80. Coupled-Cluster Methods in Quantum Chemistry

We here provide a short introduction to diagrams, which will be used in exercise 80.2. Diagrams provide an easy and visual way to derive algebraic expressions of matrix elements in second quantization. Different types of diagrams exist (Feynman, Goldstone, etc.). We will here use a diagrammatic representation suitable for coupled-cluster theory, the antisymmetrized Brandow diagrams. We start by a short recapitulation of the theory the diagrams are based upon, before proceeding to the Brandow diagrams.

Background theory

We will be working in the particle-hole formalism with the HF state $|\Psi_{\mathrm{HF}}\rangle \equiv |0\rangle$ as vacuum, rather than the true vacuum state $|\mathrm{vac}\rangle$. The quasi particles (QPs) consist of particles and holes, where particles correspond to electrons in virtual orbitals and holes correspond to the absence of electrons in occupied HF orbitals. In this picture, the HF state is a vacuum in the sense of having no particles and no holes. The elementary operator for the creation of an electron in a virtual orbital $a_a^\dagger$ corresponds to a creation of a particle $b_a^\dagger$, and annihilation of an electron in an occupied orbital a_i to a creation of a hole $b_i^\dagger$. Similarly, annihilation of an electron in a virtual orbital a_a and creation of an electron in an occupied orbital $a_i^\dagger$ correspond to annihilation of particles and holes, b_a and b_i, respectively. It then follows that

$$b_p|0\rangle = \langle 0|b_p^\dagger = 0, \tag{80.1}$$

for all QPs $p \in \{i, a\}$. All operators in second quantization involve a string of elementary operators. At the same time, we can express any state that corresponds to some Slater determinant as a string of creation operators $\ldots b_r^\dagger b_q^\dagger b_p^\dagger$ acting on $|0\rangle$.

Therefore, we can rewrite integrals involving two states and an operator string O into a vacuum expectation value (VEV) as $\langle 0|b_t b_u b_v \ldots O \ldots b_r^\dagger b_q^\dagger b_p^\dagger|0\rangle$. The VEV vanishes due to Eq. (80.1) if all creation operators are to the left of the annihilation operators. They are then said to be in *normal order*, for example, $\langle 0|b_a^\dagger b_i^\dagger b_b b_c|0\rangle = 0$. Usually, such strings contain an even number of elementary operators (which we assume in the following) but are *not* in normal order to begin with. They can, however, be *recast* into *normal-ordered form* which then makes the evaluation of the VEV very simple. For this rearrangement, we could use the anti-commutator relations directly, i.e., by permuting two operators in a string by $b_p b_q^\dagger = -b_q^\dagger b_p + \delta_{pq}$, until all operators are in normal order. For example, we

can recast the string $Y = b_p b_q b_r^\dagger b_s^\dagger$ into its normal-ordered form:

$$Y = b_r^\dagger b_s^\dagger b_p b_q - \delta_{qr} b_s^\dagger b_p + \delta_{pr} b_s^\dagger b_q + \delta_{qs} b_r^\dagger b_p - \delta_{ps} b_r^\dagger b_q + \delta_{qr}\delta_{ps} - \delta_{pr}\delta_{qs}. \tag{80.2}$$

The important point to note is that for the VEV, $\langle 0|Y|0\rangle$, only the last two terms contribute, as all other terms contain strings of creation and annihilation operators in normal order. In our example, the VEV is thus simply given by $\langle 0|Y|0\rangle = \delta_{qr}\delta_{ps} - \delta_{pr}\delta_{qs}$. Recasting strings into normal-ordered form in this way is, however, quite tedious. A simpler way to obtain that same expression is by use of Wick's theorem. A full introduction to Wick's theorem is given in chapter 9, but we still give a brief recapitulation here since it is central to the understanding of the diagrams. We start by recalling the concept of *contractions*. A contraction between two elementary operators c_p and d_q is defined as

$$\overbrace{c_p d_q} = c_p d_q - \{c_p d_q\} = \begin{cases} 0 & \text{if } c_p d_q \text{ already in normal order} \\ \delta_{pq} & \text{if } c_p d_q \text{ not in normal order} \end{cases},$$

where the curly brackets indicate normal ordering, under which permutation of two operators gives a sign change. If the operators are already in normal order, the contraction trivially vanishes. Otherwise, it follows from the anticommutator-relations that $\overbrace{b_p b_q^\dagger} = b_p b_q^\dagger - \{b_p b_q^\dagger\} = b_p b_q^\dagger + b_q^\dagger b_p = \delta_{pq}$. Note the subtle difference in wording: For $X = b_p b_q^\dagger$

$$\begin{aligned} &\text{normal ordering of } X: && \{X\} = \{b_p b_q^\dagger\} = -b_q^\dagger b_p \\ &\text{normal-ordered form of } X: && X = -b_q^\dagger b_p + \delta_{pq} = \{X\} + \delta_{pq} \end{aligned}$$

Wick's theorem now states that we can obtain the normal-ordered form of any operator string Y by summing the string in normal ordering, $\{Y\}$, with all single, double, etc. contractions of Y also in normal ordering

$$Y = \{Y\} + \sum_{\text{single}} \{\overbrace{Y}\} + \sum_{\text{double}} \{\overbrace{\overbrace{Y}}\} + \ldots \tag{80.3}$$

Comparing Wick's theorem to our result in Eq. (80.2), we see that the first term corresponds to the normal ordering of the string Y, $\{b_p b_q b_r^\dagger b_s^\dagger\}$, the next four terms are the singly-contracted terms, and the last two the doubly-contracted terms. As a contraction removes two elementary operators to yield either zero or a δ_{pq}, the result from the fully contracted terms is either zero or a product of Kronecker deltas. For the VEV, therefore, we don't even need the full expression of Y in normal-ordered form but instead only need to evaluate the fully contracted terms.

In short: To evaluate an integral between two states and some string of elementary operators we want to rewrite the integrals into VEVs because they are easily evaluated. The strings of elementary operators need to be recast into normal-ordered form and for the VEV, only the fully contracted terms need to be considered.

Brandow diagrams

Turning to the problem at hand, we recall that the Hamilton operator of an N-electron system in normal ordered form is given as

$$H = E_{\mathrm{HF}} + \sum_{pq} f_{pq} \{a_p^\dagger a_q\} + \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle \{a_p^\dagger a_q^\dagger a_s a_r\} \tag{80.4}$$

$$= E_{\mathrm{HF}} + f_N + W_N. \tag{80.5}$$

E_{HF} is the (scalar) Hartree-Fock energy, f_N the one-electron (Fock) operator, and W_N the two-electron operator. The coupled cluster (CC) energy and amplitude equations are derived by inserting the ansatz for the CC wave function $\Psi = e^T|0\rangle$ into the Schrödinger equation, multiplication from the left with e^{-T} and projection onto the reference and I-fold excited determinants $\langle\Phi_I|$, respectively:

$$\langle 0|e^{-T} H e^T|0\rangle = E \tag{80.6}$$

$$\langle \Phi_I|e^{-T} H e^T|0\rangle = 0. \tag{80.7}$$

T is the cluster operator, with $T = T_1 + T_2 + \cdots + T_N$, where $T_1 = \sum_{ai} t_i^a a_a^\dagger a_i$, $T_2 = \frac{1}{4}\sum_{ij}^{ab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$, etc. From the BCH expansion we get

$$e^{-T} H e^T = H + [H,T] + \frac{1}{2!}[[H,T],T] + \ldots \tag{80.8}$$

Wicks theorem now tells us that we can recast all commutators as

$$[H,T] = HT - TH = \{HT\} + \sum_{\text{single}} \{\overbrace{HT}\} + \cdots - \{TH\} - \sum_{\text{single}} \{\overbrace{TH}\} - \ldots \tag{80.9}$$

As $\{HT\} = \{TH\}$ and as all contractions where T is left of H vanish (the string TH is already in normal order), we see that only terms can contribute where H is left of T and where H and T have at least one contraction, symbolized as $(HT)_c$ ('c' for 'connected'). The BCH expansion then becomes

$$e^{-T} H e^T = H + (HT)_c + \frac{1}{2!}((HT)_c T)_c + \ldots \tag{80.10}$$

$$\equiv (H \exp(T))_c. \tag{80.11}$$

Inserting the Hamiltonian of Eq. (80.4), the definition of the cluster operator, as well as the expansion in (80.11) into the CC amplitude and energy equations, we could, by the use of Wicks theorem, as outlined above, arrive at algebraic expressions for Eqs. (80.6) and (80.7) by rewriting them into VEVs and forming the fully contracted terms between the different strings of QP creation and annihilation operators. A great number of these terms will, however, turn out to be equivalent or zero and it is easy to make mistakes manipulating the indices in the operator strings. With diagrams, the goal is to do these contractions in a visual way and to *only* consider such contractions that will be both non-redundant and non-zero.
In short, the procedure consists of the following four steps

1. write down the relevant equations

2. write down the diagrams and excitation level of all involved operators
3. contract diagrams to desired excitation level and number and type of external lines
4. convert diagrams to algebraic expressions

We will outline this procedure taking CCD as an example.

Step 1

In CCD we truncate the cluster operator to $T = T_2$. The energy and amplitude equations are given by

$$\begin{aligned} E &= \langle 0|(H\exp(T_2))_c|0\rangle \\ &= \langle 0|H|0\rangle + \langle 0|(HT_2)_c|0\rangle + \frac{1}{2}\langle 0|(HT_2)_cT_2)_c|0\rangle + \dots \qquad (80.12) \\ &= E_{\mathrm{HF}} + \langle 0|f_N|0\rangle + \langle 0|W_N|0\rangle + \langle 0|(f_NT_2)_c|0\rangle + \langle 0|(W_NT_2)_c|0\rangle + \dots \qquad (80.13) \\ 0 &= \langle \Phi_{ij}^{ab}|(H\exp(T_2))_c|0\rangle \\ &= \langle \Phi_{ij}^{ab}|H|0\rangle + \langle \Phi_{ij}^{ab}|(HT_2)_c|0\rangle + \frac{1}{2}\langle \Phi_{ij}^{ab}|(HT_2)_cT_2)_c|0\rangle + \dots \qquad (80.14) \\ &= \langle \Phi_{ij}^{ab}|f_N|0\rangle + \langle \Phi_{ij}^{ab}|W_N|0\rangle + \langle \Phi_{ij}^{ab}|(f_NT_2)_c|0\rangle + \dots \qquad (80.15) \end{aligned}$$

where for the amplitude equations we only project onto doubly excited determinants $\langle \Phi_{ij}^{ab}|$.

