Equations and derivations for ElemCo.jl

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Chapter 1

Introduction

1.1 General

In this document we collect the equations and derivations for methods implemented in the ElemCo.jl package. The final goal is to have a document which can be used as a reference for the equations and derivations. The final equations should also be contained in the code as docstrings or copied to the corresponding Markdown files.

1.2 Notation

We use the following notation throughout the document.

The virtual orbitals are denoted by $a, b, c, \ldots$, the occupied orbitals by $i, j, k, \ldots$, the active (open-shell) orbitals by $t, u, v, \ldots$, and the general orbital indices are denoted by p, q, r, s. The Einstein summation convention is used for repeated indices (repeated lower and upper indices are summed over). The α and β spin orbitals are denoted by p and $\bar{p}$.

The integrals are **not antisymmetrized** and denoted by v_{pq}^{rs}, where p, q, r, s are indices of orbitals, and the lower indices correspond to the creation and the upper indices to the annihilation operators in the Hamiltonian,

$$\hat{H}_N = f_p^q \left\{\hat{a}_p^\dagger \hat{a}_q\right\}_N + \frac{1}{2} v_{pq}^{rs} \left\{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\right\}_N , \tag{1.1}$$

i.e., $f_p^q = \langle p|\hat{f}|q\rangle$ and $v_{pq}^{rs} = \langle pq|rs\rangle$.

Permutation operators:

$$\begin{aligned} \mathcal{P}\,(ab)\, X_{ab}^{ij} &= X_{ba}^{ij} \\ \mathcal{P}\,(ab \to ba)\, X_{ab}^{ij} &= X_{ba}^{ij} \end{aligned} \tag{1.2}$$

Symmetrization operators:

$$\begin{aligned} \mathcal{S}\,(ab)\, X_{ab}^{ij} &= X_{ab}^{ij} + X_{ba}^{ij} \\ \mathcal{S}\,(ab, ij)\, X_{ab}^{ij} &= X_{ab}^{ij} + X_{ba}^{ji} \end{aligned} \tag{1.3}$$

Antisymmetrization operators:

$$\begin{aligned} \mathcal{A}\,(ab)\, X_{ab}^{ij} &= X_{ab}^{ij} - X_{ba}^{ij} \\ \mathcal{A}\,(ab; ij)\, X_{ab}^{ij} &= X_{ab}^{ij} - X_{ab}^{ji} - X_{ba}^{ij} + X_{ba}^{ji} \end{aligned} \tag{1.4}$$

Chapter 2

CCSD and DCSD amplitude and Λ equations

2.1 Closed-shell CCSD/DCSD Lagrangian

The singles-dressed factorization of the closed-shell CCSD and DCSD amplitude equations roughly follows the factorization from Ref. [1]. The closed-shell CCSD and DCSD Lagrangian is given by

$$\begin{aligned}
\mathcal{L} = & v_{kl}^{cd}\tilde{T}_{cd}^{kl} + \left(\hat{f}_k^c + f_k^c\right) T_c^k + \Lambda_{ij}^{ab}\hat{v}_{ab}^{ij} + \Lambda_{ij}^{ab}\left(\hat{v}_{kl}^{ij} + v_{kl}^{cd}T_{cd}^{ij}\right) T_{ab}^{kl} + \Lambda_{ij}^{ab}\hat{v}_{ab}^{cd}T_{cd}^{ij} \\
& + \Lambda_{ij}^{ab}v_{kl}^{cd}T_{ad}^{kj}T_{cb}^{il} \\
& + \Lambda_{ij}^{ab}\mathcal{S}\left(ab,ij\right)\left\{\left(\hat{f}_a^c - 2\times\frac{1}{2}v_{kl}^{cd}\tilde{T}_{ad}^{kl}\right)T_{cb}^{ij} - \left(\hat{f}_k^i + 2\times\frac{1}{2}v_{kl}^{cd}\tilde{T}_{cd}^{il}\right)T_{ab}^{kj}\right. \\
& \left. + \left(\hat{v}_{al}^{id} + \frac{1}{2}v_{kl}^{cd}\tilde{T}_{ac}^{ik}\right)\tilde{T}_{db}^{lj} - \hat{v}_{ka}^{ic}T_{cb}^{kj} - \hat{v}_{kb}^{ic}T_{ac}^{kj} - v_{kl}^{cd}T_{da}^{ki}\left(T_{cb}^{lj} - T_{bc}^{lj}\right)\right\} \\
& + \Lambda_i^a\hat{f}_a^i + \Lambda_i^a\hat{f}_j^b\tilde{T}_{ab}^{ij} + \Lambda_i^a\hat{v}_{ak}^{bc}\tilde{T}_{cb}^{ki} - \Lambda_i^a\hat{v}_{jk}^{ic}\tilde{T}_{ca}^{kj}.
\end{aligned} \tag{2.1}$$

The DCSD Lagrangian is obtained by removing terms in red.

Integrals with hats are dressed integrals, i.e. they are obtained by dressing the integrals with the singles amplitudes, and the Fock matrix is internally dressed, too, e.g.,

$$\begin{aligned}
\hat{v}_{kl}^{id} &= v_{kl}^{id} + v_{kl}^{cd}T_c^i \\
\hat{v}_{al}^{ij} &= v_{al}^{ij} - v_{kl}^{ij}T_a^k \\
\hat{f}_k^c &= h_k^c + 2\hat{v}_{kl}^{cl} - \hat{v}_{lk}^{cl} = f_k^c + \left(2v_{kl}^{cd} - v_{lk}^{cd}\right)T_d^l.
\end{aligned} \tag{2.2}$$

Note that only the **lower virtual** and **upper occupied** indices are dressed.

The amplitude equations can be obtained by taking the derivative of the Lagrangian with respect to the Lagrange multipliers Λ and setting the result to zero.

The most efficient version of CCSD/DCSD in ElemCo.jl combines the dressed factor-

ization from above with the cckext type of factorization from Ref. [2] and is given by

$$\begin{aligned}
\mathcal{L} &= v_{kl}^{cd}\tilde{T}_{cd}^{kl} + \left(\hat{f}_k^c + f_k^c\right) T_c^k + \Lambda_{ij}^{ab}\left(\hat{v}_{kl}^{ij} + v_{kl}^{cd}T_{cd}^{ij}\right) T_{ab}^{kl} + \Lambda_{ij}^{ab}K_{pq}^{ij}\delta_a^p\delta_b^q \\
&+ \Lambda_{ij}^{ab}v_{kl}^{cd}T_{ad}^{kj}T_{cb}^{il} \\
&+ \Lambda_{ij}^{ab}\mathcal{S}\left(ab,ij\right)\left\{\left(\hat{f}_a^c - 2\times\frac{1}{2}v_{kl}^{cd}\tilde{T}_{ad}^{kl}\right) T_{cb}^{ij} - \left(\hat{f}_k^i + 2\times\frac{1}{2}v_{kl}^{cd}\tilde{T}_{cd}^{il}\right) T_{ab}^{kj}\right. \\
&+ \left(\hat{v}_{al}^{id} + \frac{1}{2}v_{kl}^{cd}\tilde{T}_{ac}^{ik}\right)\tilde{T}_{db}^{lj} - \hat{v}_{ka}^{ic}T_{cb}^{kj} - \hat{v}_{kb}^{ic}T_{ac}^{kj} - v_{kl}^{cd}T_{da}^{ki}\left(T_{cb}^{lj} - T_{bc}^{lj}\right) \\
&\left. - K_{pq}^{ij}\left(\delta_k^p\delta_b^q - \frac{1}{2}\delta_k^p\delta_l^q T_b^l\right) T_a^k\right\} + \Lambda_i^a K_{pq}^{ij}\left(2\delta_a^p\delta_j^q - \delta_j^p\delta_a^q\right) \\
&- \Lambda_i^a T_a^k K_{pq}^{ij}\left(2\delta_k^p\delta_j^q - \delta_j^p\delta_k^q\right) + \Lambda_i^a\hat{h}_a^i + \Lambda_i^a\hat{f}_j^b\tilde{T}_{ab}^{ij} - \Lambda_i^a\hat{v}_{jk}^{ic}\tilde{T}_{ca}^{kj},
\end{aligned} \tag{2.3}$$

where

$$K_{pq}^{ij} = v_{pq}^{rs}\left(\left(T_{ab}^{ij} + T_a^iT_b^j\right)\delta_r^a\delta_s^b + \delta_r^iT_b^j\delta_s^b + T_a^i\delta_r^a\delta_s^j + \delta_r^i\delta_s^j\right) \tag{2.4}$$

and h is the one-particle part of the Hamiltonian.

2.2 Closed-shell CCSD/DSCD Lagrangian multipliers equations

The Λ equations are obtained by taking the derivative of the Lagrangian Eq. (2.1) with respect to the amplitudes and setting the result to zero, i.e.,

$$\begin{aligned}
\frac{\partial\mathcal{L}}{\partial T_e^m} &= 2\left(2v_{jm}^{be} - v_{jm}^{eb}\right)T_b^j + 2f_m^e - \Lambda_{ij}^{eb}\hat{v}_{mb}^{ij} - \Lambda_{ij}^{ae}\hat{v}_{am}^{ij} + \Lambda_{mj}^{ab}\hat{v}_{ab}^{ej} + \Lambda_{im}^{ab}\hat{v}_{ab}^{ie} \\
&+ \Lambda_{mj}^{ab}\hat{v}_{kl}^{ej}T_{ab}^{kl} + \Lambda_{im}^{ab}\hat{v}_{kl}^{ie}T_{ab}^{kl} - \Lambda_{ij}^{eb}\hat{v}_{mb}^{cd}T_{cd}^{ij} - \Lambda_{ij}^{ae}\hat{v}_{am}^{cd}T_{cd}^{ij} \\
&- \Lambda_{ij}^{eb}\hat{f}_m^dT_{db}^{ij} - \Lambda_{ij}^{ae}\hat{f}_m^dT_{ad}^{ij} - \Lambda_{mj}^{ab}\hat{f}_k^eT_{ab}^{kj} - \Lambda_{im}^{ab}\hat{f}_k^eT_{ab}^{ik} \\
&+ \Lambda_{ij}^{ab}\mathcal{S}\left(ab,ij\right)\left\{\left(2\hat{v}_{am}^{de} - \hat{v}_{am}^{ed}\right)T_{db}^{ij} - \left(2\hat{v}_{km}^{ie} - \hat{v}_{km}^{ei}\right)T_{ab}^{kj}\right\} \\
&- \Lambda_{ij}^{eb}\hat{v}_{ml}^{id}\tilde{T}_{db}^{lj} - \Lambda_{ij}^{ae}\hat{v}_{ml}^{jd}\tilde{T}_{ad}^{il} + \Lambda_{mj}^{ab}\hat{v}_{al}^{ed}\tilde{T}_{db}^{lj} + \Lambda_{im}^{ab}\hat{v}_{bl}^{ed}\tilde{T}_{ad}^{il} \\
&+ \Lambda_{ij}^{eb}\hat{v}_{km}^{ic}T_{cb}^{kj} - \Lambda_{mj}^{ab}\hat{v}_{ka}^{ec}T_{cb}^{kj} + \Lambda_{ij}^{ae}\hat{v}_{km}^{jc}T_{ac}^{ik} - \Lambda_{im}^{ab}\hat{v}_{kb}^{ec}T_{ac}^{ik} \\
&+ \Lambda_{ij}^{ae}\hat{v}_{km}^{ic}T_{ac}^{kj} - \Lambda_{mj}^{ab}\hat{v}_{kb}^{ec}T_{ac}^{kj} + \Lambda_{ij}^{eb}\hat{v}_{km}^{jc}T_{cb}^{ik} - \Lambda_{im}^{ab}\hat{v}_{ka}^{ec}T_{cb}^{ik} \\
&- \Lambda_i^e\hat{f}_m^i + \Lambda_m^a\hat{f}_a^e + \Lambda_i^a\left(2\hat{v}_{am}^{ie} - \hat{v}_{am}^{ei}\right) \\
&+ \Lambda_i^a\left(2v_{jm}^{be} - v_{jm}^{eb}\right)\tilde{T}_{ab}^{ij} - \Lambda_i^ev_{mk}^{bc}\tilde{T}_{cb}^{ki} - \Lambda_m^av_{jk}^{ec}\tilde{T}_{ca}^{kj}.
\end{aligned} \tag{2.5}$$

