TCC Electronic Structure Module
L5: Coupled-Cluster Theory

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February 21, 2021

Overview

These lectures introduce electronic structure theory. This is an enormous field that has undergone continuous development for near 100 years and the scope of these lectures is necessarily limited. The focus will be on the central theory as applied to molecules. The aim is to introduce you the basics of molecular electronic structure theory, which will help you understand the level of sophistication of calculations you find in the literature, and provide the foundation for further study in the field.

L1 Exact and inexact wavefunctions

L2 Hartree–Fock theory

L3 Configuration Interaction theory

L4 Møller–Plesset perturbation theory

L5 Coupled-cluster theory

L6 Properties and excited states

L7 Density Functional Theory

L8 Density Functional Approximations

Recommended books

- Good introduction to the topic: Frank Jensen, *Introduction to Computational Chemistry* (Wiley, 2007)
- Excellent concise treatise: Szabo and Ostlund, *Modern Quantum Chemistry* (Dover, 1996)
- Comprehensive reference for quantum chemistry methods (excluding DFT): Helgaker, Jørgensen and Olsen, *Molecular Electronic-Structure Theory* (Wiley, 2002)
- Excellent book for many-body correlation: Bartlett and Shavitt, *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory* (CUP, 2009)

1 Introduction

Although configuration interaction theory is conceptually simple and straightforward to implement, it is not often used to compute ground state energies. Full configuration interaction where the wavefunction is expanded in the complete Hilbert space is in general intractable because of the exponential growth of the Hilbert space with system size. Truncated configuration interaction where a subspace is selected is in general practical, but has the unfortunate feature that the error per electron incurred due to the truncated Hilbert space grows with the number of electrons that are correlated. In this lecture we will discuss this size extensivity problem and examine an alternative theory, coupled-cluster theory, where the representation of electron correlation is motived from a consideration of many-body interactions rather than through mixing electron configurations.

1.1 The inefficiency of CI theory

Let us examine the Configuration interaction wavefunction again.

$$|\mathrm{CI}\rangle = C_0|0\rangle + \sum_{ia} C^{i}_{a} |{}^{a}_{i}\rangle + \sum_{i<j,a<b} C^{ij}_{ab} |{}^{ab}_{ij}\rangle + \dots \tag{1}$$

The terms can be collected according to their physical role

$$|\theta_i\rangle = \sum_{a} C^{i}_{a} |{}^{a}_{i}\rangle \tag{2}$$

$$|\theta_{ij}\rangle = \sum_{a<b} C^{ij}_{ab} |{}^{ab}_{ij}\rangle \tag{3}$$

The terms $\sum_a C^i_a |{}^{a}_{i}\rangle$ describe the change in orbital i due to the correlation of all the electrons $\phi_i \to \phi_i + \theta_i$. Similarly, the terms $\sum_{a<b} C^{ij}_{ab} |{}^{ab}_{ij}\rangle$ describe the change in the pair function $|ij\rangle$ due to the correlation of all the electrons $|\phi_i \phi_j\rangle \to |\phi_i \phi_j\rangle + |\theta_{ij}\rangle$. Since configuration interaction theory employs a linear parameterisation of the wavefunction, a change in e.g. a quadruple function $|ijkl\rangle$ only occurs if there quadruply excitated configurations. There is a direct correspondance between the n-body configurations and the change in n-electron multiplets.

However, this parameterisation does not follow the physical process of correlation. Consider, for example, the correlation of electrons in orbitals $|ij\rangle$ is an independent process to the correlation of electrons in orbitals $|kl\rangle$. These independent pairwise correlation events occur simultaneously and result in a change in the quadruple function $|ijkl\rangle$. This product structure does not appear in the CI parameterisation and consequently it is inefficient.

