

# CCD equations (projection method)

## Derivation in KM tensor notation

The electronic Hamiltonian can be expressed as follows.

$$H_e = E_{\text{HF}} + H_c \quad E_{\text{HF}} = \langle \Phi | H_e | \Phi \rangle \quad H_c = f_p^q \tilde{a}_q^p + \frac{1}{4} \bar{g}_{pq}^{rs} \tilde{a}_{rs}^{pq} \quad (1)$$

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  $\Phi$  and  $\Phi_{ij}^{ab}$  gives the following system of equations.

$$E_c = \langle \Phi | H_c e^{\hat{T}_2} \Phi | \Phi \rangle \implies E_c = \frac{1}{4} \langle \Phi | H_c | \Phi_{kl}^{cd} \rangle t_{cd}^{kl} \quad (2)$$

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

The non-trivial terms to be evaluated are

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

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

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

$$\begin{aligned} (\tilde{a}_{ab}^{ij} \tilde{a}_q^p \tilde{a}_{kl}^{cd})_{\text{f.c.}} &= \hat{P}_{(a/b|k/l)}^{(c/d)} \tilde{a}_{a^{\circ 1} b^{\circ 3}}^{i^{\bullet 1} j^{\bullet 2}} \tilde{a}_{q^{\circ 2}}^{p^{\circ 1}} \tilde{a}_{k^{\bullet 1} l^{\bullet 2}}^{c^{\circ 2} d^{\circ 3}} + \hat{P}_{(k/l)}^{(i/j|c/d)} \tilde{a}_{a^{\circ 1} b^{\circ 2}}^{i^{\bullet 1} j^{\bullet 3}} \tilde{a}_{q^{\bullet 1}}^{p^{\bullet 2}} \tilde{a}_{k^{\circ 1} l^{\circ 3}}^{c^{\circ 1} d^{\circ 2}} \\ &= \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})_{\text{f.c.}} &= \hat{P}_{(a/b|k/l)}^{(c/d)} \tilde{a}_{a^{\circ 1} b^{\circ 2}}^{i^{\bullet 1} j^{\bullet 2}} \tilde{a}_{r^{\circ 3} s^{\circ 4}}^{p^{\circ 1} q^{\circ 2}} \tilde{a}_{k^{\bullet 1} l^{\bullet 2}}^{c^{\circ 3} d^{\circ 4}} + \hat{P}_{(k/l)}^{(i/j|c/d)} \tilde{a}_{a^{\circ 1} b^{\circ 2}}^{i^{\bullet 1} j^{\bullet 2}} \tilde{a}_{r^{\bullet 1} s^{\bullet 2}}^{p^{\bullet 3} q^{\bullet 4}} \tilde{a}_{k^{\circ 1} l^{\circ 3}}^{c^{\circ 1} d^{\circ 2}} \\ &\quad + \hat{P}_{(r/s|k/l|a/b)}^{(p/q|i/j|c/d)} \tilde{a}_{a^{\circ 1} b^{\circ 3}}^{i^{\bullet 1} j^{\bullet 3}} \tilde{a}_{r^{\bullet 1} s^{\circ 2}}^{p^{\bullet 2} q^{\circ 1}} \tilde{a}_{k^{\circ 1} l^{\circ 3}}^{c^{\circ 2} d^{\circ 3}} \\ &= \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})_{\text{f.c.}} &= 2 \hat{P}_{(k/l|m/n)}^{(c/d|e/f)} \tilde{a}_{a^{\circ 1} b^{\circ 2}}^{i^{\bullet 1} j^{\bullet 2}} \tilde{a}_{r^{\circ 3} s^{\circ 4}}^{p^{\bullet 3} q^{\bullet 4}} \tilde{a}_{k^{\circ 1} l^{\circ 2}}^{c^{\circ 1} d^{\circ 2}} \tilde{a}_{m^{\circ 3} n^{\circ 4}}^{e^{\circ 3} f^{\circ 4}} \\ &\quad + 2 \hat{P}_{(a/b|r/s|k/l|m/n)}^{(c/d|e/f)} \tilde{a}_{a^{\circ 1} b^{\circ 2}}^{i^{\bullet 1} j^{\bullet 2}} \tilde{a}_{r^{\circ 3} s^{\circ 4}}^{p^{\bullet 3} q^{\bullet 4}} \tilde{a}_{k^{\bullet 1} l^{\bullet 2}}^{c^{\circ 1} d^{\circ 3}} \tilde{a}_{m^{\bullet 3} n^{\bullet 4}}^{e^{\circ 2} f^{\circ 4}} \\ &\quad + 2 \hat{P}_{(k/l|m/n)}^{(i/j|p/q|c/d|e/f)} \tilde{a}_{a^{\circ 1} b^{\circ 2}}^{i^{\bullet 1} j^{\bullet 2}} \tilde{a}_{r^{\circ 3} s^{\circ 4}}^{p^{\bullet 3} q^{\bullet 4}} \tilde{a}_{k^{\circ 1} l^{\circ 3}}^{c^{\circ 1} d^{\circ 2}} \tilde{a}_{m^{\circ 2} n^{\circ 4}}^{e^{\circ 3} f^{\circ 4}} \\ &\quad + 2 \hat{P}_{(k/l|m/n)}^{(c/d|e/f)} \tilde{a}_{a^{\circ 1} b^{\circ 2}}^{i^{\bullet 1} j^{\bullet 2}} \tilde{a}_{r^{\circ 3} s^{\circ 4}}^{p^{\bullet 3} q^{\bullet 4}} \tilde{a}_{k^{\bullet 1} l^{\bullet 2}}^{c^{\circ 3} d^{\circ 4}} \tilde{a}_{m^{\circ 3} n^{\circ 4}}^{e^{\circ 1} f^{\circ 2}} \\ &\quad + \hat{P}_{(a/b|r/s|k/l|m/n)}^{(i/j|p/q|c/d|e/f)} \tilde{a}_{a^{\circ 1} b^{\circ 2}}^{i^{\bullet 1} j^{\bullet 2}} \tilde{a}_{r^{\circ 3} s^{\circ 4}}^{p^{\bullet 3} q^{\bullet 4}} \tilde{a}_{k^{\circ 1} l^{\circ 3}}^{c^{\circ 1} d^{\circ 3}} \tilde{a}_{m^{\circ 2} n^{\circ 4}}^{e^{\circ 2} f^{\circ 4}} \\ &= 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^d \eta_r^e \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^c \eta_b^d \eta_r^e \eta_s^f \\ &\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^d \eta_r^e \eta_s^f \end{aligned}$$