$$
\begin{aligned}
\frac{\partial \mathcal{L}}{\partial T^{mn}_{ef}} = \frac{1}{2}\mathcal{S}\left(ef,mn\right)\Big[&\Lambda^{e}_{m}\hat{f}^{f}_{n}\tilde{v}^{ef}_{mn} + \Lambda^{ef}_{ij}\left(\hat{v}^{ij}_{mn} + v^{cd}_{mn}T^{ij}_{cd}\right) + \Lambda^{ab}_{mn}v^{ef}_{kl}T^{kl}_{ab} + \Lambda^{ab}_{mn}\hat{v}^{ef}_{ab} \\
&+ \Lambda^{eb}_{in}v^{cf}_{ml}T^{il}_{cb} + \Lambda^{af}_{mj}v^{ed}_{kn}T^{kj}_{ad} \\
&+ \Lambda^{af}_{mn}\mathcal{S}\left(af,mn\right)\left(\hat{f}^{e}_{a} - 2\times\frac{1}{2}v^{ed}_{kl}\tilde{T}^{kl}_{ad}\right) - \Lambda^{eb}_{ij}\mathcal{S}\left(eb,ij\right)2\times\frac{1}{2}\tilde{v}^{cf}_{mn}T^{ij}_{cb} \\
&- \Lambda^{ef}_{in}\mathcal{S}\left(ef,in\right)\left(\hat{f}^{i}_{m} + 2\times\frac{1}{2}v^{cd}_{ml}\tilde{T}^{il}_{cd}\right) - \Lambda^{ab}_{mj}\mathcal{S}\left(ab,mj\right)2\times\frac{1}{2}\tilde{v}^{ef}_{kn}T^{kj}_{ab} \\
&+ 2\Lambda^{af}_{in}\mathcal{S}\left(af,in\right)\left(\hat{v}^{ie}_{am} + \frac{1}{2}v^{ce}_{km}\tilde{T}^{ik}_{ac}\right) - \Lambda^{af}_{im}\mathcal{S}\left(af,im\right)\left(\hat{v}^{ie}_{an} + \frac{1}{2}v^{ce}_{kn}\tilde{T}^{ik}_{ac}\right) \\
&+ 2\Lambda^{eb}_{mj}\mathcal{S}\left(eb,mj\right)\frac{1}{2}v^{fd}_{nl}\tilde{T}^{lj}_{db} - \Lambda^{eb}_{nj}\mathcal{S}\left(eb,nj\right)\frac{1}{2}v^{fd}_{ml}\tilde{T}^{lj}_{db} \\
&- \Lambda^{af}_{in}\mathcal{S}\left(af,in\right)\hat{v}^{ie}_{ma} - \Lambda^{eb}_{in}\mathcal{S}\left(eb,in\right)\hat{v}^{if}_{mb} \\
&- \Lambda^{fb}_{nj}\mathcal{S}\left(fb,nj\right)v^{ce}_{ml}\left(T^{lj}_{cb} - T^{lj}_{bc}\right) - \Lambda^{af}_{in}\mathcal{S}\left(af,in\right)v^{ed}_{km}T^{ki}_{da} \\
&+ \Lambda^{ae}_{in}\mathcal{S}\left(ab,ij\right)v^{fd}_{km}T^{ki}_{da} \\
&+ \mathcal{T}(mn)\left\{\Lambda^{e}_{m}\hat{f}^{f}_{n} + \Lambda^{a}_{n}\hat{v}^{fe}_{am} - \Lambda^{f}_{i}\hat{v}^{ie}_{nm}\right\}\Big],
\end{aligned}
\tag{2.6}
$$

with a "contravariation" operator,

$$
\mathcal{T}(mn)X^{ef}_{mn} = 2X^{ef}_{mn} - X^{ef}_{nm}. \tag{2.7}
$$

Now we can introduce useful intermediate quantities, related to the density matrices. The one-body reduced density matrices can be written as

$$
\begin{aligned}
D^{j}_{i} &= -2\Lambda^{cd}_{ik}T^{jk}_{cd}, \\
D^{b}_{a} &= 2\Lambda^{bc}_{kl}T^{kl}_{ac}, \\
D^{a}_{i} &= \Lambda^{a}_{i}, \\
D^{i}_{a} &= \Lambda^{c}_{k}\tilde{T}^{ik}_{ac}.
\end{aligned}
\tag{2.8}
$$

Note that we have excluded here terms coming from the singles amplitudes. Thus, if this density matrix is used to calculate properties, the corresponding integrals should be dressed. Alternatively, one can define "dressed" density matrices which include the singles contributions,

$$
\begin{aligned}
\hat{D}^{j}_{i} &= D^{j}_{i} - D^{c}_{i}T^{j}_{c}, \\
\hat{D}^{b}_{a} &= D^{b}_{a} + D^{b}_{k}T^{k}_{a}, \\
\hat{D}^{a}_{i} &= D^{a}_{i}, \\
\hat{D}^{i}_{a} &= D^{i}_{a} + 2T^{i}_{a} - D^{c}_{a}T^{i}_{c} + \hat{D}^{i}_{k}T^{k}_{a}.
\end{aligned}
\tag{2.9}
$$

Some parts of the two-body reduced density matrices can be written as

$$
\begin{aligned}
D^{kl}_{ij} &= \Lambda^{cd}_{ij}T^{kl}_{cd} \\
D^{aj}_{ib} &= \Lambda^{ac}_{ik}\tilde{T}^{kj}_{cb} \\
\bar{D}^{aj}_{ib} &= \Lambda^{ac}_{ik}T^{kj}_{cb} + \Lambda^{ca}_{ik}T^{kj}_{bc}
\end{aligned}
\tag{2.10}
$$

Finally, we define the following quantities which correspond to the cckext factorization and a doubles-dressing of the Fock matrix,

$$\begin{aligned} K^{rs}_{mn} &= \hat{\Lambda}^{pq}_{mn} v^{rs}_{pq} \\ \hat{\Lambda}^{pq}_{mn} &= \Lambda^{ab}_{mn}\delta^p_a\delta^q_b - \Lambda^{ab}_{mn}T^i_a\delta^p_i\delta^q_b - \Lambda^{ab}_{mn}\delta^p_a T^j_b\delta^q_j + \Lambda^{ab}_{mn}T^i_a T^j_b\delta^p_i\delta^q_j \\ x^i_m &= \tilde{T}^{il}_{cd}v^{cd}_{ml} \qquad\qquad x^e_a = \tilde{T}^{kl}_{ac}v^{ec}_{kl} \end{aligned} \tag{2.11}$$

With these definitions, the Λ equations can be written as

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial T^m_e} &= \left(2v^{pe}_{qm} - v^{ep}_{qm}\right)\hat{D}^q_p + 2f^e_m - 2\Lambda^{eb}_{ij}\hat{v}^{ij}_{mb} + 2K^{rs}_{mj}\delta^e_r\left(\delta^j_s + \delta^b_s T^j_b\right) \\ &+ 2D^{kl}_{mj}\hat{v}^{ej}_{kl} - 2\Lambda^{eb}_{ij}\left(\hat{v}^{cd}_{mb}T^{ij}_{cd}\right) - D^e_d\hat{f}^d_m + D^k_m\hat{f}^e_k - 2D^{el}_{id}\hat{v}^{id}_{ml} + 2D^{al}_{md}\hat{v}^{ed}_{al} \\ &+ 2\bar{D}^{ek}_{ic}\hat{v}^{ic}_{km} - 2\bar{D}^{ak}_{mc}\hat{v}^{ec}_{ka} - \Lambda^e_i\hat{f}^i_m + \Lambda^a_m\hat{f}^e_a - \Lambda^e_i x^i_m - \Lambda^a_m x^e_a. \end{aligned} \tag{2.12}$$

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial T^{mn}_{ef}} &= \tilde{v}^{ef}_{mn} + \Lambda^{ef}_{ij}\left(\hat{v}^{ij}_{mn} + v^{cd}_{mn}T^{ij}_{cd}\right) + D^{kl}_{mn}v^{ef}_{kl} + K^{rs}_{mn}\delta^e_r\delta^f_s \\ &+ \mathcal{S}\left(ef,mn\right)\left\{\Lambda^{af}_{mn}\left(\hat{f}^e_a - 2\times\frac{1}{2}x^e_a\right) - \Lambda^{ef}_{in}\left(\hat{f}^i_m + 2\times\frac{1}{2}x^i_m\right)\right. \\ &+ \mathcal{T}(mn)\left[2\times\frac{1}{4}v^{ef}_{kn}D^k_m - 2\times\frac{1}{4}v^{cf}_{mn}D^e_c + \Lambda^{af}_{in}\left(\hat{v}^{ie}_{am} + v^{ce}_{km}\tilde{T}^{ik}_{ac}\right)\right. \\ &\left.\left.+\frac{1}{2}\left(\Lambda^e_m\hat{f}^f_n + \Lambda^a_n\hat{v}^{fe}_{am} - \Lambda^f_i\hat{v}^{ie}_{nm}\right)\right] \right. \\ &\left. -\Lambda^{af}_{in}\hat{v}^{ie}_{ma} - \Lambda^{eb}_{in}\hat{v}^{if}_{mb} - D^{fl}_{nc}v^{ce}_{ml} + \bar{D}^{ek}_{nd}v^{fd}_{km}\right\}. \end{aligned} \tag{2.13}$$

2.3 Perturbative triples for closed-shell CCSD

The perturbative triples equations for CCSD are given by

$$\begin{aligned} E_{[T]} &= \sum_{i\le j\le k} p(i,j,k)K^{abc}_{ijk}X^{ijk}_{abc} \\ p(i,j,k) &= \begin{cases} 2 & i\neq j\neq k \\ 1 & i = j \oplus j = k \\ 0 & i = j = k \end{cases} \end{aligned} \tag{2.14}$$

X^{ijk}_{abc} and K^{abc}_{ijk} are calculated for the triangular set of indices $i \le j \le k$ (with $k = 1 : n_{occ}$),

$$\begin{aligned} K^{abc}_{ijk} = K^{ijk}_{abc} &= v^{dk}_{bc}T^{ij}_{ad} + v^{dk}_{ac}T^{ij}_{db} + v^{dj}_{cb}T^{ik}_{ad} + v^{dj}_{ab}T^{ik}_{dc} + v^{di}_{ca}T^{jk}_{bd} + v^{di}_{ba}T^{jk}_{dc} \\ &- v^{jk}_{lc}T^{li}_{ba} - v^{ik}_{lc}T^{lj}_{ab} - v^{kj}_{lb}T^{li}_{ca} - v^{ij}_{lb}T^{lk}_{ac} - v^{ki}_{la}T^{lj}_{cb} - v^{ji}_{la}T^{lk}_{bc} \\ X^{ijk}_{abc} &= \frac{4K^{ijk}_{abc} - 2K^{ijk}_{acb} - 2K^{ijk}_{cba} - 2K^{ijk}_{bac} + K^{ijk}_{cab} + K^{ijk}_{bca}}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c} \end{aligned} \tag{2.15}$$

The (T) correction contains additionally the following terms,

$$\begin{aligned} E_{(T)} = E_{[T]} + \sum_{i\le j\le k} p(i,j,k)\left[v^{bc}_{jk}X^{ijk}_{abc}T^{\dagger a}_i + v^{ac}_{ik}X^{ijk}_{abc}T^{\dagger b}_j + v^{ab}_{ij}X^{ijk}_{abc}T^{\dagger c}_k\right. \\ \left. + T^{\dagger bc}_{jk}X^{ijk}_{abc}f^a_i + T^{\dagger ac}_{ik}X^{ijk}_{abc}f^b_j + T^{\dagger ab}_{ij}X^{ijk}_{abc}f^c_k\right]. \end{aligned} \tag{2.16}$$

In case of **ΛCCSD(T)** K_{ijk}^{abc} is different from K_{abc}^{ijk} and is calculated using the Lagrange multipliers,

$$\begin{aligned} K_{ijk}^{abc} = {} & v_{dk}^{bc}\bar{\Lambda}_{ij}^{ad} + v_{dk}^{ac}\bar{\Lambda}_{ij}^{db} + v_{dj}^{cb}\bar{\Lambda}_{ik}^{ad} + v_{dj}^{ab}\bar{\Lambda}_{ik}^{dc} + v_{di}^{ca}\bar{\Lambda}_{jk}^{bd} + v_{di}^{ba}\bar{\Lambda}_{jk}^{dc} \\ & - v_{jk}^{lc}\bar{\Lambda}_{li}^{ba} - v_{ik}^{lc}\bar{\Lambda}_{lj}^{ab} - v_{kj}^{lb}\bar{\Lambda}_{li}^{ca} - v_{ij}^{lb}\bar{\Lambda}_{lk}^{ac} - v_{ki}^{la}\bar{\Lambda}_{lj}^{cb} - v_{ji}^{la}\bar{\Lambda}_{lk}^{bc}, \end{aligned} \tag{2.17}$$

where $\bar{\Lambda}_{ij}^{ab}$ are the covariant Lagrange multipliers,

$$\bar{\Lambda}_{ij}^{ab} = \frac{2}{3}\Lambda_{ij}^{ab} + \frac{1}{3}\Lambda_{ij}^{ba}. \tag{2.18}$$

Additionally, the conjugate-transposed amplitudes in Eq. (2.16) are replaced by the covariant Lagrange multipliers $\bar{\Lambda}_{ij}^{ab}$ and $\bar{\Lambda}_{i}^{a} = \frac{1}{2}\Lambda_{i}^{a}$.