1.2 Size extensivity

In addition to the CI parameterisation being inefficient, truncated CI wavefunctions are also unphysical. As you know from thermodynamics, some quantities are *intensive* and some are *extensive*. Intensive quantities are independent of the amount of matter they apply to (temperature, pressure, etc) and extensive quantities scale linearly with the amount of matter (energy, entropy, volume etc). The size extensivity of energy means that the energy of two non-interacting molecules must be the same as the sum of the energy of each molecule:

$$E_{AB} = E_A + E_B \tag{4}$$

The Hamiltonian for the dimer is simply the sum of the monomer Hamiltonians and consequently the wavefunction for the dimer must be the antisymmetrised product of the wavefunctions for the monomers

$$\hat{H}_{AB}|\Psi_{AB}\rangle = E_{AB}|\Psi_{AB}\rangle \tag{5}$$

$$(\hat{H}_A + \hat{H}_B)|\Psi_A\Psi_B\rangle = (E_A + E_B)|\Psi_A\Psi_B\rangle \tag{6}$$

Let us consider a simple example of two indentical non-interacting hydrogen molecules, and a minimal orbital basis composed of the σ_g and σ_u orbitals of each hydrogen molecule. Let us denote $|0\rangle = |\sigma_g\sigma_g\rangle$ and $|1\rangle = |\sigma_u\sigma_u\rangle$. The configuration interaction doubles (CID) wavefunction for the dimer is of the form

$$|\Psi_{\text{CID}}\rangle = c_{00}|0_A0_B\rangle + c_{10}|1_A0_B\rangle + c_{01}|0_A1_B\rangle \tag{7}$$

This wavefunction is physically incorrect since it imposes a spurious correlation whereby if the electrons of A are in σ_u, those of B must be in σ_g and vice versa. The term $|1_A1_B\rangle$ that represents the contribution where the electrons of A are in σ_u at the same time that those of B are in σ_u is missing, since this corresponds to a quadruply substituted configuration. Consequently, the CID wavefunction does not have the correct product structure

$$|\Psi_{\text{CID}}\rangle \neq |(c_0 0_A + c_1 1_A)(c_0 0_B + c_1 1_B)\rangle \tag{8}$$

and the energy of the dimer is not the sum of the energies of the monomers. This is a general problem for all truncated CI methods: they are not size extensive.

Exercise 1

Consider a hydrogen molecule in a minimal basis. The Hartree–Fock wavefunction is $|0\rangle = |\sigma_g\sigma_g\rangle$ and has energy $\langle 0|\hat{H}|0\rangle = \alpha$. The only configuration that can mix with $|0\rangle$ is $|1\rangle = |\sigma_u\sigma_u\rangle$, which is $\langle 1|\hat{H}|1\rangle = \alpha + \beta$. The energy of interaction is $\langle 0|\hat{H}|1\rangle = \gamma$. Show that the correlation energy is

$$E_c = \frac{\beta}{2}(1 - \sqrt{1 + 4\gamma^2/\beta^2}) \tag{9}$$

Consider the system of n non-interacting hydrogen molecules. What is the correct energy of this system? Show that the CID wavefunction has $n+1$ relevant configurations and that the Hamiltonian is

$$H = \begin{pmatrix} n\alpha & \gamma & \gamma & \dots & \gamma \\ \gamma & n\alpha+\beta & 0 & & 0 \\ \gamma & 0 & n\alpha+\beta & & 0 \\ \vdots & & & \ddots & \vdots \\ \gamma & 0 & 0 & \dots & n\alpha+\beta \end{pmatrix} \tag{10}$$

Thus solve the secular equation and show that the correlation energy is

$$E_c = \frac{\beta}{2}(1 - \sqrt{1 + 4n\gamma^2/\beta^2}) \tag{11}$$

What percentage of the correct correlation energy per molecule does CID recover in the limit that $n \to \infty$?

1.3 Excitation operators

To follow the physics of correlation, we need a slight paradigm shift. Instead of a linear expansion of the full n-electron wavefunction in terms of n-electron configurations, we will make a linear parameterisation of the change in a m-orbital multiplet due to m-body correlation.

