

Week 46: Many-body perturbation theory and start Coupled Cluster theory

Morten Hjorth-Jensen¹

Department of Physics and Center for Computing in Science Education, University
of Oslo, Norway¹

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Thursday:

1. Linked and unlinked diagrams, Linked diagram theorem and diagram rules, summary
2. Start coupled cluster theory
3. Second midterm at

<https://github.com/ManyBodyPhysics/FYS4480/blob/>

Friday's lecture

Friday:

1. Presentation and discussion of second midterm
2. Coupled Cluster theory
3. Relevant reading for the lectures: Shavitt abd Bartlett chapters 6 and 7 on linked and unlinked diagrams. For coupled cluster theory chapter 9 is the most relevant one. The lectures follow to a large extent the material covered in these chapters.

CCSD with twobody Hamiltonian

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

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

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

$$\begin{aligned}\hat{H} &= \sum_{pq} f_q^p \left\{ a_p^\dagger a_q \right\} + \frac{1}{4} \sum_{pqrs} \langle pq | \hat{v} | rs \rangle \left\{ a_p^\dagger a_q^\dagger a_s a_r \right\} \\ &\quad + E_0 \\ &= \hat{F}_N + \hat{V}_N + E_0 = \hat{H}_N + E_0\end{aligned}$$

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

$$\begin{aligned}f_q^p &= \langle p | \hat{h}_0 | q \rangle + \sum_i \langle pi | \hat{v} | qi \rangle \\ \langle pq || rs \rangle &= \langle pq | \hat{v} | rs \rangle\end{aligned}$$

$$E_0 = \sum_i \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij} \langle ij | \hat{v} | ij \rangle$$

Diagram equations - Derivation

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

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

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Diagram elements - Directed lines



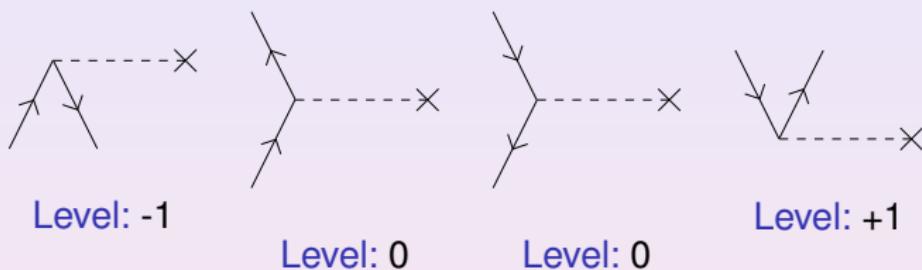
Figure: Particle line



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



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

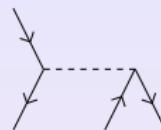
Diagram elements - Twobody Hamiltonian



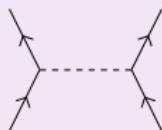
Level: -2



Level: -1



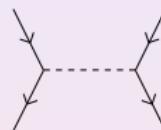
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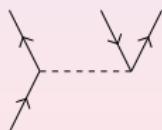
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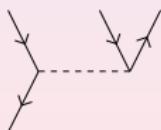
Level: 0



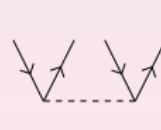
Level: 0



Level: +1



Level: +1



Level: +2

Diagram elements - Onebody cluster operator



Level: +1

- ▶ Horizontal line segment with one vertex.
- ▶ Excitation level of +1.

Diagram elements - Twobody cluster operator



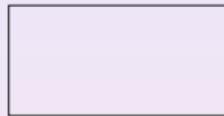
Level: +2

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

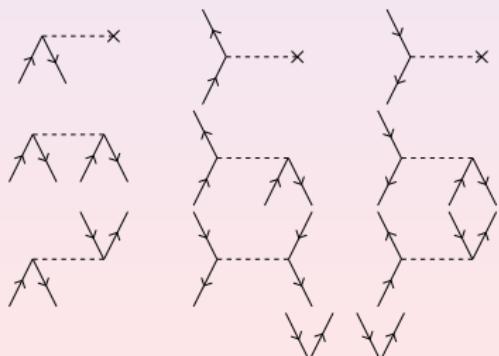
CCSD energy equation - Derivation

$$E_{\text{CCSD}} = \langle \Phi_0 || \Phi_0 \rangle$$

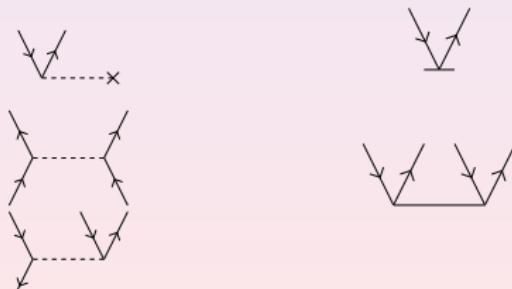
- ▶ No external lines.
- ▶ Final excitation level: 0



Elements: \hat{H}_N



Elements: \hat{T}



CCSD energy equation

$$E_{CCSD} = \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3}$$


Diagram rules

- ▶ Label all lines.
- ▶ Sum over all internal indices.
- ▶ Extract matrix elements. (f_{in}^{out} , $\langle lout, rout || lin, rin \rangle$)
- ▶ Extract cluster amplitudes with indices in the order left to right. Incoming lines are subscripts, while outgoing lines are superscripts. (t_{in}^{out} , $t_{lin,rin}^{lout,rout}$)
- ▶ Calculate the phase: $(-1)^{\text{holelines+loops}}$
- ▶ Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each equivalent vertex.