2.4 Open-shell CCSD/DSCD Lagrangian

The factorization of the open-shell CCSD/DCSD amplitude equations roughly follows the factorization of the closed-shell equations, Sec. 2.1. The open-shell CCSD and DCSD Lagrangian – i.e., spin dependent – is given by

$$\mathcal{L} = \mathcal{L}_\alpha + \mathcal{L}_\beta + \mathcal{L}_{\alpha\beta}, \tag{2.19}$$

$$\begin{aligned} \mathcal{L}_\alpha = {} & \frac{1}{2}\left[v_{kl}^{cd}T_{cd}^{kl} + \left(\hat{f}_k^c + f_k^c\right)T_c^k\right] + \frac{1}{4}\Lambda_{ij}^{ab}\left(\hat{v}_{ab}^{ij} - \hat{v}_{ab}^{ji}\right) + \frac{1}{4}\Lambda_{ij}^{ab}\left(\hat{v}_{kl}^{ij} + \frac{1}{2}v_{kl}^{cd}T_{cd}^{ij}\right)T_{ab}^{kl} \\ & + \frac{1}{4}\Lambda_{ij}^{ab}\hat{v}_{ab}^{cd}T_{cd}^{ij} + \frac{1}{4}\Lambda_{ij}^{ab}\mathcal{S}\left(ab,ij\right)\left\{\hat{x}_a^c T_{cb}^{ij} - \hat{x}_k^i T_{ab}^{kj}\right\} \\ & + \frac{1}{4}\Lambda_{ij}^{ab}\mathcal{A}\left(ab;ij\right)\left\{\left(\hat{v}_{al}^{id} - \hat{v}_{al}^{di} + \bar{x}_{al}^{id}\right)T_{db}^{lj} + \left(\hat{v}_{a\bar{l}}^{i\bar{d}} + x_{a\bar{l}}^{i\bar{d}}\right)T_{b\bar{d}}^{j\bar{l}}\right\} \\ & + \Lambda_i^a\hat{v}_{al}^{cd}T_{cd}^{il} + \Lambda_i^a\hat{v}_{a\bar{l}}^{c\bar{d}}T_{c\bar{d}}^{i\bar{l}} - \Lambda_i^a\hat{v}_{jk}^{ic}T_{ac}^{jk} - \Lambda_i^a\hat{v}_{j\bar{k}}^{i\bar{c}}T_{a\bar{c}}^{j\bar{k}} \\ & + \Lambda_i^a\hat{f}_a^i + \Lambda_i^a\hat{f}_j^b T_{ab}^{ij} + \Lambda_i^a\hat{f}_{\bar{j}}^{\bar{b}}T_{a\bar{b}}^{i\bar{j}}, \end{aligned} \tag{2.20}$$

or using the cckext factorization,

$$\begin{aligned} \mathcal{L}_\alpha = {} & \frac{1}{2}\left[v_{kl}^{cd}T_{cd}^{kl} + \left(\hat{f}_k^c + f_k^c\right)T_c^k\right] + \frac{1}{4}\Lambda_{ij}^{ab}\left(\hat{v}_{kl}^{ij} + \frac{1}{2}v_{kl}^{cd}T_{cd}^{ij}\right)T_{ab}^{kl} \\ & + \frac{1}{4}\Lambda_{ij}^{ab}K_{pq}^{ij}\left(\delta_a^p - \delta_k^p T_a^k\right)\left(\delta_b^q - \delta_l^q T_b^l\right) + \frac{1}{4}\Lambda_{ij}^{ab}\mathcal{S}\left(ab,ij\right)\left\{\hat{x}_a^c T_{cb}^{ij} - \hat{x}_k^i T_{ab}^{kj}\right\} \\ & + \frac{1}{4}\Lambda_{ij}^{ab}\mathcal{A}\left(ab;ij\right)\left\{\left(\hat{v}_{al}^{id} - \hat{v}_{al}^{di} + \bar{x}_{al}^{id}\right)T_{db}^{lj} + \left(\hat{v}_{a\bar{l}}^{i\bar{d}} + x_{a\bar{l}}^{i\bar{d}}\right)T_{b\bar{d}}^{j\bar{l}}\right\} \\ & + \Lambda_i^a\left(K_{pq}^{ij}\delta_j^q + K_{p\bar{q}}^{i\bar{j}}\delta_{\bar{j}}^{\bar{q}}\right)\left(\delta_a^p - \delta_k^p T_a^k\right) - \Lambda_i^a\hat{v}_{jk}^{ic}T_{ac}^{jk} - \Lambda_i^a\hat{v}_{j\bar{k}}^{i\bar{c}}T_{a\bar{c}}^{j\bar{k}} \\ & + \Lambda_i^a\hat{h}_a^i + \Lambda_i^a\hat{f}_j^b T_{ab}^{ij} + \Lambda_i^a\hat{f}_{\bar{j}}^{\bar{b}}T_{a\bar{b}}^{i\bar{j}}; \end{aligned} \tag{2.21}$$

$\mathcal{L}_\beta$ is obtained from $\mathcal{L}_\alpha$ by flipping the spins;

$$\begin{aligned} \mathcal{L}_{\alpha\beta} = {} & v_{k\bar{l}}^{c\bar{d}}T_{c\bar{d}}^{k\bar{l}} + \Lambda_{i\bar{j}}^{a\bar{b}}\hat{v}_{ab}^{i\bar{j}} + \Lambda_{i\bar{j}}^{a\bar{b}}\left(\hat{v}_{k\bar{l}}^{i\bar{j}} + v_{k\bar{l}}^{c\bar{d}}T_{c\bar{d}}^{i\bar{j}}\right)T_{a\bar{b}}^{k\bar{l}} + \Lambda_{i\bar{j}}^{a\bar{b}}\hat{v}_{a\bar{b}}^{c\bar{d}}T_{c\bar{d}}^{i\bar{j}} \\ & + \Lambda_{i\bar{j}}^{a\bar{b}}\left\{\hat{x}_a^c T_{c\bar{b}}^{i\bar{j}} + \hat{x}_{\bar{b}}^{\bar{d}}T_{a\bar{d}}^{i\bar{j}} - \hat{x}_k^i T_{ab}^{kj} - \hat{x}_{\bar{l}}^{\bar{j}}T_{a\bar{b}}^{i\bar{l}}\right\} \\ & + \Lambda_{i\bar{j}}^{a\bar{b}}\left\{\left(\hat{v}_{al}^{id} - \hat{v}_{al}^{di} + x_{al}^{id} + \bar{x}_{al}^{id}\right)T_{d\bar{b}}^{l\bar{j}} + \left(\hat{v}_{b\bar{l}}^{\bar{j}\bar{d}} - \hat{v}_{b\bar{l}}^{d\bar{j}} + 2x_{b\bar{l}}^{\bar{j}\bar{d}}\right)T_{ad}^{i\bar{l}}\right. \\ & \left. + \left(\hat{v}_{a\bar{l}}^{i\bar{d}} + v_{k\bar{l}}^{c\bar{d}}T_{ac}^{ik}\right)T_{d\bar{b}}^{l\bar{j}} + \hat{v}_{l\bar{b}}^{d\bar{j}}T_{ad}^{il} - \hat{v}_{a\bar{k}}^{c\bar{j}}T_{c\bar{b}}^{i\bar{k}} - \left(\hat{v}_{k\bar{b}}^{i\bar{d}} - v_{k\bar{l}}^{c\bar{d}}T_{c\bar{b}}^{i\bar{l}}\right)T_{a\bar{d}}^{k\bar{j}}\right\}, \end{aligned} \tag{2.22}$$

or using the cckext factorization,

$$\begin{aligned}\mathcal{L}_{\alpha\beta} = {} & v^{c\bar{d}}_{k\bar{l}} T^{k\bar{l}}_{c\bar{d}} + \Lambda^{a\bar{b}}_{i\bar{j}} \left(\hat{v}^{i\bar{j}}_{k\bar{l}} + v^{c\bar{d}}_{k\bar{l}} T^{i\bar{j}}_{c\bar{d}} \right) T^{k\bar{l}}_{a\bar{b}} + \Lambda^{a\bar{b}}_{i\bar{j}} K^{i\bar{j}}_{p\bar{q}} \left(\delta^p_a - \delta^p_k T^k_a \right) \left(\delta^{\bar{q}}_{\bar{b}} - \delta^{\bar{q}}_{\bar{l}} T^{\bar{l}}_{\bar{b}} \right) \\ & + \Lambda^{a\bar{b}}_{i\bar{j}} \left\{ \hat{x}^c_a T^{i\bar{j}}_{c\bar{b}} + \hat{x}^{\bar{d}}_{\bar{b}} T^{i\bar{j}}_{a\bar{d}} - \hat{x}^i_k T^{k\bar{j}}_{a\bar{b}} - \hat{x}^{\bar{j}}_{\bar{l}} T^{i\bar{l}}_{a\bar{b}} \right\} \\ & + \Lambda^{a\bar{b}}_{i\bar{j}} \left\{ \left(\hat{v}^{id}_{al} - \hat{v}^{di}_{al} + x^{id}_{al} + \bar{x}^{id}_{al} \right) T^{l\bar{j}}_{d\bar{b}} + \left(\hat{v}^{\bar{j}\bar{d}}_{\bar{b}\bar{l}} - \hat{v}^{\bar{d}\bar{j}}_{\bar{b}\bar{l}} + 2 x^{\bar{j}\bar{d}}_{\bar{b}\bar{l}} \right) T^{i\bar{l}}_{a\bar{d}} \right. \\ & \left. + \left(\hat{v}^{i\bar{d}}_{a\bar{l}} + v^{c\bar{d}}_{k\bar{l}} T^{ik}_{ac} \right) T^{l\bar{j}}_{d\bar{b}} + \hat{v}^{d\bar{j}}_{l\bar{b}} T^{il}_{ad} - \hat{v}^{c\bar{j}}_{a\bar{k}} T^{i\bar{k}}_{c\bar{b}} - \left(\hat{v}^{i\bar{d}}_{k\bar{b}} - v^{c\bar{d}}_{k\bar{l}} T^{i\bar{l}}_{c\bar{b}} \right) T^{k\bar{j}}_{a\bar{d}} \right\}.\end{aligned} \tag{2.23}$$

