CEM 993 **Spring 2023**

Assignment No. 3 (20 pts.) **Due Date: March 1, 2023**

1. (6 pts.) Let
$$H = \sum_{p,q} \langle p|z|q\rangle X_p^\dagger X_q + \tfrac{1}{2} \sum_{p,q,r,s} \langle pq|v|rs\rangle X_p^\dagger X_q^\dagger X_s X_r \tag{1}$$
be the Hamiltonian containing up to two-body terms. Use the anti-commutation relations for the creation and annihilation operators to show that if the domain of operator H is restricted to an N-electron Hilbert space with a fixed number of particles N, we can write
$$H = \tfrac{1}{2} \sum_{p,q,r,s} \langle pq|w|rs\rangle X_p^\dagger X_q^\dagger X_s X_r, \tag{2}$$
where
$$\langle pq|w|rs\rangle = \langle pq|v|rs\rangle + \frac{1}{N-1} \left(\delta_{pr} \langle q|z|s\rangle + \delta_{qs} \langle p|z|r\rangle\right). \tag{3}$$

2. (8 pts.) Let Z_N be a generic one-body operator in the normal-product form,
$$Z_N = \sum_{p,q} \langle p|z|q\rangle N[X_p^\dagger X_q], \tag{4}$$
and let T_1 be a one-body particle-hole excitation operator,
$$T_1 = \sum_{i,a} \langle a|t_1|i\rangle N[X_a^\dagger X_i]. \tag{5}$$
Use the hole-particle variant of Wick's theorem to prove that
$$[Z_N, T_1] |\Phi\rangle = \sum_{a,i} \left(\sum_b \langle a|z|b\rangle \langle b|t_1|i\rangle - \sum_j \langle a|t_1|j\rangle \langle j|z|i\rangle \right) |\Phi_i^a\rangle + \left(\sum_{a,i} \langle a|t_1|i\rangle \langle i|z|a\rangle \right) |\Phi\rangle, \tag{6}$$
where [,] is the commutator, $|\Phi\rangle$ is the Fermi vacuum state, and $|\Phi_i^a\rangle$ are the singly excited determinants relative to $|\Phi\rangle$. You will have a chance to prove the same identity using diagrams later. The above equation is a demonstration of the fact (used, for example, in coupled-cluster theory) that commutators of many-body operators produce *connected* quantities (diagrams) only.

3. (6 pts.) Use the results obtained in Problem 2, particularly Eq. (6), to derive the formulas for
$$\langle\Phi| [Z_N, T_1] |\Phi\rangle, \tag{7}$$
$$\langle\Phi_i^a| [Z_N, T_1] |\Phi\rangle, \tag{8}$$
and
$$\langle\Phi_{ij}^{ab}| [Z_N, T_1] |\Phi\rangle \tag{9}$$
in terms of matrix elements $\langle p|z|q\rangle$ and $\langle b|t_1|j\rangle$. As in Problem 2, [,] is the commutator, $|\Phi\rangle$ is the Fermi vacuum state, and $|\Phi_i^a\rangle$ is the singly excited determinant relative to

$|\Phi\rangle$. $|\Phi_{ij}^{ab}\rangle$ is the doubly excited determinant relative to $|\Phi\rangle$. The remaining definitions are the same as in Problem 2. In general, what are the values of n in the expression

$$\langle\Phi_{i_1\ldots i_n}^{a_1\ldots a_n}|\,[Z_N, T_1]\,|\Phi\rangle, \tag{10}$$

where $|\Phi_{i_1\ldots i_n}^{a_1\ldots a_n}\rangle$ is the n-tuply excited determinant relative to $|\Phi\rangle$, that produce non-zero results? Justify your answer. How would your answer change if we considered

$$\langle\Phi_{i_1\ldots i_n}^{a_1\ldots a_n}|Z_N T_1|\Phi\rangle \tag{11}$$

instead (i.e., if we replaced the commutator of Z_N and T_1 by their product)?