Step 2

In diagrams, conceptually, operators are represented by a symbol and a number of lines attached to that operator symbol, namely one line per operator in the string. The symbols for the operators are chosen as horizontal lines: the components of the Hamiltonian are represented by dotted lines and the cluster operators by solid lines. The distinction between particles and holes is made via direction (arrows) on the lines. Furthermore, the distinction between QP creation and annihilation is made by placing the lines above and below the operator symbol, respectively. More specifically, the lines are connected to vertices: for a k-electron operator, there are k vertices in its diagram, each with one incoming and one outgoing line. The rules to remember are:

a) lines from above represent particle/hole creation operators

b) lines from below particle/hole annihilation operators

c) arrows pointing upwards represent particles

d) arrows pointing downwards represent holes

e) each vertex can only have one incoming and one outgoing line (one arrow pointing towards it and one pointing away from it)

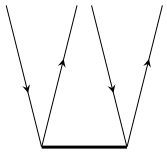
f) two diagrams are equivalent by pair-wise interchange(s) of two incoming or two outgoing lines between vertices that belong to the same operator

g) excitation level: $\frac{1}{2}$(# of lines from above − # lines from below)

We are now ready to write down all diagrams for the Hamiltonian and the T_2 cluster operator, where the latter can be expressed as

$$T_2 = \frac{1}{4}\sum_{ij}\sum_{ab} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

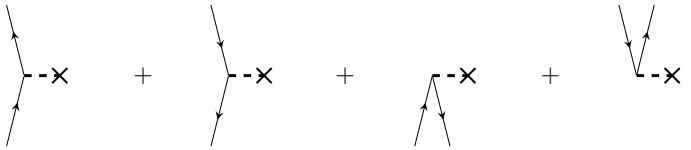
$$= \quad + 2 \quad ,$$



with the algebraic expression in the top row, the diagram in the middle row, and the excitation level in the bottom row. $E_{\rm HF}$ is simply a scalar, with excitation level 0, and has no diagrammatic representation. Turning to the one-electron part of the Hamiltonian, it can be expressed as

$$\hat{f}_N = \sum_{ab} f_{ab}\{a_a^\dagger a_b\} + \sum_{ij} f_{ij}\{a_i^\dagger a_j\} + \sum_{ai} f_{ia}\{a_i^\dagger a_a\} + \sum_{ai} f_{ai}\{a_a^\dagger a_i\}$$

$$= \quad + \quad + \quad + \quad .$$

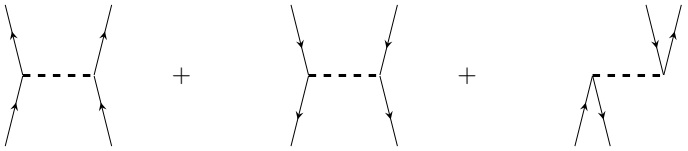


$$0 \qquad 0 \qquad -1 \qquad +1 \quad .$$

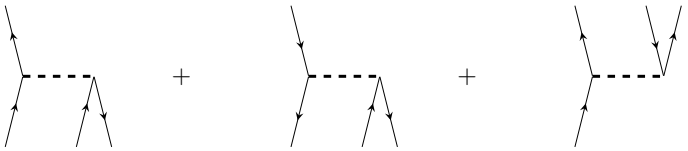
The Fock operator is represented by a dotted line with one vertex to the left, and with a cross to the right to specify that it is not an actual vertex. As can be seen, there is a clear link between the algebraic expressions and the diagrams. The excitation levels can also be easily rationalized: the first two with excitation level 0 are rotations among virtual or occupied orbitals, respectively, the third excitation level -1 diagram is a single de-excitation, and the fourth excitation level 1 diagram is a single excitation

In the same way, the two-electron operator is expressed as

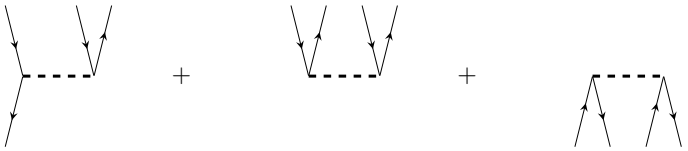
$$\begin{aligned}\hat{W}_N = \tfrac{1}{4}\,[\;& \langle ab||cd\rangle\{a_a^\dagger a_b^\dagger a_d a_c\} + \langle ij||kl\rangle\{a_i^\dagger a_j^\dagger a_l a_k\} + 4\langle ia||bj\rangle\{a_i^\dagger a_a^\dagger a_j a_b\} \\ &+ 2\langle ai||bc\rangle\{a_a^\dagger a_i^\dagger a_c a_b\} + 2\langle ij||ka\rangle\{a_i^\dagger a_j^\dagger a_a a_k\} + 2\langle ab||ci\rangle\{a_a^\dagger a_b^\dagger a_i a_c\} \\ &+ 2\langle ia||jk\rangle\{a_i^\dagger a_a^\dagger a_k a_j\} + \langle ab||ij\rangle\{a_a^\dagger a_b^\dagger a_j a_i\} + \langle ij||ab\rangle\{a_i^\dagger a_j^\dagger a_b a_a\}\;]\end{aligned}$$

$=$  $+\quad +$

$0 \qquad\qquad 0 \qquad\qquad 0$

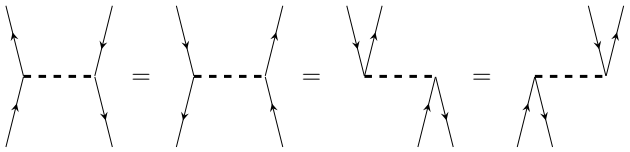
$+$  $+\quad +$

$-1 \qquad\qquad -1 \qquad\qquad +1$

$+$  $+\quad +$

$+\,1 \qquad\qquad +\,2 \qquad\qquad -\,2$

where Einstein summation is assumed for the algebraic expressions. Splitting the sum over the general indices p, q, r, s in Eq. (80.4) into occupied i, j, k, l and virtual a, b, c, d indices gives 16 terms. By exploiting the anti-symmetry as well as the rules to permute operators inside the brackets for normal ordering (sign change), we arrive at the nine terms with corresponding factors as given above. We can also understand the factors from the perspective of equivalent diagrams according to rule f): for instance, diagram 3 can be drawn in four different ways

 (80.16)

and therefore gives a factor of four.

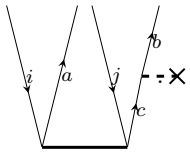
Similarly, diagrams four to seven have two equivalent diagrammatic representations, as they all have an equivalent mirror image giving a factor of two. Diagrams one, two, eight and nine are unique. You do not have to remember these factors, rather, all factors, i.e., coming from the operator definitions, the expansion in Eq. (80.11), as well as factors, permutations and signs in equivalent diagrams are included when following the rules given under step 4.

Step 3

Two operators are contracted by 'joining lines'. If we have the product AB of two operators A and B and want to consider their contractions, we will draw the diagram for A on the top and the one for B below. Meaningful (non-vanishing) contractions are then the ones where we connect lines that are *below* A (QP annihilation) and *above* B (QP creation) and that point in the same direction. We know from Wicks theorem, that only the fully contracted term can contribute to a VEV. Therefore, in principle, all lines should be connected. This is true for the CC energy equations. However, for the amplitude equations in Eq. (80.15), there is a string of operators we have not yet accounted for. The doubly excited determinant $\langle\Phi_{ij}^{ab}|$ can be expressed as $\langle 0|a_i^\dagger a_j^\dagger a_b a_a$, which would correspond to a diagram with four lines pointing down and therefore an excitation level of -2. We are, however, not going to draw this diagram but instead just keep in mind that we will need four open lines pointing up in our final diagrams for the amplitude equations, namely $a_a^\dagger a_b^\dagger a_j a_i$ to connect to $\langle\Phi_{ij}^{ab}|$ to from the remaining contractions for the VEV. In other words, the desired excitation level of the final diagrams is +2.
We will now outline how to contract the diagrams by a few example terms from the CCD amplitude equations, Eq. (80.15), and leave it to exercise 80.2 to work out the remaining terms. First, we consider the the integral

$$\langle\Phi_{ij}^{ab}|(f_N T_2)_c|0\rangle. \tag{80.17}$$

The ket side has excitation level 0 and the bra side has excitation level +2 (doubly excited determinant). Thus, the only allowed contractions must have an overall excitation level +2 (bringing either the ket side to +2 when working to the right, or the bra side to 0 when working to the left). Since the T_2 cluster operator has excitation level +2, we get non-vanishing terms only for the two f_N diagrams with excitation level 0. We will here consider the first of these, giving



(80.18)

Notice that 1) we have a contraction between the cluster operator T_2 and the one-electron component f_N of the Hamiltonian, denoted an *internal line*, over the free index c, giving a full summation over this particle index, 2) we have four open lines from above, two particle and two hole creations, to give excitation level +2, 3) the indices of the open lines match the fixed indices on the bra side, thus no summation here, and 4) the first continuous line starts with i and ends with a and the second starts with j and ends with b. Also notice that contraction of the particle creation line from the first vertex of the T_2 operator instead of on the second vertex gives an equivalent diagram, and can thus be disregarded. We will come back to the rules for the algebraic expressions under step 4, but for now let us consider a few more examples.

Let us continue by considering the third term of Eq. (80.11) for the one-electron part f_N

$$\frac{1}{2}\langle\Phi_{ij}^{ab}|((f_N T_2)_c T_2)_c|0\rangle. \tag{80.19}$$

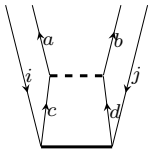
Since both T_2 operators have excitation levels +2, giving a total of +4, we cannot reach

the desired excitation level of +2 as the f_N operator has a minimum excitation level of -1 such that this term does not contribute.

We now turn to the two-electron component W_N, starting with

$$\langle \Phi_{ij}^{ab} | (W_N T_2)_c | 0 \rangle. \tag{80.20}$$

Again, T_2 has excitation level +2, so we can only match it with the W_N diagrams of excitation level 0. For the first W_N diagram of excitation level 0 we get

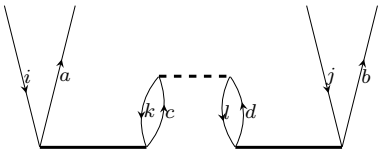


. (80.21)

The final example we give here is the integral involving the third term of the BCH expansion, Eq. (80.11), for the two-electron part of the Hamiltonian, namely

$$\frac{1}{2} \langle \Phi_{ij}^{ab} | ((W_N T_2)_c T_2)_c | 0 \rangle. \tag{80.22}$$

Since the joint excitation level of the two T_2 operators is +4, the only non-vanishing term is with the W_N diagram of excitation level -2. This term gives a total of four possible contractions, and we give only one of them as an example here



, (80.23)

with the other three left for exercise 80.2. One important thing to notice here, is that we need at least one contraction with each of the two cluster operators to give non-vanishing contributions.

Step 4

We have now outlined how to contract the diagrams, and are ready for the final step, namely to translate the diagrams into algebraic expressions. This is achieved with the following set of rules

A) assign indices. For the open lines (corresponding to the indices on the bra side), i should be connected to a, j should be connected to b, etc.

B) sum over indices of the internal lines (lines connecting two operators, the contractions)

C) assign matrix elements: Fock matrix $f_{\mathrm{out,in}} = \langle \mathrm{out} | f | \mathrm{in} \rangle$, anti-symmetrized two-electron integrals $\langle \mathrm{out}_1 \mathrm{out}_2 || \mathrm{in}_1 \mathrm{in}_2 \rangle$, cluster amplitudes $t_{\mathrm{in}_1 \mathrm{in}_2}^{\mathrm{out}_1 \mathrm{out}_2}$, etc., with '$\mathrm{in}_k$' and '$\mathrm{out}_k$' the incoming and outgoing lines on vertex k

D) factor: n equivalent internal lines give factor $1/n!$, and m equivalent operators connected in the same way give factor $1/m!$

E) sign: $(-1)^{n_{\mathrm{int,h}}+n_{\mathrm{loop}}}$, with $n_{\mathrm{int,h}}$ the number of internal hole lines and n_{loop} as the numer of loops. A loop is set of lines that begins and ends at a given vertex.

