**Department of Chemistry, Michigan State University**

**CEM 993, Spring 2023**

**Midterm Exam**

**Deadline for Emailing Solutions to the Instructor:** April 7, 2023, 11:59 pm EDT

**Name** (Last, First, Middle Initial): **SOLUTIONS (Piecuch, Piotr)**
**Student ID Number**:

## INSTRUCTIONS

- The maximum number of points that you can earn in this exam is 50. 50 points earned in this exam are equivalent to 30 % of the final grade.
- Check that your booklet contains all 18 pages.
- Write your name and student ID number in the spaces provided above.
- Answer in the spaces provided. Use the extra pages 16-18 for additional space, if necessary. If you have technical difficulties with directly using this exam booklet, write down and scan your solutions, as you normally do in the case of homework assignments, but *do not forget to write your name and student ID number on the first page of your exam.* Email your exam (this booklet or your own pages) to the instructor using the deadline described above. Late exams will not be accepted.
- Show ALL your work. Insufficient justification will result in a loss of points.
- Do not write anything in the score table given below.

| Problem | Score |
|---|---|
| 1 | /8 |
| 2 | /12 |
| 3 | /18 |
| 4 | /6 |
| 5 | /6 |
| Total | /50 |

1. (8 pts.) Calculate the following normal products without or with contractions:

(a) $n[X_a X_b X_c^\dagger X_i^\dagger X_j X_d^\dagger]$,

(b) $N[X_a X_b X_c^\dagger X_i^\dagger X_j X_d^\dagger]$,

(c) $n[X_a X_b X_c^\dagger X_i^\dagger X_j X_d^\dagger]$,

(d) $N[X_a X_b X_c^\dagger X_i^\dagger X_j X_d^\dagger]$.

*Solution*

(a) $n[X_a X_b X_c^\dagger X_i^\dagger X_j X_d^\dagger] = +X_c^\dagger X_d^\dagger X_i^\dagger X_a X_b X_j$

$\left[R = \begin{pmatrix} a & b & c & i & j & d \\ c & d & i & a & b & j \end{pmatrix} = (a\,c\,i)(b\,d\,j),\ (-1)^R = +1\right]$

(b) $N[X_a X_b X_c^\dagger X_i^\dagger X_j X_d^\dagger] = N[Y_a Y_b Y_c^\dagger Y_i Y_j^\dagger Y_d^\dagger]$

$= -Y_c^\dagger Y_d^\dagger Y_j^\dagger Y_a Y_b Y_i = -X_c^\dagger X_d^\dagger X_j X_a X_b X_i^\dagger$

$\left[R = \begin{pmatrix} a & b & c & i & j & d \\ c & d & j & a & b & i \end{pmatrix} = (a\,c\,j\,b\,d\,i),\ (-1)^R = -1\right]$.

Interestingly, we can rewrite the last result as

$-X_c^\dagger X_d^\dagger (X_j X_i^\dagger) X_a X_b = -X_c^\dagger X_d^\dagger (\delta_{ij} - X_i^\dagger X_j)$

$\times X_a X_b = -\delta_{ij} X_c^\dagger X_d^\dagger X_a X_b + X_c^\dagger X_d^\dagger X_i^\dagger X_j X_a X_b$

$= -\delta_{ij} X_c^\dagger X_d^\dagger X_a X_b + \underbrace{X_c^\dagger X_d^\dagger X_i^\dagger X_a X_b X_j}_{(a)}$.

The difference between (a) and (b) is in the $-\delta_{ij} X_c^\dagger X_d^\dagger X_a X_b$ term present in (b).

(c) $n[X_a X_b X_c^\dagger X_i^\dagger X_j X_d^\dagger] = 0$, since

$$X_i^\dagger X_j = 0.$$

(d) $N[X_a X_b X_c^\dagger X_i^\dagger X_j X_d^\dagger] = - X_a X_c^\dagger \, X_i^\dagger X_j$

$\times N[X_b X_d^\dagger] = -\pi(a)\delta_{ac}\,\chi(i)\delta_{ij} N[X_b X_d^\dagger]$,

since $R = \begin{pmatrix} a & b & c & i & j & d \\ a & c & i & j & b & d \end{pmatrix} = (a)(bcij)(d)$,

so that $(-1)^R = -1$, and $X_a X_c^\dagger = \pi(a)\,\delta_{ac}$

and $X_i^\dagger X_j = \chi(i)\,\delta_{ij}$.