The intermediate quantities are defined as follows,

$$\begin{aligned} K^{ij}_{pq} &= v^{rs}_{pq} D^{ij}_{rs} \qquad\qquad K^{i\bar{j}}_{p\bar{q}} = v^{r\bar{s}}_{p\bar{q}} D^{i\bar{j}}_{r\bar{s}} \\ D^{ij}_{rs} &= \left(T^{ij}_{ab} + T^i_a T^j_b - T^i_b T^j_a \right) \delta^a_r \delta^b_s + \mathcal{A}\left(ij;rs\right) \delta^i_r T^j_b \delta^b_s + \delta^i_r \delta^j_s - \delta^i_s \delta^j_r \\ D^{i\bar{j}}_{r\bar{s}} &= \left(T^{i\bar{j}}_{a\bar{b}} + T^i_a T^{\bar{j}}_{\bar{b}} \right) \delta^a_r \delta^{\bar{b}}_{\bar{s}} + \delta^i_r T^{\bar{j}}_{\bar{b}} \delta^{\bar{b}}_{\bar{s}} + T^i_a \delta^a_s \delta^{\bar{j}}_{\bar{s}} + \delta^i_r \delta^{\bar{j}}_{\bar{s}} \\ x^{id}_{al} &= \frac{1}{2} T^{ik}_{ac} \left(v^{cd}_{kl} - v^{dc}_{kl} \right) \\ \bar{x}^{id}_{al} &= x^{id}_{al} + T^{i\bar{k}}_{a\bar{c}} v^{d\bar{c}}_{l\bar{k}} \\ x^{i\bar{d}}_{al} &= \frac{1}{2} T^{i\bar{k}}_{a\bar{c}} \left(v^{\bar{c}\bar{d}}_{k\bar{l}} - v^{\bar{d}\bar{c}}_{k\bar{l}} \right) \\ \hat{x}^i_k &= \hat{f}^i_k + 2\times \frac{1}{2} \left(v^{cd}_{kl} T^{il}_{cd} + v^{c\bar{d}}_{k\bar{l}} T^{i\bar{l}}_{c\bar{d}} \right) \\ \hat{x}^c_a &= \hat{f}^c_a - 2\times \frac{1}{2} \left(v^{cd}_{kl} T^{kl}_{ad} + v^{c\bar{d}}_{k\bar{l}} T^{k\bar{l}}_{a\bar{d}} \right) \end{aligned} \tag{2.24}$$

2.4.1 Spin-restricted open-shell CCSD/DSCD

The spin-restricted versions `rccsd` and `rdcsd` are obtained through spin-projection of the residuals and amplitudes from the spin-dependent equations in each iteration. [3, 4]

In this section we use the following notation:

$$\begin{aligned} {}^{\alpha\alpha}T^{ij}_{ab} &= T^{ij}_{ab}, \\ {}^{\beta\beta}T^{ij}_{ab} &= T^{\bar{i}\bar{j}}_{\bar{a}\bar{b}}, \\ {}^{\alpha\beta}T^{ij}_{ab} &= T^{i\bar{j}}_{a\bar{b}}, \end{aligned} \tag{2.25}$$

and the spin-projected amplitudes are denoted by a bar, e.g., ${}^{\alpha\beta}\bar{T}^{ij}_{ab}$. Moreover, the indices $i, j, \ldots$ run in the following part of the section over the closed-shell part of occupied orbitals, $a, b, \ldots$ over the (doubly) virtual orbitals, and $t, u, \ldots$ over the singly occupied (or singly-virtual) orbitals.

The "closed-shell" part of spin-projected $\alpha\beta$ amplitudes is given by

$${}^{\alpha\beta}\bar{T}^{ij}_{ab} = \frac{1}{6}\left({}^{\alpha\alpha}T^{ij}_{ab} + {}^{\beta\beta}T^{ij}_{ab} + 2\,{}^{\alpha\beta}T^{ij}_{ab} + {}^{\alpha\beta}T^{ij}_{ba} + 2\,{}^{\alpha\beta}T^{ji}_{ba} + {}^{\alpha\beta}T^{ji}_{ab} \right) \tag{2.26}$$

The "open-shell" part of spin-projected $\alpha\beta$ amplitudes is given by

$$\begin{aligned} {}^{\alpha\beta}\bar{T}^{ij}_{at} &= \frac{1}{3}\left({}^{\beta\beta}T^{ij}_{at} + 2\,{}^{\alpha\beta}T^{ij}_{at} + {}^{\alpha\beta}T^{ji}_{at} \right) \\ {}^{\alpha\beta}\bar{T}^{tj}_{ab} &= \frac{1}{3}\left({}^{\alpha\alpha}T^{tj}_{ab} + 2\,{}^{\alpha\beta}T^{tj}_{ab} + {}^{\alpha\beta}T^{tj}_{ba} \right) \\ {}^{\alpha\beta}\bar{T}^{tj}_{au} &= {}^{\alpha\beta}T^{tj}_{au} + \frac{\delta_{tu}}{2m_s+2}\left({}^{\beta}T^{j}_{a} - {}^{\alpha}T^{j}_{a} - {}^{\alpha\beta}T^{vj}_{av} \right) \end{aligned} \tag{2.27}$$

The projection corrections for the remaining amplitudes are defined in terms of the new spin-projected $\alpha\beta$ amplitudes as follows. For singles amplitudes,

$$\begin{aligned}
{}^{\alpha}\bar{T}^{i}_{a} &= \frac{1}{2}\left({}^{\alpha}T^{i}_{a} + {}^{\beta}T^{i}_{a} - {}^{\alpha\beta}\bar{T}^{vi}_{av}\right), \\
{}^{\beta}\bar{T}^{i}_{a} &= \frac{1}{2}\left({}^{\alpha}T^{i}_{a} + {}^{\beta}T^{i}_{a} + {}^{\alpha\beta}\bar{T}^{vi}_{av}\right), \\
{}^{\alpha}\bar{T}^{t}_{a} &= {}^{\alpha}T^{t}_{a} \qquad \text{and} \qquad {}^{\beta}\bar{T}^{i}_{t} = {}^{\beta}T^{i}_{t}.
\end{aligned} \tag{2.28}$$

For the $\alpha\alpha$ and $\beta\beta$ amplitudes,

$$\begin{aligned}
{}^{\sigma\sigma}\bar{T}^{ij}_{ab} &= {}^{\alpha\beta}\bar{T}^{ij}_{ab} - {}^{\alpha\beta}\bar{T}^{ij}_{ba}, \\
{}^{\alpha\alpha}\bar{T}^{tj}_{ab} &= {}^{\alpha\alpha}\bar{T}^{jt}_{ba} = {}^{\alpha\beta}\bar{T}^{tj}_{ab} - {}^{\alpha\beta}\bar{T}^{tj}_{ba}, \\
{}^{\beta\beta}\bar{T}^{ij}_{at} &= {}^{\beta\beta}\bar{T}^{ji}_{ta} = {}^{\alpha\beta}\bar{T}^{ij}_{at} - {}^{\alpha\beta}\bar{T}^{ji}_{at}, \\
{}^{\alpha\alpha}\bar{T}^{tu}_{ab} &= {}^{\alpha\alpha}T^{tu}_{ab} \qquad \text{and} \qquad {}^{\beta\beta}\bar{T}^{ij}_{tu} = {}^{\beta\beta}T^{ij}_{tu}.
\end{aligned} \tag{2.29}$$

2.5 Open-shell CCSD/DSCD Lagrangian multipliers equations

The Lagrange multipliers equations for the open-shell CCSD/DSCD Lagrangian can be obtained by taking the derivatives with respect to the amplitudes and setting them to zero.

$$\begin{aligned}
\frac{\partial \mathcal{L}_{\alpha}}{\partial T^{m}_{e}} &= \left(v^{ce}_{km} - v^{ec}_{km}\right) T^{k}_{c} + \frac{1}{2} v^{e\bar{c}}_{m\bar{k}} T^{\bar{k}}_{\bar{c}} + f^{e}_{m} - \Lambda^{eb}_{ij}\hat{v}^{ij}_{mb} + \Lambda^{ab}_{mj}\hat{v}^{ej}_{ab} + \frac{1}{4}\Lambda^{ab}_{mj}\hat{v}^{ej}_{kl}T^{kl}_{ab} \\
&+ \frac{1}{4}\Lambda^{ab}_{im}\hat{v}^{ie}_{kl}T^{kl}_{ab} - \frac{1}{4}\Lambda^{eb}_{ij}\hat{v}^{cd}_{mb}T^{ij}_{cd} - \frac{1}{4}\Lambda^{ae}_{ij}\hat{v}^{cd}_{am}T^{ij}_{cd} - \frac{1}{2}\Lambda^{eb}_{ij}\hat{f}^{c}_{m}T^{ij}_{cb} - \frac{1}{2}\Lambda^{ab}_{mj}\hat{f}^{e}_{k}T^{kj}_{ab} \\
&+ \frac{1}{2}\Lambda^{ab}_{ij}\left\{\left(\hat{v}^{ce}_{am} - \hat{v}^{ec}_{am}\right)T^{ij}_{cb} - \left(\hat{v}^{ie}_{km} - \hat{v}^{ie}_{mk}\right)T^{kj}_{ab}\right\} \\
&- \Lambda^{eb}_{ij}\hat{v}^{id}_{ml}T^{lj}_{db} + \Lambda^{ab}_{mj}\hat{v}^{ed}_{al}T^{lj}_{db} + \Lambda^{eb}_{ij}\hat{v}^{di}_{ml}T^{lj}_{db} \\
&- \Lambda^{ab}_{mj}\hat{v}^{de}_{al}T^{lj}_{db} - \Lambda^{eb}_{ij}\hat{v}^{i\bar{d}}_{m\bar{l}}T^{j\bar{l}}_{b\bar{d}} + \Lambda^{ab}_{mj}\hat{v}^{e\bar{d}}_{a\bar{l}}T^{j\bar{l}}_{b\bar{d}} \\
&- \Lambda^{e}_{i}v^{cd}_{ml}T^{il}_{cd} - \Lambda^{e}_{i}v^{c\bar{d}}_{m\bar{l}}T^{i\bar{l}}_{c\bar{d}} - \Lambda^{a}_{m}\hat{v}^{ec}_{jk}T^{jk}_{ac} - \Lambda^{a}_{m}\hat{v}^{e\bar{c}}_{j\bar{k}}T^{j\bar{k}}_{a\bar{c}} \\
&- \Lambda^{e}_{i}\hat{f}^{i}_{m} + \Lambda^{a}_{m}\hat{f}^{e}_{a} + \Lambda^{a}_{i}\left(\hat{v}^{ie}_{am} - \hat{v}^{ei}_{am}\right) + \Lambda^{a}_{i}\left(v^{be}_{jm} - v^{eb}_{jm}\right)T^{ij}_{ab} + \Lambda^{a}_{i}v^{e\bar{b}}_{m\bar{j}}T^{i\bar{j}}_{a\bar{b}}
\end{aligned} \tag{2.30}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}_{\beta}}{\partial T^{m}_{e}} &= \frac{1}{2} v^{e\bar{c}}_{m\bar{k}} T^{\bar{k}}_{\bar{c}} + \frac{1}{2}\Lambda^{\bar{a}\bar{b}}_{\bar{i}\bar{j}}\left\{\hat{v}^{e\bar{c}}_{m\bar{a}}T^{\bar{i}\bar{j}}_{\bar{c}\bar{b}} - \hat{v}^{e\bar{i}}_{m\bar{k}}T^{\bar{k}\bar{j}}_{\bar{a}\bar{b}}\right\} \\
&+ \Lambda^{\bar{a}}_{\bar{i}}\hat{v}^{e\bar{i}}_{m\bar{a}} + \Lambda^{\bar{a}}_{\bar{i}}v^{e\bar{b}}_{m\bar{j}}T^{\bar{i}\bar{j}}_{\bar{a}\bar{b}} + \Lambda^{\bar{a}}_{\bar{i}}\left(v^{eb}_{mj} - v^{be}_{mj}\right)T^{j\bar{i}}_{b\bar{a}},
\end{aligned} \tag{2.31}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}_{\alpha\beta}}{\partial T^{m}_{e}} &= -\Lambda^{e\bar{b}}_{i\bar{j}}\hat{v}^{i\bar{j}}_{m\bar{b}} + \Lambda^{a\bar{b}}_{m\bar{j}}\hat{v}^{e\bar{j}}_{a\bar{b}} + \Lambda^{a\bar{b}}_{m\bar{j}}\hat{v}^{e\bar{j}}_{k\bar{l}}T^{k\bar{l}}_{a\bar{b}} - \Lambda^{e\bar{b}}_{i\bar{j}}\hat{v}^{c\bar{d}}_{m\bar{b}}T^{i\bar{j}}_{c\bar{d}} \\
&- \Lambda^{e\bar{b}}_{i\bar{j}}\hat{f}^{c}_{m}T^{i\bar{j}}_{c\bar{b}} - \Lambda^{a\bar{b}}_{m\bar{j}}\hat{f}^{e}_{k}T^{k\bar{j}}_{a\bar{b}} \\
&+ \Lambda^{a\bar{b}}_{i\bar{j}}\left\{\left(\hat{v}^{ce}_{am} - \hat{v}^{ec}_{am}\right)T^{i\bar{j}}_{c\bar{b}} + \hat{v}^{e\bar{d}}_{m\bar{b}}T^{i\bar{j}}_{a\bar{d}} - \left(\hat{v}^{ie}_{km} - \hat{v}^{ie}_{mk}\right)T^{k\bar{j}}_{a\bar{b}} - \hat{v}^{e\bar{j}}_{m\bar{l}}T^{i\bar{l}}_{a\bar{b}}\right\} \\
&- \Lambda^{e\bar{b}}_{i\bar{j}}\hat{v}^{id}_{ml}T^{l\bar{j}}_{d\bar{b}} + \Lambda^{a\bar{b}}_{m\bar{j}}\hat{v}^{ed}_{al}T^{l\bar{j}}_{d\bar{b}} + \Lambda^{e\bar{b}}_{i\bar{j}}\hat{v}^{di}_{ml}T^{l\bar{j}}_{d\bar{b}} - \Lambda^{a\bar{b}}_{m\bar{j}}\hat{v}^{de}_{al}T^{l\bar{j}}_{d\bar{b}} \\
&- \Lambda^{e\bar{b}}_{i\bar{j}}\hat{v}^{i\bar{d}}_{ml}T^{\bar{l}\bar{j}}_{d\bar{b}} + \Lambda^{a\bar{b}}_{m\bar{j}}\hat{v}^{e\bar{d}}_{a\bar{l}}T^{\bar{l}\bar{j}}_{d\bar{b}} + \Lambda^{e\bar{b}}_{i\bar{j}}\hat{v}^{c\bar{j}}_{m\bar{k}}T^{i\bar{k}}_{c\bar{b}} - \Lambda^{a\bar{b}}_{m\bar{j}}\hat{v}^{e\bar{d}}_{k\bar{b}}T^{k\bar{j}}_{a\bar{d}},
\end{aligned} \tag{2.32}$$