F) $P(pq) = 1 - \hat{P}_{pq}$: for unique external lines (p, q of the same type but at different operators)

with $\hat{P}_{pq}$ the permutation operator exchanging the two indices p and q. Using these rules, we can convert the diagrams of Eqs. (80.18), (80.21) and (80.23) into the algebraic expressions

$$P(ab)\sum_{c} f_{bc}t_{ij}^{ac}, \tag{80.24}$$

where we have to include $P(ab)$, since we have two unique external particle lines in Eq. (80.18),

$$\frac{1}{2}\sum_{cd}\langle ab||cd\rangle t_{ij}^{cd}, \tag{80.25}$$

where the factor $1/2$ is included since we have two equivalent internal lines in Eq. (80.21), and finally

$$\frac{1}{2}P(ij)P(ab)\sum_{cd}\sum_{kl}\langle kl||cd\rangle t_{ik}^{ac}t_{jl}^{bd}, \tag{80.26}$$

where we include both $P(ij)$ and $P(ab)$ since both the external particle and hole lines are unique, as they are connected to different T_2 operators, and where the factor $1/2$ arises since we have two equivalent operators (the T_2's) connected in the same way.

Exercise 80.1 : Essentials of CC theory (Review of the material)

a) What is the choice of the cluster operator in the CCSD ansatz and which excited determinants are considered and not considered in the wave function?

b) Discuss the differences between CCSD, CISD, and FCI wave functions and explain the terms "disconnected" and "connected" excitations.

c) Why are the CC amplitudes determined via projection techniques and not via the variation principle?

d) Describe the various steps and approximations required to obtain the so-called CCSD(T) approach. Discuss also the computational requirements of CCSD(T) and estimate for various cases (different numbers of electrons and basis functions) how much more expensive a CCSD(T) calculation is in comparison to CCSD.

Exercise 80.2 : CC equations and diagrams (medium difficulty)

Work out (in a systematic manner!) all diagrams for the CCD (for the more advanced, CCSD) amplitude equations and give the corresponding algebraic expression.

Hint: for CCSD there are 3 diagrams for the energy, 14 diagrams for the singles equations and 31 diagrams for the doubles equations.

Solution 80.2

The CCD case

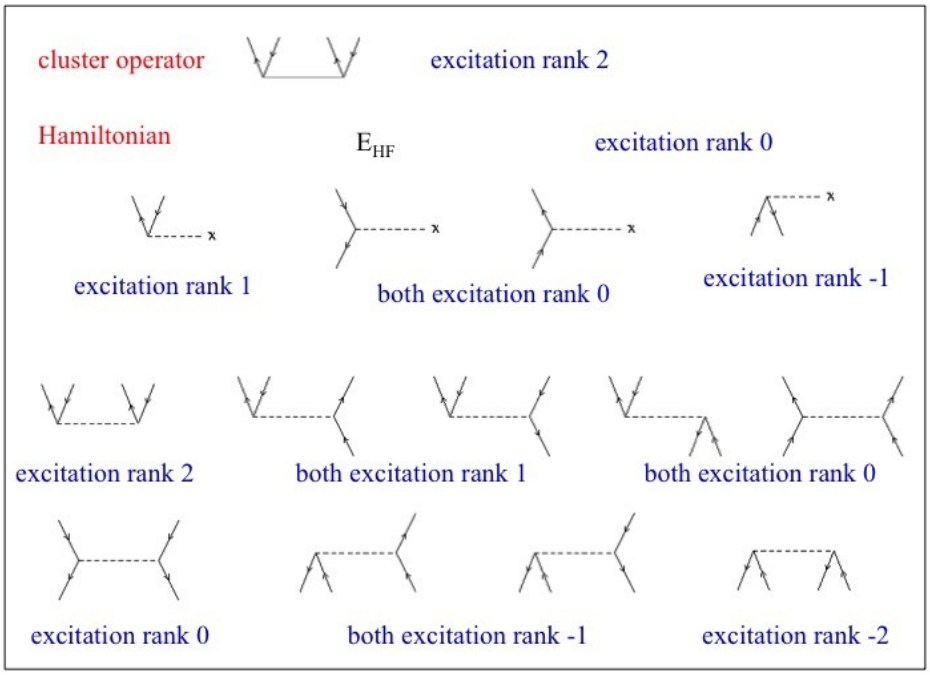
- The equations to be considered are

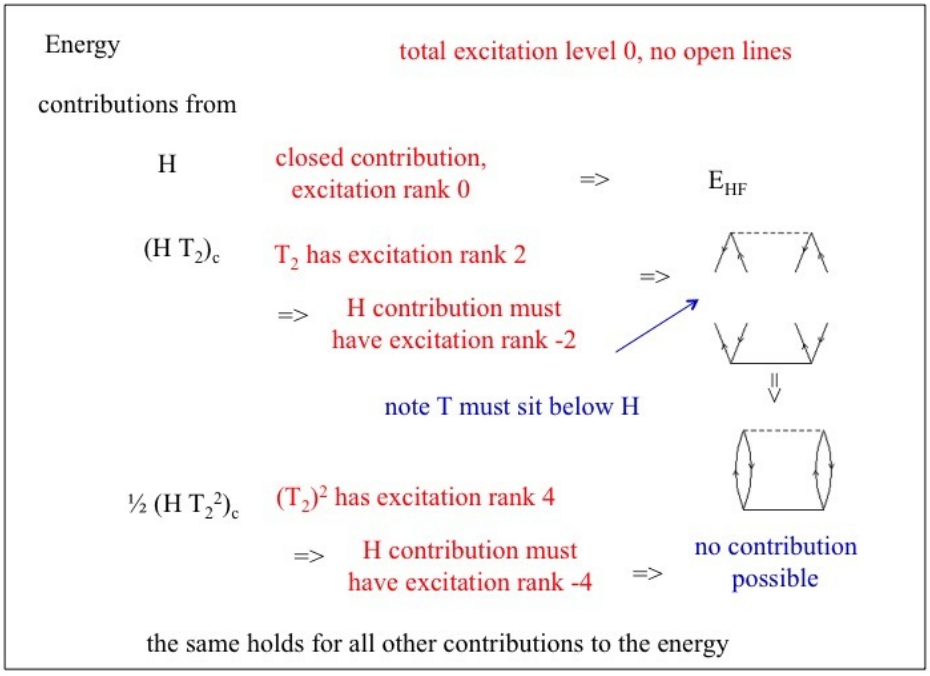
$$E = \langle 0| \left(H \ \exp(T_2)\right)_c |0\rangle; \quad 0 = \langle \Phi_{ij}^{ab}| \left(H \ \exp(T_2)\right)_c |0\rangle, \tag{80.27}$$

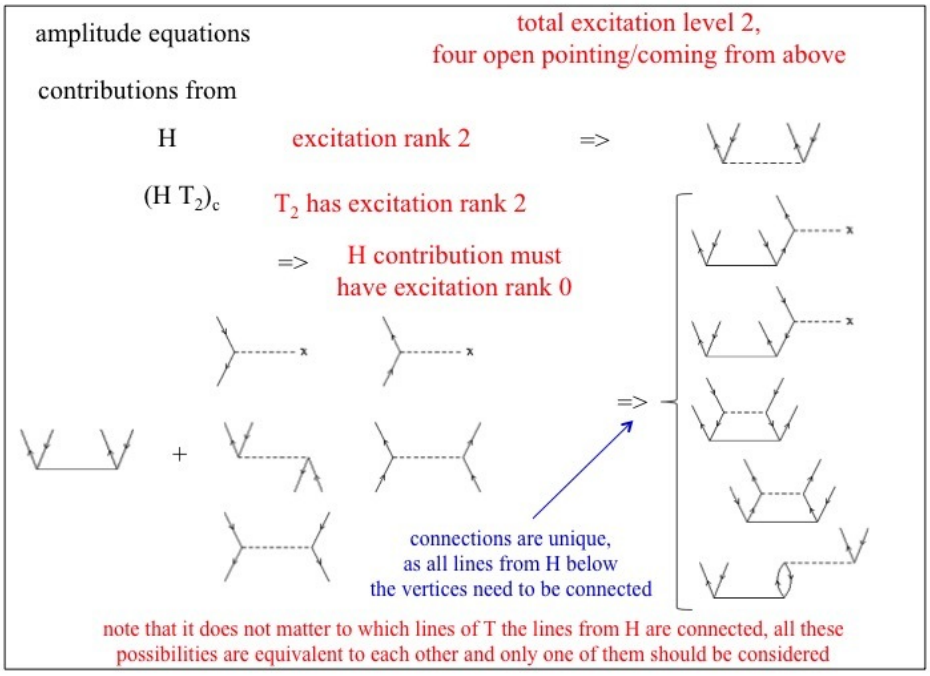
  with

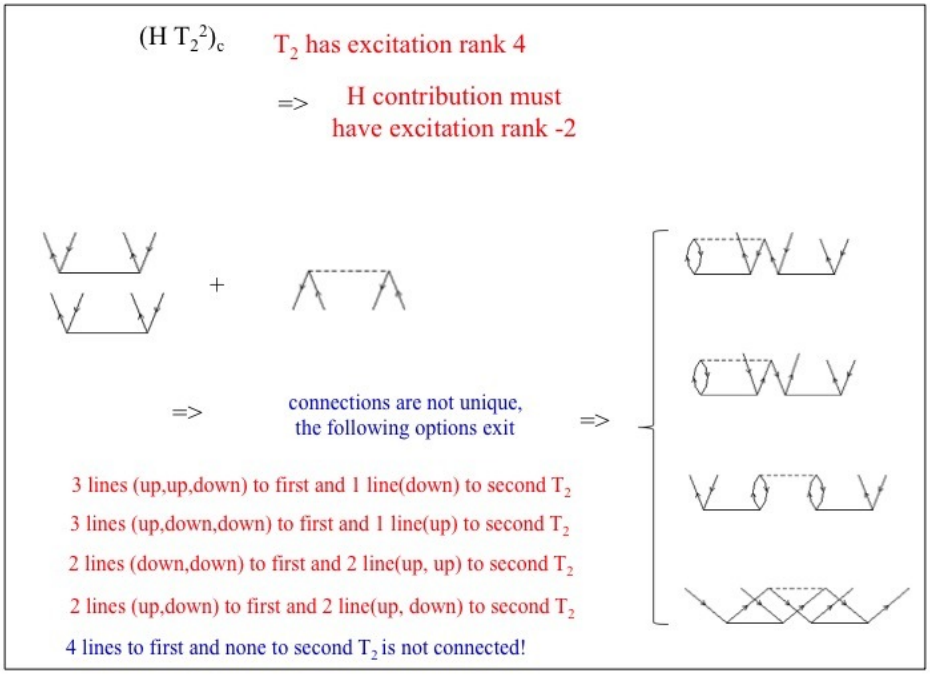
$$\left(H \ \exp(T)\right)_c = H + \left(H \ T\right)_c + \frac{1}{2!}\left(H \ T^2\right)_c + \frac{1}{3!}\left(H \ T^3\right)_c + \ldots \tag{80.28}$$

