Slides from FYS-KJM4480/9480 Lectures

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Week 48, November 25-29

Plans for week 48: coupled-cluster theory and summary of course

- ► Short repetition from last week
- ► How to write your own coupled-cluster theory code, pairing model example
- ► Coupled-cluster theory for singles and doubles excitations using a diagrammatic derivation
- ► Summary and discussion of final oral exam
- ► Suggested literature: Shavitt and Bartlett chapters 9 and 10

CCSD with twobody Hamiltonian

Truncating the cluster operator $\widehat{T}$ at the $n = 2$ level, defines CCSD approximation to the Coupled Cluster wavefunction. The coupled cluster wavefunction is now given by

$$|\Psi_{CC}\rangle = e^{\widehat{T}_1 + \widehat{T}_2}|\Phi_0\rangle$$

where

$$\hat{T}_1 = \sum_{ia} t_i^a a_a^\dagger a_i$$

$$\hat{T}_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i.$$

CCSD with twobody Hamiltonian cont.

Normal ordered Hamiltonian

$$
\widehat{H} = \sum_{pq} f_q^p \left\{ a_p^\dagger a_q \right\} + \frac{1}{4} \sum_{pqrs} \langle pq | \widehat{v} | rs \rangle \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\}
$$
$$
+ \mathrm{E}_0
$$
$$
= \widehat{F}_N + \widehat{V}_N + \mathrm{E}_0 = \widehat{H}_N + \mathrm{E}_0
$$

where (often used notations, see also Shavitt and Bartlett chapters 3-4)

$$
f_q^p = \langle p | \widehat{h}_0 | q \rangle + \sum_i \langle pi | \widehat{v} | qi \rangle
$$
$$
\langle pq || rs \rangle = \langle pq | \widehat{v} | rs \rangle
$$
$$
\mathrm{E}_0 = \sum_i \langle i | \widehat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | \widehat{v} | ij \rangle
$$

Diagram equations - Derivation

Contract $\widehat{H}_N$ with $\widehat{T}$ in all possible unique combinations that satisfy a given form. The diagram equation is the sum of all these diagrams.

- ▶ Contract one $\widehat{H}_N$ element with 0, 1 or multiple $\widehat{T}$ elements.
- ▶ All $\widehat{T}$ elements must have atleast one contraction with $\widehat{H}_N$.
- ▶ No contractions between $\widehat{T}$ elements are allowed.
- ▶ A single $\widehat{T}$ element can contract with a single element of $\widehat{H}_N$ in different ways.

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Diagram elements - Directed lines

Figure: Particle line   Figure: Hole line

- ► Represents a contraction between second quantized operators.
- ► External lines are connected to one operator vertex and infinity.
- ► Internal lines are connected to operator vertices in both ends.

Diagram elements - Onebody Hamiltonian

Level: -1

Level: 0
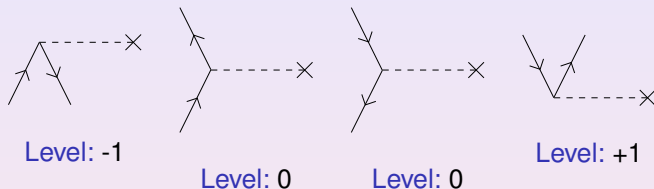
Level: 0

Level: +1

- ▶ Horisontal dashed line segment with one vertex.
- ▶ Excitation level identify the number of particle/hole pairs created by the operator.

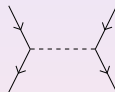# Diagram elements - Twobody Hamiltonian

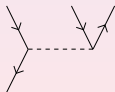Level: -2

Level: -1

Level: -1
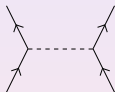
Level: 0

Level: 0

Level: 0

Level: +1

Level: +1

Level: +2

Diagram elements - Onebody cluster operator

Level: +1

- ▶ Horisontal line segment with one vertex.
- ▶ Excitation level of +1.
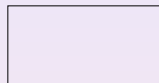
Diagram elements - Twobody cluster operator

Level: +2

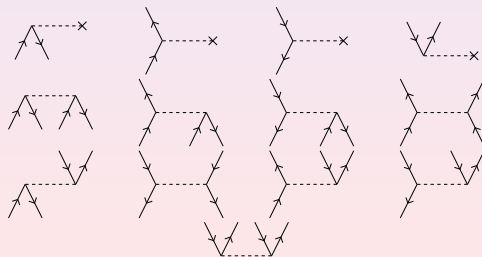- ▶ Horisontal line segment with two vertices.
- ▶ Excitation level of +2.

CCSD energy equation - Derivation
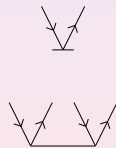
$$E_{CCSD} = \langle \Phi_0 || \Phi_0 \rangle$$

- No external lines.
- Final excitation level: 0

Elements: $\widehat{H}_N$

Elements: $\widehat{T}$

CCSD energy equation

$$E_{CCSD} = \text{} + \text{} + \text{}$$

Diagram rules

▶ Label all lines.

▶ Sum over all internal indices.

▶ Extract matrix elements. ($f_{\text{in}}^{\text{out}}$, $\langle \text{lout}, \text{rout} || \text{lin}, \text{rin} \rangle$)

▶ Extract cluster amplitudes with indices in the order left to right. Incoming lines are subscripts, while outgoing lines are superscripts. ($t_{\text{in}}^{\text{out}}$, $t_{\text{lin,rin}}^{\text{lout,rout}}$)

▶ Calculate the phase: $(-1)^{\text{holelines+loops}}$

▶ Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each equivalent vertex.

Diagram rules

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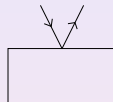
CCSD energy equation

$$E_{CCSD} = f_a^i t_i^a + \frac{1}{4}\langle ij||ab\rangle t_{ij}^{ab} + \frac{1}{2}\langle ij||ab\rangle t_i^a t_j^b$$

Note the implicit sum over repeated indices.

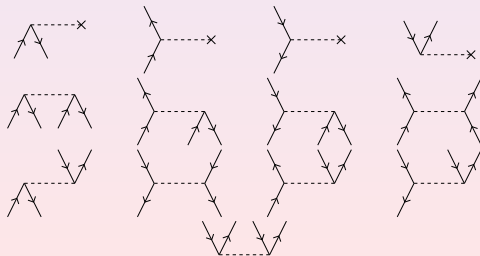# CCSD $\widehat{T}_1$ amplitude equation - Derivation
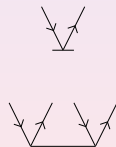
$$0 = \langle \Phi_i^a || \Phi_0 \rangle$$