The corresponding equations for the derivatives with respect to the β amplitudes are obtained by flipping the spins.

Derivatives with respect to doubles amplitudes are given by

$$\begin{aligned}
4\frac{\partial \mathcal{L}_\alpha}{\partial T^{mn}_{ef}} &= \mathcal{A}(ef;mn)\left[\frac{1}{2}v^{ef}_{mn} + \frac{1}{4}\Lambda^{ef}_{ij}\left(\hat{v}^{ij}_{mn} + \frac{1}{2}v^{cd}_{mn}T^{ij}_{cd}\right) + \frac{1}{8}\Lambda^{ab}_{mn}v^{ef}_{kl}T^{kl}_{ab}\right.\\
&+ \frac{1}{4}\Lambda^{ab}_{mn}\hat{v}^{ef}_{ab} + \frac{1}{2}\Lambda^{af}_{mn}\hat{x}^{e}_{a} - \frac{1}{2}\Lambda^{ef}_{in}\hat{x}^{i}_{m} - 2\times\frac{1}{4}\Lambda^{eb}_{ij}v^{cf}_{mn}T^{ij}_{cb} - 2\times\frac{1}{4}\Lambda^{ab}_{mj}v^{ef}_{kn}T^{kj}_{ab}\\
&+ \Lambda^{af}_{in}\left(\hat{v}^{ie}_{am} - \hat{v}^{ei}_{am} + \bar{x}^{ie}_{am}\right) + \frac{1}{2}\Lambda^{eb}_{mj}\left(v^{fd}_{nl} - v^{df}_{nl}\right)T^{lj}_{db}\\
&\left.+\Lambda^{a}_{m}\hat{v}^{ef}_{an} - \Lambda^{e}_{i}\hat{v}^{if}_{mn} + \Lambda^{e}_{m}\hat{f}^{f}_{n}\right],
\end{aligned} \tag{2.33}$$

$$\frac{\partial \mathcal{L}_\beta}{\partial T^{mn}_{ef}} = 0, \tag{2.34}$$

$$\begin{aligned}
4\frac{\partial \mathcal{L}_{\alpha\beta}}{\partial T^{mn}_{ef}} &= \mathcal{A}(ef;mn)\left[-2\times\frac{1}{2}\Lambda^{e\bar{b}}_{i\bar{j}}v^{cf}_{mn}T^{i\bar{j}}_{c\bar{b}} - 2\times\frac{1}{2}\Lambda^{a\bar{b}}_{m\bar{j}}v^{ef}_{kn}T^{k\bar{j}}_{a\bar{b}}\right.\\
&\left.+\Lambda^{e\bar{b}}_{m\bar{j}}\left(v^{fd}_{nl} - v^{df}_{nl}\right)T^{l\bar{j}}_{d\bar{b}} + \Lambda^{e\bar{b}}_{m\bar{j}}v^{f\bar{d}}_{nl}T^{\bar{l}\bar{j}}_{\bar{d}\bar{b}} + \Lambda^{e\bar{b}}_{m\bar{j}}\hat{v}^{f\bar{j}}_{n\bar{b}}\right],
\end{aligned} \tag{2.35}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}_\alpha}{\partial T^{m\bar{n}}_{e\bar{f}}} &= -2\times\frac{1}{4}\Lambda^{eb}_{ij}v^{c\bar{f}}_{m\bar{n}}T^{ij}_{cb} - 2\times\frac{1}{4}\Lambda^{ab}_{mj}v^{e\bar{f}}_{k\bar{n}}T^{kj}_{ab}\\
&+ \Lambda^{eb}_{mj}v^{d\bar{f}}_{l\bar{n}}T^{lj}_{db} + \Lambda^{ae}_{im}\left(\hat{v}^{i\bar{f}}_{a\bar{n}} + x^{i\bar{f}}_{a\bar{n}}\right) + \frac{1}{2}\Lambda^{eb}_{mj}\left(v^{\bar{f}\bar{d}}_{\bar{n}\bar{l}} - v^{\bar{d}\bar{f}}_{\bar{n}\bar{l}}\right)T^{j\bar{l}}_{b\bar{d}}\\
&+ \Lambda^{a}_{m}\hat{v}^{e\bar{f}}_{a\bar{n}} - \Lambda^{e}_{i}\hat{v}^{i\bar{f}}_{m\bar{n}} + \Lambda^{e}_{m}\hat{f}^{\bar{f}}_{\bar{n}},
\end{aligned} \tag{2.36}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}_\beta}{\partial T^{m\bar{n}}_{e\bar{f}}} &= -2\times\frac{1}{4}\Lambda^{\bar{f}\bar{b}}_{\bar{i}\bar{j}}v^{e\bar{c}}_{m\bar{n}}T^{\bar{i}\bar{j}}_{\bar{c}\bar{b}} - 2\times\frac{1}{4}\Lambda^{\bar{a}\bar{b}}_{\bar{n}\bar{j}}v^{e\bar{f}}_{m\bar{k}}T^{\bar{k}\bar{j}}_{\bar{a}\bar{b}}\\
&+ \Lambda^{\bar{f}\bar{b}}_{\bar{n}\bar{j}}v^{e\bar{d}}_{m\bar{l}}T^{\bar{l}\bar{j}}_{\bar{d}\bar{b}} + \Lambda^{\bar{a}\bar{f}}_{\bar{i}\bar{n}}\left(\hat{v}^{e\bar{i}}_{m\bar{a}} + x^{\bar{i}e}_{\bar{a}m}\right) + \frac{1}{2}\Lambda^{\bar{f}\bar{b}}_{\bar{n}\bar{j}}\left(v^{ed}_{ml} - v^{de}_{ml}\right)T^{l\bar{j}}_{d\bar{b}}\\
&+ \Lambda^{\bar{a}}_{\bar{n}}\hat{v}^{\bar{f}e}_{\bar{a}m} - \Lambda^{\bar{f}}_{\bar{i}}\hat{v}^{\bar{i}e}_{\bar{n}m} + \Lambda^{\bar{f}}_{\bar{n}}\hat{f}^{e}_{m},
\end{aligned} \tag{2.37}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}_{\alpha\beta}}{\partial T^{m\bar{n}}_{e\bar{f}}} &= v^{e\bar{f}}_{m\bar{n}} + \Lambda^{e\bar{f}}_{i\bar{j}}\left(\hat{v}^{i\bar{j}}_{m\bar{n}} + v^{c\bar{d}}_{m\bar{n}}T^{i\bar{j}}_{c\bar{d}}\right) + \Lambda^{a\bar{b}}_{m\bar{n}}v^{e\bar{f}}_{k\bar{l}}T^{k\bar{l}}_{a\bar{b}} + \Lambda^{a\bar{b}}_{m\bar{n}}\hat{v}^{e\bar{f}}_{a\bar{b}}\\
&+ \Lambda^{a\bar{f}}_{m\bar{n}}\hat{x}^{e}_{a} - 2\times\frac{1}{2}\Lambda^{e\bar{b}}_{i\bar{j}}v^{c\bar{f}}_{m\bar{n}}T^{i\bar{j}}_{cb} + \Lambda^{e\bar{b}}_{m\bar{n}}\hat{x}^{\bar{f}}_{\bar{b}} - 2\times\frac{1}{2}\Lambda^{a\bar{f}}_{i\bar{j}}v^{e\bar{d}}_{m\bar{n}}T^{i\bar{j}}_{ad}\\
&- \Lambda^{e\bar{f}}_{i\bar{n}}\hat{x}^{i}_{m} - 2\times\frac{1}{2}\Lambda^{a\bar{b}}_{m\bar{j}}v^{e\bar{f}}_{k\bar{n}}T^{k\bar{j}}_{a\bar{b}} - \Lambda^{e\bar{f}}_{m\bar{j}}\hat{x}^{\bar{j}}_{\bar{n}} - 2\times\frac{1}{2}\Lambda^{a\bar{b}}_{i\bar{n}}v^{e\bar{f}}_{m\bar{l}}T^{i\bar{l}}_{a\bar{b}}\\
&+ \Lambda^{a\bar{f}}_{i\bar{n}}\left(\hat{v}^{ie}_{am} - \hat{v}^{ei}_{am} + x^{ie}_{am} + \bar{x}^{ie}_{am}\right) + \Lambda^{e\bar{b}}_{m\bar{j}}v^{d\bar{f}}_{l\bar{n}}T^{l\bar{j}}_{d\bar{b}} + \Lambda^{e\bar{b}}_{m\bar{j}}\left(\hat{v}^{\bar{j}\bar{f}}_{\bar{b}\bar{n}} - \hat{v}^{\bar{f}\bar{j}}_{\bar{b}\bar{n}} + 2x^{\bar{j}\bar{f}}_{\bar{b}\bar{n}}\right)\\
&- \Lambda^{a\bar{f}}_{m\bar{j}}\hat{v}^{e\bar{j}}_{a\bar{n}} - \Lambda^{e\bar{b}}_{i\bar{n}}\left(\hat{v}^{i\bar{f}}_{m\bar{b}} - v^{c\bar{f}}_{m\bar{l}}T^{i\bar{l}}_{c\bar{b}}\right) + \Lambda^{a\bar{f}}_{m\bar{j}}v^{e\bar{d}}_{k\bar{n}}T^{k\bar{j}}_{ad},
\end{aligned} \tag{2.38}$$

and the derivatives with respect to the $\beta\beta$ amplitudes are obtained by flipping the spins.