- Consider the excitation levels of the diagrams to be evaluated:
  - Energy expression:
    the total excitation level (projection on references) needs to be zero
  - Amplitude equation:
    the total excitation level (projection on doubles) needs to be two
- Consider the number of open lines in the diagrams to be evaluated
  - Energy expression:
    no open lines, closed diagrams
  - Amplitude equation:
    four open lines, two pointing upwards and two coming from above
- Get complete list of diagrams for T_2 and H together with their excitation rank (see below)


cluster operator
excitation rank 2
Hamiltonian
E_{HF}
excitation rank 0
excitation rank 1
both excitation rank 0
excitation rank -1
excitation rank 2
both excitation rank 1
both excitation rank 0
excitation rank 0
both excitation rank -1
excitation rank -2


Energy
total excitation level 0, no open lines
contributions from
H
closed contribution,
excitation rank 0
=>
E_{HF}
$(H\ T_2)_c$
T_2 has excitation rank 2
=>
=> H contribution must
have excitation rank -2
note T must sit below H
$½\ (H\ T_2^2)_c$
$(T_2)^2$ has excitation rank 4
=> H contribution must
have excitation rank -4
=>
no contribution
possible
the same holds for all other contributions to the energy


amplitude equations
total excitation level 2,
four open pointing/coming from above
contributions from
H
excitation rank 2
=>
$(H T_2)_c$
T_2 has excitation rank 2
=>
H contribution must
have excitation rank 0
+
=>
connections are unique,
as all lines from H below
the vertices need to be connected
note that it does not matter to which lines of T the lines from H are connected, all these
possibilities are equivalent to each other and only one of them should be considered

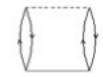

$(H T_2^2)_c$
T_2 has excitation rank 4
=>
H contribution must
have excitation rank -2
+
=>
connections are not unique,
the following options exit
=>
3 lines (up,up,down) to first and 1 line(down) to second T_2
3 lines (up,down,down) to first and 1 line(up) to second T_2
2 lines (down,down) to first and 2 line(up, up) to second T_2
2 lines (up,down) to first and 2 line(up, down) to second T_2
4 lines to first and none to second T_2 is not connected!

$(H\,T_2^3)_c$ T_2 has excitation rank 6

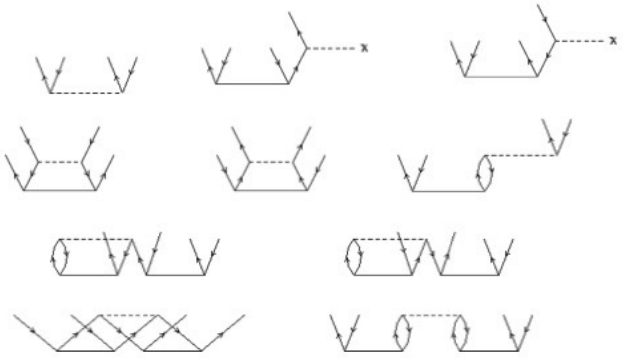
=> H contribution must have excitation rank -4 => no contribution possible

final result

CC energy:

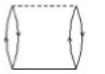


CC equations:



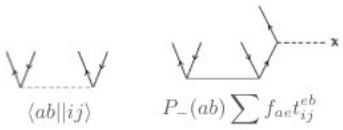
algebraic expressions

CC energy:



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

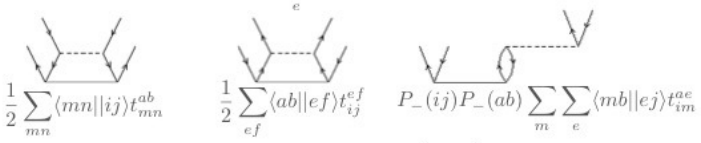
CC equations:



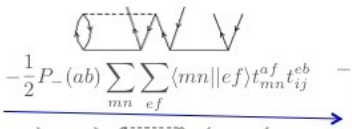
$$\langle ab||ij\rangle \qquad P_-(ab)\sum_e f_{ae}t_{ij}^{eb} \qquad -P_-(ij)\sum_m f_{mi}t_{mj}^{ab}$$

straighforward application of rules

make sure that i connects to a and j connects to b

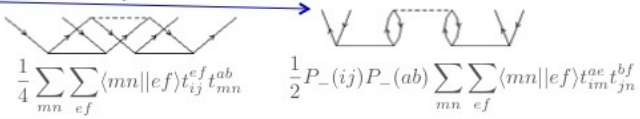


$$\frac{1}{2}\sum_{mn}\langle mn||ij\rangle t_{mn}^{ab} \qquad \frac{1}{2}\sum_{ef}\langle ab||ef\rangle t_{ij}^{ef} \qquad P_-(ij)P_-(ab)\sum_m\sum_e\langle mb||ej\rangle t_{im}^{ae}$$



$$-\frac{1}{2}P_-(ab)\sum_{mn}\sum_{ef}\langle mn||ef\rangle t_{mn}^{af}t_{ij}^{eb} \qquad -\frac{1}{2}P_-(ij)\sum_{mn}\sum_{ef}\langle mn||ef\rangle t_{in}^{ef}t_{mj}^{ab}$$

note that this is the only diagram with equivalent operators



$$\frac{1}{4}\sum_{mn}\sum_{ef}\langle mn||ef\rangle t_{ij}^{ef}t_{mn}^{ab} \qquad \frac{1}{2}P_-(ij)P_-(ab)\sum_{mn}\sum_{ef}\langle mn||ef\rangle t_{im}^{ae}t_{jn}^{bf}$$

The CCSD case

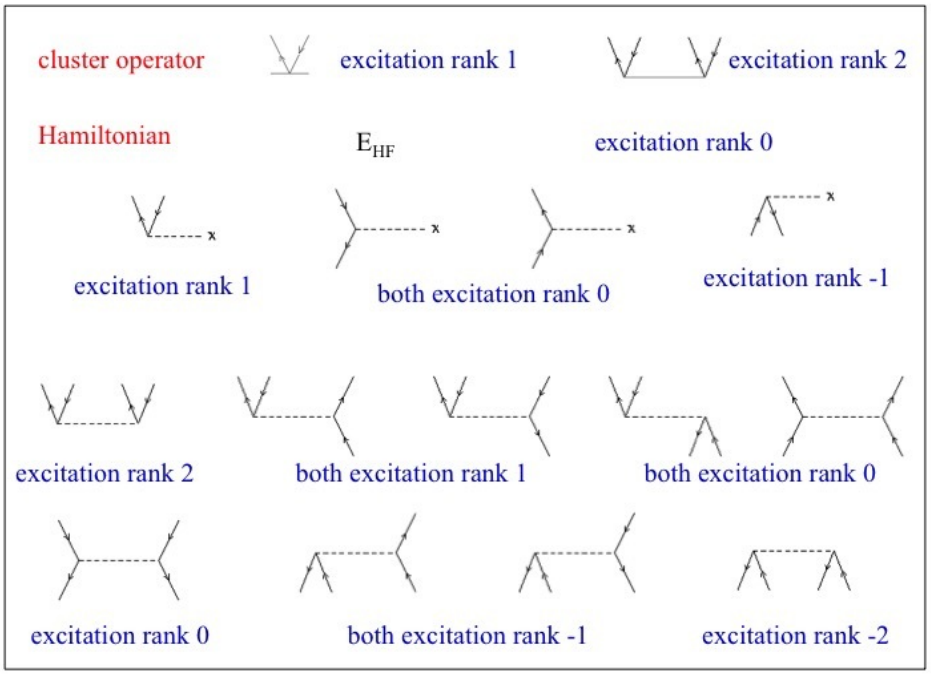
- The equations to be considered are

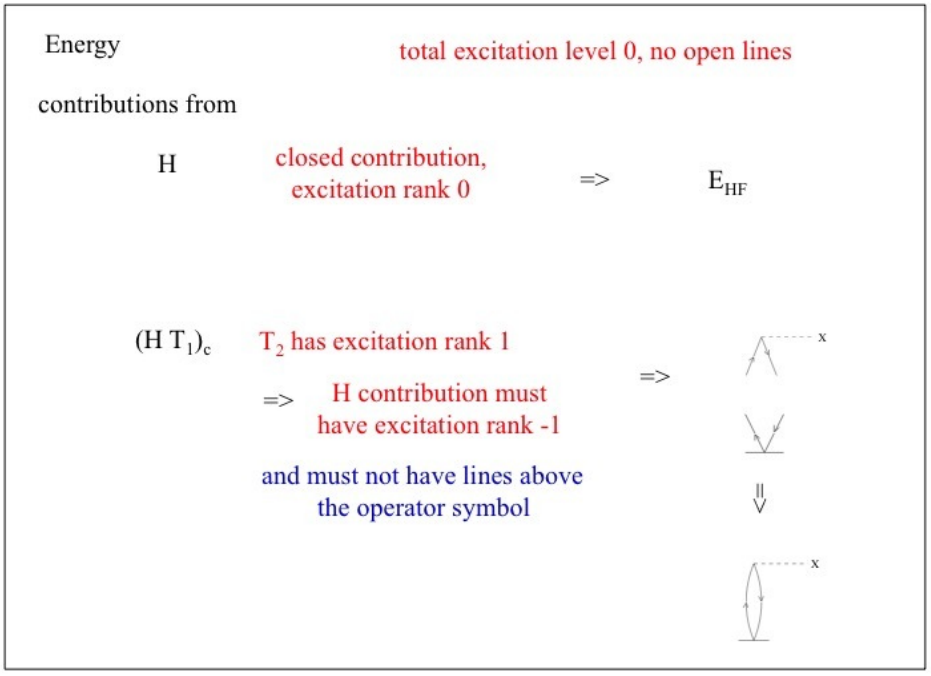
$$\begin{aligned} E &= \langle 0| \left(H \ \exp(T_1+T_2)\right)_c |0\rangle \\ 0 &= \langle \Phi_i^a| \left(H \ \exp(T_1+T_2)\right)_c |0\rangle \\ 0 &= \langle \Phi_{ij}^{ab}| \left(H \ \exp(T_1+T_2)\right)_c |0\rangle \end{aligned}$$