- One pair of particle/hole external lines.
- Final excitation level: +1

Elements: $\widehat{H}_N$

Elements: $\widehat{T}$

Diagram rules

- ▶ Label all lines.
- ▶ Sum over all internal indices.
- ▶ Extract matrix elements. $(f_{\text{in}}^{\text{out}}, \langle \text{lout}, \text{rout} || \text{lin}, \text{rin} \rangle)$
- ▶ Extract cluster amplitudes with indices in the order left to right. Incoming lines are subscripts, while outgoing lines are superscripts. $(t_{\text{in}}^{\text{out}}, t_{\text{lin,rin}}^{\text{lout,rout}})$
- ▶ Calculate the phase: $(-1)^{\text{holelines+loops}}$
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CCSD $\widehat{T}_1$ amplitude equation

$$
\begin{aligned}
0 = {} & f_i^a + f_e^a t_i^e - f_i^m t_m^a + \langle ma||ei\rangle t_m^e + f_e^m t_{im}^{ae} + \frac{1}{2}\langle am||ef\rangle t_{im}^{ef} \\
& - \frac{1}{2}\langle mn||ei\rangle t_{mn}^{ea} - f_e^m t_i^e t_m^a + \langle am||ef\rangle t_i^e t_m^f - \langle mn||ei\rangle t_m^e t_n^a \\
& + \langle mn||ef\rangle t_m^e t_{ni}^{fa} - \frac{1}{2}\langle mn||ef\rangle t_i^e t_{mn}^{af} - \frac{1}{2}\langle mn||ef\rangle t_n^a t_{mi}^{ef} \\
& - \langle mn||ef\rangle t_i^e t_m^a t_n^f
\end{aligned}
$$

CCSD $\widehat{T}_2$ amplitude equation - Derivation

$$0 = \langle \Phi_{ij}^{ab} || \Phi_0 \rangle$$

- ▶ Two pairs of particle/hole external lines.
- ▶ Final excitation level: +2
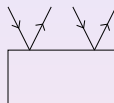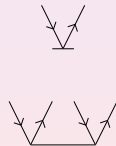
CCSD $\widehat{T}_2$ amplitude equation

$$0 = \vee \cdots \vee \; + \; \bigvee \cdots \vee + \; \vee \cdots \bigvee + \; \bigvee \cdots \times + \; \times \cdots \bigvee + \; \bigvee \cdots \bigvee \; + \; \bigvee \cdots$$
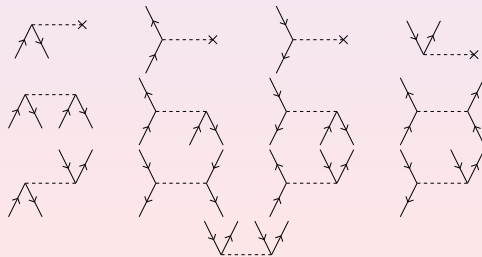
Diagram rules

▶ Label all lines.

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▶ Extract matrix elements. ($f_{\text{in}}^{\text{out}}$, $\langle \text{lout}, \text{rout} || \text{lin}, \text{rin} \rangle$)

▶ Extract cluster amplitudes with indices in the order left to right. Incoming lines are subscripts, while outgoing lines are superscripts. ($t_{\text{in}}^{\text{out}}$, $t_{\text{lin,rin}}^{\text{lout,rout}}$)

▶ Calculate the phase: $(-1)^{\text{holelines+loops}}$

▶ Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each equivalent vertex.

▶ Antisymmetrize a pair of external particle/hole line that does not connect to the same operator.

Diagram rules

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- ▶ Antisymmetrize a pair of external particle/hole line that does not connect to the same operator.

CCSD $\widehat{T}_2$ amplitude equation

$$
\begin{aligned}
0 =\ & \langle ab||ij\rangle + P(ij)\langle ab||ej\rangle t_i^e - P(ab)\langle am||ij\rangle t_m^b + P(ab)f_e^b t_{ij}^{ae} - P(ij)f_i^m t_{mj}^{ab} \\
& + \frac{1}{2}\langle ab||ef\rangle t_{ij}^{ef} + \frac{1}{2}\langle mn||ij\rangle t_{mn}^{ab} + P(ij)P(ab)\langle mb||ej\rangle t_{im}^{ae} \\
& + \frac{1}{2}P(ij)\langle ab||ef\rangle t_i^e t_j^f + \frac{1}{2}P(ab)\langle mn||ij\rangle t_m^a t_n^b - P(ij)P(ab)\langle mb||ej\rangle t_i^e t_m^a \\
& + \frac{1}{4}\langle mn||ef\rangle t_{ij}^{ef} t_{mn}^{ab} + \frac{1}{2}P(ij)P(ab)\langle mn||ef\rangle t_{im}^{ae} t_{nj}^{fb} - \frac{1}{2}P(ab)\langle mn||ef\rangle t_{ij}^{ae} t_{mn}^{bf} \\
& - \frac{1}{2}P(ij)\langle mn||ef\rangle t_{mi}^{ef} t_{nj}^{ab} - P(ij)f_e^m t_i^e t_{mj}^{ab} - P(ab)f_e^m t_{ij}^{ae} t_m^b \\
& + P(ij)P(ab)\langle am||ef\rangle t_i^e t_{mj}^{fb} - \frac{1}{2}P(ab)\langle am||ef\rangle t_{ij}^{ef} t_m^b + P(ab)\langle bm||ef\rangle t_{ij}^{ae} t_m^f \\
& - P(ij)P(ab)\langle mn||ej\rangle t_{im}^{ae} t_n^b + \frac{1}{2}P(ij)\langle mn||ej\rangle t_i^e t_{mn}^{ab} - P(ij)\langle mn||ei\rangle t_m^e t_{nj}^{ab} \\
& - \frac{1}{2}P(ij)P(ab)\langle am||ef\rangle t_i^e t_j^f t_m^b + \frac{1}{2}P(ij)P(ab)\langle mn||ej\rangle t_i^e t_m^a t_n^b \\
& + \frac{1}{4}P(ij)\langle mn||ef\rangle t_i^e t_{mn}^{ab} t_j^f - P(ij)P(ab)\langle mn||ef\rangle t_i^e t_m^a t_{nj}^{fb} \\
& + \frac{1}{4}P(ab)\langle mn||ef\rangle t_m^a t_{ij}^{ef} t_n^b - P(ij)\langle mn||ef\rangle t_m^e t_i^f t_{nj}^{ab} - P(ab)\langle mn||ef\rangle t_{ij}^{ae} t_m^b t_n^f \\
& + \frac{1}{4}P(ij)P(ab)\langle mn||ef\rangle t_i^e t_m^a t_j^f t_n^b
\end{aligned}
$$

The expansion

$$E_{CC} = \langle \Psi_0 | \left(\hat{H}_N + \left[\hat{H}_N, \hat{T} \right] + \frac{1}{2} \left[\left[\hat{H}_N, \hat{T} \right], \hat{T} \right] + \frac{1}{3!} \left[\left[\left[\hat{H}_N, \hat{T} \right], \hat{T} \right], \hat{T} \right] \right.$$
$$\left. + \frac{1}{4!} \left[\left[\left[\left[\hat{H}_N, \hat{T} \right], \hat{T} \right], \hat{T} \right], \hat{T} \right] + + \right) | \Psi_0 \rangle$$

$$0 = \langle \Psi_{ij\cdots}^{ab\cdots} | \left(\hat{H}_N + \left[\hat{H}_N, \hat{T} \right] + \frac{1}{2} \left[\left[\hat{H}_N, \hat{T} \right], \hat{T} \right] + \frac{1}{3!} \left[\left[\left[\hat{H}_N, \hat{T} \right], \hat{T} \right], \hat{T} \right] \right.$$
$$\left. + \frac{1}{4!} \left[\left[\left[\left[\hat{H}_N, \hat{T} \right], \hat{T} \right], \hat{T} \right], \hat{T} \right] + + \right) | \Psi_0 \rangle$$

