1. Expand the electronic Hamiltonian H in terms of Φ-normal-ordered operators using Wick's theorem for graphs, writing the core Hamiltonian and electron repulsion operators as $\boxtimes\!\!-\!\!\langle \equiv h_p^q a_q^p$ and $\{\!\!\sim\!\!\} \equiv \frac{1}{4}\bar{g}_{pq}^{rs} a_{rs}^{pq}$.

$$H = \boxtimes\!\!-\!\!\langle + \{\!\!\sim\!\!\} = ?$$

Answer:

$$\boxtimes\!\!-\!\!\langle + \{\!\!\sim\!\!\} = \boxtimes\!\!-\!\!\langle + \boxtimes\!\!-\!\!\bigcirc + \{\!\!\sim\!\!\} + \bigcirc\!\!\sim\!\!\langle + \bigcirc\!\!\sim\!\!\bigcirc$$

$$= h_p^q \tilde{a}_q^p + h_i^i + \tfrac{1}{4}\bar{g}_{pq}^{rs}\tilde{a}_{rs}^{pq} + \bar{g}_{ip}^{iq}\tilde{a}_q^p + \tfrac{1}{2}\bar{g}_{ij}^{ij}$$

The degeneracy factors were derived as follows: The third term has two pairs of equivalent linesI', yielding a degeneracy of $2^2 = 4$. The fifth term has just one pair of equivalent lines, yielding a degeneracy of 2.

2. Evaluate the following using Wick's theorem for graphs. Fully simplify your answer assuming the indices refer to a basis of canonical Hartree-Fock spin-orbitals.

$$\langle \Phi_{ijk}^{abc}|F_{\mathrm{c}}\,C_3|\Phi\rangle = ?$$

$$F_{\mathrm{c}} \equiv f_p^q \tilde{a}_q^p$$

$$C_3 \equiv \left(\tfrac{1}{3!}\right)^2 c_{def}^{lmn}\tilde{a}_{lmn}^{def}$$

Answer:

$$\langle \Phi_{ijk}^{abc}|F_{\mathrm{c}}\,C_3|\Phi\rangle =$$

$$= \hat{P}_{(a/bc)} f_a^d c_{dbc}^{ijk} - \hat{P}^{(i/jk)} f_l^i c_{abc}^{ljk}$$

These are the reduced antisymmetrizers, which means we have cancelled the degeneracy factors coming from equivalent coefficient lines (a set of three and a set of two in each graph). For canonical orbitals, Brillouin's theorem holds and this can be further simplified.

$$\begin{aligned}
\langle \Phi_{ijk}^{abc}|F_{\mathrm{c}}\,C_3|\Phi\rangle &= \hat{P}_{(a/bc)}\epsilon_a c_{abc}^{ijk} - \hat{P}^{(i/jk)}\epsilon_i c_{abc}^{ijk}\\
&= \epsilon_a c_{abc}^{ijk} - \epsilon_b c_{bac}^{ijk} - \epsilon_c c_{cba}^{ijk} - \epsilon_i c_{abc}^{ijk} + \epsilon_j c_{abc}^{jik} + \epsilon_k c_{abc}^{kji}\\
&= (\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k)c_{abc}^{ijk}
\end{aligned}$$

The last step follows from the fact that c_{abc}^{ijk} is antisymmetric in its upper and lower indices.

3. (a) Explain how to get from the projected CCD Schrödinger equation

$$E_{\rm c}\, t_{ab}^{ij} = \langle \Phi_{ij}^{ab} | H_{\rm c} \exp(T_2) | \Phi \rangle \qquad\qquad H_{\rm c} = F_{\rm c} + V_{\rm c} \qquad\qquad \begin{aligned} F_{\rm c} &\equiv f_p^q \tilde{a}_q^p \\ V_{\rm c} &\equiv \tfrac{1}{4} \bar{g}_{pq}^{rs} \tilde{a}_{rs}^{pq} \end{aligned} \qquad (1)$$

to the working equation for CCD amplitudes

$$t_{ab}^{ij} = (\mathcal{E}_{ab}^{ij})^{-1} \langle \Phi_{ij}^{ab} | V_{\rm c} \exp(T_2) | \Phi \rangle_{\rm L} \qquad\qquad \mathcal{E}_{ab}^{ij} \equiv \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b \qquad (2)$$

assuming a canonical Hartree-Fock reference.[1]