To this end we introduce m-body excitation operators $\hat{\tau}_{ijk\ldots}^{abc\ldots}$ that performs the m orbital replacement from $ijk\cdots$ to $abc\cdots$. The order m of each operator is called the excitation rank. In this notation, the CI wavefunction is

$$|\mathrm{CI}\rangle = C_0|0\rangle + \sum_{ia} C_a^i \hat{\tau}_i^a|0\rangle + \sum_{i<j,a<b} C_{ab}^{ij}\hat{\tau}_{ij}^{ab}|0\rangle + \ldots \tag{12}$$

The operator $\hat{\tau}_i^a = \hat{a}_a^\dagger \hat{a}_i$ removes (annihilates) an electron from an occupied orbital i and adds (creates) an electron in the virtual orbital a and is called a singles excitation operator

$$\hat{\tau}_i^a|0\rangle = |{}^{a}_{i}\rangle, \qquad \hat{\tau}_i^a|{}^{b}_{j}\rangle = |{}^{ab}_{ij}\rangle, \qquad \hat{\tau}_i^b|{}^{a}_{i}\rangle = 0, \qquad \hat{\tau}_j^a|{}^{a}_{i}\rangle = 0 \tag{13}$$

Similarly, $\hat{\tau}_{ij}^{ab}$ is a doubles excitation operator and $\hat{\tau}_{ijk}^{abc}$ is a triples excitation operator and so on. A general excitation operator will be denoted as $\hat{\tau}_\mu$.

Exercise 2
Show that all excitation operators commute $[\hat{\tau}_\mu, \hat{\tau}_\nu] = 0$ and are nilpotent $\hat{\tau}_\mu^2 = 0$.

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2 The coupled-cluster wavefunction

We require a wavefunction where correlation processes can happen simultaneously rather than one by one. Each m-body correlation process is parameterised by a modification of the m-body multiplet

$$|ijk\cdots\rangle \rightarrow |ijk\cdots\rangle + |\theta_{ijk\ldots}\rangle = (1 + \sum_{a<b<c\ldots} t_{abc\ldots}^{ijk\ldots}\tau_{ijk\ldots}^{abc\ldots})|0\rangle \tag{14}$$

The coupled-cluster wavefunction is the wavefunction where all such m-body correlation processes occur simultaneously and has the general form

$$|\mathrm{CC}\rangle = \prod_\mu (1 + t_\mu \hat{\tau}_\mu)|0\rangle \tag{15}$$

The CC wavefunction is conveniently expressed as an exponential

$$|\mathrm{CC}\rangle = e^{\hat{T}}|0\rangle \tag{16}$$

$$\hat{T} = \sum_\mu t_\mu \hat{\tau}_\mu \tag{17}$$

$\hat{T}$ is called the cluster operator. If all excitations are included in $\hat{T}$, the CC wavefunction is identical to the CI wavefunction. The cluster operator can be decomposed into singles, doubles, triples, etc contributions

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \hat{T}_4 + \dots \tag{18}$$

$\hat{T}_1$ parameterises the correlation induced orbital relaxation. $\hat{T}_2$ parameterises two-body correlation, $\hat{T}_3$ three-body correlation and so on. The correspondance between the CC operators $\hat{T}_m$ and the CI operaotrs $\hat{C}_m$ reveals the many-body structure in the CC wavefunction

$$\hat{C}_1 = \hat{T}_1, \qquad \hat{C}_2 = \hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2, \qquad \hat{C}_3 = \hat{T}_3 + \hat{T}_1\hat{T}_2 + \tfrac{1}{6}\hat{T}_1^3 \tag{19}$$

The CC amplitudes decay much more quickly with excitation rank than the CI coefficients. A heiarchy of approximate CC wavefunctions are defined by truncating $\hat{T}$ to a given order: CCS, CCSD, CCSDT, CCSDTQ etc, where up to single, double, triple, quadruple excitations etc are included in $\hat{T}$. Note that in all of these wavefunctions, configurations with n-fold excitations for n-electrons appear due to the product structure. However, the coefficients for these highly excited configurations are generated as sums of products of the retained low-order excitation amplitudes.

Exercise 3
Show that $\prod_\mu (1 + t_\mu \hat{\tau}_\mu)|0\rangle = e^{\hat{T}}|0\rangle$. Hint: the operators are nilpotent and $e^{\hat{A}}e^{\hat{B}} = e^{\hat{A}+\hat{B}}$ if $[\hat{A},\hat{B}] = 0$.