The CCSD energy equation revisited

The expanded CC energy equation involves an infinite sum over nested commutators

$$
\begin{aligned}
E_{CC} = \langle \Psi_0 | \Big(& \hat{H}_N + \left[\hat{H}_N, \hat{T} \right] + \frac{1}{2} \left[\left[\hat{H}_N, \hat{T} \right], \hat{T} \right] \\
& + \frac{1}{3!} \left[\left[\left[\hat{H}_N, \hat{T} \right], \hat{T} \right], \hat{T} \right] \\
& + \frac{1}{4!} \left[\left[\left[\left[\hat{H}_N, \hat{T} \right], \hat{T} \right], \hat{T} \right], \hat{T} \right] + + \Big) | \Psi_0 \rangle,
\end{aligned}
$$

but fortunately we can show that it truncates naturally, depending on the Hamiltonian.

The first term is zero by construction.

$$
\langle \Psi_0 | \widehat{H}_N | \Psi_0 \rangle = 0
$$

The CCSD energy equation revisited.

The second term can be split up into different pieces

$$\langle \Psi_0 | \left[\hat{H}_N, \hat{T} \right] | \Psi_0 \rangle = \langle \Psi_0 | \left(\left[\hat{F}_N, \hat{T}_1 \right] + \left[\hat{F}_N, \hat{T}_2 \right] + \left[\hat{V}_N, \hat{T}_1 \right] + \left[\hat{V}_N, \hat{T}_2 \right] \right) | \Psi_0 \rangle$$

Since we need the explicit expressions for the commutators both in the next term and in the amplitude equations, we calculate them separately.

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p a_p^\dagger a_q t_i^a a_a^\dagger a_i - t_i^a a_a^\dagger a_i f_q^p a_p^\dagger a_q\right)$$

$$= \sum_{pqia} f_q^p t_i^a \left(a_p^\dagger a_q a_a^\dagger a_i - a_a^\dagger a_i a_p^\dagger a_q\right)$$

$$\left\{a_a^\dagger a_i\right\} \left\{a_p^\dagger a_q\right\} = a_a^\dagger a_i a_p^\dagger a_q = a_p^\dagger a_q a_a^\dagger a_i$$

$$a_p^\dagger a_q a_a^\dagger a_i = a_p^\dagger a_q a_a^\dagger a_i$$

$$+ \; a_p^\dagger a_q a_a^\dagger a_i + a_p^\dagger a_q a_a^\dagger a_i$$

$$+ \; a_p^\dagger a_q a_a^\dagger a_i$$

$$= a_p^\dagger a_q a_a^\dagger a_i + \delta_{qa} a_p^\dagger a_i + \delta_{pi} a_q a_a^\dagger + \delta_{qa}\delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p a_p^\dagger a_q t_i^a a_a^\dagger a_i - t_i^a a_a^\dagger a_i f_q^p a_p^\dagger a_q \right)$$

$$= \sum_{pqia} f_q^p t_i^a \left(a_p^\dagger a_q a_a^\dagger a_i - a_a^\dagger a_i a_p^\dagger a_q \right)$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = a_a^\dagger a_i a_p^\dagger a_q = a_p^\dagger a_q a_a^\dagger a_i$$

$$a_p^\dagger a_q a_a^\dagger a_i = a_p^\dagger a_q a_a^\dagger a_i$$

$$+ a_p^\dagger a_q a_a^\dagger a_i + a_p^\dagger a_q a_a^\dagger a_i$$

$$+ a_p^\dagger a_q a_a^\dagger a_i$$

$$= a_p^\dagger a_q a_a^\dagger a_i + \delta_{qa} a_p^\dagger a_i + \delta_{pi} a_q a_a^\dagger + \delta_{qa} \delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p a_p^\dagger a_q t_i^a a_a^\dagger a_i - t_i^a a_a^\dagger a_i f_q^p a_p^\dagger a_q \right)$$
$$= \sum_{pqia} f_q^p t_i^a \left(a_p^\dagger a_q a_a^\dagger a_i - a_a^\dagger a_i a_p^\dagger a_q \right)$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = a_a^\dagger a_i a_p^\dagger a_q = a_p^\dagger a_q a_a^\dagger a_i$$

$$a_p^\dagger a_q a_a^\dagger a_i = a_p^\dagger a_q a_a^\dagger a_i$$
$$+ \overbrace{a_p^\dagger a_q a_a^\dagger a_i}^{} + a_p^\dagger \overbrace{a_q a_a^\dagger a_i}^{}$$
$$+ \overbrace{a_p^\dagger a_q a_a^\dagger a_i}^{}$$
$$= a_p^\dagger a_q a_a^\dagger a_i + \delta_{qa} a_p^\dagger a_i + \delta_{pi} a_q a_a^\dagger + \delta_{qa} \delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p a_p^\dagger a_q t_i^a a_a^\dagger a_i - t_i^a a_a^\dagger a_i f_q^p a_p^\dagger a_q \right)$$

$$= \sum_{pqia} f_q^p t_i^a \left(a_p^\dagger a_q a_a^\dagger a_i - a_a^\dagger a_i a_p^\dagger a_q \right)$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = a_a^\dagger a_i a_p^\dagger a_q = a_p^\dagger a_q a_a^\dagger a_i$$

$$a_p^\dagger a_q a_a^\dagger a_i = a_p^\dagger a_q a_a^\dagger a_i$$

$$+ \overbracket{a_p^\dagger a_q a_a^\dagger} a_i + a_p^\dagger \overbracket{a_q a_a^\dagger} a_i$$

$$+ \overbracket{a_p^\dagger a_q a_a^\dagger a_i}$$

$$= a_p^\dagger a_q a_a^\dagger a_i + \delta_{qa} a_p^\dagger a_i + \delta_{pi} a_q a_a^\dagger + \delta_{qa} \delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1 \right]$

$$\left[\hat{F}_N, \hat{T}_1 \right] = \sum_{pqia} \left(f_q^p a_p^\dagger a_q t_i^a a_a^\dagger a_i - t_i^a a_a^\dagger a_i f_q^p a_p^\dagger a_q \right)$$

$$= \sum_{pqia} f_q^p t_i^a \left(a_p^\dagger a_q a_a^\dagger a_i - a_a^\dagger a_i a_p^\dagger a_q \right)$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = a_a^\dagger a_i a_p^\dagger a_q = a_p^\dagger a_q a_a^\dagger a_i$$

$$a_p^\dagger a_q a_a^\dagger a_i = a_p^\dagger a_q a_a^\dagger a_i$$

$$+ \overset{\frown}{a_p^\dagger a_q a_a^\dagger} a_i + a_p^\dagger \overset{\frown}{a_q a_a^\dagger} a_i$$

