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}^{(c/d)}_{(a/b|k/l)} \vdots \tilde{a}^{i^{\bullet 1} j^{\bullet 2}}_{a^{\circ 1} b^{\circ 3}} \tilde{a}^{p^{\circ 1}}_{q^{\circ 2}} \tilde{a}^{c^{\circ 2} d^{\circ 3}}_{k^{\bullet 1} l^{\bullet 2}} \vdots + \hat{P}^{(i/j|c/d)}_{(k/l)} \vdots \tilde{a}^{i^{\bullet 1} j^{\bullet 3}}_{a^{\circ 1} b^{\circ 2}} \tilde{a}^{p^{\bullet 2}}_{q^{\bullet 1}} \tilde{a}^{c^{\circ 1} d^{\circ 2}}_{k^{\bullet 2} l^{\bullet 3}} \vdots \\
&= \hat{P}^{(c/d)}_{(a/b|k/l)} \eta_a^p \eta_q^c \eta_b^d \gamma_k^i \gamma_l^j - \hat{P}^{(i/j|c/d)}_{(k/l)} \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}^{(c/d)}_{(a/b|k/l)} \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 + \hat{P}^{(i/j|c/d)}_{(k/l)} \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 \\
&\quad + \hat{P}^{(p/q|i/j|c/d)}_{(r/s|k/l|a/b)} \vdots \tilde{a}^{i^{\bullet 1} j^{\bullet 3}}_{a^{\circ 1} b^{\circ 3}} \tilde{a}^{p^{\bullet 2} q^{\circ 1}}_{r^{\bullet 1} s^{\circ 2}} \tilde{a}^{c^{\circ 2} d^{\circ 3}}_{k^{\bullet 2} l^{\bullet 3}} \vdots \\
&= \hat{P}^{(c/d)}_{(a/b|k/l)} \eta_a^p \eta_b^q \eta_r^c \eta_s^d \gamma_k^i \gamma_l^j + \hat{P}^{(i/j|c/d)}_{(k/l)} \gamma_r^i \gamma_s^j \gamma_k^p \gamma_l^q \eta_a^c \eta_b^d - \hat{P}^{(p/q|i/j|c/d)}_{(r/s|k/l|a/b)} \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}^{(c/d|e/f)}_{(k/l|m/n)} \vdots \tilde{a}^{i^{\bullet 1} j^{\bullet 2}}_{a^{\circ 1} b^{\circ 2}} \tilde{a}^{p^{\bullet 3} q^{\bullet 4}}_{r^{\circ 3} s^{\circ 4}} \tilde{a}^{c^{\circ 1} d^{\circ 2}}_{k^{\bullet 1} l^{\bullet 2}} \tilde{a}^{e^{\circ 3} f^{\circ 4}}_{m^{\bullet 3} n^{\bullet 4}} \vdots \\
&\quad + 2\hat{P}^{(c/d|e/f)}_{(a/b|r/s|k/l|m/n)} \vdots \tilde{a}^{i^{\bullet 1} j^{\bullet 2}}_{a^{\circ 1} b^{\circ 2}} \tilde{a}^{p^{\bullet 3} q^{\bullet 4}}_{r^{\circ 3} s^{\circ 4}} \tilde{a}^{c^{\circ 1} d^{\circ 3}}_{k^{\bullet 1} l^{\bullet 2}} \tilde{a}^{e^{\circ 2} f^{\circ 4}}_{m^{\bullet 3} n^{\bullet 4}} \vdots \\
&\quad + 2\hat{P}^{(i/j|p/q|c/d|e/f)}_{(k/l|m/n)} \vdots \tilde{a}^{i^{\bullet 1} j^{\bullet 2}}_{a^{\circ 1} b^{\circ 2}} \tilde{a}^{p^{\bullet 3} q^{\bullet 4}}_{r^{\circ 3} s^{\circ 4}} \tilde{a}^{c^{\circ 1} d^{\circ 2}}_{k^{\bullet 1} l^{\bullet 3}} \tilde{a}^{e^{\circ 3} f^{\circ 4}}_{m^{\bullet 2} n^{\bullet 4}} \vdots \\
&\quad + 2\hat{P}^{(c/d|e/f)}_{(k/l|m/n)} \vdots \tilde{a}^{i^{\bullet 1} j^{\bullet 2}}_{a^{\circ 1} b^{\circ 2}} \tilde{a}^{p^{\bullet 3} q^{\bullet 4}}_{r^{\circ 3} s^{\circ 4}} \tilde{a}^{c^{\circ 3} d^{\circ 4}}_{k^{\bullet 1} l^{\bullet 2}} \tilde{a}^{e^{\circ 1} f^{\circ 2}}_{m^{\bullet 3} n^{\bullet 4}} \vdots \\
&\quad + \hat{P}^{(i/j|p/q|c/d|e/f)}_{(a/b|r/s|k/l|m/n)} \vdots \tilde{a}^{i^{\bullet 1} j^{\bullet 2}}_{a^{\circ 1} b^{\circ 2}} \tilde{a}^{p^{\bullet 3} q^{\bullet 4}}_{r^{\circ 3} s^{\circ 4}} \tilde{a}^{c^{\circ 1} d^{\circ 3}}_{k^{\bullet 1} l^{\bullet 3}} \tilde{a}^{e^{\circ 2} f^{\circ 4}}_{m^{\bullet 2} n^{\bullet 4}} \vdots \\
&= 2\hat{P}^{(c/d|e/f)}_{(k/l|m/n)} \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}^{(c/d|e/f)}_{(a/b|r/s|k/l|m/n)} \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}^{(i/j|p/q|c/d|e/f)}_{(k/l|m/n)} \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}^{(c/d|e/f)}_{(k/l|m/n)} \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}^{(i/j|p/q|c/d|e/f)}_{(a/b|r/s|k/l|m/n)} \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.

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

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

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.

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

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

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

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