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3 The coupled-cluster equations

Since the coupled-cluster wavefunction has contributions from the full Hilbert space, optimising the excitation amplitudes using the Rayleigh–Ritz variational procedure incurs the same cost as full CI. Instead, a system of m equations that determine the m unknown amplitudes t_μ are obtained by projecting the Schrödinger equation onto a m-dimensional manifold: $\langle 0|\hat{\tau}_\mu^\dagger e^{-\hat{T}}$

$$\hat{H}e^{\hat{T}}|0\rangle \approx Ee^{\hat{T}}|0\rangle \quad \rightarrow \quad \langle 0|\hat{\tau}_\mu^\dagger e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle = 0 \tag{20}$$

This yields a set of coupled non-linear equations for the amplitudes, which must be solved self consistently. Once solved, can be used to compute the energy by projecting the Schrödinger equation onto $\langle 0|e^{-\hat{T}}$

$$\langle 0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle = E_{\mathrm{CC}} \tag{21}$$

In these equations the Hamiltonian operator is similarity transformed by the cluster operator $\tilde{H} = e^{-\hat{T}}\hat{H}e^{\hat{T}}$. The similarity transformed Hamiltonian has the Hartree–Fock wavefunction as its ground state but produces a correlated energy, which becomes exact if $\hat{T}$ is not truncated. Because $\hat{H}$ is a two-body operator, $\tilde{H}$ has a terminating Baker-Campbell-Hausdorff expansion

$$\tilde{H} = \hat{H} + [\hat{H},\hat{T}] + \frac{1}{2}[[\hat{H},\hat{T}],\hat{T}] + \frac{1}{6}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] + \frac{1}{24}[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}] \tag{22}$$

The amplitude equations are therefore coupled fourth order polynomials.

Note that, the equations for each order $\hat{T}_m$ are coupled to all other orders included in the wavefunction. Thus the $\hat{T}_m$ parameterise the m-body correlation function, which has relaxed due the effect of all orders of correlation processes accounted for in the CC wavefunction.

3.1 The coupled cluster energy

Let us now examine the amplitude and energy equations in detail. We start with the equation for the energy. Inserting the BCH expansion for $\tilde{H}$ we obtain

$$E_{\text{CC}} = \langle 0|\hat{H} + [\hat{H},\hat{T}] + \tfrac{1}{2}[[\hat{H},\hat{T}],\hat{T}] + \tfrac{1}{6}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] + \tfrac{1}{24}[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}]|0\rangle \tag{23}$$

We first note that $\langle 0|\hat{T} = 0$, since excitation operators on ket states act as de-excitation operators on bra states. Thus only one term from each set of nested commutators survives.

$$E_{\text{CC}} = \langle 0|\hat{H} + \hat{H}\hat{T} + \tfrac{1}{2}\hat{H}\hat{T}^2 + \tfrac{1}{6}\hat{H}\hat{T}^3 + \tfrac{1}{24}\hat{H}\hat{T}^4|0\rangle \tag{24}$$

Secondly, since $\hat{H}$ can de-excite at most two electrons, all contributions from combinations of excitation operators resulting in triple or higher-order excited configurations vanish.

$$E_{\text{CC}} = \langle 0|\hat{H} + \hat{H}\hat{T}_1 + \hat{H}\hat{T}_2 + \tfrac{1}{2}\hat{H}\hat{T}_1^2|0\rangle \tag{25}$$

The term $\langle 0|\hat{H}\hat{T}_1|0\rangle = 0$ when the Brillouin condition applies, which is the case for references optimised using RHF or UHF theory.

$$E_{\text{CC}} = E_{\text{HF}} + \langle 0|\hat{H}\hat{T}_2 + \tfrac{1}{2}\hat{H}\hat{T}_1^2|0\rangle \tag{26}$$

The energy formula only contains singles and doubles amplitudes, irrespective of the order of the coupled-cluster method. Higher-order excitations affect the energy indirectly because the singles and doubles are coupled to the triple and higher amplitudes through the amplitude equations.