$$+ \overset{\frown}{a_p^\dagger a_q a_a^\dagger a_i}$$

$$= a_p^\dagger a_q a_a^\dagger a_i + \delta_{qa} a_p^\dagger a_i + \delta_{pi} a_q a_a^\dagger + \delta_{qa} \delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p a_p^\dagger a_q t_i^a a_a^\dagger a_i - t_i^a a_a^\dagger a_i f_q^p a_p^\dagger a_q\right)$$

$$= \sum_{pqia} f_q^p t_i^a \left(a_p^\dagger a_q a_a^\dagger a_i - a_a^\dagger a_i a_p^\dagger a_q\right)$$

$$\left\{a_a^\dagger a_i\right\} \left\{a_p^\dagger a_q\right\} = a_a^\dagger a_i a_p^\dagger a_q = a_p^\dagger a_q a_a^\dagger a_i$$

$$a_p^\dagger a_q a_a^\dagger a_i = a_p^\dagger a_q a_a^\dagger a_i$$

$$+ \overbrace{a_p^\dagger a_q a_a^\dagger a_i} + a_p^\dagger \overbrace{a_q a_a^\dagger} a_i$$

$$+ \overbrace{a_p^\dagger a_q a_a^\dagger a_i}$$

$$= a_p^\dagger a_q a_a^\dagger a_i + \delta_{qa} a_p^\dagger a_i + \delta_{pi} a_q a_a^\dagger + \delta_{qa}\delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pqia} \left(f_q^p a_p^\dagger a_q t_i^a a_a^\dagger a_i - t_i^a a_a^\dagger a_i f_q^p a_p^\dagger a_q \right)$$

$$= \sum_{pqia} f_q^p t_i^a \left(a_p^\dagger a_q a_a^\dagger a_i - a_a^\dagger a_i a_p^\dagger a_q \right)$$

$$\left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = a_a^\dagger a_i a_p^\dagger a_q = a_p^\dagger a_q a_a^\dagger a_i$$

$$a_p^\dagger a_q a_a^\dagger a_i = a_p^\dagger a_q a_a^\dagger a_i$$

$$+ \overbrace{a_p^\dagger a_q a_a^\dagger a_i} + a_p^\dagger \overbrace{a_q a_a^\dagger a_i}$$

$$+ \overbrace{a_p^\dagger \overbrace{a_q a_a^\dagger a_i}}$$

$$= a_p^\dagger a_q a_a^\dagger a_i + \delta_{qa} a_p^\dagger a_i + \delta_{pi} a_q a_a^\dagger + \delta_{qa} \delta_{pi}$$

The expansion - $\left[\hat{F}_N, \hat{T}_1 \right]$

Wicks theorem gives us

$$\left\{ a_p^\dagger a_q \right\} \left\{ a_a^\dagger a_i \right\} - \left\{ a_a^\dagger a_i \right\} \left\{ a_p^\dagger a_q \right\} = \delta_{qa} \left\{ a_p^\dagger a_i \right\} + \delta_{pi} \left\{ a_q a_a^\dagger \right\} + \delta_{qa}\delta_{pi}.$$

Inserted into the original expression, we arrive at the explicit value of the commutator

$$\left[\hat{F}_N, \hat{T}_1 \right] = \sum_{pai} f_a^p t_i^a a_p^\dagger a_i + \sum_{qai} f_q^i t_i^a a_q a_a^\dagger + \sum_{ai} f_a^i t_i^a$$

$$= \left(\hat{F}_N \hat{T}_1 \right)_c.$$

The subscript means that the product only includes terms where the operators are connected by atleast one shared index.

The expansion - $\left[\hat{F}_N, \hat{T}_2 \right]$

$$\left[\hat{F}_N, \hat{T}_2 \right] = \left[\sum_{pq} f_q^p a_p^\dagger a_q, \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i \right]$$

$$= \frac{1}{4} \sum_{\substack{pq \\ ijab}} \left[a_p^\dagger a_q, a_a^\dagger a_b^\dagger a_j a_i \right]$$

$$= \frac{1}{4} \sum_{\substack{pq \\ ijab}} f_q^p t_{ij}^{ab} \left(a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i - a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q \right)$$

The expansion - $\left[\hat{F}_N, \hat{T}_2 \right]$

$$a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q = a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q$$
$$= a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i$$

$$a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i = a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i + \left\{ a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i \right\}$$

$$= a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i - \delta_{pj} a_q a_a^\dagger a_b^\dagger a_i + \delta_{pi} a_q a_a^\dagger a_b^\dagger a_j$$
$$+ \delta_{qa} a_p^\dagger a_b^\dagger a_j a_i - \delta_{qb} a_p^\dagger a_a^\dagger a_j a_i - \delta_{pj} \delta_{qa} a_b^\dagger a_i$$
$$+ \delta_{pi} \delta_{qa} a_b^\dagger a_j + \delta_{pj} \delta_{qb} a_a^\dagger a_i - \delta_{pi} \delta_{qb} a_a^\dagger a_j$$

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$$a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q = a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q$$
$$= a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i$$

$$a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i = a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i + \left\{ \overbracket{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overbracket{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\}$$

$$+ \left\{ a_p^\dagger \overbracket{a_q a_a^\dagger} a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger \overbracket{a_q a_a^\dagger a_b^\dagger} a_j a_i \right\} + \left\{ \overbracket{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\}$$

$$+ \left\{ \overbracket{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overbracket{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overbracket{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\}$$

$$= a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i - \delta_{pj} a_q a_a^\dagger a_b^\dagger a_i + \delta_{pi} a_q a_a^\dagger a_b^\dagger a_j$$
$$+ \delta_{qa} a_p^\dagger a_b^\dagger a_j a_i - \delta_{qb} a_p^\dagger a_a^\dagger a_j a_i - \delta_{pj} \delta_{qa} a_b^\dagger a_i$$
$$+ \delta_{pi} \delta_{qa} a_b^\dagger a_j + \delta_{pj} \delta_{qb} a_a^\dagger a_i - \delta_{pi} \delta_{qb} a_a^\dagger a_j$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q = a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q$$
$$= a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i$$

$$a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i = a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i + \left\{ \overline{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overline{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\}$$

$$+ \left\{ a_p^\dagger \overline{a_q a_a^\dagger} a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger \overline{a_q a_a^\dagger a_b^\dagger} a_j a_i \right\} + \left\{ \overline{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\}$$

$$+ \left\{ \overline{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overline{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overline{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\}$$

$$= a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i - \delta_{pj} a_q a_a^\dagger a_b^\dagger a_i + \delta_{pi} a_q a_a^\dagger a_b^\dagger a_j$$
$$+ \delta_{qa} a_p^\dagger a_b^\dagger a_j a_i - \delta_{qb} a_p^\dagger a_a^\dagger a_j a_i - \delta_{pj}\delta_{qa} a_b^\dagger a_i$$
$$+ \delta_{pi}\delta_{qa} a_b^\dagger a_j + \delta_{pj}\delta_{qb} a_a^\dagger a_i - \delta_{pi}\delta_{qb} a_a^\dagger a_j$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q = a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q$$
$$= a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i$$

