} f_k^i t_{ab}^{kj} \\
\left(\tfrac{1}{4}\right)^2 \overline{g}_{pq}^{rs} t_{cd}^{kl} (\tilde{a}_{ab}^{ij} \tilde{a}_{rs}^{pq} \tilde{a}_{kl}^{cd})_{\text{f.c.}} &= \tfrac{1}{4} \overline{g}_{pq}^{rs} t_{cd}^{kl} \hat{P}_{(a/b)} \eta_a^p \eta_b^q \eta_r^c \eta_s^d \gamma_k^i \gamma_l^j + \tfrac{1}{4} \overline{g}_{pq}^{rs} t_{cd}^{kl} \hat{P}^{(i/j)} \gamma_r^i \gamma_s^j \gamma_k^p \gamma_l^q \eta_a^c \eta_b^d \\
&\quad - \overline{g}_{pq}^{rs} t_{cd}^{kl} \hat{P}_{(a/b)}^{(i/j)} \gamma_r^i \gamma_k^p \gamma_l^j \eta_a^q \eta_s^c \eta_b^d \\
&= \tfrac{1}{4} \hat{P}_{(a/b)} \overline{g}_{ab}^{cd} t_{cd}^{ij} + \tfrac{1}{4} \hat{P}^{(i/j)} \overline{g}_{kl}^{ij} t_{ab}^{kl} - \hat{P}_{(a/b)}^{(i/j)} \overline{g}_{ka}^{ic} t_{cb}^{kj} \\
&= \tfrac{1}{2} \overline{g}_{ab}^{cd} t_{cd}^{ij} + \tfrac{1}{2} \overline{g}_{kl}^{ij} t_{ab}^{kl} + \hat{P}_{(a/b)}^{(i/j)} \overline{g}_{ak}^{ic} t_{bc}^{jk} \\
\tfrac{1}{2} \left(\tfrac{1}{4}\right)^3 \overline{g}_{pq}^{rs} t_{cd}^{kl} t_{ef}^{mn} (\tilde{a}_{ab}^{ij} \tilde{a}_{rs}^{pq} \tilde{a}_{kl}^{cd} \tilde{a}_{mn}^{ef})_{\text{f.c.}} &= \quad \tfrac{1}{4} \overline{g}_{pq}^{rs} t_{cd}^{kl} t_{ef}^{mn} \gamma_k^i \gamma_l^j \gamma_m^p \gamma_n^q \eta_a^c \eta_b^d \eta_r^e \eta_s^f \\
&\quad - \tfrac{1}{2} \overline{g}_{pq}^{rs} t_{cd}^{kl} t_{ef}^{mn} \hat{P}_{(a/b)} \gamma_k^i \gamma_l^j \gamma_m^p \gamma_n^q \eta_a^c \eta_b^e \eta_r^d \eta_s^f \\
&\quad - \tfrac{1}{2} \overline{g}_{pq}^{rs} t_{cd}^{kl} t_{ef}^{mn} \hat{P}^{(i/j)} \gamma_k^i \gamma_m^j \gamma_l^p \gamma_n^q \eta_a^c \eta_b^d \eta_r^e \eta_s^f \\
&\quad + \tfrac{1}{4} \overline{g}_{pq}^{rs} t_{cd}^{kl} t_{ef}^{mn} \gamma_k^i \gamma_l^j \gamma_m^p \gamma_n^q \eta_a^e \eta_b^f \eta_r^c \eta_s^d \\
&\quad + \tfrac{1}{2} \overline{g}_{pq}^{rs} t_{cd}^{kl} t_{ef}^{mn} \hat{P}_{(a/b)}^{(i/j)} \gamma_k^i \gamma_m^j \gamma_l^p \gamma_n^q \eta_a^c \eta_b^e \eta_r^d \eta_s^f \\
&= \tfrac{1}{4} \overline{g}_{mn}^{ef} t_{ab}^{ij} t_{ef}^{mn} - \tfrac{1}{2} \hat{P}_{(a/b)} \overline{g}_{mn}^{df} t_{ad}^{ij} t_{bf}^{mn} - \tfrac{1}{2} \hat{P}^{(i/j)} \overline{g}_{ln}^{ef} t_{ab}^{il} t_{ef}^{jn} \\
&\quad + \tfrac{1}{4} \overline{g}_{mn}^{cd} t_{cd}^{ij} t_{ab}^{mn} + \tfrac{1}{2} \hat{P}_{(a/b)}^{(i/j)} \overline{g}_{ln}^{df} t_{ad}^{il} t_{bf}^{jn} \\
&= \left(\tfrac{1}{4} \overline{g}_{kl}^{cd} t_{cd}^{kl} \right) t_{ab}^{ij} - \tfrac{1}{2} \hat{P}_{(a/b)} \overline{g}_{kl}^{cd} t_{ac}^{ij} t_{bd}^{kl} - \tfrac{1}{2} \hat{P}^{(i/j)} \overline{g}_{kl}^{cd} t_{ab}^{ik} t_{cd}^{jl} \\
&\quad + \tfrac{1}{4} \overline{g}_{kl}^{cd} t_{cd}^{ij} t_{ab}^{kl} + \hat{P}^{(i/j)} \overline{g}_{kl}^{cd} t_{ac}^{ik} t_{bd}^{jl}
\end{aligned}
$$

