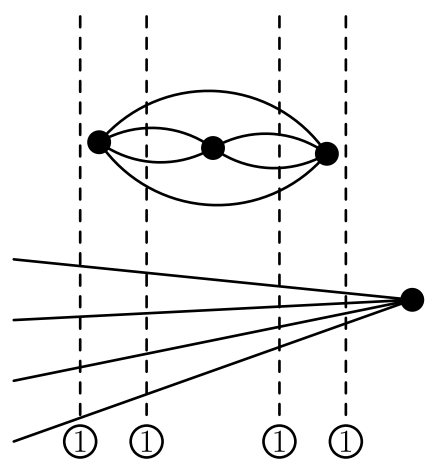
CEM 993 **Spring 2023**

Assignment No. 6 (20 pts.) **Due Date: April 28, 2023**

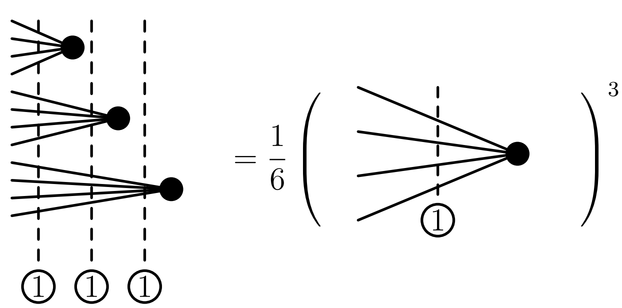
1. (8 pts.) Draw the Hugenholtz and Brandow diagrams for the second-order MBPT correction to the wave function, $|\Psi_0^{(2)}\rangle$, assuming that the perturbation operator W consists of only two-body part, $W = V_N$, and write the complete algebraic expression for each of the resulting diagrams. Distinguish between the wave function contributions corresponding to different excitation levels (i.e., the second-order MBPT corrections due to singly excited determinants, the second-order MBPT corrections due to doubly excited determinants, etc.).

2. (4 pts.) Among the unlinked contributions that originate from the principal term in the fourth-order MBPT correction to the wave function, $|\Psi_0^{(4)}\rangle$, there is a group of diagrams represented by the skeleton



and all time versions of the first kind associated with it. Perform suitable diagram factorization for this group and identify the specific renormalization term contributing to $|\Psi_0^{(4)}\rangle$ that this group cancels out.

3. (4 pts.) Prove the following diagram factorization:



4. (4 pts.) Let us assume that the reference determinant $|\Phi_0\rangle$ used in MBPT as the unperturbed wave function is a Hartree-Fock state, i.e., the perturbation operator

W consists of only two-body part, $W = V_N$. In this case, among the Hugenholtz diagrams representing the second-order MBPT correction to the wave function, $|\Psi_0^{(2)}\rangle$, there are two that correspond to the second-order estimate of the singly excited cluster operator T_1, i.e., $T_1^{(2)}$. Identify these diagrams and provide the corresponding algebraic expressions for them (you can copy this information from your solution of Problem 1 if you like). Use the resulting formula for $T_1^{(2)}$ in terms of the antisymmetrized matrix elements $v_{pq}^{rs} \equiv \langle pq|v|rs\rangle_{\mathcal{A}}$, unperturbed spin-orbital energies ε_p, and particle-hole excitation operators $E_i^a = X_a^\dagger X_i$ relevant to the problem to determine the explicit formula for the second-order MBPT estimate of the singly excited cluster amplitude $t_a^i \equiv \langle a|t_1|i\rangle$, i.e., ${}^{(2)}t_a^i \equiv \langle a|t_1^{(2)}|i\rangle$.