$$a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i = a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i + \left\{ \overbracket{a_p^\dagger a_q a_a^\dagger a_b^\dagger} a_j a_i \right\} + \left\{ \overbracket{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j} a_i \right\}$$

$$+ \left\{ a_p^\dagger \overbracket{a_q a_a^\dagger} a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger \overbracket{a_q a_a^\dagger a_b^\dagger} a_j a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i \right\}$$

$$+ \left\{ a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i \right\}$$

$$= a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i - \delta_{pj} a_q a_a^\dagger a_b^\dagger a_i + \delta_{pi} a_q a_a^\dagger a_b^\dagger a_j$$
$$+ \delta_{qa} a_p^\dagger a_b^\dagger a_j a_i - \delta_{qb} a_p^\dagger a_a^\dagger a_j a_i - \delta_{pj} \delta_{qa} a_b^\dagger a_i$$
$$+ \delta_{pi} \delta_{qa} a_b^\dagger a_j + \delta_{pj} \delta_{qb} a_a^\dagger a_i - \delta_{pi} \delta_{qb} a_a^\dagger a_j$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q = a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q$$
$$= a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i$$

$$a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i = a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i + \left\{ \overbrace{a_p^\dagger a_q a_a^\dagger a_b^\dagger} a_j a_i \right\} + \left\{ \overbrace{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j} a_i \right\}$$

$$+ \left\{ a_p^\dagger \overbrace{a_q a_a^\dagger} a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger \overbrace{a_q a_a^\dagger a_b^\dagger} a_j a_i \right\} + \left\{ \overbrace{a_p^\dagger a_q a_a^\dagger a_b^\dagger} a_j a_i \right\}$$

$$+ \left\{ a_p^\dagger \overbrace{a_q a_a^\dagger} a_b^\dagger a_j a_i \right\} + \left\{ \overbrace{a_p^\dagger a_q a_a^\dagger a_b^\dagger} a_j a_i \right\} + \left\{ \overbrace{a_p^\dagger a_q a_a^\dagger a_b^\dagger} a_j a_i \right\}$$

$$= a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i - \delta_{pj} a_q a_a^\dagger a_b^\dagger a_i + \delta_{pi} a_q a_a^\dagger a_b^\dagger a_j$$
$$+ \delta_{qa} a_p^\dagger a_b^\dagger a_j a_i - \delta_{qb} a_p^\dagger a_a^\dagger a_j a_i - \delta_{pj} \delta_{qa} a_b^\dagger a_i$$
$$+ \delta_{pi} \delta_{qa} a_b^\dagger a_j + \delta_{pj} \delta_{qb} a_a^\dagger a_i - \delta_{pi} \delta_{qb} a_a^\dagger a_j$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

$$a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q = a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q$$
$$= a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i$$

$$a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i = a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i + \left\{ \overline{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overline{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\}$$

$$+ \left\{ a_p^\dagger \overline{a_q a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ a_p^\dagger \overline{a_q a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overline{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\}$$

$$+ \left\{ \overline{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overline{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overline{a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i} \right\}$$

$$= a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i - \delta_{pj} a_q a_a^\dagger a_b^\dagger a_i + \delta_{pi} a_q a_a^\dagger a_b^\dagger a_j$$
$$+ \delta_{qa} a_p^\dagger a_b^\dagger a_j a_i - \delta_{qb} a_p^\dagger a_a^\dagger a_j a_i - \delta_{pj} \delta_{qa} a_b^\dagger a_i$$
$$+ \delta_{pi} \delta_{qa} a_b^\dagger a_j + \delta_{pj} \delta_{qb} a_a^\dagger a_i - \delta_{pi} \delta_{qb} a_a^\dagger a_j$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

Wicks theorem gives us

$$
\begin{aligned}
\left(a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i - a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q \right) = \\
- \delta_{pj} a_q a_a^\dagger a_b^\dagger a_i + \delta_{pi} a_q a_a^\dagger a_b^\dagger a_j + \delta_{qa} a_p^\dagger a_b^\dagger a_j a_i \\
- \delta_{qb} a_p^\dagger a_a^\dagger a_j a_i - \delta_{pj} \delta_{qa} a_b^\dagger a_i + \delta_{pi} \delta_{qa} a_b^\dagger a_j + \delta_{pj} \delta_{qb} a_a^\dagger a_i \\
- \delta_{pi} \delta_{qb} a_a^\dagger a_j
\end{aligned}
$$

Inserted into the original expression, we arrive at

$$
\begin{aligned}
\left[\widehat{F}_N, \widehat{T}_2 \right] = \frac{1}{4} \sum_{\substack{pq \\ abij}} f_q^p t_{ij}^{ab} \Big(-\delta_{pj} a_q a_a^\dagger a_b^\dagger a_i + \delta_{pi} a_q a_a^\dagger a_b^\dagger a_j \\
+ \delta_{qa} a_p^\dagger a_b^\dagger a_j a_i - \delta_{qb} a_p^\dagger a_a^\dagger a_j a_i - \delta_{pj} \delta_{qa} a_b^\dagger a_i \\
+ \delta_{pi} \delta_{qa} a_b^\dagger a_j + \delta_{pj} \delta_{qb} a_a^\dagger a_i - \delta_{pi} \delta_{qb} a_a^\dagger a_j \Big).
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

Wicks theorem gives us

$$
\begin{aligned}
\Big(a_p^\dagger a_q a_a^\dagger a_b^\dagger a_j a_i - a_a^\dagger a_b^\dagger a_j a_i a_p^\dagger a_q\Big) = & \\
& - \delta_{pj} a_q a_a^\dagger a_b^\dagger a_i + \delta_{pi} a_q a_a^\dagger a_b^\dagger a_j + \delta_{qa} a_p^\dagger a_b^\dagger a_j a_i \\
& - \delta_{qb} a_p^\dagger a_a^\dagger a_j a_i - \delta_{pj}\delta_{qa} a_b^\dagger a_i + \delta_{pi}\delta_{qa} a_b^\dagger a_j + \delta_{pj}\delta_{qb} a_a^\dagger a_i \\
& - \delta_{pi}\delta_{qb} a_a^\dagger a_j
\end{aligned}
$$

Inserted into the original expression, we arrive at

$$
\begin{aligned}
\left[\hat{F}_N, \hat{T}_2\right] = \frac{1}{4} \sum_{\substack{pq \\ abij}} f_q^p t_{ij}^{ab} \Big(& -\delta_{pj} a_q a_a^\dagger a_b^\dagger a_i + \delta_{pi} a_q a_a^\dagger a_b^\dagger a_j \\
& + \delta_{qa} a_p^\dagger a_b^\dagger a_j a_i - \delta_{qb} a_p^\dagger a_a^\dagger a_j a_i - \delta_{pj}\delta_{qa} a_b^\dagger a_i \\
& + \delta_{pi}\delta_{qa} a_b^\dagger a_j + \delta_{pj}\delta_{qb} a_a^\dagger a_i - \delta_{pi}\delta_{qb} a_a^\dagger a_j \Big).
\end{aligned}
$$

The expansion - $\left[\hat{F}_N, \hat{T}_2\right]$

After renaming indices and changing the order of operators, we arrive at the explicit expression

$$\begin{aligned}
\left[\hat{F}_N, \hat{T}_2\right] &= \frac{1}{2} \sum_{qijab} f_q^i t_{ij}^{ab} a_q a_a^\dagger a_b^\dagger a_j + \frac{1}{2} \sum_{pijab} f_a^p t_{ij}^{ab} a_p^\dagger a_b^\dagger a_j a_i \\
&\quad + \sum_{ijab} f_a^i t_{ij}^{ab} a_b^\dagger a_j \\
&= \left(\hat{F}_N \hat{T}_2\right)_c.
\end{aligned}$$

The subscript implies that only the connected terms from the product contribute.