Substituting these terms, along with the second Slater rule ($\langle \Phi_{ij}^{ab} | H_c | \Phi \rangle = \overline{g}_{ab}^{ij}$ and $\langle \Phi | H_c | \Phi_{kl}^{cd} \rangle = \overline{g}_{kl}^{cd}$), into equations 2 and 3 gives the following.

$$
E_c = \tfrac{1}{4} \overline{g}_{kl}^{cd} t_{cd}^{kl} \tag{6}
$$

$$
\begin{aligned}
E_c t_{ab}^{ij} = \overline{g}_{ab}^{ij} &+ \hat{P}_{(a/b)} f_a^c t_{cb}^{ij} - \hat{P}^{(i/j)} f_k^i t_{ab}^{kj} + \tfrac{1}{2} \overline{g}_{ab}^{cd} t_{cd}^{ij} + \tfrac{1}{2} \overline{g}_{kl}^{ij} t_{ab}^{kl} + \hat{P}_{(a/b)}^{(i/j)} \overline{g}_{ak}^{ic} t_{bc}^{jk} \\
&+ \left(\tfrac{1}{4} \overline{g}_{kl}^{cd} t_{cd}^{kl} \right) t_{ab}^{ij} - \tfrac{1}{2} \hat{P}_{(a/b)} \overline{g}_{kl}^{cd} t_{ac}^{ij} t_{bd}^{kl} - \tfrac{1}{2} \hat{P}^{(i/j)} \overline{g}_{kl}^{cd} t_{ab}^{ik} t_{cd}^{jl} + \tfrac{1}{4} \overline{g}_{kl}^{cd} t_{cd}^{ij} t_{ab}^{kl} + \hat{P}^{(i/j)} \overline{g}_{kl}^{cd} t_{ac}^{ik} t_{bd}^{jl}
\end{aligned} \tag{7}
$$

Finally, using the energy expression 6 allows us to cancel the left-hand side of equation 7 with the seventh term on the right, leaving the traditional CCD $\hat{T}_2$ amplitude equations.

$$
\begin{aligned}
0 = \overline{g}_{ab}^{ij} &+ \hat{P}_{(a/b)} f_a^c t_{cb}^{ij} - \hat{P}^{(i/j)} f_k^i t_{ab}^{kj} + \tfrac{1}{2} \overline{g}_{ab}^{cd} t_{cd}^{ij} + \tfrac{1}{2} \overline{g}_{kl}^{ij} t_{ab}^{kl} + \hat{P}_{(a/b)}^{(i/j)} \overline{g}_{ak}^{ic} t_{bc}^{jk} - \tfrac{1}{2} \hat{P}_{(a/b)} \overline{g}_{kl}^{cd} t_{ac}^{ij} t_{bd}^{kl} \\
&- \tfrac{1}{2} \hat{P}^{(i/j)} \overline{g}_{kl}^{cd} t_{ab}^{ik} t_{cd}^{jl} + \tfrac{1}{4} \overline{g}_{kl}^{cd} t_{cd}^{ij} t_{ab}^{kl} + \hat{P}^{(i/j)} \overline{g}_{kl}^{cd} t_{ac}^{ik} t_{bd}^{jl}
\end{aligned} \tag{8}
$$

Assuming a canonical HF reference wavefunction (so that $f_a^c = \varepsilon_a \delta_a^c$ and $f_k^i = \varepsilon_i \delta_k^i$) and moving the second and third terms to the left-hand side gives the CCD working equations

$$
t_{ab}^{ij} = \mathcal{E}_{ab}^{ij} \Big(\overline{g}_{ab}^{ij} + \tfrac{1}{2} \overline{g}_{ab}^{cd} t_{cd}^{ij} + \tfrac{1}{2} \overline{g}_{kl}^{ij} t_{ab}^{kl} + \hat{P}_{(a/b)}^{(i/j)} \overline{g}_{ak}^{ic} t_{bc}^{jk} - \tfrac{1}{2} \hat{P}_{(a/b)} \overline{g}_{kl}^{cd} t_{ac}^{ij} t_{bd}^{kl} - \tfrac{1}{2} \hat{P}^{(i/j)} \overline{g}_{kl}^{cd} t_{ab}^{ik} t_{cd}^{jl} \tag{9}
$$

$$
+ \tfrac{1}{4} \overline{g}_{kl}^{cd} t_{cd}^{ij} t_{ab}^{kl} + \hat{P}^{(i/j)} \overline{g}_{kl}^{cd} t_{ac}^{ik} t_{bd}^{jl} \Big) \qquad \text{where } \mathcal{E}_{ab}^{ij} = \frac{1}{\varepsilon_i + \varepsilon_i - \varepsilon_a - \varepsilon_b}. \tag{10}
$$