SOLUTIONS

1. Let us substitute Eq. (3) into Eq. (2). We obtain,

$$H = \frac{1}{2} \sum_{pqrs} \langle pq | w | rs \rangle X_p^+ X_q^+ X_s X_r$$

$$= \frac{1}{2} \sum_{pqrs} \langle pq | v | rs \rangle X_p^+ X_q^+ X_s X_r$$

$$+ \frac{1}{2(N-1)} \sum_{pqrs} \left(\delta_{pr} \langle q | z | s \rangle + \delta_{qs} \langle p | z | r \rangle \right) \times$$

$$\times X_p^+ X_q^+ X_s X_r =$$

$$= \frac{1}{2} \sum_{pqrs} \langle pq | v | rs \rangle X_p^+ X_q^+ X_s X_r$$

$$+ \frac{1}{2(N-1)} \sum_{pqrs} \delta_{pr} \langle q | z | s \rangle X_p^+ X_q^+ X_s X_r$$

$$+ \frac{1}{2(N-1)} \sum_{pqrs} \delta_{qs} \langle p | z | r \rangle X_p^+ X_q^+ X_s X_r$$

$$= \frac{1}{2} \sum_{pqrs} \langle pq|v|rs \rangle X_p^\dagger X_q^\dagger X_s X_r$$

$$+ \frac{1}{2(N-1)} \sum_{pqs} \langle q|z|s \rangle X_p^\dagger X_q^\dagger X_s X_p$$

$$+ \frac{1}{2(N-1)} \sum_{pqr} \langle p|z|r \rangle X_p^\dagger X_q^\dagger X_q X_r .$$

$$= \frac{1}{2} \sum_{pqrs} \langle pq|v|rs \rangle X_p^\dagger X_q^\dagger X_s X_r$$

$$+ \frac{1}{2(N-1)} \sum_{pqs} \langle q|z|s \rangle X_q^\dagger X_p^\dagger X_p X_s$$

$$+ \frac{1}{2(N-1)} \sum_{pqr} \langle p|z|r \rangle X_p^\dagger X_q^\dagger X_q X_r .$$

Note that

$$\frac{1}{2(N-1)} \sum_{pqs} \langle q|z|s \rangle X_q^\dagger X_p^\dagger X_p X_s$$

$$\overset{q \leftrightarrow p}{\underset{s \to r}{=}} \frac{1}{2(N-1)} \sum_{pqr} \langle p|z|r \rangle X_p^\dagger X_q^\dagger X_q X_r .$$

Thus,

$$H = \frac{1}{2} \sum_{pqrs} \langle pq | v | rs \rangle X_p^\dagger X_q^\dagger X_s X_r + \frac{1}{N-1} \sum_{pqr} \langle p | z | r \rangle X_p^\dagger \hat{N}_q X_r , \tag{A}$$

where
$$\hat{N}_q = X_q^\dagger X_q$$
is the number operator for state q.

Let us recall that

$$\begin{aligned}
[\hat{N}_q , X_r] &= X_q^\dagger X_q X_r - X_r X_q^\dagger X_q \\
&= - X_q^\dagger X_r X_q - X_r X_q^\dagger X_q \\
&= - \underbrace{\left(X_q^\dagger X_r + X_r X_q^\dagger \right)}_{\{X_q^\dagger , X_r\} = \delta_{qr}} X_q \\
&= - \delta_{qr} X_q .
\end{aligned}$$

Thus,
$$\hat{N}_q X_r = X_r \hat{N}_q - \delta_{qr} X_q .$$

Substituting this result into Eq. (A), we obtain

$$H = \frac{1}{2}\sum_{pqrs}\langle pq|v|rs\rangle X_p^{+}X_q^{+}X_s X_r + \frac{1}{N-1}\sum_{pqr}\langle p|z|r\rangle X_p^{+}\left(X_r\hat{N}_q - \delta_{qr}X_q\right)$$

