

1. Expand the electronic Hamiltonian  $H$  in terms of  $\Phi$ -normal-ordered operators using Wick's theorem for graphs, writing the core Hamiltonian and electron repulsion operators as  $\boxtimes \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \equiv h_p^q a_q^p$  and  $\begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \text{---} \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \equiv \frac{1}{4} \bar{g}_{pq}^{rs} a_{rs}^{pq}$ .

$$H = \boxtimes \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \text{---} \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} = ?$$

**Answer:**

$$\begin{aligned} \boxtimes \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \text{---} \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} &= \boxtimes \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \boxtimes \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \text{---} \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \text{---} \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \text{---} \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \text{---} \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \text{---} \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \text{---} \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} + \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \text{---} \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \text{---} \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \text{---} \begin{array}{c} \uparrow \\ \circ \\ \downarrow \end{array} \\ &= h_p^q \tilde{a}_q^p + h_i^i + \frac{1}{4} \bar{g}_{pq}^{rs} \tilde{a}_{rs}^{pq} + \bar{g}_{ip}^{iq} \tilde{a}_q^p + \frac{1}{2} \bar{g}_{ij}^{ij} \end{aligned}$$

The degeneracy factors were derived as follows: The third term has two pairs of equivalent lines, 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.

$$\langle \Phi_{ijk}^{abc} | F_c C_3 | \Phi \rangle = ?$$

$$F_c \equiv f_p^q \tilde{a}_q^p$$

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

**Answer:**

$$\begin{aligned} \langle \Phi_{ijk}^{abc} | F_c C_3 | \Phi \rangle &= \text{Diagram 1} = \text{Diagram 2} + \text{Diagram 3} \\ &= \hat{P}_{(a/bc)} f_a^d c_{dbc}^{ijk} - \hat{P}^{(i/jk)} f_l^i c_{abc}^{ljk} \end{aligned}$$

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.

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

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

$$E_c t_{ab}^{ij} = \langle \Phi_{ij}^{ab} | H_c \exp(T_2) | \Phi \rangle \quad H_c = F_c + V_c \quad \begin{aligned} F_c &\equiv f_p^q \tilde{a}_q^p \\ V_c &\equiv \frac{1}{4} \bar{g}_{pq}^{rs} \tilde{a}_{rs}^{pq} \end{aligned} \quad (1)$$

to the working equation for CCD amplitudes

$$t_{ab}^{ij} = (\mathcal{E}_{ab}^{ij})^{-1} \langle \Phi_{ij}^{ab} | V_c \exp(T_2) | \Phi \rangle_L \quad \mathcal{E}_{ab}^{ij} \equiv \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b \quad (2)$$

assuming a canonical Hartree-Fock reference.<sup>1</sup>

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

$$\langle \Phi_{ij}^{ab} | H_c \exp(T_2) | \Phi \rangle_U = \left( \begin{array}{c} \text{diagram with two vertices and a wavy line} \\ \text{exp} \left( \begin{array}{c} \text{diagram with two vertices and a wavy line} \end{array} \right) \end{array} \right)_U = \begin{array}{c} \text{diagram with two vertices and a wavy line} \\ \text{diagram with two vertices and a wavy line} \end{array}$$

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  $\langle \Phi | H_c \exp(T_2) | \Phi \rangle = E_c$ . Therefore,

$$0 = E_c t_{ab}^{ij} - \langle \Phi_{ij}^{ab} | H_c \exp(T_2) | \Phi \rangle_U = \langle \Phi_{ij}^{ab} | H_c \exp(T_2) | \Phi \rangle_L$$

which implies the following.

$$-\langle \Phi_{ij}^{ab} | F_c \exp(T_2) | \Phi \rangle_L = \langle \Phi_{ij}^{ab} | V_c \exp(T_2) | \Phi \rangle_L \quad (3)$$

The term on the left evaluates as follows.

$$\begin{aligned} \langle \Phi_{ij}^{ab} | F_c \exp(T_2) | \Phi \rangle_L &= \begin{array}{c} \text{diagram with two vertices and a wavy line} \\ \text{diagram with two vertices and a wavy line} \end{array} = \begin{array}{c} \text{diagram with two vertices and a wavy line} \\ \text{diagram with two vertices and a wavy line} \end{array} + \begin{array}{c} \text{diagram with two vertices and a wavy line} \\ \text{diagram with two vertices and a wavy line} \end{array} \\ &= \hat{P}_{(a/b)} f_a^c t_{cb}^{ij} - \hat{P}^{(i/j)} f_k^i t_{ab}^{kj} \\ &= \epsilon_a t_{ab}^{ij} - \epsilon_b t_{ba}^{ij} - \epsilon_i t_{ab}^{ij} + \epsilon_j t_{ab}^{ji} \\ &= -\mathcal{E}_{ab}^{ij} t_{ab}^{ij} \end{aligned}$$

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  $^{[n]}t_{ab}^{ij} = (\mathcal{E}_{ab}^{ij})^{-1} \langle \Phi_{ij}^{ab} | V_c \exp(^{[n-1]}T_2) | \Phi \rangle_L$ .
- ii. If  $|^{[n]}t_2 - ^{[n-1]}t_2|$  is less than the convergence threshold, increment  $n$  and return to step i.

<sup>1</sup>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.

$$\begin{aligned} \vdots \cdots a_{a^\bullet}^r a_s^{a^\bullet} \cdots \vdots &= - \vdots \cdots a_s^r (-\eta_a^a) \cdots \vdots = + \vdots \cdots a_s^r \cdots \vdots \quad \text{or} \\ \vdots \cdots a_s^{i^\circ} a_{i^\circ}^r \cdots \vdots &= - \vdots \cdots a_s^r (+\gamma_i^i) \cdots \vdots = - \vdots \cdots a_s^r \cdots \vdots \end{aligned}$$

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  $(-)^{h_i} a_{a^\bullet}^{a^\bullet} = (-)^{h_i} (-\eta_a^a) = (-)^{h_i+1}$ .