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

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Week 46, November 10-14

Week 46, November 10-14, 2025

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/`
4. Video of lecture at `https://youtu.be/x9kJ_o9exLM`
5. Whiteboard notes at `https://github.com/ManyBodyPhysics/FYS4480/blob/`

Friday's lecture

Friday:

1. Presentation and discussion of second midterm
2. Coupled Cluster theory
3. Video of lecture at `https://youtu.be/KvM0vCI_8HU`
4. Whiteboard notes at
   `https://github.com/ManyBodyPhysics/FYS4480/blob/`
5. 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.

Definitions

The basics, Normal ordered Hamiltonian

Twobody Hamiltonian

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

where

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

Definitions

The basics, Normal ordered Hamiltonian

Twobody Hamiltonian

The amplitudes are given by

$$f_q^p = \langle p|\hat{h}_0|q\rangle + \sum_i \langle pi|\hat{v}|qi\rangle$$

$$\langle pq||rs\rangle = \langle pq|\hat{v}|rs\rangle$$

In relation to the Hamiltonian, $\hat{H}_N$ is given by

$$\begin{aligned}
\hat{H}_N &= \hat{H} - E_0 \\
E_0 &= \langle \Phi_0|\hat{H}|\Phi_0\rangle \\
&= \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij} \langle ij|\hat{v}|ij\rangle
\end{aligned}$$

where E_0 is the energy expectation value between reference states.

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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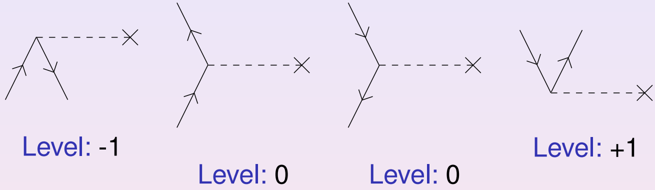
Diagram elements - Directed lines

Figure: Particle line

Figure: Hole line

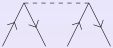
- Represents a contraction between second quantized operators.
- External lines are connected to one operator vertex and infinity.
- Internal lines are connected to operator vertices in both ends.

Diagram elements - Onebody Hamiltonian



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

Diagram elements - Twobody Hamiltonian



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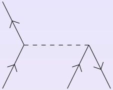

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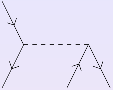

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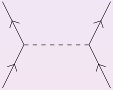
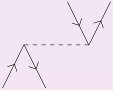
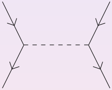


Level: 0



Level: 0



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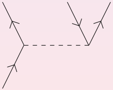
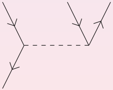


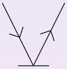
Level: +1



Level: +1

Level: +2

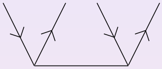
Diagram elements - Onebody cluster operator



Level: +1

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

Diagram elements - Twobody cluster operator



Level: +2

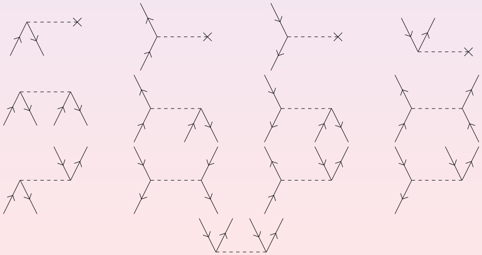
- Horisontal line segment with two vertices.
- Excitation level of +2.

CCSD energy equation - Derivation

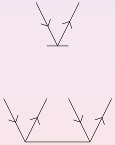
$$E_{\mathrm{CCSD}} = \langle \Phi_0 | | \Phi_0 \rangle$$

- No external lines.
- Final excitation level: 0

Elements: $\widehat{H}_N$



Elements: $\widehat{T}$



CCSD energy equation

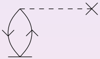
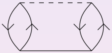
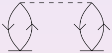
$E_{CCSD} =$  $+$  $+$ 

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. ($t_{\text{in}}^{\text{out}}$, $t_{\text{lin},\text{rin}}^{\text{lout},\text{rout}}$)
- Calculate the phase: $(-1)^{\text{holelines}+\text{loops}}$
- Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each ecuivalent vertex.

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CCSD energy equation

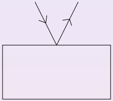
$$E_{CCSD} = f^i_a t^a_i + \frac{1}{4}\langle ij||ab\rangle t^{ab}_{ij} + \frac{1}{2}\langle ij||ab\rangle t^a_i t^b_j$$

Note the implicit sum over repeated indices.