$$= \frac{1}{2}\sum_{pqrs}\langle pq|v|rs\rangle X_p^{+}X_q^{+}X_s X_r + \frac{1}{N-1}\left[\sum_{pqr}\langle p|z|r\rangle X_p^{+}X_r\hat{N}_q - \sum_{pqr}\delta_{qr}\langle p|z|r\rangle X_p^{+}X_q\right]$$

$$= \frac{1}{2}\sum_{pqrs}\langle pq|v|rs\rangle X_p^{+}X_q^{+}X_s X_r + \frac{1}{N-1}\left[\sum_{pr}\langle p|z|r\rangle X_p^{+}X_r\hat{N} - \sum_{pr}\langle p|z|r\rangle X_p^{+}X_r\right],$$ where

$\hat{N} = \sum_q \hat{N}_q$ is the total number operator.

Thus,

$$H = \frac{1}{2} \sum_{pqrs} \langle pq|v|rs\rangle X_p^\dagger X_q^\dagger X_s X_r + \frac{1}{N-1} \sum_{pr} \langle p|z|r\rangle X_p^\dagger X_r (\hat{N}-1).$$

Now, if the domain of H is restricted to an N-electron Hilbert space with a fixed number of particles N, then in this domain $\hat{N} = N$ (every wave function $|\Psi\rangle$ in this domain satisfies

$$\hat{N}|\Psi\rangle = N|\Psi\rangle).$$

In consequence,

$$H = \frac{1}{2} \sum_{pqrs} \langle pq|v|rs\rangle X_p^\dagger X_q^\dagger X_s X_r + \cancel{\frac{1}{N-1}} \sum_{pr} \langle p|z|r\rangle X_p^\dagger X_r \cancel{(N-1)}$$

$$= \frac{1}{2} \sum_{pqrs} \langle pq|\hat{v}|rs\rangle X_p^\dagger X_q^\dagger X_s X_r$$

$$+ \sum_{pr} \langle p|z|r\rangle X_p^\dagger X_r ,$$

which is exactly the standard form of the Hamiltonian, Eq. (1). We proved that Eqs. (1) and (2) are equivalent as long as the domain of H is restricted to an N-electron Hilbert space.

2. We must determine

$$[Z_N, T_1] = Z_N T_1 - T_1 Z_N .$$

We obtain,

$$Z_N T_1 = \sum_{pq} \langle p|z|q\rangle N[X_p^\dagger X_q] \times$$

$$\times \sum_{a,i} \langle a|t_1|i\rangle N[X_a^\dagger X_i] =$$

$$= \sum_{pqai} \langle p|z|q\rangle \langle a|t_1|i\rangle$$

$$\times N[X_p^\dagger X_q] N[X_a^\dagger X_i]$$

$$N[X_p^\dagger X_q] N[X_a^\dagger X_i] \overset{GWT}{=} N[X_p^\dagger X_q X_a^\dagger X_i]$$

$$+ \quad N[X_p^\dagger X_q X_a^\dagger X_i]$$

$$+ \quad N[X_p^\dagger X_q X_a^\dagger X_i]$$

$$+ \quad N[X_p^\dagger X_q X_a^\dagger X_i]$$

$$= N[X_p^\dagger X_q X_a^\dagger X_i] \quad +$$

$$+ \chi(p)\, \delta_{pi}\; N[X_q X_a^\dagger]$$

$$+ \pi(q)\, \delta_{qa}\; N[X_p^\dagger X_i]$$

$$+ \chi(p)\pi(q)\, \delta_{pi}\, \delta_{qa}$$

Thus,

$$Z_N T_1 = \sum_{pqai} \langle p|z|q\rangle\langle a|t_1|i\rangle N[X_p^\dagger X_q X_a^\dagger X_i]$$

$$- \sum_{pqai} \chi(p)\, \delta_{pi} \langle p|z|q\rangle\langle a|t_1|i\rangle N[X_a^\dagger X_q$$

$$+ \sum_{pqai} \pi(q)\, \delta_{qa} \langle p|z|q\rangle\langle a|t_1|i\rangle N[X_p^\dagger X_i]$$