Thus,

$$N[X_a X_b X_c^\dagger X_i^\dagger X_j X_d^\dagger] = -\delta_{ac}\,\delta_{ij}\, N[Y_b Y_d^\dagger]$$

$$= +\delta_{ac}\,\delta_{ij}\, Y_d^\dagger Y_b = +\delta_{ac}\,\delta_{ij}\, X_d^\dagger X_b .$$

2. (12 pts.) (a) Let $Z_N$ be a one-body operator in the normal-product form,

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

and let $T_2$ be a two-body particle-hole excitation operator,

$$T_2 = \tfrac{1}{4} \sum_{j,k,b,c} \langle bc|t_2|jk\rangle_{\mathcal{A}} N[X_b^\dagger X_j X_c^\dagger X_k].$$

Use the hole-particle variant of Wick's theorem to derive the formula for

$$\langle \Phi_i^a|\, [Z_N, T_2]\, |\Phi\rangle \tag{1}$$

in terms of matrix elements $\langle p|z|q\rangle$ and $\langle bc|t_2|jk\rangle_{\mathcal{A}}$. Here, $[\ ,\ ]$ is the commutator, $|\Phi\rangle$ is the Fermi vacuum state, and $|\Phi_i^a\rangle$ is the singly excited determinant relative to $|\Phi\rangle$. [8 pts.]
(b) Use the diagrammatic method based on drawing the Hugenholtz (and Brandow) diagrams to calculate the matrix element given by Eq. (1). Compare the results obtained in (a) and (b). [4 pts.]

*Solution*

(a) $\langle \Phi_i^a|\, [Z_N, T_2]\, |\Phi\rangle = \langle \Phi_i^a|\, Z_N T_2 - T_2 Z_N\, |\Phi\rangle$

$$= \frac{1}{4} \sum_{pq} \sum_{jkbc} \langle p|z|q\rangle \langle bc|t_2|jk\rangle_A$$

$$\times \Big( \underbrace{\langle \Phi| N[X_i^\dagger X_a] N[X_p^\dagger X_q] N[X_b^\dagger X_j X_c^\dagger X_k] |\Phi\rangle}_{A}$$

$$- \underbrace{\langle \Phi| N[X_i^\dagger X_a] N[X_b^\dagger X_j X_c^\dagger X_k] N[X_p^\dagger X_q] |\Phi\rangle}_{B} \Big)$$

$$A = \langle \Phi| N[X_i^\dagger X_a X_p^\dagger X_q X_b^\dagger X_j X_c^\dagger X_k] |\Phi\rangle$$

$$+ \langle \Phi| N[X_i^\dagger X_a X_p^\dagger X_q X_b^\dagger X_j X_c^\dagger X_k] |\Phi\rangle$$

$$+ \langle \Phi | N[x_i^\dagger x_a \, x_p^\dagger x_q \, x_b^\dagger x_j \, x_c^\dagger x_k] | \Phi \rangle$$

$$+ \langle \Phi | N[x_i^\dagger x_a \, x_p^\dagger x_q \, x_b^\dagger x_j \, x_c^\dagger x_k] | \Phi \rangle$$

$$= \overset{\nearrow 1}{\chi(p)} \, \delta_{pj} \, \overset{\nearrow 1}{\pi(q)} \, \delta_{qb} \, \overset{\nearrow 1}{\chi(i)} \, \delta_{ik} \, \overset{\nearrow 1}{\pi(a)} \, \delta_{ac}$$

$$- \overset{\nearrow 1}{\chi(p)} \, \delta_{pk} \, \overset{\nearrow 1}{\pi(q)} \, \delta_{qb} \, \overset{\nearrow 1}{\chi(i)} \, \delta_{ij} \, \overset{\nearrow 1}{\pi(a)} \, \delta_{ac}$$

$$- \overset{\nearrow 1}{\chi(p)} \, \delta_{pj} \, \overset{\nearrow 1}{\pi(q)} \, \delta_{qc} \, \overset{\nearrow 1}{\chi(i)} \, \delta_{ik} \, \overset{\nearrow 1}{\pi(a)} \, \delta_{ab}$$

$$+ \overset{\nearrow 1}{\chi(p)} \, \delta_{pk} \, \overset{\nearrow 1}{\pi(q)} \, \delta_{qc} \, \overset{\nearrow 1}{\chi(i)} \, \delta_{ij} \, \overset{\nearrow 1}{\pi(a)} \, \delta_{ab}$$

$$= \delta_{pj} \delta_{qb} \delta_{ik} \delta_{ac} - \delta_{pk} \delta_{qb} \delta_{ij} \delta_{ac}$$

$$- \delta_{pj} \delta_{qc} \delta_{ik} \delta_{ab} + \delta_{pk} \delta_{qc} \delta_{ij} \delta_{ab} \, .$$