The one-body reduced density matrix (without singles contributions) is given by

$$\begin{aligned}
D^{j}_{i} &= -\frac{1}{2}\Lambda^{cd}_{ik}T^{jk}_{cd} - \Lambda^{c\bar{d}}_{i\bar{k}}T^{j\bar{k}}_{c\bar{d}}\\
D^{b}_{a} &= \frac{1}{2}\Lambda^{bc}_{kl}T^{kl}_{ac} + \Lambda^{b\bar{c}}_{k\bar{l}}T^{k\bar{l}}_{a\bar{c}}\\
D^{a}_{i} &= \Lambda^{a}_{i}\\
D^{i}_{a} &= \Lambda^{c}_{k}T^{ik}_{ac} + \Lambda^{\bar{c}}_{\bar{k}}T^{i\bar{k}}_{a\bar{c}}
\end{aligned} \tag{2.39}$$

and the β 1RDM is obtained by flipping the spins.

The full (dressed) one-body reduced density matrix is given by

$$\begin{aligned}
\hat{D}_i^j &= D_i^j - D_i^c T_c^j, \\
\hat{D}_a^b &= D_a^b + D_k^b T_a^k, \\
\hat{D}_i^a &= D_i^a, \\
\hat{D}_a^i &= D_a^i + T_a^i - D_a^c T_c^i + \hat{D}_k^i T_a^k.
\end{aligned} \tag{2.40}$$

Additionally, we define intermediates related to the two-body reduced density matrix,

$$\begin{aligned}
D_{ij}^{kl} &= \frac{1}{2}\Lambda_{ij}^{cd} T_{cd}^{kl} \\
D_{i\bar{j}}^{k\bar{l}} &= \Lambda_{i\bar{j}}^{c\bar{d}} T_{c\bar{d}}^{k\bar{l}} \\
D_{ib}^{aj} &= \Lambda_{ik}^{ac} T_{bc}^{jk} + \Lambda_{i\bar{k}}^{a\bar{c}} T_{b\bar{c}}^{j\bar{k}} \\
\bar{D}_{i\bar{b}}^{a\bar{j}} &= \Lambda_{ik}^{ac} T_{c\bar{b}}^{k\bar{j}} + \Lambda_{i\bar{k}}^{a\bar{c}} T_{\bar{b}\bar{c}}^{\bar{j}\bar{k}}
\end{aligned} \tag{2.41}$$

and doubles-dressed Fock matrix,

$$\begin{aligned}
x_k^i &= v_{kl}^{cd} T_{cd}^{il} + v_{k\bar{l}}^{c\bar{d}} T_{c\bar{d}}^{i\bar{l}} \\
x_a^c &= v_{kl}^{cd} T_{ad}^{kl} + v_{k\bar{l}}^{c\bar{d}} T_{a\bar{d}}^{k\bar{l}}.
\end{aligned} \tag{2.42}$$

The intermediates for the cckext factorization are given by

$$\begin{aligned}
K_{mn}^{rs} &= \hat{\Lambda}_{mn}^{pq} v_{pq}^{rs} \\
\hat{\Lambda}_{mn}^{pq} &= \Lambda_{mn}^{ab} \delta_a^p \delta_b^q - \Lambda_{mn}^{ab} T_a^i \delta_i^p \delta_b^q - \Lambda_{mn}^{ab} \delta_a^p T_b^j \delta_j^q + \Lambda_{mn}^{ab} T_a^i T_b^j \delta_i^p \delta_j^q.
\end{aligned} \tag{2.43}$$

$K_{m\bar{n}}^{r\bar{s}}$ and $K_{\bar{m}\bar{n}}^{\bar{r}\bar{s}}$ are obtained by flipping the spins.

Finally, we define useful intermediates which can be precalculated and reused in the equations,

$$\begin{aligned}
\hat{y}_{am}^{ie} &= \hat{v}_{am}^{ie} - \hat{v}_{am}^{ei} + \bar{x}_{am}^{ie} + x_{am}^{ie} \\
\hat{y}_{\bar{b}n}^{\bar{j}f} &= v_{n\bar{l}}^{f\bar{d}} T_{d\bar{b}}^{\bar{l}\bar{j}} + \hat{v}_{n\bar{b}}^{f\bar{j}} + 2x_{\bar{b}n}^{\bar{j}f}
\end{aligned} \tag{2.44}$$

With these intermediates the equations for the α Lagrange multipliers are given by

$$\begin{aligned}
\frac{\partial \mathcal{L}}{\partial T_e^m} &= \left(v_{pm}^{qe} - v_{pm}^{eq}\right) \hat{D}_q^p + v_{m\bar{p}}^{e\bar{q}} \hat{D}_{\bar{q}}^{\bar{p}} + f_m^e - \Lambda_{ij}^{eb} \hat{v}_{mb}^{ij} - \Lambda_{i\bar{j}}^{e\bar{b}} \hat{v}_{m\bar{b}}^{i\bar{j}} \\
&\quad + K_{mj}^{rs} \delta_r^e \left(\delta_s^j + \delta_s^b T_b^j\right) + K_{m\bar{j}}^{r\bar{s}} \delta_r^e \left(\delta_{\bar{s}}^{\bar{j}} + \delta_{\bar{s}}^{\bar{b}} T_{\bar{b}}^{\bar{j}}\right) + D_{mj}^{kl} \hat{v}_{kl}^{ej} + D_{m\bar{j}}^{k\bar{l}} \hat{v}_{k\bar{l}}^{e\bar{j}} \\
&\quad - \frac{1}{2}\Lambda_{ij}^{eb} \left(\hat{v}_{mb}^{cd} T_{cd}^{ij}\right) - \Lambda_{i\bar{j}}^{e\bar{b}} \left(\hat{v}_{m\bar{b}}^{c\bar{d}} T_{c\bar{d}}^{i\bar{j}}\right) - D_c^e \hat{f}_m^c + D_m^k \hat{f}_k^e \\
&\quad + D_{id}^{el} \left(\hat{v}_{ml}^{di} - \hat{v}_{lm}^{di}\right) + D_{md}^{al} \left(\hat{v}_{al}^{ed} - \hat{v}_{al}^{de}\right) - \bar{D}_{i\bar{d}}^{e\bar{l}} \hat{v}_{m\bar{l}}^{i\bar{d}} + \bar{D}_{m\bar{d}}^{a\bar{l}} \hat{v}_{a\bar{l}}^{e\bar{d}} \\
&\quad + \Lambda_{i\bar{j}}^{e\bar{b}} \hat{v}_{m\bar{k}}^{c\bar{j}} T_{c\bar{b}}^{i\bar{k}} - \Lambda_{m\bar{j}}^{a\bar{b}} \hat{v}_{k\bar{b}}^{e\bar{d}} T_{a\bar{d}}^{k\bar{j}} \\
&\quad - \Lambda_i^e \hat{f}_m^i + \Lambda_m^a \hat{f}_a^e - \Lambda_i^e x_m^i - \Lambda_m^a x_a^e
\end{aligned} \tag{2.45}$$

$$
\begin{aligned}
4\frac{\partial \mathcal{L}}{\partial T^{mn}_{ef}} &= v^{ef}_{mn} - v^{ef}_{nm} + \Lambda^{ef}_{ij}\left(\hat{v}^{ij}_{mn} + \frac{1}{2} v^{cd}_{mn} T^{ij}_{cd}\right) + D^{kl}_{mn} v^{ef}_{kl} + K^{rs}_{mn}\delta^{e}_{r}\delta^{f}_{s} \\
&+ \mathcal{S}\left(ef, mn\right)\left\{\Lambda^{af}_{mn}\hat{x}^{e}_{a} - \Lambda^{ef}_{in}\hat{x}^{i}_{m}\right\} \\
&+ \mathcal{A}\left(ef; mn\right)\left\{2\times\frac{1}{2} D^{k}_{m} v^{ef}_{kn} - 2\times\frac{1}{2} D^{e}_{c} v^{cf}_{mn} + \Lambda^{af}_{in}\hat{y}^{ie}_{am} + \Lambda^{e\bar{b}}_{m\bar{j}}\hat{y}^{\bar{j}f}_{\bar{b}n}\right. \\
&\left. + \Lambda^{a}_{m}\hat{v}^{ef}_{an} - \Lambda^{e}_{i}\hat{v}^{if}_{mn} + \Lambda^{e}_{m}\hat{f}^{f}_{n}\right\}
\end{aligned}
\tag{2.46}
$$

The equations for the β Lagrange multipliers are obtained by flipping the spins. The equations for the $\alpha\beta$ Lagrange multipliers are given by

$$
\begin{aligned}
\frac{\partial \mathcal{L}}{\partial T^{m\bar{n}}_{e\bar{f}}} &= v^{e\bar{f}}_{m\bar{n}} + \Lambda^{e\bar{f}}_{i\bar{j}}\left(\hat{v}^{i\bar{j}}_{m\bar{n}} + v^{c\bar{d}}_{m\bar{n}} T^{i\bar{j}}_{c\bar{d}}\right) + D^{k\bar{l}}_{m\bar{n}} v^{e\bar{f}}_{k\bar{l}} + K^{r\bar{s}}_{m\bar{n}}\delta^{e}_{r}\delta^{\bar{f}}_{\bar{s}} \\
&+ \Lambda^{a\bar{f}}_{m\bar{n}}\hat{x}^{e}_{a} + \Lambda^{e\bar{b}}_{m\bar{n}}\hat{x}^{\bar{f}}_{\bar{b}} - \Lambda^{e\bar{f}}_{i\bar{n}}\hat{x}^{i}_{m} - \Lambda^{e\bar{f}}_{m\bar{j}}\hat{x}^{\bar{j}}_{\bar{n}} \\
&+ 2\times\frac{1}{2}\left(D^{k}_{m} v^{e\bar{f}}_{k\bar{n}} + D^{\bar{k}}_{\bar{n}} v^{e\bar{f}}_{m\bar{k}} - D^{e}_{c} v^{c\bar{f}}_{m\bar{n}} - D^{\bar{f}}_{\bar{c}} v^{e\bar{c}}_{m\bar{n}}\right) \\
&+ \Lambda^{a\bar{f}}_{i\bar{n}}\hat{y}^{ie}_{am} + \Lambda^{e\bar{b}}_{m\bar{j}}\hat{y}^{\bar{j}\bar{f}}_{\bar{b}\bar{n}} + \Lambda^{ae}_{im}\hat{y}^{i\bar{f}}_{a\bar{n}} + \Lambda^{\bar{a}\bar{f}}_{\bar{i}\bar{n}}\hat{y}^{\bar{i}e}_{\bar{a}m} \\
&- \Lambda^{a\bar{f}}_{m\bar{j}}\left(\hat{v}^{e\bar{j}}_{a\bar{n}} - v^{e\bar{d}}_{k\bar{n}} T^{k\bar{j}}_{a\bar{d}}\right) - \Lambda^{e\bar{b}}_{i\bar{n}}\left(\hat{v}^{i\bar{f}}_{m\bar{b}} - v^{c\bar{f}}_{m\bar{l}} T^{i\bar{l}}_{c\bar{b}}\right) \\
&+ \Lambda^{a}_{m}\hat{v}^{e\bar{f}}_{a\bar{n}} - \Lambda^{e}_{i}\hat{v}^{i\bar{f}}_{m\bar{n}} + \Lambda^{e}_{m}\hat{f}^{\bar{f}}_{\bar{n}} + \Lambda^{\bar{a}}_{\bar{n}}\hat{v}^{\bar{f}e}_{\bar{a}m} - \Lambda^{\bar{f}}_{\bar{i}}\hat{v}^{\bar{i}e}_{\bar{n}m} + \Lambda^{\bar{f}}_{\bar{n}}\hat{f}^{e}_{m}.
\end{aligned}
\tag{2.47}
$$

2.6 Perturbative triples for unrestricted CCSD

The perturbative triples equations for unrestricted CCSD are given by

$$
E_{[T]} = \frac{1}{6}\sum_{i<j<k} K^{abc}_{ijk} T^{ijk}_{abc} + \frac{1}{6}\sum_{\bar{i}<\bar{j}<\bar{k}} K^{\bar{a}\bar{b}\bar{c}}_{\bar{i}\bar{j}\bar{k}} T^{\bar{i}\bar{j}\bar{k}}_{\bar{a}\bar{b}\bar{c}} + \frac{1}{2}\sum_{i<j;\bar{k}} K^{ab\bar{c}}_{ij\bar{k}} X^{ij\bar{k}}_{ab\bar{c}} + \frac{1}{2}\sum_{\bar{i}<\bar{j};k} K^{\bar{a}\bar{b}c}_{\bar{i}\bar{j}k} X^{\bar{i}\bar{j}k}_{\bar{a}\bar{b}c}. \tag{2.48}
$$