The expansion - $\frac{1}{2}\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pai} f_a^p t_i^a a_p^\dagger a_i + \sum_{qai} f_q^i t_i^a a_q a_a^\dagger + \sum_{ai} f_a^i t_i^a$$

$$\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right] = \left[\sum_{pai} f_a^p t_i^a a_p^\dagger a_i + \sum_{qai} f_q^i t_i^a a_q a_a^\dagger + \sum_{ai} f_a^i t_i^a, \sum_{jb} t_j^b a_b^\dagger a_j\right]$$

$$= \left[\sum_{pai} f_a^p t_i^a a_p^\dagger a_i + \sum_{qai} f_q^i t_i^a a_q a_a^\dagger, \sum_{jb} t_j^b a_b^\dagger a_j\right]$$

$$= \sum_{pabij} f_a^p t_i^a t_j^b \left[a_p^\dagger a_i, a_b^\dagger a_j\right] + \sum_{qabij} f_q^i t_i^a t_j^b \left[a_q a_a^\dagger, a_b^\dagger a_j\right]$$

$$a_b^\dagger a_j a_p^\dagger a_i = a_b^\dagger a_j a_p^\dagger a_i = a_p^\dagger a_i a_b^\dagger a_j$$

$$a_b^\dagger a_j a_q a_a^\dagger = a_b^\dagger a_j a_q a_a^\dagger = a_q a_a^\dagger a_b^\dagger a_j$$

The expansion - $\frac{1}{2}\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pai} f_a^p t_i^a a_p^\dagger a_i + \sum_{qai} f_q^i t_i^a a_q a_a^\dagger + \sum_{ai} f_a^i t_i^a$$

$$\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right] = \left[\sum_{pai} f_a^p t_i^a a_p^\dagger a_i + \sum_{qai} f_q^i t_i^a a_q a_a^\dagger + \sum_{ai} f_a^i t_i^a, \sum_{jb} t_j^b a_b^\dagger a_j\right.$$

$$= \left[\sum_{pai} f_a^p t_i^a a_p^\dagger a_i + \sum_{qai} f_q^i t_i^a a_q a_a^\dagger, \sum_{jb} t_j^b a_b^\dagger a_j\right]$$

$$= \sum_{pabij} f_a^p t_i^a t_j^b \left[a_p^\dagger a_i, a_b^\dagger a_j\right] + \sum_{qabij} f_q^i t_i^a t_j^b \left[a_q a_a^\dagger, a_b^\dagger a_j\right]$$

$$a_b^\dagger a_j a_p^\dagger a_i = a_b^\dagger a_j a_p^\dagger a_i = a_p^\dagger a_i a_b^\dagger a_j$$

$$a_b^\dagger a_j a_q a_a^\dagger = a_b^\dagger a_j a_q a_a^\dagger = a_q a_a^\dagger a_b^\dagger a_j$$

The expansion - $\frac{1}{2}\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pai} f_a^p t_i^a a_p^\dagger a_i + \sum_{qai} f_q^i t_i^a a_q a_a^\dagger + \sum_{ai} f_a^i t_i^a$$

$$\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right] = \left[\sum_{pai} f_a^p t_i^a a_p^\dagger a_i + \sum_{qai} f_q^i t_i^a a_q a_a^\dagger + \sum_{ai} f_a^i t_i^a, \sum_{jb} t_j^b a_b^\dagger a_j\right.$$

$$= \left[\sum_{pai} f_a^p t_i^a a_p^\dagger a_i + \sum_{qai} f_q^i t_i^a a_q a_a^\dagger, \sum_{jb} t_j^b a_b^\dagger a_j\right.$$

$$= \sum_{pabij} f_a^p t_i^a t_j^b \left[a_p^\dagger a_i, a_b^\dagger a_j\right] + \sum_{qabij} f_q^i t_i^a t_j^b \left[a_q a_a^\dagger, a_b^\dagger a_j\right]$$

$$a_b^\dagger a_j a_p^\dagger a_i = a_b^\dagger a_j a_p^\dagger a_i = a_p^\dagger a_i a_b^\dagger a_j$$
$$a_b^\dagger a_j a_q a_a^\dagger = a_b^\dagger a_j a_q a_a^\dagger = a_q a_a^\dagger a_b^\dagger a_j$$

The expansion - $\frac{1}{2}\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right]$

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pai} f_a^p t_i^a a_p^\dagger a_i + \sum_{qai} f_q^i t_i^a a_q a_a^\dagger + \sum_{ai} f_a^i t_i^a$$

$$\begin{aligned}
\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right] &= \left[\sum_{pai} f_a^p t_i^a a_p^\dagger a_i + \sum_{qai} f_q^i t_i^a a_q a_a^\dagger + \sum_{ai} f_a^i t_i^a, \sum_{jb} t_j^b a_b^\dagger a_j\right] \\
&= \left[\sum_{pai} f_a^p t_i^a a_p^\dagger a_i + \sum_{qai} f_q^i t_i^a a_q a_a^\dagger, \sum_{jb} t_j^b a_b^\dagger a_j\right] \\
&= \sum_{pabij} f_a^p t_i^a t_j^b \left[a_p^\dagger a_i, a_b^\dagger a_j\right] + \sum_{qabij} f_q^i t_i^a t_j^b \left[a_q a_a^\dagger, a_b^\dagger a_j\right]
\end{aligned}$$

$$a_b^\dagger a_j a_p^\dagger a_i = a_b^\dagger a_j a_p^\dagger a_i = a_p^\dagger a_i a_b^\dagger a_j$$
$$a_b^\dagger a_j a_q a_a^\dagger = a_b^\dagger a_j a_q a_a^\dagger = a_q a_a^\dagger a_b^\dagger a_j$$

The expansion - $\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right]$

$$
\begin{aligned}
\frac{1}{2}\left[\left[\widehat{F}_N, \widehat{T}_1\right], \widehat{T}_1\right] &= \frac{1}{2}\left(\sum_{pabij} f_a^p t_i^a t_j^b \delta_{pj} a_i a_b^\dagger - \sum_{qabij} f_q^i t_i^a t_j^b \delta_{qb} a_a^\dagger a_j\right) \\
&= -\frac{1}{2}2\sum_{abij} f_b^j t_j^a t_i^b a_a^\dagger a_i \\
&= -\sum_{abij} f_b^j t_j^a t_i^b a_a^\dagger a_i \\
&= \frac{1}{2}\left(\widehat{F}_N \widehat{T}_1^2\right)_c
\end{aligned}
$$