$B = 0$, since one cannot obtain a nonzero fully contracted expression from

$$\langle \Phi | N[x_i^\dagger x_a] N[x_b^\dagger x_j x_c^\dagger x_k] N[x_p^\dagger x_q] | \Phi \rangle .$$

Thus,
$$\langle \Phi_i^a | [Z_N, T_2] | \Phi \rangle = \frac{1}{4} \sum_{pq} \sum_{jkbc} \langle p | \hat{z} | q \rangle$$

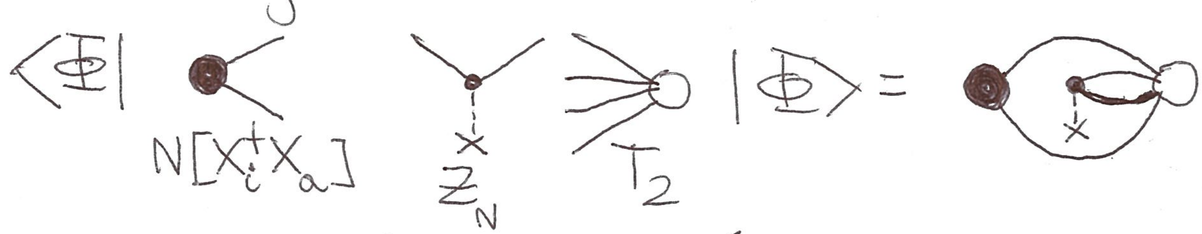
$$\times \langle bc | t_2 | jk \rangle_A \times A$$

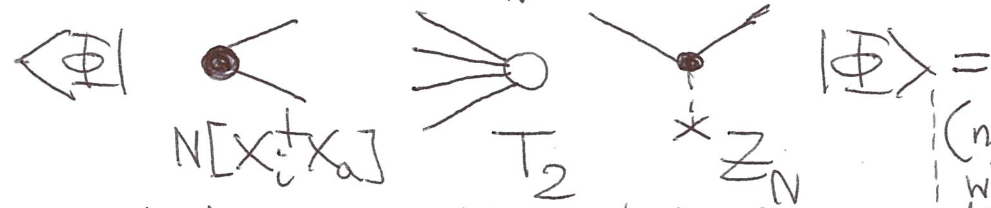
$$= \frac{1}{4}\Big( \sum_{jb} \langle j|\hat{z}|b\rangle \langle ba|t_2|ji\rangle_A - \sum_{kb} \langle k|\hat{z}|b\rangle \langle ba|t_2|ik\rangle_A - \sum_{jc} \langle j|\hat{z}|c\rangle \langle ac|t_2|ji\rangle_A + \sum_{kc} \langle k|\hat{z}|c\rangle \langle ac|t_2|ik\rangle_A \Big)$$

$$= \sum_{jb} \langle j|\hat{z}|b\rangle \langle ab|t_2|ij\rangle_A$$

(b) $$\langle \Phi_i^a|[Z_N, T_2]|\Phi\rangle = \underbrace{\langle \Phi|N[X_i^\dagger X_a]\, Z_N T_2|\Phi\rangle}_{\mathrm{I}} - \underbrace{\langle \Phi|N[X_i^\dagger X_a]\, T_2 Z_N|\Phi\rangle}_{\mathrm{II}}$$

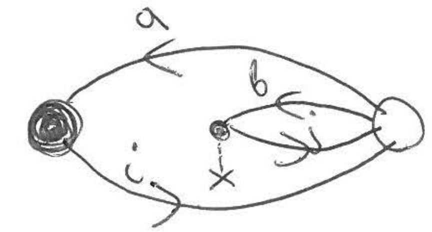
Non-oriented Hugenholtz skeletons:

I: 


II: 


(no skeletons without external lines can be formed)

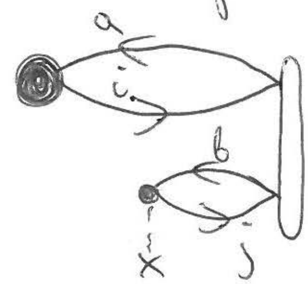
Thus, we only have one Hugenholtz diagram:




, $b, j$ - free
$a, i$ - fixed

$W_H = 1$

Brandow diagram is :




$S_B = (-1)^{2+2} = +1$.