$$+ \sum_{pqai} \chi(p)\pi(q)\, \delta_{pi}\, \delta_{qa} \langle p|z|q\rangle\langle a|t_1|i\rangle$$

$$= \sum_{pqai} \langle p|z|q\rangle\langle a|t_1|i\rangle\; N[X_p^\dagger X_q X_a^\dagger X_i]$$

$$- \sum_{qai} \langle i|z|q\rangle\langle a|t_1|i\rangle N[X_a^\dagger X_q]$$

$$+ \sum_{pai} \langle p|z|a\rangle\langle a|t_1|i\rangle N[X_p^\dagger X_i]$$

$$+ \sum_{ai} \langle i|z|a\rangle\langle a|t_1|i\rangle ,$$

so that

$$Z_N T_1 |\Phi\rangle = \sum_{pqai} \langle p|z|q\rangle\langle a|t_1|i\rangle N[X_p^\dagger X_q X_a^\dagger X_i]|\Phi\rangle$$

$$- \sum_{qai} \langle i|z|q\rangle\langle a|t_1|i\rangle N[X_a^\dagger X_q]|\Phi\rangle$$

$$+ \sum_{pai} \langle p|z|a\rangle\langle a|t_1|i\rangle N[X_p^\dagger X_i]|\Phi\rangle$$

$$+ \sum_{ai} \langle i|z|a\rangle\langle a|t_1|i\rangle |\Phi\rangle .$$

Note that q in the second term has to be occupied. If q is unoccupied,

$$N[X_a^\dagger X_q]|\Phi\rangle = N[Y_a^\dagger Y_q]|\Phi\rangle$$
$$= Y_a^\dagger Y_q|\Phi\rangle = 0.$$

Thus, $\sum_q$ in the second term reduces to

$\sum_j$ (q becomes $j \in$ occ.).

Similarly, p in the third term must be unoccupied. If p is occupied,

$$N[X_p^\dagger X_i]|\Phi\rangle = N[Y_p Y_i^\dagger]|\Phi\rangle$$
$$= -Y_i^\dagger Y_p|\Phi\rangle = 0.$$

Thus, $\sum_p$ in the third term reduces to

$\sum_b$ (p becomes $b \in$ unocc.).

As a result, we can write,

$$Z_N T_1 |\Phi\rangle = \sum_{pqai} \langle p|z|q\rangle \langle a|t_1|i\rangle \times$$

$$\times N[X_p^\dagger X_q X_a^\dagger X_i] |\Phi\rangle - \sum_{aij} \langle i|z|j\rangle \times$$

$$\times \langle a|t_1|i\rangle \; N[X_a^\dagger X_j] |\Phi\rangle$$

$$+ \sum_{abi} \langle b|z|a\rangle \langle a|t_1|i\rangle N[X_b^\dagger X_i] |\Phi\rangle$$

$$+ \sum_{ai} \langle i|z|a\rangle \langle a|t_1|i\rangle |\Phi\rangle .$$

If we switch i with j in the second term and a with b in the third term, we obtain,

$$Z_N T_1 |\Phi\rangle = \sum_{pqai} \langle p|z|q\rangle \langle a|t_1|i\rangle$$

$$\times N[X_p^\dagger X_q X_a^\dagger X_i] |\Phi\rangle$$

$$- \sum_{aij} \langle j|z|i\rangle \langle a|t_1|j\rangle |\Phi_i^a\rangle$$

$$+ \sum_{abi} \langle a|z|b\rangle \langle b|t_1|i\rangle |\Phi_i^a\rangle$$

$$+ \sum_{ai} \langle i|z|a\rangle \langle a|t_1|i\rangle |\Phi\rangle . \qquad (B)$$