We can express the coupled-cluster energy in terms of coupled-cluster density matrices.

$$E_{\text{CC}} = \sum_{pq} \bar{D}_{pq} h_{pq} + \frac{1}{4}\sum_{pqrs} \bar{d}_{pqrs} g_{pq}^{rs} \tag{27}$$

$$\bar{D}_{pq} = \langle 0|\hat{a}_p^\dagger \hat{a}_q|\text{CC}\rangle \tag{28}$$

$$\bar{d}_{pqrs} = \langle 0|\hat{a}_p^\dagger \hat{a}_q^\dagger a_s a_r|\text{CC}\rangle \tag{29}$$

The coupled-cluster density matrices are not Hermitian.

To obtain an explicit formula for the energy, we can follow the algebra of second quantisation. It is convenient to rearrange the terms of the Hamiltonian into *normal order* with respect to the Hartree–Fock reference, where all quasi-annihilation operators (those that remove a vacancy in an occupied orbital or remove a particle from a virtual orbital) appear on the right of all quasi-creation operators (those that create a vacancy in an occupied orbital or create a particle in a virtual orbital). In this way Wick's theorem can be used efficiently to identify and evaluate all terms that contribute to the integral.

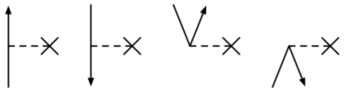
$$\hat{H}_N = E_{\text{HF}} + \hat{F}_N + \hat{G}_N \tag{30}$$

We will not go into the details here, but instead apply the diagrammatic techniques introduced for perturbation theory.

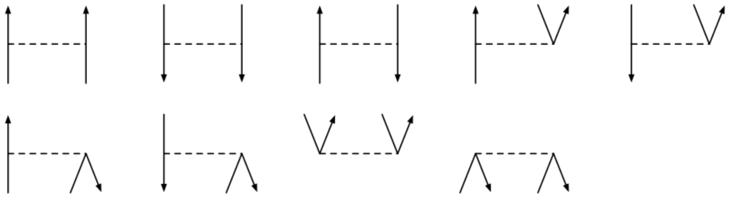
Recall that a Hamiltonian interaction is depicted as a dotted line with lines entering and leaving denoting it's action. Lines above the interaction denote quasi-creation operations that create a hole in the occupied space or create a particle in the virtual space. Lines below the interaction denote quasi-annihilation operations that fill a hole in the occupied space or remove a particle from the virtual space.

In addition, lines are given arrows to denote whether they refer to the occupied or virtual space, with upward arrows denoting virtual and downward arrows denoting occupied. All particle number conserving operators must have an equal number of arrows entering as leaving.

Using Goldstones notation, the one-body component of the normal-ordered Hamiltonian, which is the Fock operator, has four terms

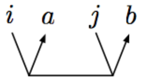


the two-body component of the Hamiltonian has nine different terms



Whereas in perturbation theory, a probability amplitude was represented as an interaction and a resolvent, in coupled-cluster theory we denote an excitation amplitude with a solid line with particle lines above, it because an excitation is a purely quasi-creation operation: it creates hole(s) in the occupied space and creates particle(s) in the virtual space.

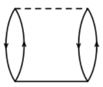
$$t^{ij}_{ab} \equiv$$



Exercise 4
Write down the second quantised expression for the four components of the Fock operator $\hat{F}_N$

To evaluate the integral $\langle 0|\hat{H}\hat{T}_2|0\rangle$ we have to connect the amplitude to the various interaction lines contributing to the Hamiltonian in every way possible such that there are no free lines. This corresponds to all excitations from the reference ket being de-excited to return to the reference bra. Only the last of the Hamiltonian diagrams can do this and in only one distinct way:

$$\langle 0|\hat{H}\hat{T}_2|0\rangle =$$



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

The contributions from the singles amplitudes are effective double excitations because $\hat{\tau}_i^a \tau_j^b = \hat{t}_{ij}^{ab}$ so that

$$E_{\mathrm{CC}} = E_{\mathrm{HF}} + \frac{1}{4}\sum_{ijab}(t^{ij}_{ab} + 2t^a_i t^b_j)\langle ab||ij\rangle \tag{31}$$

3.2 The amplitude equations

We now turn to the amplitude equations. Use the notation $\langle 0|\hat{\tau}_\mu^\dagger = \langle \mu|$ and inserting the BCH expansion, we must evaluate

$$\langle \mu|\hat{H} + [\hat{H},\hat{T}] + \tfrac{1}{2}[[\hat{H},\hat{T}],\hat{T}] + \tfrac{1}{6}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] + \tfrac{1}{24}[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}]|0\rangle = 0 \tag{32}$$