We obtain

$$\sum_{jb} \langle j|\hat{z}|b\rangle \langle ab|t_2|ij\rangle_A ,$$ in agreement with (a).

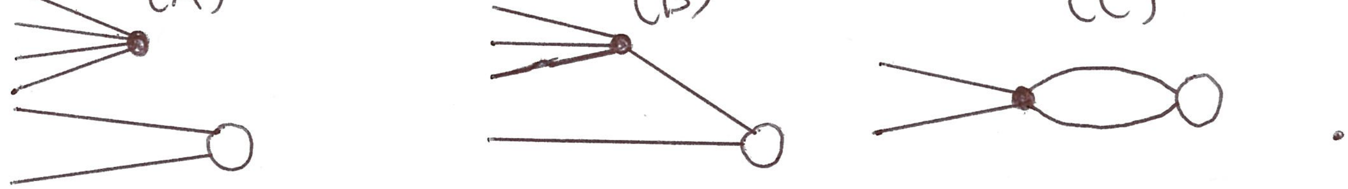
This finding agrees with the fact that $[Z_N, T_2]$ is a connected quantity $(Z_N T_2)_C$.

3. (18 pts.) Use the diagrammatic method based on drawing Goldstone diagrams to calculate $V_N C_1|\Phi\rangle$, where $V_N = \frac{1}{2}\sum_{p,q,r,s} \langle pq|v|rs\rangle\, N[X_p^\dagger X_r X_q^\dagger X_s]$ is a two-body part of the normal-ordered form of the Hamiltonian and $C_1 = \sum_{a,i} \langle a|c_1|i\rangle\, N[X_a^\dagger X_i]$ is a single excitation operator, in terms of matrix elements $\langle pq|v|rs\rangle$ and $\langle a|c_1|i\rangle$. In deriving the relevant Goldstone diagrams, go through the Hugenholtz skeletons and diagrams as intermediate steps. Remember, however, that the final resulting diagrams must be of the Goldstone type.

*Solution*

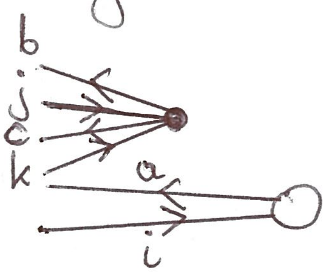
We can start from non-oriented Hugenholtz skeletons obtained from  and , representing $V_N$ and $C_1$, respectively. The resulting skeletons are as follows:

(A) (B) (C)

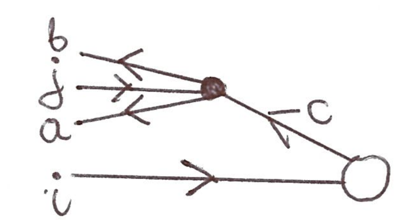


(no contractions) (one contraction) (two contractions)

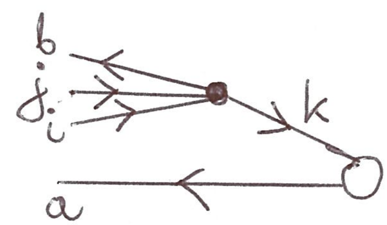
We used the fact that external lines must extend to the left. The above three skelitons result in the following Hugenholtz diagrams (all labels are free):



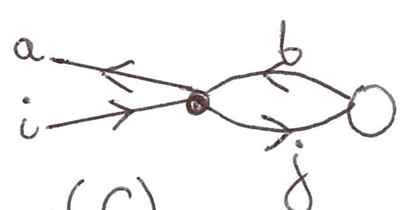

(A)




(B1)



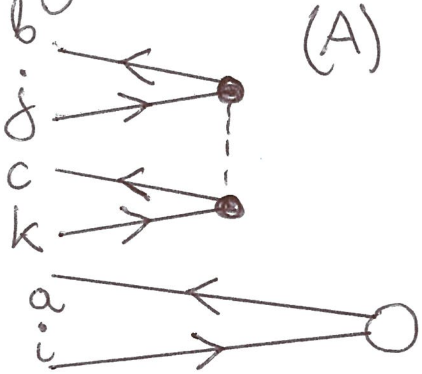

(B2)