giving the following.

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

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

$$E_c = \frac{1}{4} \bar{g}_{kl}^{cd} t_{cd}^{kl} \quad (6)$$

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

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.

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

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

$$t_{ab}^{ij} = \mathcal{E}_{ab}^{ij} \left( \bar{g}_{ab}^{ij} + \frac{1}{2} \bar{g}_{ab}^{cd} t_{cd}^{ij} + \frac{1}{2} \bar{g}_{kl}^{ij} t_{ab}^{kl} + \hat{P}_{(a/b)}^{(i/j)} \bar{g}_{ak}^{ic} t_{bc}^{jk} - \frac{1}{2} \hat{P}_{(a/b)} \bar{g}_{kl}^{cd} t_{ac}^{ij} t_{bd}^{kl} - \frac{1}{2} \hat{P}^{(i/j)} \bar{g}_{kl}^{cd} t_{ab}^{ik} t_{cd}^{jl} \right. \quad (9)$$

$$\left. + \frac{1}{4} \bar{g}_{kl}^{cd} t_{cd}^{ij} t_{ab}^{kl} + \hat{P}^{(i/j)} \bar{g}_{kl}^{cd} t_{ac}^{ik} t_{bd}^{jl} \right) \quad \text{where } \mathcal{E}_{ab}^{ij} = \frac{1}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}. \quad (10)$$