SOLUTIONS

1. $|\Psi_0^{(2)}\rangle = \{(R^{(0)}W)^2\}_L |\Phi_0\rangle$,

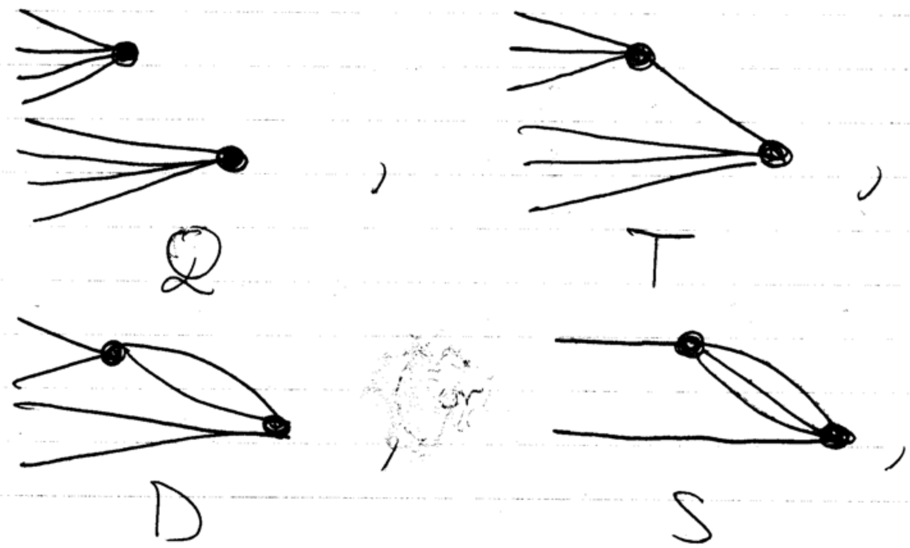
where L indicates linked diagrams.

In our case, $W = V_N$, so that

$$|\Psi_0^{(2)}\rangle = \{(R^{(0)}V_N)^2\}_L |\Phi_0\rangle$$
$$= (R^{(0)}V_N)^2 |\Phi_0\rangle,$$

since we cannot produce unlinked diagrams from two V_N vertices (we could, but this would produce "dangerous denominators", the  situation).

Nonoriented Hugenholtz skeletons corresponding to $(R^{(0)}V_N)^2|\Phi_0\rangle$:



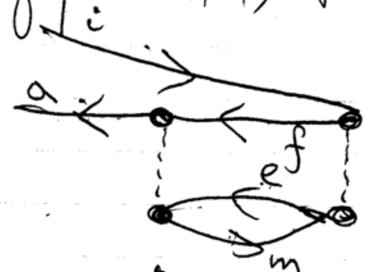
where Q, T, D, and S designate contributions due to quadruply excited configurations, triply excited configurations, doubly excited configurations, and singly excited configurations, respectively.

Oriented Hugenholtz and Brandow diagrams and the corresponding algebraic expressions:

$$|\Psi_0^{(2)}\rangle = |\Psi_0^{(2)}(S)\rangle + |\Psi_0^{(2)}(D)\rangle + |\Psi_0^{(2)}(T)\rangle + |\Psi_0^{(2)}(Q)\rangle .$$

The $|\Psi_0^{(2)}(S)\rangle$ (singly excited) terms are;

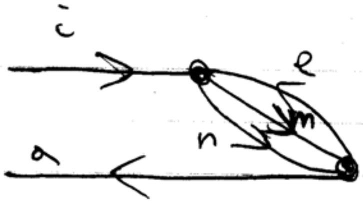
Hugenholtz



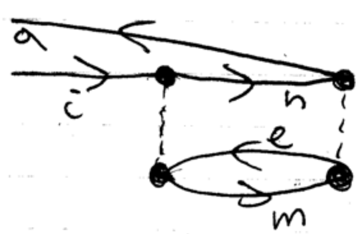
Brandow

Expression;

$$\frac{1}{2}\sum_{aef,im} \langle ma|\hat{v}|ef\rangle_A \langle ef|\hat{v}|mi\rangle_A \Delta^{(1)}(i;a) \times \Delta^{(1)}(i,m;e,f)\ |\Phi_i^a\rangle$$



Hugenholtz

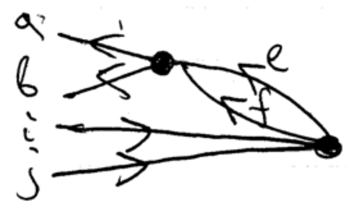


Brandow

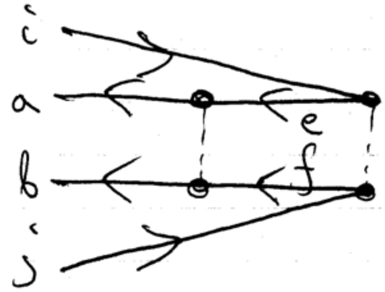
Expression;

$$-\frac{1}{2}\sum_{ae,imn} \langle ea|\hat{v}|mn\rangle_A \langle mn|\hat{v}|ei\rangle_A \Delta^{(1)}(i;a) \times \Delta^{(1)}(m,n;a,e)\ |\Phi_i^a\rangle$$