(C)

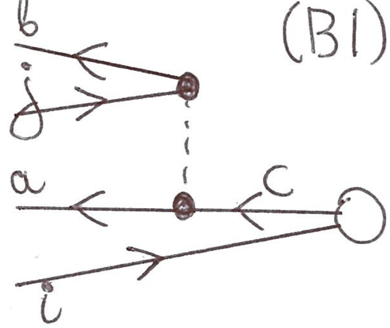
And now, we replace each Hugenholtz resulting diagram by Goldstone diagram(s), using line exchanges at $V_N$ as necessary to see if additional Goldstone diagrams can be generated (outgoing lines at $V_N$ will be exchanged):

(A)



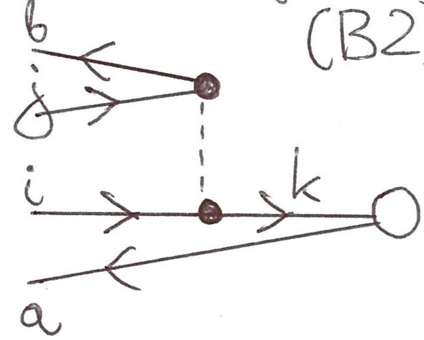

(exchange of b and c lines at $V_N$ gives no new diagram)

(B1)



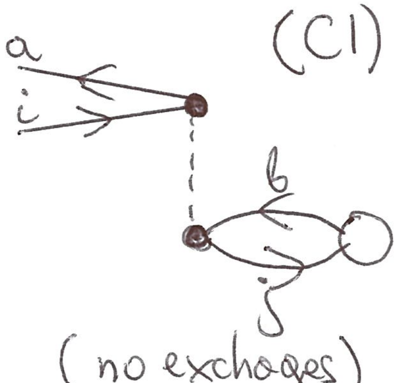

(exchange of b and a lines at $V_N$ gives no new diagram)

(B2)



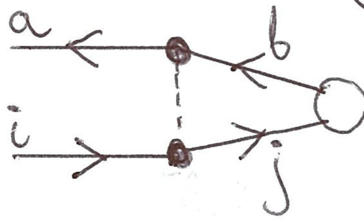

(exchange of b and k lines at $V_N$ gives no new diagram; one could also exchange lines i and j at $V_N$ with the same outcome)

(C1)




(no exchoges)

(C2)




(after exchanging outgoing lines at $V_N$ in (C1))

Diagram weights ($w_R$) and signs ($s_R$):

(A) $w_R = \frac{1}{2}$, $s_R = +1$ $(l_R = 0,\ h_R = 0)$

(B1) $w_R = 1$, $s_R = +1$ $(l_R = 0,\ h_R = 0)$

(B2) $w_R = 1$, $s_R = -1$ $(l_R = 0,\ h_R = 1)$

(C1) $w_R = 1$, $s_R = +1$ $(l_R = 1,\ h_R = 1)$

(C2) $w_R = 1$, $s_R = -1$ $(l_R = 0,\ h_R = 1)$

The formula for $V_N C_1 |\Phi\rangle$ is:

$$V_N C_1 |\Phi\rangle = (A) + (B1) + (B2) + (C1) + (C2)$$

$$= \frac{1}{2} \sum_{abc,ijk} \langle bc|\hat{v}|jk\rangle \langle a|\hat{c}_1|i\rangle N[X_a^\dagger X_i X_b^\dagger X_j X_c^\dagger X_k] |\Phi\rangle$$

$$+ \sum_{abc,ij} \langle ab|\hat{v}|cj\rangle \langle c|\hat{c}_1|i\rangle N[X_a^\dagger X_i X_b^\dagger X_j] |\Phi\rangle$$

$$- \sum_{ab,ijk} \langle kb|\hat{v}|ij\rangle \langle a|\hat{c}_1|k\rangle N[X_a^\dagger X_i X_b^\dagger X_j] |\Phi\rangle$$

$$+ \sum_{ab,ij} \langle aj|\hat{v}|ib\rangle \langle b|\hat{c}_1|j\rangle N[X_a^\dagger X_i] |\Phi\rangle$$

$$- \sum_{ab,ij} \langle aj|\hat{v}|bi\rangle\langle b|\hat{c}_1|j\rangle \, N[X_a^\dagger X_i] \, |\Phi\rangle .$$