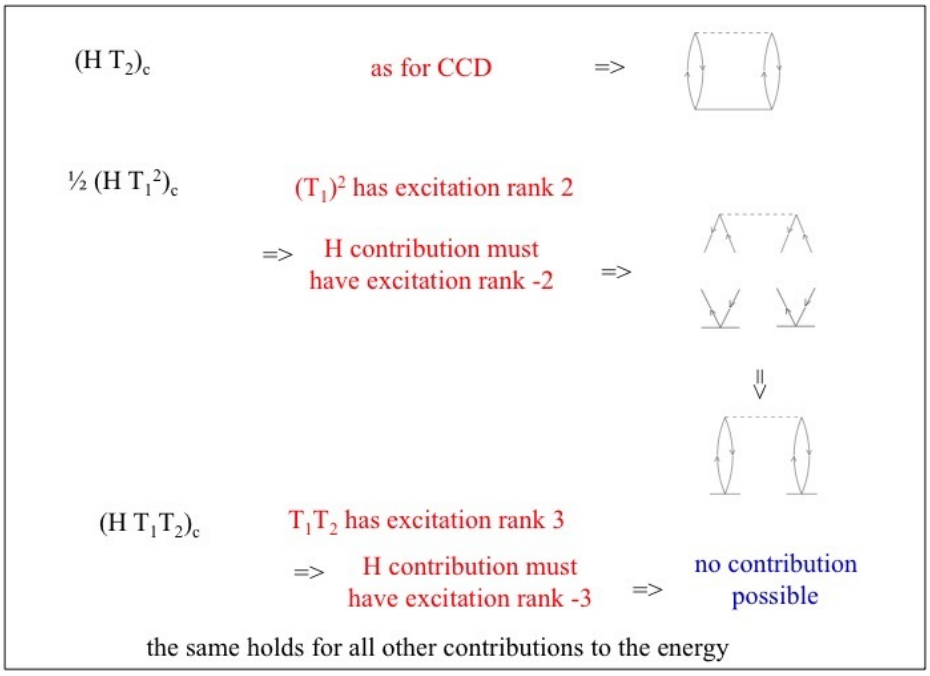
  with

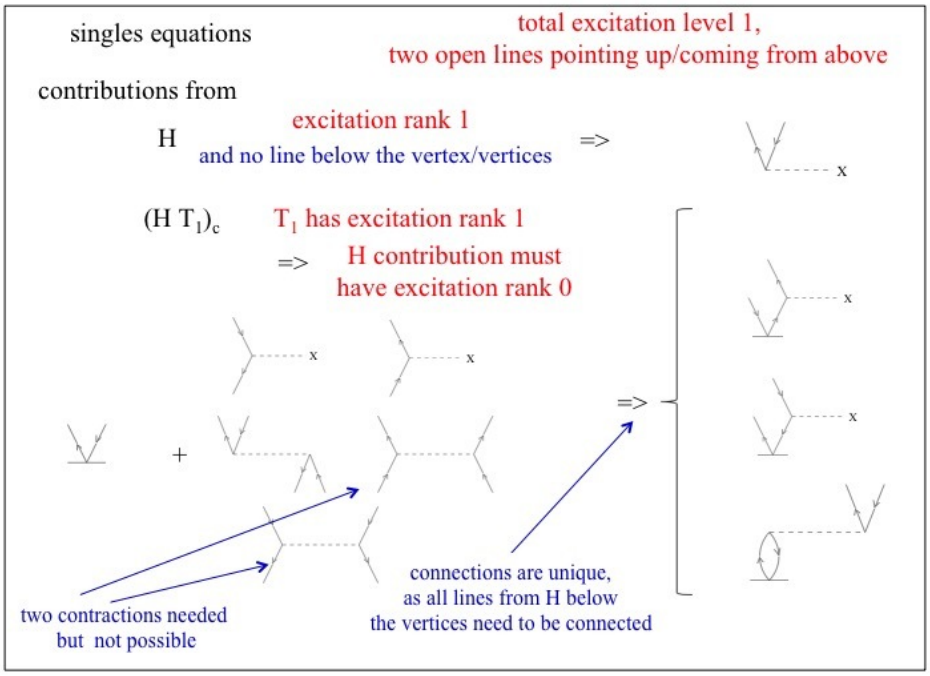
$$\left(H \ \exp(T)\right)_c = H + \left(H \ T\right)_c + \frac{1}{2!}\left(H \ T^2\right)_c + \frac{1}{3!}\left(H \ T^3\right)_c + \ldots \tag{80.29}$$

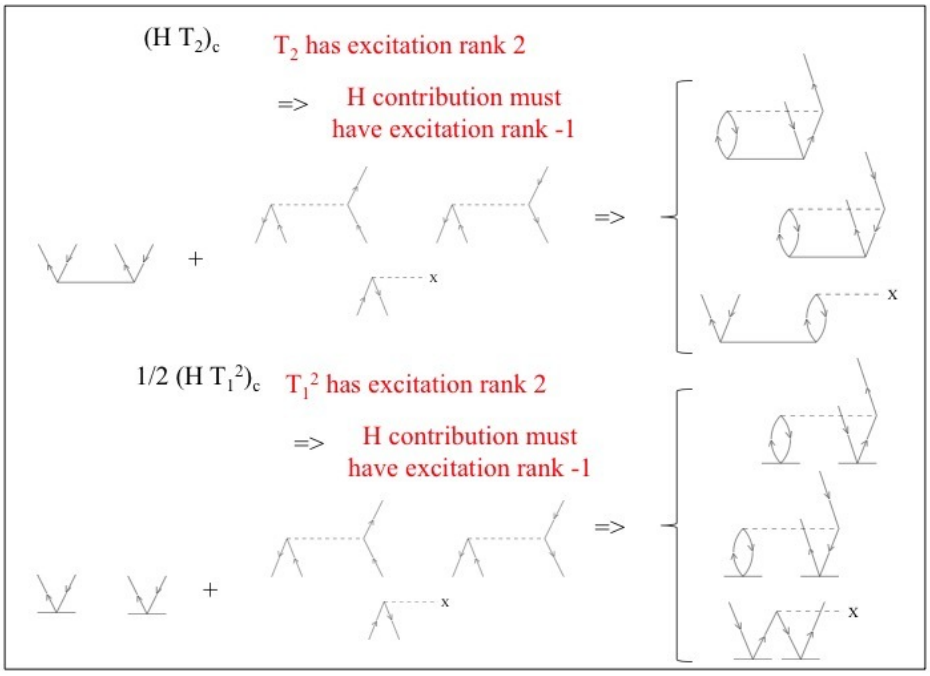
- Consider the excitation levels of the diagrams to be evaluated:
  - Energy expression:
    the total excitation level (projection on references) needs to be zero
  - Singles equation:
    the total excitation level (projection on singles) needs to be one
  - Doubles equation:
    the total excitation level (projection on doubles) needs to be two
- Consider the number of open lines in the diagrams to be evaluated
  - Energy expression:
    no open lines, closed diagrams
  - Singles equation:
    two open lines, one pointing upwards and one coming from above
  - Singles equation:
    four open lines, two pointing upwards and two coming from above
- Get complete list of diagrams for T_1, T_2 and H together with their excitation rank, as shown in the following. Note that we add comments concerning contractions such as, e.g. $(2,1,1)$, meaning two contractions to first T, and one to second and third. Sometimes, in the following, we also provide information about the arrow direction of the contraction: 'u' means upwards and 'd' downwards.

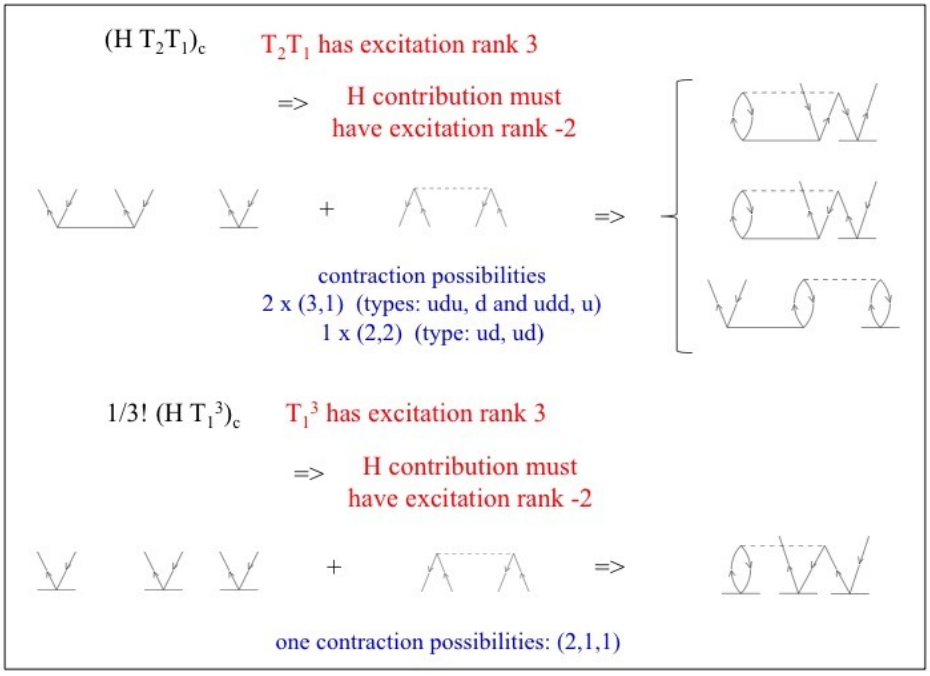

cluster operator
excitation rank 1
excitation rank 2
Hamiltonian
E_{HF}
excitation rank 0
excitation rank 1
both excitation rank 0
excitation rank -1
excitation rank 2
both excitation rank 1
both excitation rank 0
excitation rank 0
both excitation rank -1
excitation rank -2

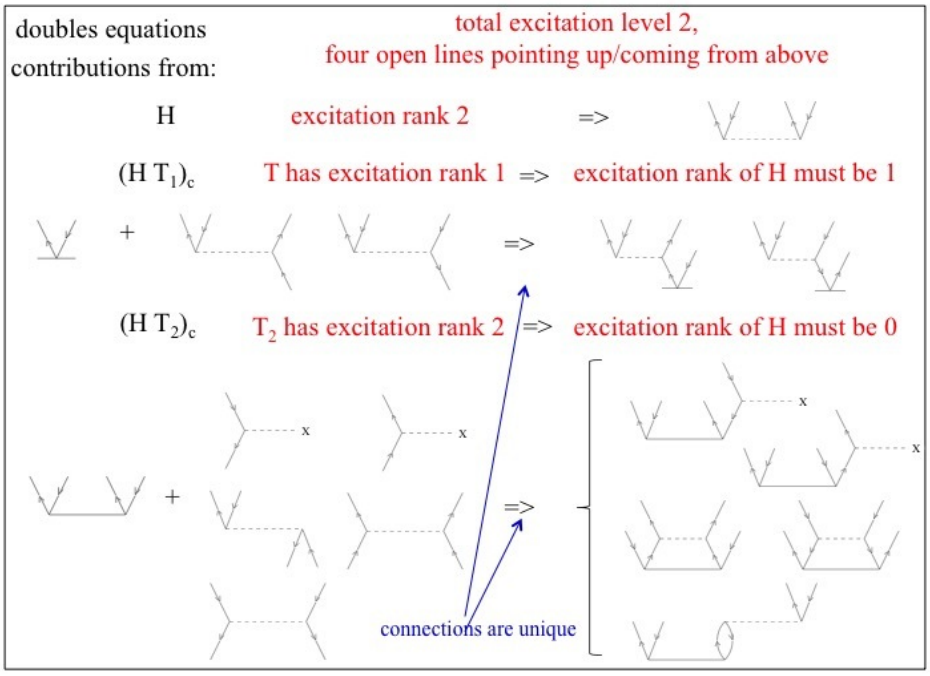

Energy
total excitation level 0, no open lines
contributions from
H
closed contribution,
excitation rank 0
=>
E_{HF}
$(H\ T_1)_c$
T_2 has excitation rank 1
=> H contribution must
have excitation rank -1
and must not have lines above
the operator symbol
=>