Now,

$$T_1 Z_N = \sum_{pqai} \langle a|t_1|i\rangle \langle p|z|q\rangle N[X_a^\dagger X_i] N[X_p^\dagger X_q]$$

$$= \sum_{pqai} \langle a|t_1|i\rangle \langle p|z|q\rangle N[X_a^\dagger X_i X_p^\dagger X_q],$$

since

$$N[X_a^\dagger \overbrace{X_i X_p^\dagger} X_q] = \overset{0}{\pi(i)} \delta_{ip} N[X_a^\dagger X_q]$$

$$= 0$$

$$N[\overbrace{X_a^\dagger X_i X_p^\dagger X_q}] = \overset{0}{\eta(a)} \delta_{aq} N[X_i X_p^\dagger]$$

$$= 0$$

$$N[X_a^\dagger X_i X_p^\dagger X_q] = \overset{0}{\eta(a)} \overset{0}{\pi(i)} \delta_{aq} \delta_{ip}$$

$$= 0$$

Thus,

$$T_1 Z_N = \sum_{pqai} \langle a|t_1|i\rangle\langle p|z|q\rangle$$

$$\times N[X_a^\dagger X_i X_p^\dagger X_q] = \sum_{pqai} \langle a|t_1|i\rangle\langle p|z|q\rangle$$

$$\times N[X_p^\dagger X_q X_a^\dagger X_i] \; ,$$

so that

$$T_1 Z_N|\Phi\rangle = \sum_{pqai} \langle p|z|q\rangle\langle a|t_1|i\rangle$$

$$\times N[X_p^\dagger X_q X_a^\dagger X_i]|\Phi\rangle \; . \quad (C).$$

Subtracting Eq. (C) from (B), we obtain

$$[Z_N, T_1]|\Phi\rangle = \sum_{abi} \langle a|z|b\rangle\langle b|t_1|i\rangle|\Phi_i^a\rangle$$

$$- \sum_{aij} \langle a|t_1|j\rangle\langle j|z|i\rangle|\Phi_i^a\rangle$$

$$+ \sum_{ai} \langle i|z|a\rangle \langle a|t_1|i\rangle |\Phi\rangle$$

$$= \sum_{ai} \left(\sum_b \langle a|z|b\rangle\langle b|t_1|i\rangle - \right.$$

$$\left. - \sum_j \langle a|t_1|j\rangle\langle j|z|i\rangle \right) |\Phi_i^a\rangle$$

$$+ \sum_{ai} \langle a|t_1|i\rangle\langle i|z|a\rangle \; |\Phi\rangle,$$

which completes the proof of Eq. (6).

Expressions,

$$\sum_{\underline{\underline{b}}} \langle a|z|\underline{\underline{b}}\rangle\langle \underline{\underline{b}}|t_1|i\rangle$$ (b is shared between $\langle a|z|b\rangle$ & $\langle b|t_1|i\rangle$ and summed over),

$$\sum_{\underline{\underline{j}}} \langle a|t_1|\underline{\underline{j}}\rangle\langle \underline{\underline{j}}|z|i\rangle$$ (j is shared between $\langle a|t_1|j\rangle$ & $\langle j|z|i\rangle$ and summed over),

and

$$\sum_{a,i} \langle a|t_1|i\rangle \langle i|z|a\rangle$$ (a and i are shared between $\langle a|t_1|i\rangle$ & $\langle i|z|a\rangle$ and summed over)

represent the examples of CONNECTED quantities.

3. $[Z_N, T_1]|\Phi\rangle$, Eq. (6), has a form of a CI expansion,

$$[Z_N, T_1]|\Phi\rangle = c_0|\Phi\rangle + \sum_{n=1}^{N} \sum_{\substack{i_1<\cdots<i_n \\ a_1<\cdots<a_n}} c^{i_1\cdots i_n}_{a_1\cdots a_n} |\Phi^{a_1\cdots a_n}_{i_1\cdots i_n}\rangle, \quad (A)$$

where

$$c_0 = \langle\Phi|[Z_N, T_1]|\Phi\rangle, \quad (B)$$

$$c^{i_1\cdots i_n}_{a_1\cdots a_n} = \langle\Phi^{a_1\cdots a_n}_{i_1\cdots i_n}|[Z_N, T_1]|\Phi\rangle, \quad n \geq 1. \quad (C)$$