K^{abc}_{ijk} and T^{ijk}_{abc} (and the all-β-counterparts) are calculated for a triangular set of indices $i<j<k$ (with $k = 3:n_\alpha$),

$$
\begin{aligned}
K^{abc}_{ijk} &= K^{ijk}_{abc} = \mathcal{A}\left(abc\right)\left\{v^{dk}_{bc} T^{ij}_{ad} + v^{dj}_{cb} T^{ik}_{ad} + v^{di}_{ba} T^{jk}_{dc} - \frac{1}{2}\left(\bar{v}^{kj}_{cl} T^{il}_{ab} + \bar{v}^{ki}_{cl} T^{lj}_{ab} + \bar{v}^{ij}_{al} T^{kl}_{cb}\right)\right\}, \\
\bar{v}^{ij}_{al} &= v^{ij}_{al} - v^{ji}_{al}, \\
T^{ijk}_{abc} &= \frac{K^{ijk}_{abc}}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}
\end{aligned}
\tag{2.49}
$$

$K^{ab\bar{c}}_{ij\bar{k}}$ and $T^{ij\bar{k}}_{ab\bar{c}}$ (and the spin-flipped counterparts) are calculated for a triangular set of first two indices $i<j$ (with $j = 2:n_\alpha$),

$$
\begin{aligned}
K^{ab\bar{c}}_{ij\bar{k}} &= K^{ij\bar{k}}_{ab\bar{c}} = \mathcal{A}\left(ab\right)\left\{v^{d\bar{k}}_{b\bar{c}} T^{ij}_{ad} + v^{di}_{ba} T^{j\bar{k}}_{d\bar{c}} + v^{dj}_{ab} T^{i\bar{k}}_{d\bar{c}} + v^{i\bar{d}}_{a\bar{c}} T^{j\bar{k}}_{b\bar{d}} + v^{j\bar{d}}_{b\bar{c}} T^{i\bar{k}}_{a\bar{d}} - \bar{v}^{ij}_{al} T^{l\bar{k}}_{b\bar{c}}\right. \\
&\left. - v^{j\bar{k}}_{b\bar{l}} T^{i\bar{l}}_{a\bar{c}} - v^{i\bar{k}}_{a\bar{l}} T^{j\bar{l}}_{b\bar{c}}\right\} - v^{j\bar{k}}_{l\bar{c}} T^{il}_{ab} - v^{i\bar{k}}_{l\bar{c}} T^{lj}_{ab}, \\
T^{ij\bar{k}}_{ab\bar{c}} &= \frac{K^{ij\bar{k}}_{ab\bar{c}}}{\epsilon_i + \epsilon_j + \epsilon_{\bar{k}} - \epsilon_a - \epsilon_b - \epsilon_{\bar{c}}}
\end{aligned}
\tag{2.50}
$$

The (T) correction contains additionally the following terms,

$$\begin{aligned} E_{(T)} = E_{[T]} + \sum_{i<j<k} \Big[& v_{jk}^{bc} T_{abc}^{ijk} T_i^{\dagger a} + v_{ik}^{ac} T_{abc}^{ijk} T_j^{\dagger b} + v_{ij}^{ab} T_{abc}^{ijk} T_k^{\dagger c} \\ & + \frac{1}{2} \left(T_{jk}^{\dagger bc} T_{abc}^{ijk} f_i^a + T_{ik}^{\dagger ac} T_{abc}^{ijk} f_j^b + T_{ij}^{\dagger ab} T_{abc}^{ijk} f_k^c \right) \Big] \\ & + \sum_{i<j;\bar{k}} \Big[v_{j\bar{k}}^{b\bar{c}} T_{ab\bar{c}}^{ij\bar{k}} T_i^{\dagger a} + v_{i\bar{k}}^{a\bar{c}} T_{ab\bar{c}}^{ij\bar{k}} T_j^{\dagger b} + v_{ij}^{ab} T_{ab\bar{c}}^{ij\bar{k}} T_{\bar{k}}^{\dagger \bar{c}} \\ & + T_{j\bar{k}}^{\dagger b\bar{c}} T_{ab\bar{c}}^{ij\bar{k}} f_i^a + T_{i\bar{k}}^{\dagger a\bar{c}} T_{ab\bar{c}}^{ij\bar{k}} f_j^b + \frac{1}{2} T_{ij}^{\dagger ab} T_{ab\bar{c}}^{ij\bar{k}} f_{\bar{k}}^{\bar{c}} \Big] \\ & + \text{spin-flipped terms.} \end{aligned} \tag{2.51}$$

In case of **ΛUCCSD(T)**, K_{ijk}^{abc} and T_{abc}^{ijk} etc are different from K_{ijk}^{abc} and T_{abc}^{ijk} and can be calculated by replacing amplitudes with Lagrange multipliers (and integrals with transpose integrals) in the above equations,

$$\begin{aligned} K_{ijk}^{abc} &= \mathcal{A}(abc) \left\{ v_{dk}^{bc} \Lambda_{ij}^{ad} + v_{dj}^{cb} \Lambda_{ik}^{ad} + v_{di}^{ba} \Lambda_{jk}^{dc} - \frac{1}{2} \left(\bar{v}_{kj}^{cl} \Lambda_{il}^{ab} + \bar{v}_{ki}^{cl} \Lambda_{lj}^{ab} + \bar{v}_{ij}^{al} \Lambda_{kl}^{cb} \right) \right\}, \\ K_{ij\bar{k}}^{ab\bar{c}} &= \mathcal{A}(ab) \Big\{ v_{d\bar{k}}^{b\bar{c}} \Lambda_{ij}^{ad} + v_{di}^{ba} \Lambda_{j\bar{k}}^{d\bar{c}} + v_{dj}^{ab} \Lambda_{i\bar{k}}^{d\bar{c}} + v_{i\bar{d}}^{a\bar{c}} \Lambda_{j\bar{k}}^{b\bar{d}} + v_{j\bar{d}}^{b\bar{c}} \Lambda_{i\bar{k}}^{a\bar{d}} - \bar{v}_{ij}^{al} \Lambda_{l\bar{k}}^{b\bar{c}} \\ &\quad - v_{j\bar{k}}^{b\bar{l}} \Lambda_{i\bar{l}}^{a\bar{c}} - v_{i\bar{k}}^{a\bar{l}} \Lambda_{j\bar{l}}^{b\bar{c}} \Big\} - v_{j\bar{k}}^{l\bar{c}} \Lambda_{il}^{ab} - v_{i\bar{k}}^{l\bar{c}} \Lambda_{lj}^{ab}, \end{aligned} \tag{2.52}$$

and the conjugate-transpose of the amplitudes in Eq. (2.51) are replaced with the Lagrange multipliers.

Chapter 3

Two determinant coupled cluster

Amplitudes are normal ordered with respect to the formal reference with two active orbitals t and $\bar{u}$. The occupied $(i, j, \ldots)$ and virtual $(a, b, \ldots)$ spaces do not contain the active orbitals. The equations follow the equations presented in Ref.[5]. Differences because of fixed typos or other reasons are coloured blue. Terms we have added to ensure energy invariance with respect to the reference choice and which are not explicitly listed in Ref.[5] are coloured magenta. Terms we have added to ensure proper antisymmetry and which are not explicitly listed in Ref.[5] are coloured green. IAS terms, which are terms including the all internal singles, are coloured brown.

$$\begin{aligned} R_a^i &= \langle {}^A\Phi_a^i | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle_C - \left(\langle {}^A\Phi_a^i | e^{\hat{T}_B} | {}^B\Phi \rangle \langle {}^B\Phi | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle \right)_C \\ &\equiv \langle {}^A\Phi_a^i | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle_C + M_a^i W = 0, \end{aligned} \tag{3.1}$$

$$\begin{aligned} R_{ab}^{ij} &= \langle {}^A\Phi_{ab}^{ij} | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle_C - \left(\langle {}^A\Phi_{ab}^{ij} | e^{\hat{T}_B} | {}^B\Phi \rangle \langle {}^B\Phi | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle \right)_C \\ &- \mathcal{A}\,(ij;ab) \left[\langle {}^A\Phi_a^i | e^{\hat{T}_A} | {}^A\Phi \rangle \left(\langle {}^A\Phi_b^j | e^{\hat{T}_B} | {}^B\Phi \rangle \langle {}^B\Phi | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle \right)_C \right. \\ &\left. - \hat{R}(ia) \langle {}^B\Phi_a^i | e^{\hat{T}_B} | {}^B\Phi \rangle \left(\langle {}^A\Phi_b^j | e^{\hat{T}_B} | {}^B\Phi \rangle \langle {}^B\Phi | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle \right)_C \right] \\ &\equiv \langle {}^A\Phi_{ab}^{ij} | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle_C + M_{ab}^{ij} W = 0, \end{aligned} \tag{3.2}$$

The operator $\hat{R}(ia)$ excludes the active orbitals from the corresponding orbital spaces. The following intermediates are used:

$$\tau_a^i = T_a^i - T_{\bar{a}}^{\bar{i}}, \tag{3.3}$$

$$\tau_{\bar{a}}^{\bar{i}} = T_{\bar{a}}^{\bar{i}} - T_a^i, \tag{3.4}$$

$$\tau_{ab}^{ij} = T_{ab}^{ij} + T_a^i T_b^j. \tag{3.5}$$

The singles M tensor is built as follows,

$$M_u^i = T_{u\bar{t}}^{t\bar{i}}, \tag{3.6}$$
$$M_u^i = T_u^t T_{\bar{t}}^{\bar{i}}, \tag{3.7}$$
$$M_a^t = -T_{u\bar{a}}^{t\bar{u}}, \tag{3.8}$$
$$M_a^t = -T_u^t T_{\bar{a}}^{\bar{u}}, \tag{3.9}$$
$$M_a^i = T_{\bar{a}}^{\bar{u}} T_{ut}^{t\bar{i}} + T_{\bar{t}}^{\bar{i}} T_{u\bar{a}}^{t\bar{u}}, \tag{3.10}$$
$$M_a^i = T_u^t T_{\bar{a}\bar{t}}^{\bar{u}\bar{i}}, \tag{3.11}$$
$$M_a^i = T_u^t T_{\bar{a}}^{\bar{u}} T_{\bar{t}}^{\bar{i}}, \tag{3.12}$$
$$M_u^t = T_u^t. \tag{3.13}$$

$$M_{\bar{t}}^{\bar{i}} = T_{u\bar{t}}^{i\bar{u}}, \tag{3.14}$$
$$M_{\bar{t}}^{\bar{i}} = T_{\bar{t}}^{\bar{u}} T_u^i, \tag{3.15}$$
$$M_{\bar{a}}^{\bar{u}} = -T_{a\bar{t}}^{t\bar{u}}, \tag{3.16}$$
$$M_{\bar{a}}^{\bar{u}} = -T_{\bar{t}}^{\bar{u}} T_a^t, \tag{3.17}$$
$$M_{\bar{a}}^{\bar{i}} = T_a^t T_{ut}^{i\bar{u}} + T_u^i T_{a\bar{t}}^{t\bar{u}}, \tag{3.18}$$
$$M_{\bar{a}}^{\bar{i}} = T_{\bar{t}}^{\bar{u}} T_{au}^{ti}, \tag{3.19}$$
$$M_{\bar{a}}^{\bar{i}} = T_{\bar{t}}^{\bar{u}} T_a^t T_u^i, \tag{3.20}$$
$$M_{\bar{t}}^{\bar{u}} = T_{\bar{t}}^{\bar{u}}. \tag{3.21}$$