Thus,

$$V_N C_1 |\Phi\rangle = \frac{1}{2} \sum_{abc,ijk} \langle bc|\hat{v}|jk\rangle\langle a|\hat{c}_1|i\rangle \, |\Phi_{ijk}^{abc}\rangle$$
$$+ \sum_{abc,ij} \langle ab|\hat{v}|cj\rangle\langle c|\hat{c}_1|i\rangle \, |\Phi_{ij}^{ab}\rangle$$
$$- \sum_{ab,ijk} \langle kb|\hat{v}|ij\rangle\langle a|\hat{c}_1|k\rangle \, |\Phi_{ij}^{ab}\rangle$$
$$+ \sum_{ab,ij} \langle aj|\hat{v}|ib\rangle_A \langle b|\hat{c}_1|j\rangle \, |\Phi_i^a\rangle$$

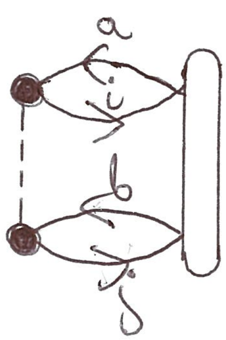
or

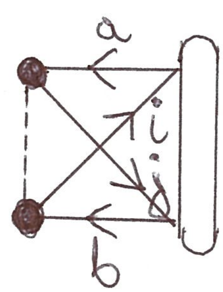
$$V_N C_1 |\Phi\rangle = \frac{1}{2} \sum_{abc,ijk} \langle bc|\hat{v}|jk\rangle\langle a|\hat{c}_1|i\rangle \, |\Phi_{ijk}^{abc}\rangle$$
$$+ \sum_{ab,ij} \Big( \sum_c \langle ab|\hat{v}|cj\rangle\langle c|\hat{c}_1|i\rangle - \sum_k \langle kb|\hat{v}|ij\rangle\langle a|\hat{c}_1|k\rangle \Big) |\Phi_{ij}^{ab}\rangle$$
$$+ \sum_{ab,ij} \langle aj|\hat{v}|ib\rangle_A \langle b|\hat{c}_1|j\rangle \, |\Phi_i^a\rangle .$$

4. (6 pts.) Consider the expression $\langle\Phi|V_N C_2|\Phi\rangle$ for a $(2n)$-electron closed-shell system described by a spin-orbital basis $|p\rangle$ obtained by multiplying spatial functions (orbitals) $|P\rangle$ by the spin-up and spin-down states, $|\alpha\rangle = |\frac{1}{2},\frac{1}{2}\rangle$ and $|\beta\rangle = |\frac{1}{2},-\frac{1}{2}\rangle$, respectively, so that $|p\rangle = |P\rangle \otimes |\sigma_p\rangle$, where $|\sigma_p\rangle = |\alpha\rangle$ or $|\beta\rangle$. As you know from our lectures, $\langle\Phi|V_N C_2|\Phi\rangle$ results in two Goldstone diagrams. Assuming that the Fermi vacuum state $|\Phi\rangle$ is built from $n$ doubly occupied orbitals $|I\rangle$, where $I = 1,\ldots,n$, and that the two-body part of the normal-ordered form of the Hamiltonian, $V_N$, and the double excitation operator $C_2$ are both spin-free operators, use the Goldstone diagrams representing $\langle\Phi|V_N C_2|\Phi\rangle$ to derive the spin-free form of it in terms of spin-independent matrix elements $\langle PQ|v|RS\rangle$ and $\langle AB|c_2|IJ\rangle$ of $V_N$ and $C_2$. If you remember the two Goldstone diagrams corresponding to $\langle\Phi|V_N C_2|\Phi\rangle$, you do not have to rederive them. You do, however, have to convert them into the corresponding and properly labeled orbital diagrams, which must be shown as part of your solution, before deriving and reporting the final spin-free formula for $\langle\Phi|V_N C_2|\Phi\rangle$.