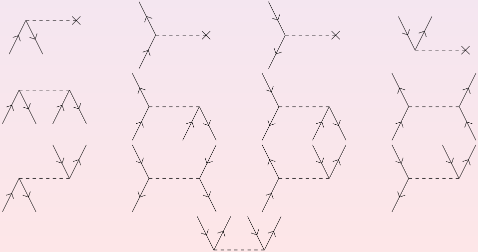
CCSD $\widehat{T}_1$ amplitude equation - Derivation

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

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



Elements: $\widehat{H}_N$



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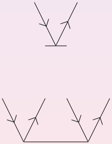

CCSD $\widehat{T}_1$ amplitude equation

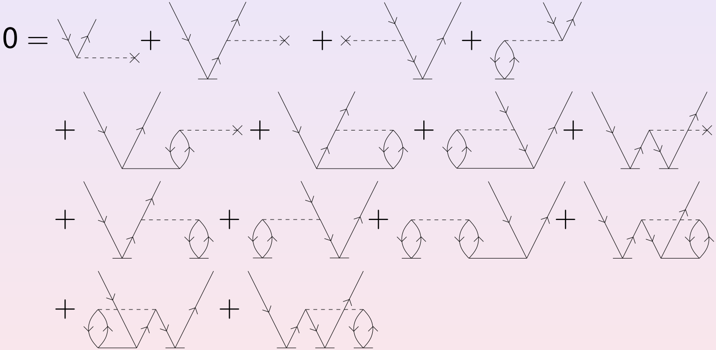

Diagram rules

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- Calculate the phase: $(-1)^{\text{holelines}+\text{loops}}$
- Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each ecuivalent vertex.

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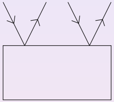
CCSD $\widehat{T}_1$ amplitude equation

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

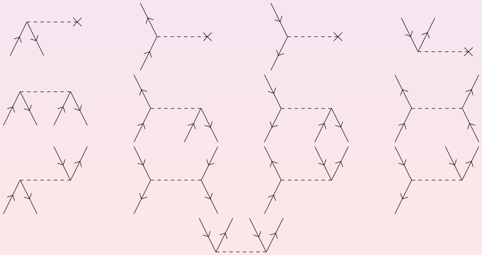
CCSD $\widehat{T}_2$ amplitude equation - Derivation

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

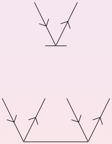
- Two pairs of particle/hole external lines.
- Final excitation level: +2



Elements: $\widehat{H}_N$



Elements: $\widehat{T}$



CCSD $\widehat{T}_2$ amplitude equation

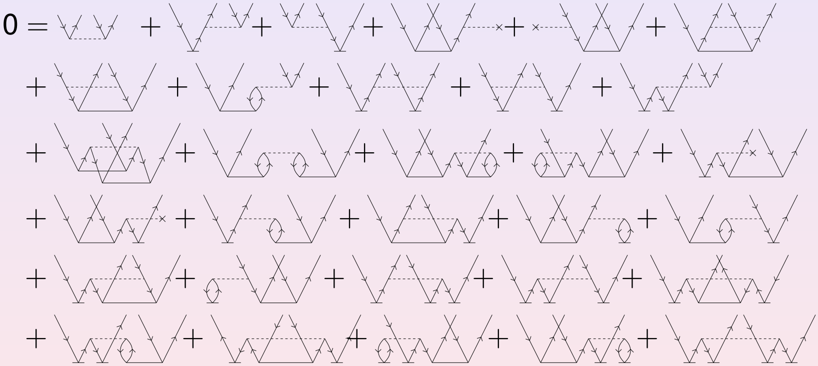


Diagram rules

- Label all lines.
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- Extract cluster amplitudes with indices in the order left to right. Incoming lines are subscripts, while outgoing lines are superscripts. ($t_{\mathrm{in}}^{\mathrm{out}}$, $t_{\mathrm{lin,rin}}^{\mathrm{lout,rout}}$)
- Calculate the phase: $(-1)^{\mathrm{holelines}+\mathrm{loops}}$
- Multiply by a factor of $\frac{1}{2}$ for each equivalent line and each ecuivalent vertex.
- Antisymmetrize a pair of external particle/hole line that does not connect to the same operator.

CCSD $\widehat{T}_2$ amplitude equation

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