The all alpha part of the doubles part is built as follows,

$$M^{ij}_{ua} = \mathcal{A}(ij)\,\tau^{i}_{a} T^{t\bar{j}}_{u\bar{t}} + \mathcal{A}(ij)\,T^{\bar{i}}_{\bar{t}} T^{t\bar{j}}_{u\bar{a}}, \tag{3.22}$$

$$M^{ij}_{ua} = T^{t}_{u} T^{\bar{i}\bar{j}}_{\bar{t}\bar{a}}, \tag{3.23}$$

$$M^{ij}_{au} = -\mathcal{A}(ij)\,\tau^{i}_{a} T^{t\bar{j}}_{u\bar{t}} - \mathcal{A}(ij)\,T^{\bar{i}}_{\bar{t}} T^{t\bar{j}}_{u\bar{a}}, \tag{3.24}$$

$$M^{ij}_{au} = -T^{t}_{u} T^{\bar{i}\bar{j}}_{\bar{t}\bar{a}}, \tag{3.25}$$

$$M^{ti}_{ab} = \mathcal{A}(ab)\,\tau^{i}_{b} T^{t\bar{u}}_{u\bar{a}} + \mathcal{A}(ab)\,T^{\bar{u}}_{\bar{b}} T^{t\bar{i}}_{u\bar{a}}, \tag{3.26}$$

$$M^{ti}_{ab} = T^{t}_{u} T^{\bar{u}\bar{i}}_{\bar{b}\bar{a}}, \tag{3.27}$$

$$M^{it}_{ab} = -\mathcal{A}(ab)\,\tau^{i}_{b} T^{t\bar{u}}_{u\bar{a}} - \mathcal{A}(ab)\,T^{\bar{u}}_{\bar{b}} T^{t\bar{i}}_{u\bar{a}}, \tag{3.28}$$

$$M^{it}_{ab} = -T^{t}_{u} T^{\bar{u}\bar{i}}_{\bar{b}\bar{a}}, \tag{3.29}$$

$$\begin{aligned} M^{ij}_{ab} = &- \mathcal{A}(ij;ab)\,\tau^{j}_{b}\left(T^{\bar{u}}_{\bar{a}} T^{t\bar{i}}_{u\bar{t}} + T^{\bar{i}}_{\bar{t}} T^{t\bar{u}}_{u\bar{a}}\right) - \mathcal{A}\left(\bar{i}\bar{j};\bar{a}\bar{b}\right)\left(T^{\bar{u}\bar{i}}_{\bar{t}\bar{a}} T^{t\bar{j}}_{u\bar{b}}\right) \\ &- \mathcal{A}\left(\bar{i}\bar{j}\right) T^{\bar{u}\bar{i}}_{\bar{a}\bar{b}} T^{t\bar{j}}_{u\bar{t}} - \mathcal{A}(ab)\,T^{\bar{i}\bar{j}}_{\bar{t}\bar{a}} T^{t\bar{u}}_{u\bar{b}} - \mathcal{A}\left(\bar{i}\bar{j};\bar{a}\bar{b}\right) T^{\bar{u}}_{\bar{a}} T^{\bar{j}}_{\bar{t}} T^{t\bar{i}}_{u\bar{b}}, \end{aligned} \tag{3.30}$$

$$\begin{aligned} M^{ij}_{ab} = &-\mathcal{A}\left(\bar{i}\bar{j};\bar{a}\bar{b}\right)\tau^{\bar{i}}_{\bar{a}}\left(T^{\bar{u}}_{\bar{t}} T^{t\bar{j}}_{u\bar{b}} + T^{t}_{u} T^{\bar{u}\bar{j}}_{\bar{t}\bar{b}}\right) \\ &-\mathcal{A}\left(\bar{i}\bar{j}\right) T^{t}_{u} T^{\bar{j}}_{\bar{t}} T^{\bar{u}\bar{i}}_{\bar{a}\bar{b}} - \mathcal{A}\left(\bar{a}\bar{b}\right) T^{t}_{u} T^{\bar{u}}_{\bar{b}} T^{\bar{i}\bar{j}}_{\bar{t}\bar{a}}, \end{aligned} \tag{3.31}$$

$$M^{it}_{au} = -T^{t\bar{i}}_{u\bar{a}}, \tag{3.32}$$

$$M^{ti}_{au} = T^{t\bar{i}}_{u\bar{a}}, \tag{3.33}$$

$$M^{it}_{ua} = T^{t\bar{i}}_{u\bar{a}}, \tag{3.34}$$

$$M^{ti}_{ua} = -T^{t\bar{i}}_{u\bar{a}}, \tag{3.35}$$

$$M^{it}_{au} = -\tau^{\bar{i}}_{\bar{a}} T^{t}_{u}, \tag{3.36}$$

$$M^{it}_{ua} = +\tau^{\bar{i}}_{\bar{a}} T^{t}_{u}, \tag{3.37}$$

$$M^{ti}_{au} = +\tau^{\bar{i}}_{\bar{a}} T^{t}_{u}, \tag{3.38}$$

$$M^{ti}_{ua} = -\tau^{\bar{i}}_{\bar{a}} T^{t}_{u}. \tag{3.39}$$

The all beta part of the doubles M tensor is obtained from the all alpha part analogously to the presented singles M tensor.

The alpha beta part is calculated as follows,

$$M^{i\bar{j}}_{u\bar{a}} = -\tau^{\bar{j}}_{\bar{a}} T^{t\bar{i}}_{ut} - T^{j}_{u} T^{t\bar{i}}_{a\bar{t}} - T^{t}_{a} \tau^{j\bar{i}}_{u\bar{t}} - T^{\bar{i}}_{\bar{t}} T^{tj}_{au}, \tag{3.40}$$

$$M^{i\bar{j}}_{u\bar{a}} = T^{t}_{u} T^{j\bar{i}}_{a\bar{t}}, \tag{3.41}$$

$$M^{j\bar{i}}_{a\bar{t}} = -\tau^{j}_{a} T^{i\bar{u}}_{u\bar{t}} - T^{\bar{j}}_{\bar{t}} T^{i\bar{u}}_{u\bar{a}} - T^{\bar{u}}_{\bar{a}} \tau^{i\bar{j}}_{u\bar{t}} - T^{i}_{u} T^{\bar{j}\bar{u}}_{\bar{t}\bar{a}}, \tag{3.42}$$

$$M^{j\bar{i}}_{a\bar{t}} = T^{\bar{u}}_{\bar{t}} T^{i\bar{j}}_{u\bar{a}}, \tag{3.43}$$

$$M^{t\bar{i}}_{a\bar{b}} = \tau^{\bar{i}}_{\bar{b}} T^{t\bar{u}}_{u\bar{a}} + T^{t}_{b} T^{i\bar{u}}_{u\bar{a}} + T^{i}_{u} \tau^{t\bar{u}}_{b\bar{a}} + T^{\bar{u}}_{\bar{a}} T^{it}_{ub}, \tag{3.44}$$

$$M^{t\bar{i}}_{a\bar{b}} = -T^{t}_{u} T^{i\bar{u}}_{b\bar{a}}, \tag{3.45}$$

$$M^{i\bar{u}}_{b\bar{a}} = \tau^{i}_{b} T^{t\bar{u}}_{a\bar{t}} + T^{\bar{u}}_{\bar{b}} T^{t\bar{i}}_{a\bar{t}} + T^{\bar{i}}_{\bar{t}} \tau^{t\bar{u}}_{a\bar{b}} + T^{t}_{a} T^{\bar{i}\bar{u}}_{\bar{t}\bar{b}}, \tag{3.46}$$

$$M^{i\bar{u}}_{b\bar{a}} = -T^{\bar{u}}_{\bar{t}} T^{t\bar{i}}_{a\bar{b}}, \tag{3.47}$$

$$\begin{aligned} M^{i\bar{j}}_{a\bar{b}} = &-\tau^{\bar{j}}_{\bar{b}} (T^{\bar{u}}_{\bar{a}} T^{t\bar{i}}_{ut} + T^{\bar{i}}_{\bar{t}} T^{t\bar{u}}_{u\bar{a}}) - \tau^{i}_{a} (T^{j\bar{u}}_{ut} T^{t}_{b} + T^{t\bar{u}}_{b\bar{t}} T^{j}_{u}) \\ &+ T^{\bar{i}}_{\bar{t}} T^{\bar{u}}_{\bar{a}} T^{tj}_{ub} + T^{t}_{b} T^{j}_{u} T^{\bar{u}\bar{i}}_{\bar{t}\bar{a}} - T^{j}_{u} T^{\bar{u}}_{\bar{a}} T^{t\bar{i}}_{b\bar{t}} - T^{t}_{b} T^{\bar{i}}_{\bar{t}} T^{j\bar{u}}_{u\bar{a}} \\ &- \tau^{j\bar{i}}_{u\bar{t}} \tau^{t\bar{u}}_{b\bar{a}} + T^{j\bar{u}}_{ut} T^{t\bar{i}}_{b\bar{a}} + T^{t\bar{i}}_{u\bar{t}} T^{j\bar{u}}_{b\bar{a}} + T^{t\bar{u}}_{b\bar{t}} T^{j\bar{i}}_{u\bar{a}} \\ &+ T^{t\bar{u}}_{u\bar{a}} T^{j\bar{i}}_{b\bar{t}} - T^{tj}_{ub} T^{\bar{u}\bar{i}}_{\bar{t}\bar{a}} - T^{t\bar{i}}_{u\bar{a}} T^{j\bar{u}}_{b\bar{t}} - T^{j\bar{u}}_{u\bar{a}} T^{t\bar{i}}_{b\bar{t}}, \end{aligned} \tag{3.48}$$

$$\begin{aligned} M^{i\bar{j}}_{a\bar{b}} = &-\tau^{\bar{j}}_{\bar{b}} T^{t}_{u} T^{\bar{u}\bar{i}}_{\bar{a}\bar{t}} - \tau^{i}_{a} T^{\bar{u}}_{\bar{t}} T^{jt}_{ub} + T^{t}_{u} T^{\bar{i}}_{\bar{t}} T^{j\bar{u}}_{b\bar{a}} + T^{t}_{u} T^{\bar{u}}_{\bar{a}} T^{j\bar{i}}_{b\bar{t}} \\ &+ T^{\bar{u}}_{\bar{t}} T^{t}_{b} T^{j\bar{i}}_{u\bar{a}} + T^{\bar{u}}_{\bar{t}} T^{j}_{u} T^{t\bar{i}}_{b\bar{a}}, \end{aligned} \tag{3.49}$$

$$M^{t\bar{i}}_{ut} = T^{i}_{u}, \tag{3.50}$$

$$M^{i\bar{u}}_{ut} = T^{\bar{i}}_{\bar{t}}, \tag{3.51}$$

$$M^{t\bar{i}}_{u\bar{a}} = \tau^{it}_{ua}, \tag{3.52}$$

$$M^{i\bar{u}}_{a\bar{t}} = \tau^{\bar{i}\bar{u}}_{\bar{t}\bar{a}}, \tag{3.53}$$

$$M^{t\bar{i}}_{at} = \tau^{i\bar{u}}_{u\bar{a}}, \tag{3.54}$$

$$M^{i\bar{u}}_{u\bar{a}} = \tau^{t\bar{i}}_{a\bar{t}}, \tag{3.55}$$

$$M^{t\bar{u}}_{u\bar{a}} = -T^{t}_{a}, \tag{3.56}$$

$$M^{t\bar{u}}_{a\bar{t}} = -T^{\bar{u}}_{\bar{a}}, \tag{3.57}$$

$$M^{i\bar{j}}_{ut} = -\tau^{j\bar{i}}_{ut}, \tag{3.58}$$

$$M^{t\bar{u}}_{a\bar{b}} = -\tau^{t\bar{u}}_{b\bar{a}}. \tag{3.59}$$

The effective Hamiltonian W is just the all active part of the residuum,

$$W = R^{t\bar{u}}_{ut}. \tag{3.60}$$

The all internal doubles $T^{t\bar{u}}_{ut}$ coupled cluster amplitude is set to zero at the beginning of every iteration. At the end of every iteration the all internal doubles residuum $R^{t\bar{u}}_{ut}$ is set to zero.
IAS contribution to the energy,

$$\Delta E_{\mathrm{IAS}} = -W^{t\bar{u}}_{ut} T^{t}_{u} T^{\bar{u}}_{\bar{t}}. \tag{3.61}$$

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