The $|\Psi_0^{(2)}(D)\rangle$ (doubly excited) terms are:



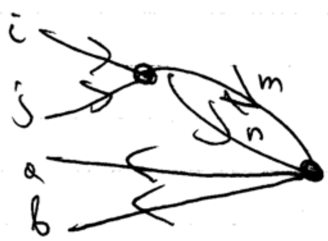
Hugenholtz



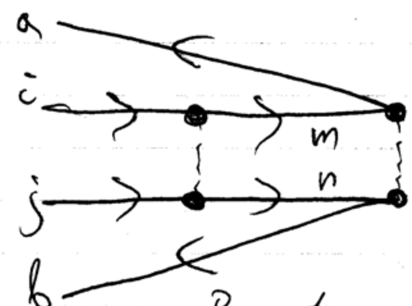
Brandow

Expression:

$$\frac{1}{8}\sum_{abefij}\langle ab|\hat{v}|ef\rangle_A\langle ef|\hat{v}|ij\rangle_A\,\Delta^{(1)}(ij;a,b)$$
$$\times\,\Delta^{(1)}(ij;e,f)\;|\Phi_{ij}^{ab}\rangle$$

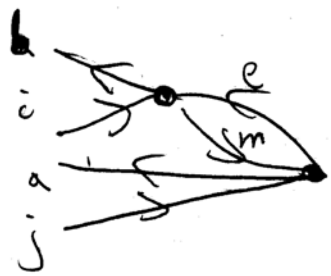


Hugenholtz

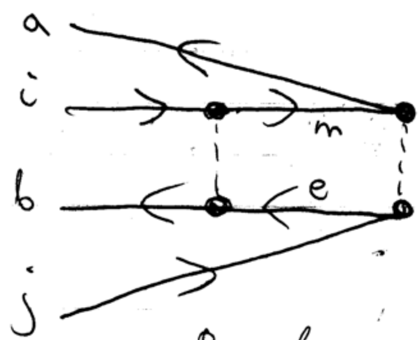


Brandow

Expression: $$\frac{1}{8}\sum_{ab,ijmn}\langle ab|\hat{v}|mn\rangle_A\langle mn|\hat{v}|ij\rangle_A\,\Delta^{(1)}(ij;a,b)$$
$$\times\,\Delta^{(1)}(m,n;a,b)\;|\Phi_{ij}^{ab}\rangle$$



Hugenholtz

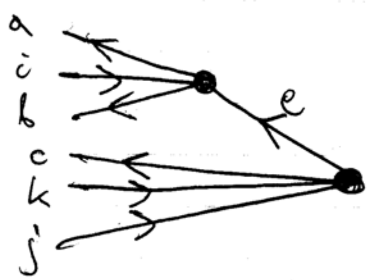


Brandow

Expression:

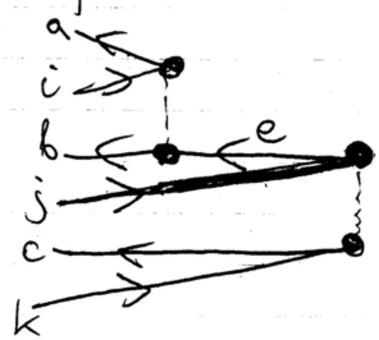
$$-\sum_{abe,ijm}\langle ae|\hat{v}|mj\rangle_A\langle mb|\hat{v}|ie\rangle_A\,\Delta^{(1)}(jm;a,e)\times\Delta^{(1)}(ij;a,b)\;|\Phi_{ij}^{ab}\rangle$$

The $|\Psi_0^{(2)}(T)\rangle$ (triply excited) terms are:



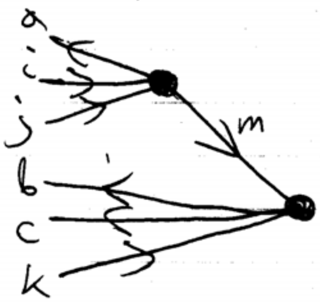
Hugenholtz

Brandow

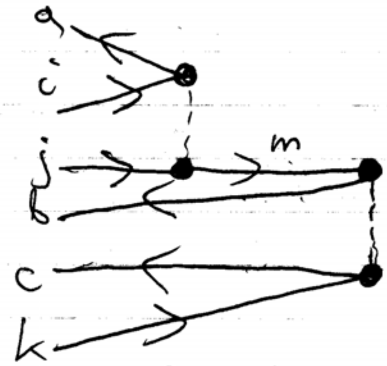


Expression:

$$\frac{1}{4}\sum_{abce,ijk}\langle ab|\hat{v}|ie\rangle_A\langle ec|\hat{v}|jk\rangle_A\,\Delta^{(1)}(ijk;a,b,c)\times\Delta^{(1)}(jk;c,e)\;|\Phi_{ijk}^{abc}\rangle$$



Hugenholtz

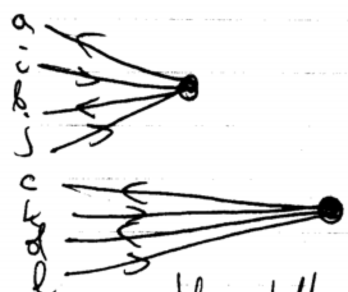


Brandow

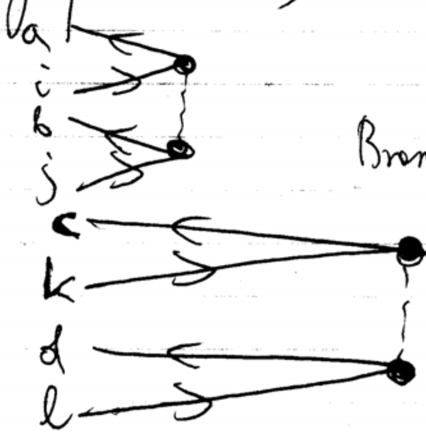
Expression:

$$-\frac{1}{4}\sum_{abc,ijkm}\langle bc|\hat{v}|mk\rangle_A\langle am|\hat{v}|ij\rangle_A\,\Delta^{(1)}(i,j,k;a,b,c)$$
$$\times\,\Delta^{(1)}(k,m;b,c)\,|\Phi_{ijk}^{abc}\rangle$$

The $|\Psi_0^{(2)}(Q)\rangle$ (quadruply excited) terms are:

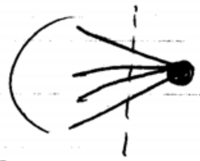


Hugenholtz



Brandow

Expression: $$\frac{1}{16}\sum_{abcd,ijkl}\langle ab|\hat{v}|ij\rangle_A\langle cd|\hat{v}|kl\rangle_A$$
$$\times\,\Delta^{(1)}(i,j,k,l;a,b,c,d)\,\Delta^{(1)}(k,l;c,d)\,|\Phi_{ijkl}^{abcd}\rangle$$

As shown in the class, the $|\Psi^{(2)}(Q)\rangle$ term factorizes into $\frac{1}{2}\Big($  $\Big)^2$ to give:

$\frac{1}{2}$  $\times$  $=$

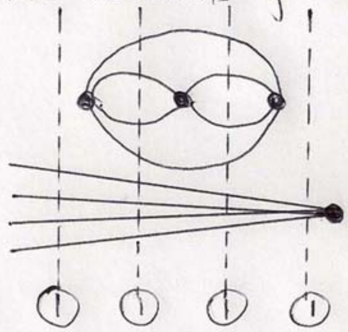
$$= \frac{1}{32} \sum_{abij} \sum_{cdkl} \langle ab|\hat{v}|ij\rangle_A \, \Delta^{(1)}(i,j;a,b) \times \langle cd|\hat{v}|kl\rangle_A \, \Delta^{(1)}(k,l;c,d) \times |\Phi_{ijkl}^{ab\,cd}\rangle$$

$$= \frac{1}{2} \left(T_2^{(1)}\right)^2 |\Phi_0\rangle,$$ where

$$T_2^{(1)} = \frac{1}{4} \sum_{abij} \langle ab|\hat{v}|ij\rangle_A \, \Delta^{(1)}(i,j;a,b) \times E_{ij}^{ab}$$

