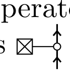
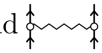
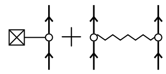
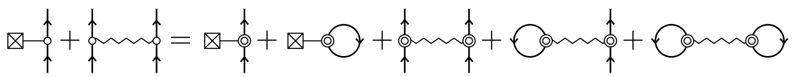
1. Expand the electronic Hamiltonian H_e in terms of Φ-normal-ordered operators using Wick's theorem for graphs, writing the core Hamiltonian and electron repulsion operators as  $\equiv h^q_p a^p_q$ and  $\equiv \frac{1}{4}\overline{g}^{rs}_{pq} a^{pq}_{rs}$.

$H_e =$  $= ?$

Answer:



$$= h^q_p \tilde{a}^p_q + h^i_i + \tfrac{1}{4}\overline{g}^{rs}_{pq}\tilde{a}^{pq}_{rs} + \overline{g}^{iq}_{ip}\tilde{a}^p_q + \tfrac{1}{2}\overline{g}^{ij}_{ij}$$

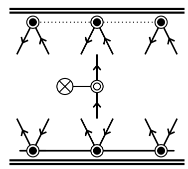
The degeneracy factors were derived as follows: The third term has two pairs of equivalent linesI', yielding a degeneracy of $2^2 = 4$. The fifth term has just one pair of equivalent lines, yielding a degeneracy of 2.

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.

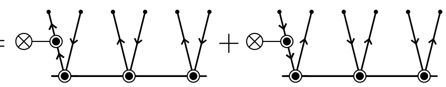
$$\langle\Phi_{ijk}^{abc}|F_{\mathrm{c}}\,C_3|\Phi\rangle = \,? \qquad\qquad \begin{aligned} F_{\mathrm{c}} &\equiv f_p^q\tilde{a}_q^p \\ C_3 &\equiv (\tfrac{1}{3!})^2 c_{def}^{lmn}\tilde{a}_{lmn}^{def} \end{aligned}$$

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

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

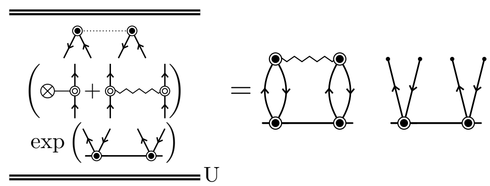
to the working equation for CCD amplitudes

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

assuming a canonical Hartree-Fock reference.[1]

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

$$\langle \Phi_{ij}^{ab} | H_\mathrm{c} \exp(T_2) | \Phi \rangle_\mathrm{U} =$$



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_c or $\tilde{a}_{ab}^{ij}$. The first factor on the right is the only diagram arising from $\langle \Phi | H_\mathrm{c} \exp(T_2) | \Phi \rangle = E_\mathrm{c}$. Therefore,

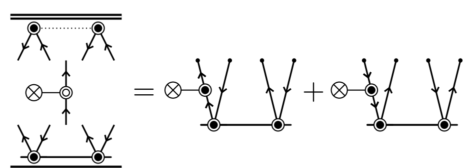
$$0 = E_\mathrm{c}\, t_{ab}^{ij} - \langle \Phi_{ij}^{ab} | H_\mathrm{c} \exp(T_2) | \Phi \rangle_\mathrm{U} = \langle \Phi_{ij}^{ab} | H_\mathrm{c} \exp(T_2) | \Phi \rangle_\mathrm{L}$$

which implies the following.

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

The term on the left evaluates as follows.

$$\langle \Phi_{ij}^{ab} | F_\mathrm{c} \exp(T_2) | \Phi \rangle_\mathrm{L} =$$



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

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

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

[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 $(-)^{h_i} a^p_q$ 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.

$$\begin{aligned} \vdots \cdots a^r_{a\bullet} a^{a\bullet}_s \cdots \vdots &= -\vdots \cdots a^r_s(-\eta^a_a) \cdots \vdots = +\vdots \cdots a^r_s \cdots \vdots \quad \text{or} \\ \vdots \cdots a^{i\circ}_s a^r_{i\circ} \cdots \vdots &= -\vdots \cdots a^r_s(+\gamma^i_i) \cdots \vdots = -\vdots \cdots a^r_s \cdots \vdots \end{aligned}$$

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