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CCSD energy equation

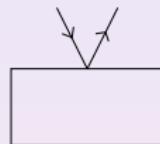
$$E_{CCSD} = f_a^i t_i^a + \frac{1}{4} \langle ij || ab \rangle t_{ij}^{ab} + \frac{1}{2} \langle ij || ab \rangle t_i^a t_j^b$$

Note the implicit sum over repeated indices.

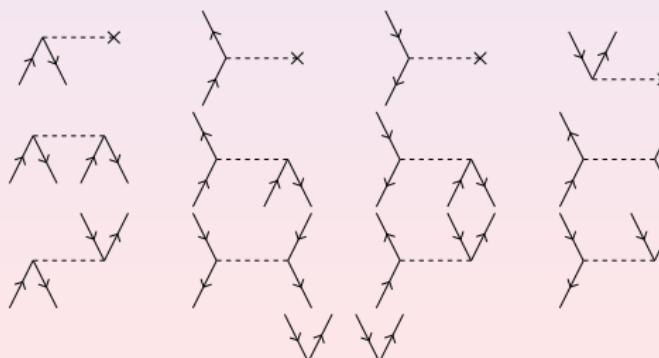
CCSD \hat{T}_1 amplitude equation - Derivation

$$0 = \langle \Phi_i^a | | \Phi_0 \rangle$$

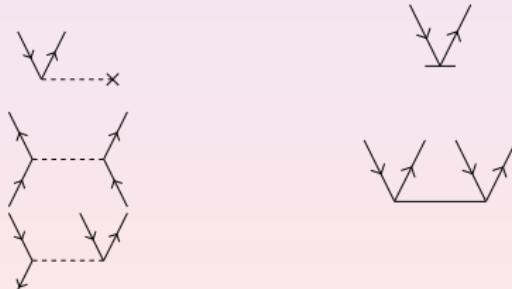
- ▶ One pair of particle/hole external lines.
- ▶ Final excitation level: +1



Elements: \hat{H}_N



Elements: \hat{T}



CCSD \hat{T}_1 amplitude equation

$$0 = \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3} + \text{Diagram 4} + \text{Diagram 5}$$
$$+ \text{Diagram 6} + \text{Diagram 7} + \text{Diagram 8} + \text{Diagram 9}$$
$$+ \text{Diagram 10} + \text{Diagram 11} + \text{Diagram 12} + \text{Diagram 13}$$
$$+ \text{Diagram 14} + \text{Diagram 15}$$

Diagram rules

- ▶ Label all lines.
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- ▶ Extract matrix elements. (f_{in}^{out} , $\langle lout, rout || lin, rin \rangle$)
- ▶ Extract cluster amplitudes with indices in the order left to right. Incoming lines are subscripts, while outgoing lines are superscripts. (t_{in}^{out} , $t_{lin,rin}^{lout,rout}$)
- ▶ Calculate the phase: $(-1)^{\text{holelines+loops}}$
- ▶ Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each equivalent vertex.

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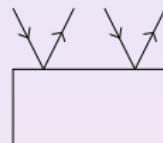
CCSD \hat{T}_1 amplitude equation

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

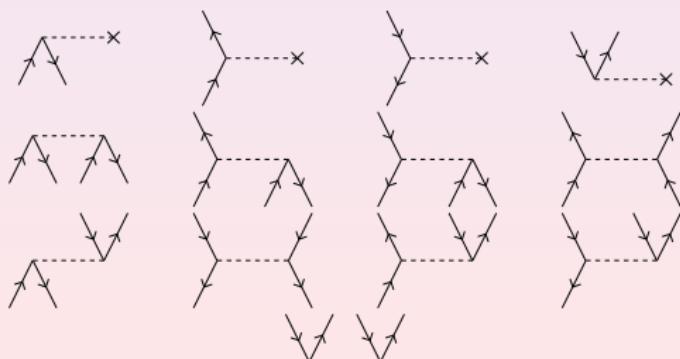
CCSD \hat{T}_2 amplitude equation - Derivation

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

- ▶ Two pairs of particle/hole external lines.
- ▶ Final excitation level: +2



Elements: \hat{H}_N



Elements: \hat{T}



CCSD \hat{T}_2 amplitude equation

$$0 = \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3} + \text{Diagram 4} + \text{Diagram 5} + \text{Diagram 6} + \text{Diagram 7} + \text{Diagram 8} + \text{Diagram 9} + \text{Diagram 10} + \text{Diagram 11} + \text{Diagram 12} + \text{Diagram 13} + \text{Diagram 14} + \text{Diagram 15} + \text{Diagram 16} + \text{Diagram 17} + \text{Diagram 18} + \text{Diagram 19} + \text{Diagram 20}$$

Diagram rules

- ▶ Label all lines.
- ▶ Sum over all internal indices.
- ▶ Extract matrix elements. ($t_{in}^{out}, \langle lout, rout || lin, rin \rangle$)
- ▶ Extract cluster amplitudes with indices in the order left to right. Incoming lines are subscripts, while outgoing lines are superscripts. ($t_{in}^{out}, t_{lin,rin}^{lout,rout}$)
- ▶ 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.

CCSD \hat{T}_2 amplitude equation

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