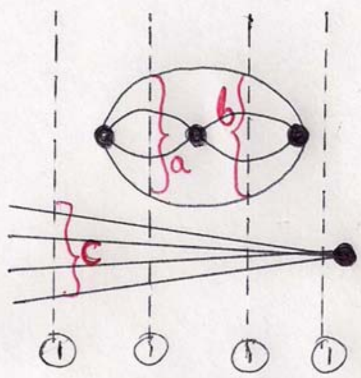
is the first-order estimate to the pair-cluster operator T_2.

2. Here are the skeletons obtained by forming time versions of the first kind from

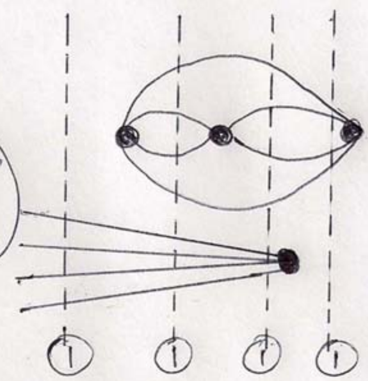


:

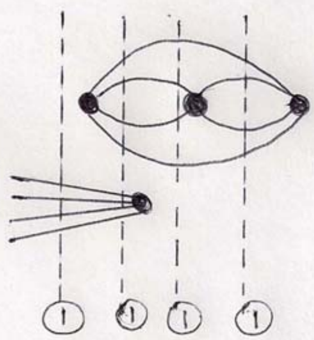
I



II



III



, where we use a, b, and c to designate the contributions to MBPT denominators from the corresponding fermion lines.

Let us use N to designate the numerator parts of the algebraic expressions associated with the above diagrams (products of weights, signs, and

matrix elements that each digram produces).
Then, we can write:

$$\mathrm{I} = \frac{N}{c(a+c)(b+c)c}, \quad \mathrm{II} = \frac{N}{c(a+c)(b+c)b},$$

and

$$\mathrm{III} = \frac{N}{c(a+c)ab},$$

summed over the appropriate indices of all the lines.
We obtain,

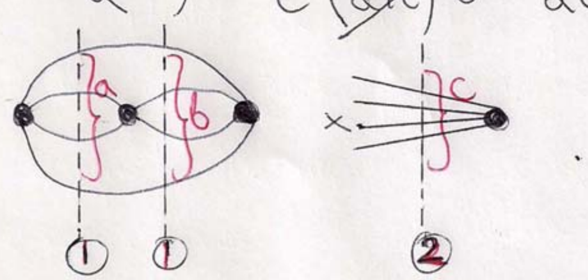
$$\mathrm{I} + \mathrm{II} + \mathrm{III} = \frac{N}{c(a+c)(b+c)c} + \frac{N}{c(a+c)(b+c)b}$$

$$+ \frac{N}{c(a+c)ab} = \frac{N}{c(a+c)(b+c)}\left(\frac{1}{c} + \frac{1}{b}\right)$$

$$+ \frac{N}{c(a+c)ab} = \frac{N}{c(a+c)\cancel{(b+c)}} \cdot \frac{\cancel{(b+c)}}{b \cdot c} + \frac{N}{c(a+c)ab}$$

$$= \frac{N}{c(a+c)b}\left(\frac{1}{c} + \frac{1}{a}\right) = \frac{N}{c\cancel{(a+c)}b} \cdot \frac{\cancel{(a+c)}}{ac}$$

$$= \frac{N}{ab \cdot c^2} =$$



.