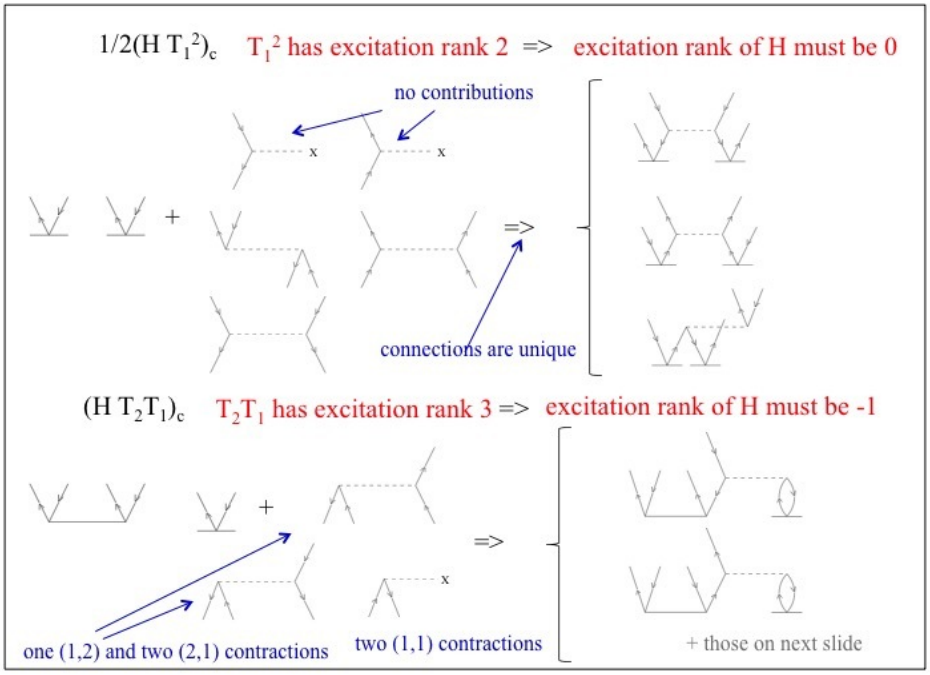

$(H\,T_2)_c$
as for CCD
=>
½ $(H\,T_1^2)_c$
$(T_1)^2$ has excitation rank 2
=> H contribution must have excitation rank -2
=>
$(H\,T_1T_2)_c$
T_1T_2 has excitation rank 3
=> H contribution must have excitation rank -3
=>
no contribution possible
the same holds for all other contributions to the energy

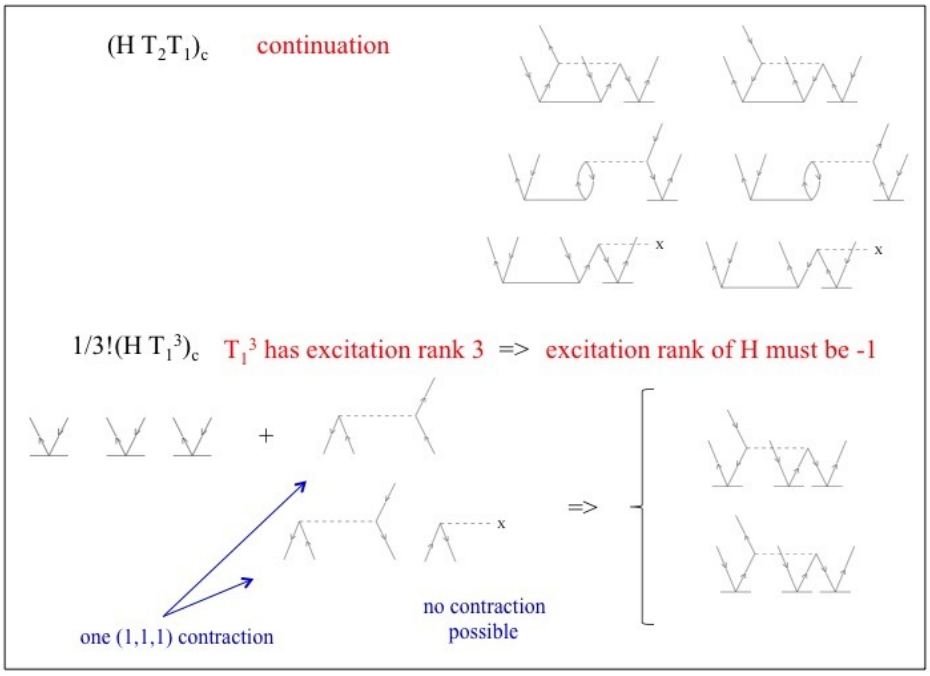

singles equations
total excitation level 1,
two open lines pointing up/coming from above
contributions from
H
excitation rank 1
and no line below the vertex/vertices
=>
x
$(H\,T_1)_c$
T_1 has excitation rank 1
=> H contribution must have excitation rank 0
x
x
+
=>
x
x
two contractions needed but not possible
connections are unique, as all lines from H below the vertices need to be connected

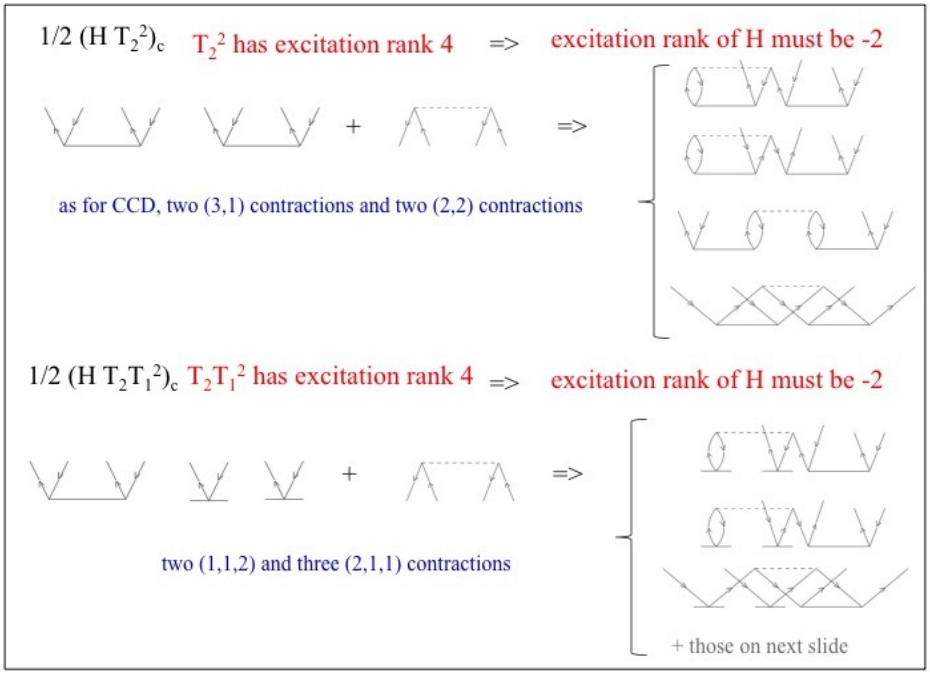

$(H\ T_2)_c$
T_2 has excitation rank 2
=> H contribution must have excitation rank -1
+
x
=>
x
$1/2\ (H\ T_1^2)_c$
T_1^2 has excitation rank 2
=> H contribution must have excitation rank -1
+
x
=>
x


$(H\ T_2T_1)_c$
T_2T_1 has excitation rank 3
=> H contribution must have excitation rank -2
+
=>
contraction possibilities
2 x (3,1) (types: udu, d and udd, u)
1 x (2,2) (type: ud, ud)
$1/3!\ (H\ T_1^3)_c$
T_1^3 has excitation rank 3
=> H contribution must have excitation rank -2
+
=>
one contraction possibilities: (2,1,1)

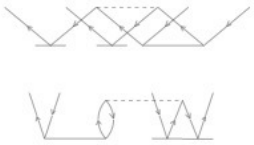

doubles equations
contributions from:
total excitation level 2,
four open lines pointing up/coming from above
H
excitation rank 2
=>
(H T1)c
T has excitation rank 1 => excitation rank of H must be 1
+
=>
(H T2)c
T2 has excitation rank 2 => excitation rank of H must be 0
x
x
+
=>
x
x
connections are unique


1/2(H T1^2)c
T1^2 has excitation rank 2 => excitation rank of H must be 0
no contributions
x
x
+
=>
connections are unique
(H T2T1)c
T2T1 has excitation rank 3 => excitation rank of H must be -1
+
=>
x
one (1,2) and two (2,1) contractions
two (1,1) contractions
+ those on next slide

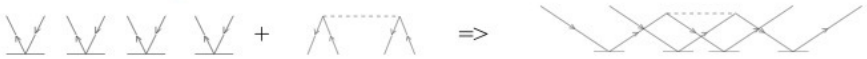

$(H\ T_2T_1)_c$ continuation
x
x
$1/3!(H\ T_1^3)_c$ T_1^3 has excitation rank 3 => excitation rank of H must be -1
+
x
=>
one (1,1,1) contraction
no contraction possible


$1/2\ (H\ T_2^2)_c$ T_2^2 has excitation rank 4 => excitation rank of H must be -2
+
=>
as for CCD, two (3,1) contractions and two (2,2) contractions
$1/2\ (H\ T_2T_1^2)_c$ $T_2T_1^2$ has excitation rank 4 => excitation rank of H must be -2
+
=>
two (1,1,2) and three (2,1,1) contractions
+ those on next slide

$1/2\ (H\ T_2 T_1^2)_c$ continuation



$¼!\ (H\ T_1^4)_c$ T_1^4 has excitation rank 4 => excitation rank of H must be -2

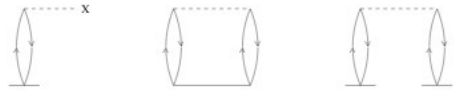


one contraction (1,1,1,1)

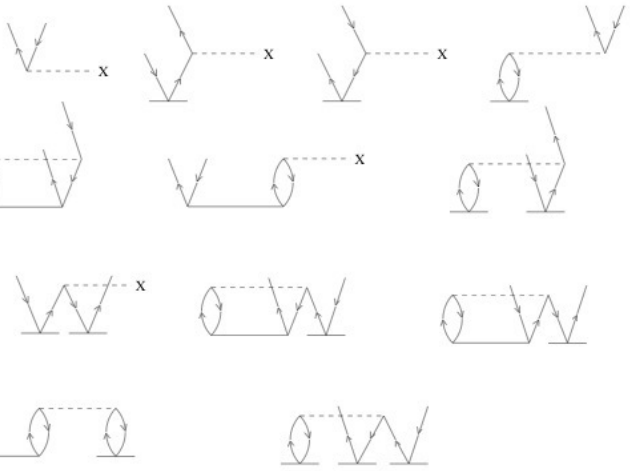
⇒ a total of 3 diagrams for the energy, 14 diagrams for the singles equation and 31 diagrams for the doubles equation

final set of diagrams

CC energy:

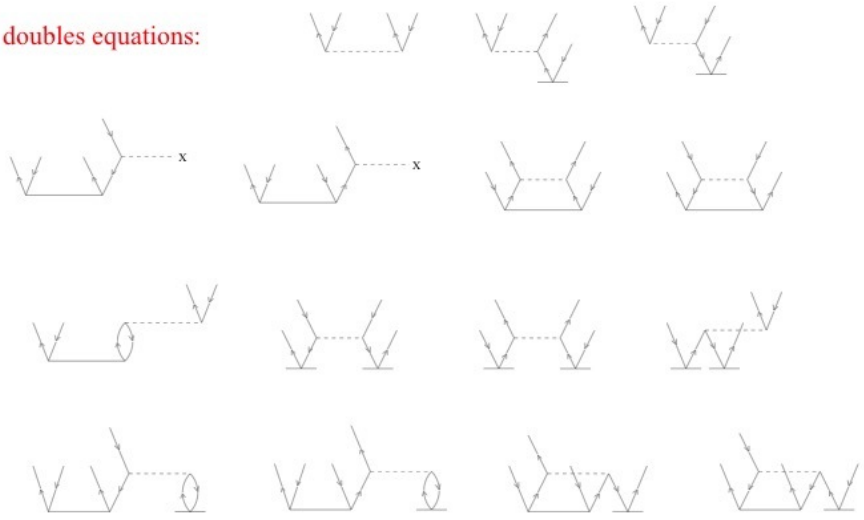


singles equations:

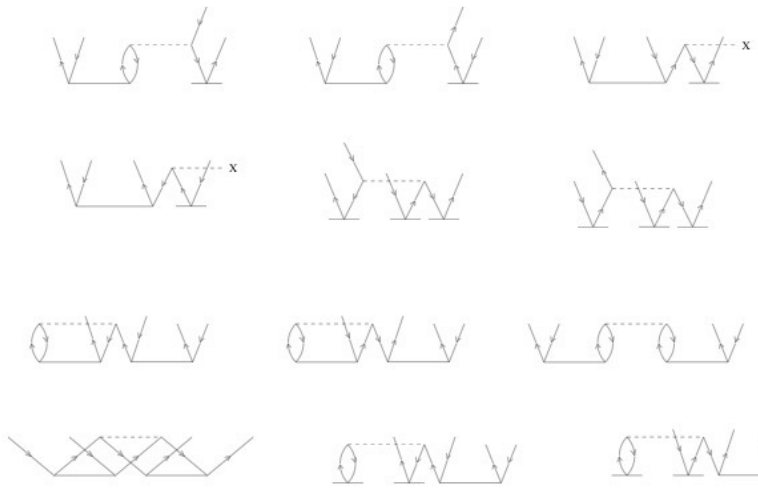


final set of diagrams

doubles equations:



final set of diagrams, cont'd



final set of diagrams, cont'd

Exercise 80.3 : CC theory and spin contamination (advanced, more difficult)

CC theory in its standard formulation provides only spin eigenfunctions in the case of closed-shell systems, while open-shell treatments suffer from spin contamination. This observation can be explained by analyzing the commutator $[S^2, T]$.

a) Show that $[S^2, T] = 0$ implies that the CC wave function is a spin eigenfunction provided that the reference determinant is a spin eigenfunction.

b) What are the commutator with S^2 for a simple excitation operator such as $a^\dagger_{a\sigma} a_{i\sigma}$ (notation $p\alpha$ denotes a spatial orbital with index p combined with an α spin function) and for the generators of the unitary group, $E^a_i = \sum_\sigma a^\dagger_{a\sigma} a_{i\sigma}$?

Hint: The operator S^2 is a two-electron operator and actually best used in the form

$$S^2 = S_+ S_- + S_z^2 - S_z. \tag{80.30}$$

In second quantization the corresponding operators are given as

$$S_+ = \sum_p a^\dagger_{p\alpha} a_{p\beta}; \quad S_- = \sum_p a^\dagger_{p\beta} a_{p\alpha}; \quad S_z = \frac{1}{2} \sum_p (a^\dagger_{p\alpha} a_{p\alpha} - a^\dagger_{p\beta} a_{p\beta}). \tag{80.31}$$

To reduce the amount of work, consider the commutators with S_-, S_+, and S_z.

c) Show that in the closed-shell case the cluster operator (with the given relationships between the amplitudes) can be rewritten in terms of E^a_i.

d) Discuss how a standard open-shell CC treatment could be modified in order to obtain a properly spin-adapted CC wavefunction. Discuss the consequences in particular with respect to the normal-ordered representation of products of cluster operators.

Solution 80.3

a. A CC wave function is a spin eigenfunction (i.e., eigenfunction of S^2, the case of S_z is trivial and not discussed) when the following eigenvalue equation holds

$$S^2 \exp(T)|0\rangle = s(s+1) \exp(T)|0\rangle$$

With the assumption that the reference determinant is a spin eigenfunction

$$S^2|0\rangle = s(s+1)|0\rangle$$

and that the commutator

$$\left[S^2, T\right] = 0$$

vanishes*, it follows that the CC wave function is a spin eigenfunction:

$$S^2 \exp(T)|0\rangle = \exp(T) S^2|0\rangle = \exp(T) s(s+1)|0\rangle = s(s+1) \exp(T)|0\rangle$$

*This implies $\left[S^2, \exp(T)\right] = 0$

b. The spin operator S^2 can be rewritten as (see standard textbooks of quantum chemistry) as

$$S^2 = \frac{1}{2}\left(S_+S_- + S_-S_+\right) + S_z^2 = S_+S_- + S_z^2 - S_z.$$

The second-quantized form of these erators is given as:

$$S_+ = \sum_p a^\dagger_{p\alpha}a_{p\beta}; \quad S_- = \sum_p a^\dagger_{p\beta}a_{p\alpha}; \quad S_z = \frac{1}{2}\sum_p \left(a^\dagger_{p\alpha}a_{p\alpha} - a^\dagger_{p\beta}a_{p\beta}\right)$$

To be evaluated are now the commutators of these operators with

$$a^\dagger_{a\alpha}a_{i\alpha}, a^\dagger_{a\beta}a_{i\beta}, \text{ and } E^a_i = a^\dagger_{a\alpha}a_{i\alpha} + a^\dagger_{a\beta}a_{i\beta}$$

It suffices to compute the commutators of $a^\dagger_{a\alpha}a_{i\alpha}$ with S_+, S_- and S_z and infer from this the other commutators. The commutators can be computed using the anticommutator relations, but the best way is probably to use Wick's theorem, as discussed in Chapter 9 (hint: use normal ordering with respect to the real vacuum and realize that only contracted contributions survive in the commutator). This yields:

$$\begin{aligned}
\left[S_+, a^\dagger_{a\alpha}a_{i\alpha}\right] &= \sum_p \left(a^\dagger_{p\alpha}a_{p\beta}a^\dagger_{a\alpha}a_{i\alpha} - a^\dagger_{a\alpha}a_{i\alpha}a^\dagger_{p\alpha}a_{p\beta}\right) \\
&= \sum_p \left(N(a^\dagger_{p\alpha}\overbrace{a_{p\beta}a^\dagger_{a\alpha}}a_{i\alpha}) - N(a^\dagger_{a\alpha}\overbrace{a_{i\alpha}a^\dagger_{p\alpha}}a_{p\beta})\right) \\
&= -a^\dagger_{a\alpha}a_{i\beta},
\end{aligned}$$

Continuing in the same manner we find

$$\begin{aligned}
\left[S_-, a^\dagger_{a\alpha}a_{i\alpha}\right] &= \sum_p \left(a^\dagger_{p\beta}a_{p\alpha}a^\dagger_{a\alpha}a_{i\alpha} - a^\dagger_{a\alpha}a_{i\alpha}a^\dagger_{p\beta}a_{p\alpha}\right) \\
&= \sum_p \left(N(a^\dagger_{p\beta}\overbrace{a_{p\alpha}a^\dagger_{a\alpha}}a_{i\alpha}) - N(a^\dagger_{a\alpha}\overbrace{a_{i\alpha}a^\dagger_{p\beta}}a_{p\alpha})\right) \\
&= a^\dagger_{a\beta}a_{i\alpha}
\end{aligned}$$

In the final commutator with S_z it suffices to consider the α part of S_z, since the β part obviously commutes:

$$\begin{aligned}
\left[S_z, a^\dagger_{a\alpha}a_{i\alpha}\right] &= \frac{1}{2}\sum_p \left(a^\dagger_{p\alpha}a_{p\alpha}a^\dagger_{a\alpha}a_{i\alpha} - a^\dagger_{a\alpha}a_{i\alpha}a^\dagger_{p\alpha}a_{p\alpha}\right) \\
&= \frac{1}{2}\sum_p \left(N(a^\dagger_{p\alpha}\overbrace{a_{p\alpha}a^\dagger_{a\alpha}}a_{i\alpha}) - N(a^\dagger_{a\alpha}\overbrace{a_{i\alpha}a^\dagger_{p\alpha}}a_{p\alpha})\right) \\
&= 0.
\end{aligned}$$

Proceeding in analogous manner we find

$$\left[S_+, a^\dagger_{a\beta}a_{i\beta}\right] = a^\dagger_{a\alpha}a_{i\beta} \quad \left[S_-, a^\dagger_{a\beta}a_{i\beta}\right] = -a^\dagger_{a\beta}a_{i\alpha} \quad \left[S_z, a^\dagger_{a\beta}a_{i\beta}\right] = 0,$$

as well as

$$[S_+, E_i^a] = 0 \quad [S_-, E_i^a] = 0 \quad [S_z, E_i^a] = 0.$$

From the results obtained so far, it already follows that E_i^a commutes with S^2, while for the individual excitation operators the (actually non-vanishing) commutator with S_+S_- needs to be evaluated as well (to be skipped)

$$\begin{aligned}\left[S_+S_-, a_{a\alpha}^\dagger a_{i\alpha}\right] &= S_+\left[S_-, a_{a\alpha}^\dagger a_{i\alpha}\right] + \left[S_+, a_{a\alpha}^\dagger a_{i\alpha}\right] S_- \\ &= \ldots = \sum_p \Big(N(a_{p\alpha}^\dagger a_{p\beta} a_{a\beta}^\dagger a_{i\alpha}) - N(a_{a\alpha}^\dagger a_{i\beta} a_{p\beta}^\dagger a_{p\alpha})\Big) \neq 0\end{aligned}$$

c. The task is to rewrite the closed-shell cluster operator (CCSD case) in terms of the generators of the unitary group. We proceed by limiting summations to indices of spatial orbitals only, and writing out explicitly all spin combinations.