The CCSD energy equation revisited

$$\langle \Phi_0 | \left[\hat{V}_N, \hat{T}_1 \right] | \Phi_0 \rangle = \langle \Phi_0 | \left[\frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle a_p^\dagger a_q^\dagger a_s a_r, \sum_{ia} t_i^a a_a^\dagger a_i \right] | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{\substack{pqr \\ sia}} \langle pq || rs \rangle t_i^a \langle \Phi_0 | \left[a_p^\dagger a_q^\dagger a_s a_r, a_a^\dagger a_i \right] | \Phi_0 \rangle$$

$$= 0$$

The CCSD energy equation revisited

$$\langle \Phi_0 | \left[\hat{V}_N, \hat{T}_1 \right] | \Phi_0 \rangle = \langle \Phi_0 | \left[\frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle a_p^\dagger a_q^\dagger a_s a_r, \sum_{ia} t_i^a a_a^\dagger a_i \right] | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{\substack{pqr \\ sia}} \langle pq || rs \rangle t_i^a \langle \Phi_0 | \left[a_p^\dagger a_q^\dagger a_s a_r, a_a^\dagger a_i \right] | \Phi_0 \rangle$$

$$= 0$$

The CCSD energy equation revisited

$$\langle \Phi_0 | \left[\hat{V}_N, \hat{T}_1 \right] | \Phi_0 \rangle = \langle \Phi_0 | \left[\frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle a_p^\dagger a_q^\dagger a_s a_r, \sum_{ia} t_i^a a_a^\dagger a_i \right] | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{\substack{pqr \\ sia}} \langle pq||rs \rangle t_i^a \langle \Phi_0 | \left[a_p^\dagger a_q^\dagger a_s a_r, a_a^\dagger a_i \right] | \Phi_0 \rangle$$

$$= 0$$

The CCSD energy equation revisited

$\langle\Phi_0|\left[\hat{V}_N, \hat{T}_2\right]|\Phi_0\rangle =$

$\langle\Phi_0|\left[\dfrac{1}{4}\sum_{pqrs}\langle pq||rs\rangle a_p^\dagger a_q^\dagger a_s a_r, \dfrac{1}{4}\sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i\right]|\Phi_0\rangle$

$= \dfrac{1}{16}\sum_{\substack{pqr\\sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\left[a_p^\dagger a_q^\dagger a_s a_r, a_a^\dagger a_b^\dagger a_j a_i\right]|\Phi_0\rangle$

$= \dfrac{1}{16}\sum_{\substack{pqr\\sijab}}\langle pq||rs\rangle t_{ij}^{ab}\langle\Phi_0|\Bigg(\left\{\overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i}\right\} + \left\{\overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i}\right\}$

$\left\{\overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i}\right\} + \left\{\overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i}\right\}\Bigg)|\Phi_0\rangle$

$= \dfrac{1}{4}\sum_{ijab}\langle ij||ab\rangle t_{ij}^{ab}$

The CCSD energy equation revisited

$$\langle \Phi_0 | \left[\hat{V}_N, \hat{T}_2 \right] | \Phi_0 \rangle =$$

$$\langle \Phi_0 | \left[\frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle a_p^\dagger a_q^\dagger a_s a_r, \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i \right] | \Phi_0 \rangle$$

$$= \frac{1}{16} \sum_{\substack{pqr \\ sijab}} \langle pq || rs \rangle t_{ij}^{ab} \langle \Phi_0 | \left[a_p^\dagger a_q^\dagger a_s a_r, a_a^\dagger a_b^\dagger a_j a_i \right] | \Phi_0 \rangle$$

$$= \frac{1}{16} \sum_{\substack{pqr \\ sijab}} \langle pq || rs \rangle t_{ij}^{ab} \langle \Phi_0 | \left(\left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} \right.$$

$$\left. \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} \right) | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}$$

The CCSD energy equation revisited

$\langle \Phi_0 | \left[\hat{V}_N, \hat{T}_2 \right] | \Phi_0 \rangle =$

$\langle \Phi_0 | \left[\dfrac{1}{4} \sum_{pqrs} \langle pq || rs \rangle a_p^\dagger a_q^\dagger a_s a_r, \dfrac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i \right] | \Phi_0 \rangle$

$= \dfrac{1}{16} \sum_{\substack{pqr \\ sijab}} \langle pq || rs \rangle t_{ij}^{ab} \langle \Phi_0 | \left[a_p^\dagger a_q^\dagger a_s a_r, a_a^\dagger a_b^\dagger a_j a_i \right] | \Phi_0 \rangle$

$= \dfrac{1}{16} \sum_{\substack{pqr \\ sijab}} \langle pq || rs \rangle t_{ij}^{ab} \langle \Phi_0 | \Big(\left\{ \overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i} \right\}$

$\left\{ \overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i} \right\} + \left\{ \overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i} \right\} \Big) | \Phi_0 \rangle$

$= \dfrac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}$

The CCSD energy equation revisited

$$\langle \Phi_0 | \left[\hat{V}_N, \hat{T}_2 \right] | \Phi_0 \rangle =$$

$$\langle \Phi_0 | \left[\frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle a_p^\dagger a_q^\dagger a_s a_r, \frac{1}{4} \sum_{ijab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i \right] | \Phi_0 \rangle$$

$$= \frac{1}{16} \sum_{\substack{pqr \\ sijab}} \langle pq || rs \rangle t_{ij}^{ab} \langle \Phi_0 | \left[a_p^\dagger a_q^\dagger a_s a_r, a_a^\dagger a_b^\dagger a_j a_i \right] | \Phi_0 \rangle$$

$$= \frac{1}{16} \sum_{\substack{pqr \\ sijab}} \langle pq || rs \rangle t_{ij}^{ab} \langle \Phi_0 | \left(\left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} \right.$$

$$\left. \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i \right\} \right) | \Phi_0 \rangle$$

$$= \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}$$

The CCSD energy equation revisited

The CCSD energy get two contributions from $\left(\widehat{H}_N \widehat{T} \right)_c$

$$E_{CC} \Leftarrow \langle \Phi_0 | \left[\hat{H}_N, \hat{T} \right] | \Phi_0 \rangle$$

$$= \sum_{ia} f_a^i t_i^a + \frac{1}{4} \sum_{ijab} \langle ij || ab \rangle t_{ij}^{ab}$$