Thus,

$$\mathrm{I} + \mathrm{II} + \mathrm{III} = \langle \Phi_0 | V_N R^{(0)} V_N R^{(0)} V_N | \Phi_0 \rangle \, R^{(0)^2} V_N | \Phi_0 \rangle .$$

As we can see, the sum of diagrams I, II and III gives the $\langle \Phi_0 | V_N R^{(0)} V_N R^{(0)} V_N | \Phi_0 \rangle \, R^{(0)2} V_N | \Phi_0 \rangle$ contribution to the

$$\langle \Phi_0 | W R^{(0)} W R^{(0)} W | \Phi_0 \rangle \, R^{(0)^2} W | \Phi_0 \rangle$$

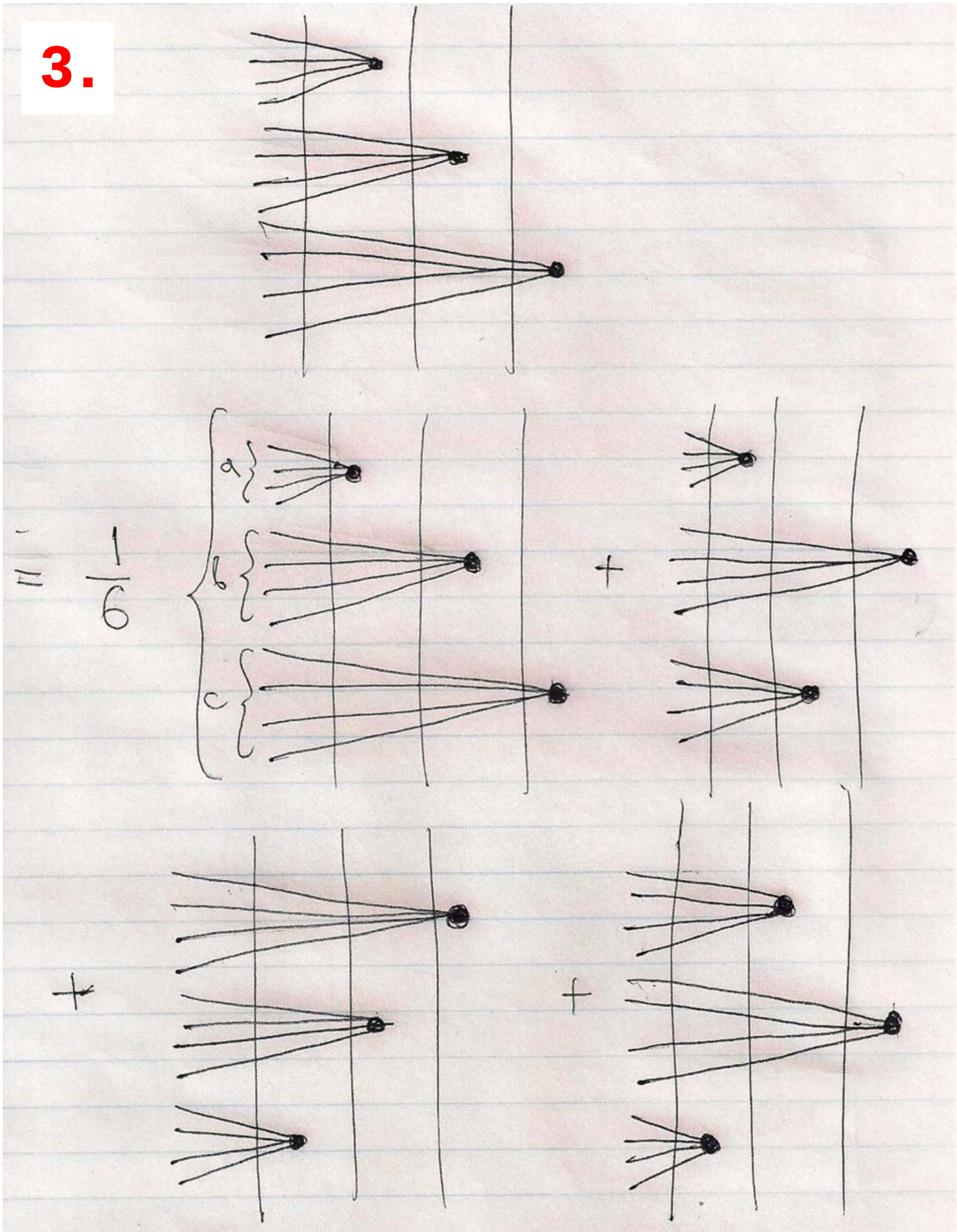
term, which is identical to one of the renormalization terms in $|\Psi_0^{(4)}\rangle$ except for the sign. In other words, the sum of diagrams I, II, and III originating from the principal term of $|\Psi_0^{(4)}\rangle$ cancels the