Answer: The only way to form a unlinked diagram from the operators in $\langle \Phi_{ij}^{ab} | H_{\rm c} \exp(T_2) | \Phi \rangle$ is

because we need at least two operators on bottom to form a disconnected part, and one of them must be fully contracted with either $V_{\rm c}$ or $\tilde{a}_{ab}^{ij}$. The first factor on the right is the only diagram arising from $\langle \Phi | H_{\rm c} \exp(T_2) | \Phi \rangle = E_{\rm c}$. Therefore,

$$0 = E_{\rm c}\, t_{ab}^{ij} - \langle \Phi_{ij}^{ab} | H_{\rm c} \exp(T_2) | \Phi \rangle_{\rm U} = \langle \Phi_{ij}^{ab} | H_{\rm c} \exp(T_2) | \Phi \rangle_{\rm L}$$

which implies the following.

$$-\langle \Phi_{ij}^{ab} | F_{\rm c} \exp(T_2) | \Phi \rangle_{\rm L} = \langle \Phi_{ij}^{ab} | V_{\rm c} \exp(T_2) | \Phi \rangle_{\rm L} \qquad (3)$$

The term on the left evaluates as follows.

$$= \hat{P}_{(a/b)} f_a^c t_{cb}^{ij} - \hat{P}^{(i/j)} f_k^i t_{ab}^{kj}$$
$$= \epsilon_a t_{ab}^{ij} - \epsilon_b t_{ba}^{ij} - \epsilon_i t_{ab}^{ij} + \epsilon_j t_{ab}^{ji}$$
$$= - \mathcal{E}_{ab}^{ij} t_{ab}^{ij}$$

Substituting this into equation 3 and dividing both sides by $\mathcal{E}_{ab}^{ij}$ leads to equation 2.

(b) Write out an algorithm to numerically solve equation 2.

Answer: Starting from $^{[0]}t_{ab}^{ij} = 0$ and $n = 1$, do the following.

i. Update amplitudes as $^{[n]}t_{ab}^{ij} = (\mathcal{E}_{ab}^{ij})^{-1} \langle \Phi_{ij}^{ab} | V_{\rm c} \exp(^{[n-1]}T_2) | \Phi \rangle_{\rm L}$.

ii. If $|^{[n]}\boldsymbol{t}_2 - {}^{[n-1]}\boldsymbol{t}_2|$ is less than the convergence threshold, increment n and return to step i.

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[1]Hint: You only need to evaluate three diagrams to answer this question.

Extra Credit: Derive the following interpretation rule in your own words:

> Each open cycle in a graph contributes $(-)^{h_i} a_q^p$ to the normal-ordered product of operators, where p and q label the free ends and h_i is the number of hole contractions in the cycle. A closed cycle (loop) contributes $(-)^{h_i+1}$.

Answer: The single-excitation operators involved in a contraction can be brought together with no sign change, since they each contain two operators. The contracted operators can then be eliminated as follows.

$$\vdots \cdots a_{a\bullet}^r a_s^{a\bullet} \cdots \vdots = -\vdots \cdots a_s^r(-\eta_a^a) \cdots \vdots = +\vdots \cdots a_s^r \cdots \vdots \quad \text{or}$$

$$\vdots \cdots a_s^{i\circ} a_{i\circ}^r \cdots \vdots = -\vdots \cdots a_s^r(+\gamma_i^i) \cdots \vdots = -\vdots \cdots a_s^r \cdots \vdots$$

Applying this result to each contraction line in an open cycle yields $(-)^{h_i} a_q^p$. Applying it to all but one particle line in a loop yields $(-)^{h_i} a_{a\bullet}^{a\bullet} = (-)^{h_i}(-\eta_a^a) = (-)^{h_i+1}$.