From a direct comparison of Eq. (6) with Eqs. (A)-(C), we immediately obtain,

$$C_0 = \sum_{a,i} \langle a|t_1|i\rangle\langle i|z|a\rangle , \quad (D)$$

$$C_a^i = \sum_b \langle a|z|b\rangle\langle b|t_1|i\rangle \quad (E)$$

$$- \sum_j \langle a|t_1|j\rangle\langle j|z|i\rangle ,$$

$$C_{ab}^{ij} = 0 , \quad (F)$$

and, in general,

$$C_{a_1 \cdots a_n}^{i_1 \cdots i_n} = 0 \quad \text{for} \quad n \geqslant 2. \quad (G)$$

Eq. (D) gives us a formula for Eq. (7).
Eq. (E) gives ~~us~~ an expression for Eq. (8).
Eq. (F) gives us an expression for Eq. (9),
i.e., $\langle \Phi_{ij}^{ab} | [Z_N, T_1] | \Phi \rangle = 0$,
Eq. (G) tells us that $\langle \Phi_{i_1 \cdots i_n}^{a_1 \cdots a_n} | [Z_N, T_1] | \Phi \rangle$
is ~~no~~nzero only when $n = 0$ or 1.

When we reexamine the solution of Problem 2, we can find out that $Z_N T_1 |\Phi\rangle$, in addition to the $\sum_{a,i} c_a^i |\Phi_i^a\rangle + c_0 |\Phi\rangle$ contributions, where c_a^i and c_0 are given by Eqs. (E) and (D), respectively, has an extra term

$$\sum_{abij} \langle a|t_1|i\rangle \langle b|z|j\rangle |\Phi_{ij}^{ab}\rangle,$$

which can be written as

$$\sum_{abij} \tilde{c}_{ab}^{ij} |\Phi_{ij}^{ab}\rangle, \text{ where}$$

$\tilde{c}_{ab}^{ij} = \langle a|t_1|i\rangle \langle b|z|j\rangle$, or, after simple manipulations, as

$$\sum_{a<b,\, i<j} c_{ab}^{ij} |\Phi_{ij}^{ab}\rangle, \text{ where}$$

$$c^{ij}_{ab} = \tilde{c}^{ij}_{ab} - \tilde{c}^{ij}_{ba} - \tilde{c}^{ji}_{ab} + \tilde{c}^{ji}_{ba}$$

$$= \mathcal{A}^{ij} \mathcal{A}_{ab} \, \tilde{c}^{ij}_{ab}, \quad \text{with}$$

$\mathcal{A}^{pq} \equiv \mathcal{A}_{pq} = 1 - (pq)$ representing the index antisymmetrizer [(pq) is a transposition of p and q]. The expressions, such as

$$c^{ij}_{ab} = \mathcal{A}^{ij} \mathcal{A}_{ab} \langle a|t_1|i\rangle \langle b|\hat{z}|j\rangle,$$

are examples of <u>disconnected</u> quantities that factorize into linear combinations of product terms (no index sharing between $\langle a|t_1|i\rangle$ and $\langle b|z|j\rangle$). In other words, the $Z_N T_1 |\Phi\rangle$ function, in addition to the connected $(Z_N T_1)_C |\Phi\rangle$

term, which is equivalent to $[Z_N, T_1]|\Phi\rangle$ and given by Eq. (6), contains the disconnected term (abbreviated by DC),

$$(Z_N T_1)_{DC} = \sum_{a<b,\, i<j} C_{ab}^{ij} |\Phi_{ij}^{ab}\rangle,$$

where

$$C_{ab}^{ij} = \mathcal{A}^{ij} \mathcal{A}_{ab} \langle a|t_1|i\rangle \langle b|z|j\rangle .$$

This immediately implies that

$$\langle \Phi_{i_1 \cdots i_n}^{a_1 \cdots a_n} | Z_N T_1 | \Phi\rangle \quad \text{is nonzero}$$

for $n = 0, 1,$ and 2, while vanishing when $n \geq 3$.