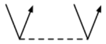
In order for a term to connect $\langle \mu|$ with $|0\rangle$, the excitation rank must match that of $\hat{\tau}_\mu$. For the purposes of illustration, we examine the amplitude equations for the CCD method where $\hat{T} = \hat{T}_2$. First we observe that the Hamiltonian can de-excite at most two electrons, so the commutators $[[[\hat{H},\hat{T}_2],\hat{T}_2],\hat{T}_2]$ and $[[[[\hat{H},\hat{T}_2],\hat{T}_2],\hat{T}_2],\hat{T}_2]$ cannot connect $\langle {}^{ab}_{ij}|$ with $|0\rangle$.

$$\langle \mu|\hat{H} + [\hat{H},\hat{T}_2] + \frac{1}{2}[[\hat{H},\hat{T}_2],\hat{T}_2]|0\rangle = 0 \tag{33}$$

Now we examine each remaining contribution in turn and identify all diagrams that combine the amplitudes with Hamiltonian interactions to leave two particle lines and two hole lines.

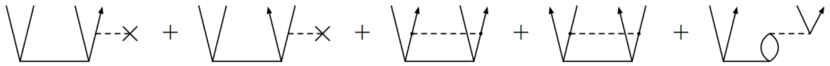
For the first term, the only Hamiltonian term that contributes is that corresponding to a double excitation

$$\langle \mu|\hat{H}|0\rangle =$$



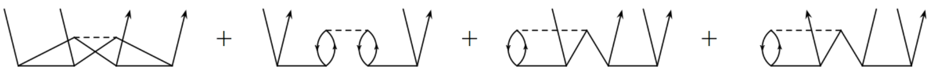
For the $[\hat{H},\hat{T}_2]$ commutator, both the one-electron and two-electron Hamiltonian interactions contribute.

$$\langle \mu|[\hat{H},\hat{T}_2]|0\rangle =$$



For the $[[\hat{H},\hat{T}_2],\hat{T}_2]$ double commutator, we find

$$\frac{1}{2}\langle \mu|[[\hat{H},\hat{T}_2],\hat{T}_2]|0\rangle =$$



The equations are coupled quadratic equations and are solved iteratively using a quasi-Newton procedure together with convergence acceleration methods. This requires storing multiple versions of the double amplitudes t_{ab}^{ij} on disk, which can become a computational bottleneck. The CCD equations can be evaluated using steps that scale as O^3V^3 and O^2V^4 where O and V are the number of occupied and virtual orbitals, respectively. This requires a factorisation of the equations and temporary storage of four-index intermediates. The CCD method is rarely used because single excitations account for orbital relaxation due to correlation. The CCSD equations are more complicated, but can be derived in the same way.

3.3 Perturbative triples energy

The cost of CCSDT is usually prohibitive, not least because the equations scale as N^8 with the number of orbitals N and because six index objects (e.g. the t_3 amplitudes) must be stored on disk. A cost effective alternative that is a very good approximation, is to estimate the contribution from the t_3 contributions using perturbation theory. The energy can be evaluated without iteration and the method scales as N^7.

For completeness, the energy formula is given below:

$$E_{(T)} = -\frac{1}{36} \sum_{ijkabc} t^{ijk}_{abc} t^{ijk}_{abc} (\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k) + \frac{1}{4} \sum_{ijkabc} \langle jk||bc \rangle t^i_a t^{abc}_{ijk} \tag{34}$$

where the triples amplitudes t^{ijk}_{abc} are evaluated from the converged CCSD amplitudes t^i_a and t^{ij}_{ab}.

$$(\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k) t^{ijk}_{abc} = -P_{abc} P_{ijk} \left[\sum_d \langle bc||di \rangle t^{jk}_{ad} - \sum_l \langle la||jk \rangle t^{il}_{bc} + t^i_a \langle bc||jk \rangle \right] \tag{35}$$

where P_{pqr} makes the permutations $pqr + rpq + qrp$.