The CCSD energy equation revisited

$$E_{CC} \Leftarrow \langle \Phi_0 | \frac{1}{2} \left(\widehat{H}_N \widehat{T}^2 \right)_c | \Phi_0 \rangle$$

$$\langle \Phi_0 | \frac{1}{2} \left(\widehat{V}_N \widehat{T}_1^2 \right)_c | \Phi_0 \rangle =$$

$$\frac{1}{8} \sum_{pqrs} \sum_{ijab} \langle pq || rs \rangle t_i^a t_j^b \langle \Phi_0 | \left(a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right)_c | \Phi_0 \rangle$$

$$= \frac{1}{8} \sum_{pqrs} \sum_{ijab} \langle pq || rs \rangle t_i^a t_j^b \langle \Phi_0 |$$

$$\left(\left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} \right.$$

$$\left. + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} \right) | \Phi_0 \rangle$$

$$= \frac{1}{2} \sum_{ijab} \langle ij || ab \rangle t_i^a t_j^b$$

The CCSD energy equation revisited

$$E_{CC} \Leftarrow \langle \Phi_0 | \frac{1}{2} \left(\widehat{H}_N \widehat{T}^2 \right)_c | \Phi_0 \rangle$$

$$\langle \Phi_0 | \frac{1}{2} \left(\widehat{V}_N \widehat{T}_1^2 \right)_c | \Phi_0 \rangle =$$

$$\frac{1}{8} \sum_{pqrs} \sum_{ijab} \langle pq || rs \rangle t_i^a t_j^b \langle \Phi_0 | \left(a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right)_c | \Phi_0 \rangle$$

$$= \frac{1}{8} \sum_{pqrs} \sum_{ijab} \langle pq || rs \rangle t_i^a t_j^b \langle \Phi_0 |$$

$$\left(\left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} \right.$$

$$\left. + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} \right) | \Phi_0 \rangle$$

$$= \frac{1}{2} \sum_{ijab} \langle ij || ab \rangle t_i^a t_j^b$$

The CCSD energy equation revisited

$$E_{CC} \Leftarrow \langle \Phi_0 | \frac{1}{2} \left(\widehat{H}_N \widehat{T}^2 \right)_c | \Phi_0 \rangle$$

$$\langle \Phi_0 | \frac{1}{2} \left(\widehat{V}_N \widehat{T}_1^2 \right)_c | \Phi_0 \rangle =$$

$$\frac{1}{8} \sum_{pqrs} \sum_{ijab} \langle pq || rs \rangle t_i^a t_j^b \langle \Phi_0 | \left(a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right)_c | \Phi_0 \rangle$$

$$= \frac{1}{8} \sum_{pqrs} \sum_{ijab} \langle pq || rs \rangle t_i^a t_j^b \langle \Phi_0 |$$

$$\left(\left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} \right.$$

$$\left. + \left\{ a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j \right\} \right) | \Phi_0 \rangle$$

$$= \frac{1}{2} \sum_{ijab} \langle ij || ab \rangle t_i^a t_j^b$$

The CCSD energy equation revisited

$$E_{CC} \Leftarrow \langle\Phi_0|\frac{1}{2}\left(\widehat{H}_N\widehat{T}^2\right)_c|\Phi_0\rangle$$

$$\langle\Phi_0|\frac{1}{2}\left(\widehat{V}_N\widehat{T}_1^2\right)_c|\Phi_0\rangle =$$

$$\frac{1}{8}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_i^a t_j^b\langle\Phi_0|\left(a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j\right)_c|\Phi_0\rangle$$

$$=\frac{1}{8}\sum_{pqrs}\sum_{ijab}\langle pq||rs\rangle t_i^a t_j^b\langle\Phi_0|$$

$$\left(\left\{\overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j}\right\} + \left\{\overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j}\right\} + \left\{\overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j}\right\}\right.$$

$$\left. + \left\{\overline{a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j}\right\}\right)|\Phi_0\rangle$$

$$=\frac{1}{2}\sum_{ijab}\langle ij||ab\rangle t_i^a t_j^b$$

The CCSD energy equation revisited

- ▶ No contractions possible between cluster operators.
- ▶ Cluster operators need to contract with free indices to the left.
- ▶ Disconnected parts automatically cancel in the commutator.
- ▶ Onebody operators can connect to maximum two cluster operators.
- ▶ Twobody operators can connect to maximum four cluster operators.
- ▶ Different terms in the expansion contributes to different equations.

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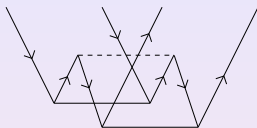
Diagram (2.12)

$$= \frac{1}{4}\langle mn|\widehat{v}|ef\rangle t_{ij}^{ef} t_{mn}^{ab}$$

Diagram (2.26)

$$= \frac{1}{4}P(ij)\langle mn|\widehat{v}|ef\rangle t_i^e t_{mn}^{ab} t_j^f$$

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$$= \frac{1}{4}P(ij)P(ab)\langle mn|\widehat{v}|ef\rangle t_i^e t_m^a t_j^f t_n^b$$
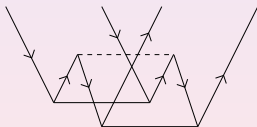
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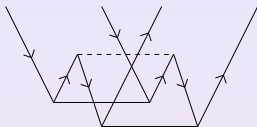
$$= \frac{1}{4} \langle mn|\widehat{v}|ef\rangle t_{ij}^{ef} t_{mn}^{ab}$$

Diagram cost: $n_p^4 n_h^4$

Diagram (2.12) - Factored

$$= \frac{1}{4} \langle mn|\widehat{v}|ef\rangle t_{ij}^{ef} t_{mn}^{ab}$$

$$= \frac{1}{4} \left(\langle mn|\widehat{v}|ef\rangle t_{ij}^{ef} \right) t_{mn}^{ab}$$

$$= \frac{1}{4} X_{ij}^{mn} t_{mn}^{ab}$$

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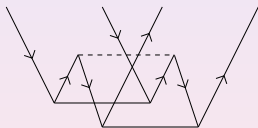
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Factoring, Classification

A diagram is classified by how many hole and particle lines between a $\hat{T}_i$ operator and the interaction ($T_i(p^{np}h^{nh})$).

Diagram (2.12) Classification

$$= \frac{1}{4}\langle mn|\widehat{v}|ef\rangle t_{ij}^{ef} t_{mn}^{ab}$$

This diagram is classified as $T_2(p^2) \times T_2(h^2)$

Factoring, Classification

Diagram (2.26)

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This diagram is classified as $T_1(p) \times T_1(p) \times T_1(h) \times T_1(h)$

Coupled Cluster algorithm

7.7cm   Setup modelspace
Calculate f and v amplitudes
$$t_i^a \leftarrow 0; \; t_{ij}^{ab} \leftarrow 0$$
$$E \leftarrow 1; \; E_{old} \leftarrow 0$$
$$E_{ref} \leftarrow \sum_i \langle i | \hat{t} | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | \hat{v} | ij \rangle$$
while not converged $(E - E_{old} > \epsilon)$
  Calculate intermediates
  $$t_i^a \leftarrow \text{calculated value}$$
  $$t_{ij}^{ab} \leftarrow \text{calculated value}$$
  $$E_{old} \leftarrow E$$
  $$E \leftarrow f_a^i t_i^a + \frac{1}{4} \langle ij || ab \rangle t_{ij}^{ab} + \frac{1}{2} \langle ij || ab \rangle t_i^a t_j^b$$
  end while
  $$E_{GS} \leftarrow E_{ref} + E$$

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