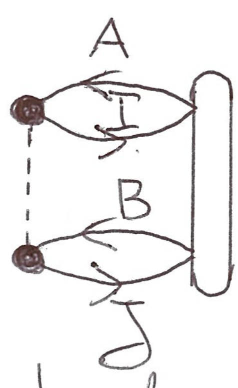
*Solution*

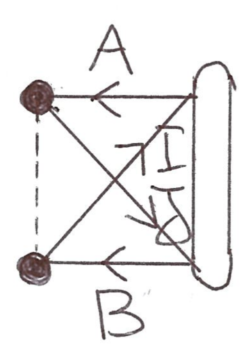
We start from the Goldstone diagrams representing $\langle\Phi|V_N C_2|\Phi\rangle$ in a spin-orbital form:




Conversion to orbital, spin-free, form gives:




$W_R = \frac{1}{2}$, $l_R = 2$, $h_R = 2$, $S_R = +1$

$W_R = \frac{1}{2}$, $l_R = 1$, $h_R = 2$, $S_R = -1$.

Remembering that we also have to incorporate $2^{l_R}$ in each of the resulting expressions, we obtain,

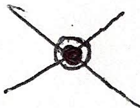
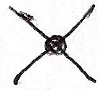
$$\langle \Phi | V_N C_2 | \Phi \rangle = \frac{1}{2} \cdot 2^2 \sum_{ABIJ} \langle IJ | \hat{v} | AB \rangle \langle AB | \hat{c}_2 | IJ \rangle$$

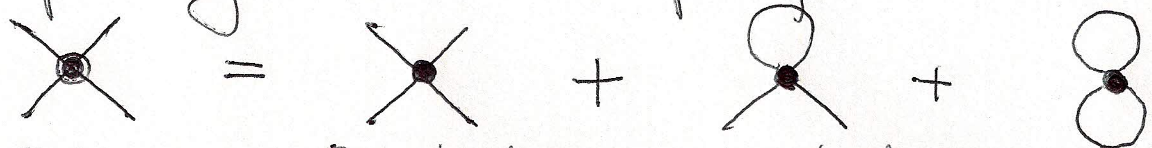
$$- \frac{1}{2} \cdot 2^1 \sum_{ABIJ} \langle IJ | \hat{v} | BA \rangle \langle AB | \hat{c}_2 | IJ \rangle$$

$$= \sum_{ABIJ} \left( 2 \langle IJ | \hat{v} | AB \rangle - \langle IJ | \hat{v} | BA \rangle \right) \times \langle AB | \hat{c}_2 | IJ \rangle .$$

5. (6 pts.) Use the diagrammatic method based on drawing Hugenholtz/Brandow diagrams to derive the relationship between the standard and normal-ordered forms of a two-body operator, $V$ and $V_N$, respectively.

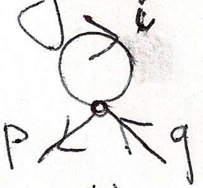
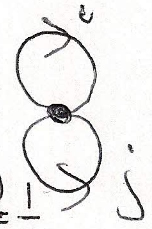
*Solution*

Let us use  to represent $V$ and  to represent $V_N$. The non-oriented Hugenholtz skeletons representing the relationship of $V$ and $V_N$ are



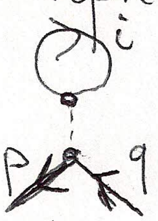
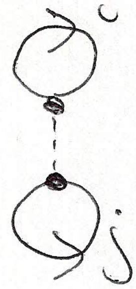
(V) = 0 contractions ($V_N$) + 1 contraction + 2 contractions.

Thus, after introducing arrows and labels, we obtain

$V = V_N +$  $+$ , or,

$W^{(H)} = 1$, $W^{(H)} = \frac{1}{2}$

in a Brandow representation,

$V = V_N +$  $+$ .

$W^{(H)} = 1$, $S^{(B)} = (-1)^{1+1} = +1$; $W^{(H)} = \frac{1}{2}$, $S^{(B)} = (-1)^{2+2} = +1$

After reading the Brandow diagrams, we can write

$$V = V_N + \sum_{p,q}\left(\sum_i \langle pi|\hat{v}|qi\rangle_A\right) N[X_p^\dagger X_q] + \frac{1}{2}\sum_{i,j}\langle ij|\hat{v}|ij\rangle_A = V_N + G_N + \langle\Phi|V|\Phi\rangle,$$

where

$$G_N = \sum_{p,q} \langle p|\hat{g}|q\rangle N[X_p^\dagger X_q],$$

with

$$\langle p|\hat{g}|q\rangle = \sum_i \langle pi|\hat{v}|qi\rangle_A,$$

and

$$\langle \Phi|V|\Phi\rangle = \frac{1}{2}\sum_{ij} \langle ij|\hat{v}|ij\rangle_A,$$

which is a desired result.