- In the case of singles, we use

$$t_{i\alpha}^{a\alpha} = t_{i\beta}^{a\beta}.$$

allowing us to define

$$T_i^a = t_{i\alpha}^{a\alpha} = t_{i\beta}^{a\beta}.$$

We therefore have

$$\begin{aligned}T_1 &= \sum_a \sum_i \Big(t_{i\alpha}^{a\alpha} a_{a\alpha}^\dagger a_{i\alpha} + t_{i\beta}^{a\beta} a_{a\beta}^\dagger a_{i\beta}\Big) \\ &= \sum_a \sum_i T_i^a \Big(a_{a\alpha}^\dagger a_{i\alpha} + a_{a\beta}^\dagger a_{i\beta}\Big) = \sum_a \sum_i T_i^a E_i^a\end{aligned}$$

- In the case ouf doubles, we use

$$t_{i\alpha j\alpha}^{a\alpha b\alpha} = t_{i\beta j\beta}^{a\beta b\beta}; \quad t_{i\alpha j\beta}^{a\alpha b\beta} = t_{j\beta i\alpha}^{b\beta a\alpha} = -t_{i\alpha j\beta}^{b\beta a\alpha} = -t_{j\beta i\alpha}^{a\alpha b\beta}$$

and

$$t_{i\alpha j\alpha}^{a\alpha b\alpha} = t_{i\alpha j\beta}^{a\alpha b\beta} - t_{i\alpha j\beta}^{b\alpha a\beta}; \quad t_{i\alpha j\beta}^{a\alpha b\beta} = t_{j\alpha i\beta}^{b\alpha a\beta}.$$

We now define

$$T_{ij}^{ab} = t_{i\alpha j\beta}^{a\alpha b\beta}.$$

The T_2 operator is expanded as

$$\begin{aligned}T_2 &= \frac{1}{4}\sum_{a,b}\sum_{i,j}\Big(t_{i\alpha j\alpha}^{a\alpha b\alpha} a_{a\alpha}^\dagger a_{b\alpha}^\dagger a_{j\alpha} a_{i\alpha} + t_{i\beta j\beta}^{a\beta b\beta} a_{a\beta}^\dagger a_{b\beta}^\dagger a_{j\beta} a_{i\beta} + t_{i\alpha j\beta}^{a\alpha b\beta} a_{a\alpha}^\dagger a_{b\beta}^\dagger a_{j\beta} a_{i\alpha} \\ &+ t_{i\alpha j\beta}^{a\beta b\alpha} a_{a\beta}^\dagger a_{b\alpha}^\dagger a_{j\beta} a_{i\alpha} + t_{i\beta j\alpha}^{a\alpha b\beta} a_{a\alpha}^\dagger a_{b\beta}^\dagger a_{j\alpha} a_{i\beta} + t_{i\beta j\alpha}^{a\beta b\alpha} a_{a\beta}^\dagger a_{b\alpha}^\dagger a_{j\alpha} a_{i\beta}\Big)\end{aligned}$$

Rewritten in terms of T-amplitudes defined above, we obtain

$$\begin{aligned}T_2 &= \frac{1}{4}\sum_{a,b}\sum_{i,j}\Big((T_{ij}^{ab} - T_{ij}^{ba}) a_{a\alpha}^\dagger a_{b\alpha}^\dagger a_{j\alpha} a_{i\alpha} + (T_{ij}^{ab} - T_{ij}^{ba}) a_{a\beta}^\dagger a_{b\beta}^\dagger a_{j\beta} a_{i\beta} \\ &+ T_{ij}^{ab} a_{a\alpha}^\dagger a_{b\beta}^\dagger a_{j\beta} a_{i\alpha} - T_{ij}^{ba} a_{a\beta}^\dagger a_{b\alpha}^\dagger a_{j\beta} a_{i\alpha} \\ &+ T_{ji}^{ab} a_{a\alpha}^\dagger a_{b\beta}^\dagger a_{j\alpha} a_{i\beta} - T_{ji}^{ba} a_{a\beta}^\dagger a_{b\alpha}^\dagger a_{j\alpha} a_{i\beta}\Big)\end{aligned}$$

We now regroup terms and reorder creation/annihilation operators to obtain

$$\begin{aligned} T_2 &= \frac{1}{4}\sum_{a,b}\sum_{i,j} T_{ij}^{ab}\left(a_{a\alpha}^\dagger a_{b\alpha}^\dagger a_{j\alpha}a_{i\alpha} + a_{a\beta}^\dagger a_{b\beta}^\dagger a_{j\beta}a_{i\beta} + a_{a\alpha}^\dagger a_{b\beta}^\dagger a_{j\beta}a_{i\alpha} + a_{b\alpha}^\dagger a_{a\beta}^\dagger a_{i\beta}a_{j\alpha}\right) \\ &+ \frac{1}{4}\sum_{a,b}\sum_{i,j} T_{ij}^{ba}\left(a_{b\alpha}^\dagger a_{a\alpha}^\dagger a_{j\alpha}a_{i\alpha} + a_{b\beta}^\dagger a_{a\beta}^\dagger a_{j\beta}a_{i\beta} + a_{b\alpha}^\dagger a_{a\beta}^\dagger a_{j\beta}a_{i\alpha} + a_{a\alpha}^\dagger a_{b\beta}^\dagger a_{i\beta}a_{j\alpha}.\right) \end{aligned}$$

This factorizes to give

$$\begin{aligned} T_2 &= \frac{1}{4}\sum_{a,b}\sum_{i,j} T_{ij}^{ab}\left(a_{a\alpha}^\dagger a_{i\alpha} + a_{a\beta}^\dagger a_{i\beta}\right)\left(a_{b\alpha}^\dagger a_{j\alpha} + a_{b\beta}^\dagger a_{j\beta}\right) \\ &+ \frac{1}{4}\sum_{a,b}\sum_{i,j} T_{ij}^{ba}\left(a_{a\alpha}^\dagger a_{i\alpha} + a_{b\beta}^\dagger a_{i\beta}\right)\left(a_{a\alpha}^\dagger a_{j\alpha} + a_{a\beta}^\dagger a_{j\beta}\right), \end{aligned}$$

and can therefore be rewritten in terms of generators of the unitary group

$$T_2 = \frac{1}{4}\sum_{a,b}\sum_{i,j} T_{ij}^{ab}E_i^a E_j^b + \frac{1}{4}\sum_{a,b}\sum_{i,j} T_{ij}^{ba}E_i^b E_j^a = \frac{1}{2}\sum_{a,b}\sum_{i,j} T_{ij}^{ab}E_i^a E_j^b$$

This means that in the closed-shell case, the cluster operator can be written in terms of the generators, and the CC wave function is the spin adapted.

d. If one rewrites the cluster operator in terms of the generators of the unitary group, a spin-adapted open-shell CC theory is possible (see Jansen & Schaefer, Paldus and co-workers). However, the use of the generators requires that each spatial orbitalis included for both spin case in the same way. While a singlu occupied orbital in the doublet case is for the alpha spin case *occupied* and for the beta spin case *virtual*, the use of the generators would then involve this orbital in the cluster operator for both spin cases (!) as annihilation and creation operator. A consequence is that different components of the cluster operator do no longer commute and that the BCH expansion does not terminate after the quartic terms. Consequently such CC theories are significantly more complicated and can usually only be implemented using automatic-implementation techniques.

Exercise 80.4 : Factorization and computational cost (medium difficulty)

Show that the cost (in terms of number of operations) for evaluating

$$Z_{ij}^{ab} = \frac{1}{4}\sum_{m,n}\sum_{e,f}\langle mn||ef\rangle t_{ij}^{ef} t_{mn}^{ab} \qquad \text{for all } i,j,a,b \text{ combinations} \tag{80.32}$$

is $2n_{occ}^4 N_{virt}^2$ and thus only of the order N^6. N denotes here the total number of orbitals, n_{occ} stands for the number of occupied orbitals (indices i,j,m,n) and N_{virt} denotes the number of virtual orbitals (indices a,b,e,f).
Analyze in an analogous manner all quadratic terms in the CCD equations and show in this way that the cost for a CCD calculation is indeed only of the order N^6.

Exercise 80.5 : The similarity-transformed Hamiltonian (Part I) (medium difficulty)

The similarity-transformed Hamiltonian,

$$\bar{H} = e^{-\hat{T}} \hat{H}_N e^{\hat{T}}, \tag{80.33}$$

is central to the conventional formulations of coupled cluster (CC) theory. Here $\hat{H}_N$ is the normal-ordered Hamiltonian,

$$\begin{aligned} \hat{H}_N &= \hat{F}_N + \hat{V}_N \\ &= \sum_{pq} f_{pq} \{a_p^\dagger a_q\} + \frac{1}{4} \sum_{pqrs} \{a_p^\dagger a_q^\dagger a_s a_r\}, \end{aligned} \tag{80.34}$$

and the cluster operator contains excitation operators appropriate for the given level of coupled cluster theory, *e.g.*, for CCSD,

$$\begin{aligned} \hat{T} &= \hat{T}_1 + \hat{T}_2 \\ &= \sum_{ia} t_i^a \{a_a^\dagger a_i\} + \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \{a_a^\dagger a_b^\dagger a_j a_i\}. \end{aligned} \tag{80.35}$$

While the Hamiltonian contains one- ($\hat{F}_N$) and two-body ($\hat{V}_N$) operators, the similarity transformation has the potential to introduce higher-body contributions.

While the power-series expansion of $e^{\hat{T}}$ truncates only at the number of electrons (or, more precisely, at the number of occupied spin-orbitals), the commutator expansion of $\bar{H}$ [the Campbell-Baker-Hausdorff (CBH)] expansion] truncates at the fourth-order commutator, *i.e*,

$$\begin{aligned} \bar{H} = \hat{H} &+ \left[\hat{H}, \hat{T}\right] + \frac{1}{2!} \left[\left[\hat{H}, \hat{T}\right], \hat{T}\right] + \frac{1}{3!} \left[\left[\left[\hat{H}, \hat{T}\right], \hat{T}\right], \hat{T}\right] \\ &+ \frac{1}{4!} \left[\left[\left[\left[\hat{H}, \hat{T}\right], \hat{T}\right], \hat{T}\right], \hat{T}\right], \end{aligned} \tag{80.36}$$

because the Hamiltonian is a two-body operator at most, and provided that the cluster operators commute, *e.g.*,

$$\left[\hat{T}_1, \hat{T}_2\right] = 0. \tag{80.37}$$

(This commutator holds for conventional formulations of CC theory using RHF or UHF reference determinants/orbitals. The formulation is much more complicated for ROHF references where spin-adapted CC wave functions are sought.)

a) Show explicitly using only the anticommutation relations,

$$a_p^\dagger a_q + a_q a_p^\dagger = \delta_{pq}, \quad a_p^\dagger a_q^\dagger + a_q^\dagger a_p^\dagger = 0, \quad \text{and} \quad a_p a_q + a_q a_p = 0 \tag{80.38}$$

that the commutator between the Fock operator, $\hat{F}_N$, and the single-excitation cluster operator, $\hat{T}_1$,

$$\left[\hat{F}_N, \hat{T}_1\right] = \sum_{pq} \sum_{ia} f_{pq} t_i^a \left[a_p^\dagger a_q, a_a^\dagger a_i\right], \tag{80.39}$$

reduces the number of *general-orbital* annihilation/creation operators (those that could be either occupied or virtual orbitals) by one. (Note that normal ordering is not necessary for this analysis, so you can ignore it here.)

b) Using the above result, the fact that the Hamiltonian is a two-body operator, and the assumption that the cluter operators commute, explain why the CBH expansion of $\bar{H}$ truncates at the quadruply nested commutator.

Exercise 80.6 : The similarity-transformed Hamiltonian (Part II) (medium difficulty)

While the normal-ordered Hamiltonian contains one- ($\hat{F}_N$) and two-body ($\hat{V}_N$) operators, the similarity transformation has the potential to introduce higher-body contributions.

a) It is convenient in some specific CC formulations (such as CC2 and CC3) to make use of the $\hat{T}_1$-similarity-transformed Hamiltonian, *viz.*,

$$\bar{H}_{\hat{T}_1} = e^{-\hat{T}_1} \hat{H}_N e^{\hat{T}}. \tag{80.40}$$

Show, using either Wick's theorem or diagrammatic techniques, that this transformation leaves the normal-ordered Hamiltonian as a two-body operator at most.

b) Show, using either Wick's theorem of diagrammatic techniques, that the CCSD similarity-transformed Hamiltonian contains up to *six-body* terms:

$$\bar{H}_{\text{CCSD}} = e^{-\hat{T}_1 - \hat{T}_2} \hat{H}_N e^{\hat{T}_1 + \hat{T}_2}. \tag{80.41}$$