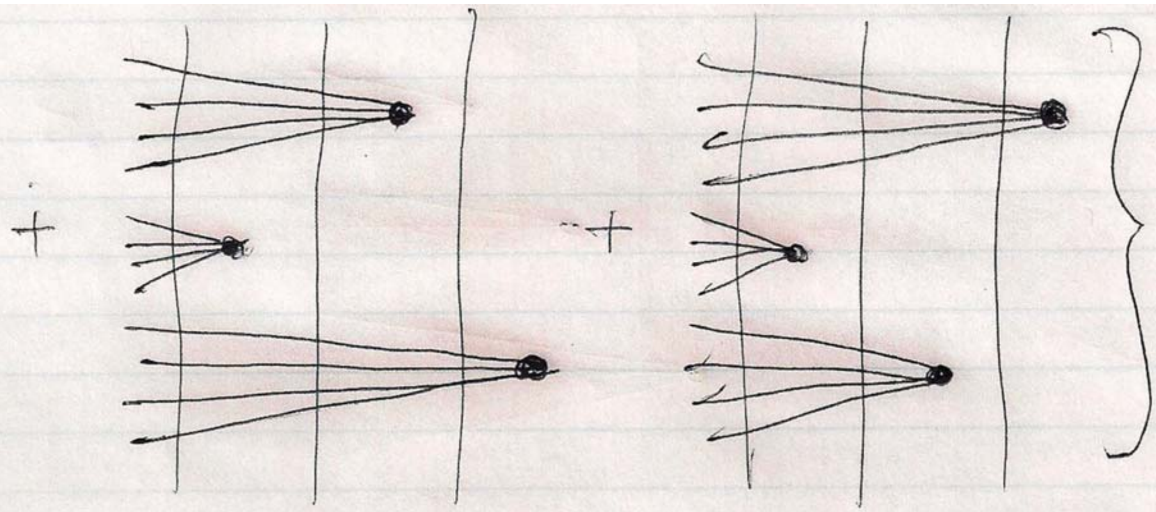
$$[- \langle \Phi_0 | V_N R^{(0)} V_N R^{(0)} V_N | \Phi_0 \rangle \, R^{(0)^2} V_N | \Phi_0 \rangle]$$

contribution to the

$$[- \langle \Phi_0 | W R^{(0)} W R^{(0)} W | \Phi_0 \rangle \, R^{(0)^2} W | \Phi_0 \rangle]$$

renormalization term in $|\Psi_0^{(4)}\rangle$.


3.



$$= \frac{1}{6}\left\{ \frac{N}{(a+b+c)(b+c)c} + \frac{N}{(a+b+c)(b+c)b} \right.$$

$$+ \frac{N}{(a+b+c)(a+b)a} + \frac{N}{(a+b+c)(a+b)b}$$

$$\left. + \frac{N}{(a+b+c)(a+c)c} + \frac{N}{(a+b+c)(a+c)a} \right\}$$

$$= \frac{1}{6}\left\{ \frac{N}{(a+b+c)(b+c)} \underbrace{\left(\frac{1}{c} + \frac{1}{b}\right)}_{=\frac{b+c}{bc}} \right.$$

$$+ \frac{N}{(a+b+c)(a+b)} \underbrace{\left(\frac{1}{a} + \frac{1}{b}\right)}_{= \frac{a+b}{ab}}$$

$$+ \frac{N}{(a+b+c)(a+c)} \underbrace{\left(\frac{1}{c} + \frac{1}{a}\right)}_{= \frac{a+c}{ac}} \Bigg\}$$

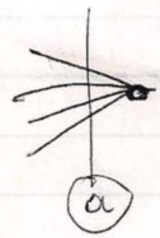
$$= \frac{1}{6} \left\{ \frac{N}{(a+b+c)bc} + \frac{N}{(a+b+c)ab} \right.$$

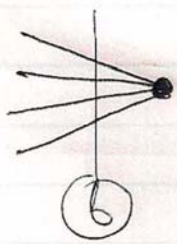
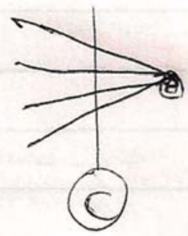
$$\left. + \frac{N}{(a+b+c)ac} \right\}$$

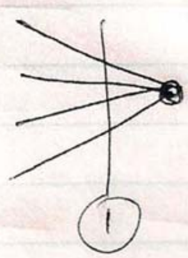
$$= \frac{1}{6} \frac{N}{(a+b+c)} \left\{ \frac{1}{ab} + \frac{1}{bc} + \frac{1}{ca} \right\}$$

$$= \frac{1}{6} \frac{N}{(a+b+c)} \frac{abc^2 + a^2bc + ab^2c}{a^2b^2c^2}$$

$$= \frac{1}{6} \frac{N}{\cancel{(a+b+c)}} \frac{\cancel{(a+b+c)}\, abc}{a^2 b^2 c^2}$$

$$= \frac{1}{6} \frac{N}{abc} = \frac{1}{6}$$ 

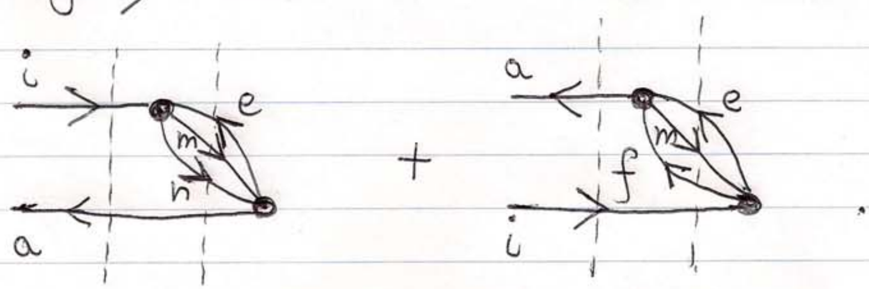
$\times$  $\times$ 

$$= \frac{1}{6} \Bigg($$  $$\Bigg)^3$$

4. According to our general considerations in class,

$$T_1^{(2)}|\Phi_0\rangle = \{(R^{(0)}V_N)^2\}_{C,1}|\Phi_0\rangle.$$

The two diagrams that correspond to this expression and that originate from $|\Psi_0^{(2)}\rangle$ are



According to the solution of Problem 1, we can write

$$T_1^{(2)} = -\frac{1}{2}\sum_{aeimn} \langle ea|\hat{v}|mn\rangle_A \langle mn|\hat{v}|ei\rangle_A$$

$$\times \Delta^{(1)}(i;a)\, \Delta^{(1)}(m,n;a,e)\, E_i^a$$

$$+ \frac{1}{2} \sum_{aef\, im} \langle ma|\hat{v}|ef\rangle_A \langle ef|\hat{v}|mi\rangle_A$$

$$\times \Delta^{(1)}(i;a)\, \Delta^{(1)}(i,m;e,f)\, E_i^a$$

Thus,

$$T_1^{(2)} = \sum_{a,i} \langle a|t_1^{(2)}|i\rangle E_i^a ,$$

where

$$\langle a|t_1^{(2)}|i\rangle \equiv {}^{(2)}t_a^i = \frac{1}{2} \sum_{efm} \langle ma|\hat{v}|ef\rangle_A$$

$$\times \langle ef|\hat{v}|mi\rangle_A\, \Delta^{(1)}(i;a)\, \Delta^{(1)}(i,m;e,f)$$

$$- \frac{1}{2} \sum_{emn} \langle ea|\hat{v}|mn\rangle_A \langle mn|\hat{v}|ei\rangle_A$$

$$\times \Delta^{(1)}(i;a)\, \Delta^{(1)}(m,n;a,e) .$$

We can simplify this result by writing

$$
{}^{(2)}t_a^{\,i} = \frac{1}{2}\,\Delta^{(1)}(i;a)
$$

$$
\times \sum_{em}\left\{ \sum_{f} v_{ma}^{ef}\, v_{ef}^{mi}\, \Delta^{(1)}(i,m;e,f) \right.
$$

$$
\left. - \sum_{n} v_{ea}^{mn}\, v_{mn}^{ei}\, \Delta^{(1)}(m,n;a,e) \right\}
$$

Clearly,

$$
{}^{(2)}t_a^{\,i} \equiv \langle a | t_1^{(2)} | i \rangle
$$

$$
= \langle \Phi_i^a | T_1^{(2)} | \Phi_0 \rangle .
$$