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 $v_{pq}^{rs} = \langle pq|rs\rangle$.

Symmetrization operators:

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

Antisymmetrization operators:

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

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

$$\begin{aligned}\mathcal{L} = & v^{cd}_{kl}\tilde{T}^{kl}_{cd} + \left(\hat{f}^c_k + f^c_k\right) T^k_c + \Lambda^{ab}_{ij}\left(\hat{v}^{ij}_{kl} + v^{cd}_{kl}T^{ij}_{cd}\right) T^{kl}_{ab} + \Lambda^{ab}_{ij} K^{ij}_{pq}\delta^p_a\delta^q_b \\ & + \Lambda^{ab}_{ij} v^{cd}_{kl} T^{kj}_{ad} T^{il}_{cb} \\ & + \Lambda^{ab}_{ij}\mathcal{S}(ab,ij)\left\{\left(\hat{f}^c_a - 2\times\frac{1}{2}v^{cd}_{kl}\tilde{T}^{kl}_{ad}\right)T^{ij}_{cb} - \left(\hat{f}^i_k + 2\times\frac{1}{2}v^{cd}_{kl}\tilde{T}^{il}_{cd}\right)T^{kj}_{ab}\right. \\ & + \left(\hat{v}^{id}_{al} + \frac{1}{2}v^{cd}_{kl}\tilde{T}^{ik}_{ac}\right)\tilde{T}^{lj}_{db} - \hat{v}^{ic}_{ka}T^{kj}_{cb} - \hat{v}^{ic}_{kb}T^{kj}_{ac} - v^{cd}_{kl}T^{ki}_{da}\left(T^{lj}_{cb} - T^{lj}_{bc}\right) \\ & \left. - K^{ij}_{pq}\left(\delta^p_k\delta^q_b - \frac{1}{2}\delta^p_k\delta^q_l T^l_b\right)T^k_a\right\} + \Lambda^a_i K^{ij}_{pq}\left(2\delta^p_a\delta^q_j - \delta^p_j\delta^q_a\right) \\ & - \Lambda^a_i T^k_a K^{ij}_{pq}\left(2\delta^p_k\delta^q_j - \delta^p_j\delta^q_k\right) + \Lambda^a_i\hat{h}^i_a + \Lambda^a_i\hat{f}^b_j\tilde{T}^{ij}_{ab} - \Lambda^a_i\hat{v}^{ic}_{jk}\tilde{T}^{kj}_{ca},\end{aligned} \tag{2.3}$$

where

$$K^{ij}_{pq} = v^{rs}_{pq}\left(\left(T^{ij}_{ab} + T^i_a T^j_b\right)\delta^a_r\delta^b_s + \delta^i_r T^j_b\delta^b_s + T^i_a\delta^a_r\delta^j_s + \delta^i_r\delta^j_s\right) \tag{2.4}$$

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.,

$$\begin{aligned}\frac{\partial\mathcal{L}}{\partial T^m_e} = & 2\left(2v^{be}_{jm} - v^{eb}_{jm}\right)T^j_b + 2f^e_m - \Lambda^{eb}_{ij}\hat{v}^{ij}_{mb} - \Lambda^{ae}_{ij}\hat{v}^{ij}_{am} + \Lambda^{ab}_{mj}\hat{v}^{ej}_{ab} + \Lambda^{ab}_{im}\hat{v}^{ie}_{ab} \\ & + \Lambda^{ab}_{mj}\hat{v}^{ej}_{kl}T^{kl}_{ab} + \Lambda^{ab}_{im}\hat{v}^{ie}_{kl}T^{kl}_{ab} - \Lambda^{eb}_{ij}\hat{v}^{cd}_{mb}T^{ij}_{cd} - \Lambda^{ae}_{ij}\hat{v}^{cd}_{am}T^{ij}_{cd} \\ & - \Lambda^{eb}_{ij}\hat{f}^d_m T^{ij}_{db} - \Lambda^{ae}_{ij}\hat{f}^d_m T^{ij}_{ad} - \Lambda^{ab}_{mj}\hat{f}^e_k T^{kj}_{ab} - \Lambda^{ab}_{im}\hat{f}^e_k T^{ik}_{ab} \\ & + \Lambda^{ab}_{ij}\mathcal{S}(ab,ij)\left\{\left(2\hat{v}^{de}_{am} - \hat{v}^{ed}_{am}\right)T^{ij}_{db} - \left(2\hat{v}^{ie}_{km} - \hat{v}^{ei}_{km}\right)T^{kj}_{ab}\right\} \\ & - \Lambda^{eb}_{ij}\hat{v}^{id}_{ml}\tilde{T}^{lj}_{db} - \Lambda^{ae}_{ij}\hat{v}^{jd}_{ml}\tilde{T}^{il}_{ad} + \Lambda^{ab}_{mj}\hat{v}^{ed}_{al}\tilde{T}^{lj}_{db} + \Lambda^{ab}_{im}\hat{v}^{ed}_{bl}\tilde{T}^{il}_{ad} \\ & + \Lambda^{eb}_{ij}\hat{v}^{ic}_{km}T^{kj}_{cb} - \Lambda^{ab}_{mj}\hat{v}^{ec}_{ka}T^{kj}_{cb} + \Lambda^{ae}_{ij}\hat{v}^{jc}_{km}T^{ik}_{ac} - \Lambda^{ab}_{im}\hat{v}^{ec}_{kb}T^{ik}_{ac} \\ & + \Lambda^{ae}_{ij}\hat{v}^{ic}_{km}T^{kj}_{ac} - \Lambda^{ab}_{mj}\hat{v}^{ec}_{kb}T^{kj}_{ac} + \Lambda^{eb}_{ij}\hat{v}^{jc}_{km}T^{ik}_{cb} - \Lambda^{ab}_{im}\hat{v}^{ec}_{ka}T^{ik}_{cb} \\ & - \Lambda^e_i\hat{f}^i_m + \Lambda^a_m\hat{f}^e_a + \Lambda^a_i\left(2\hat{v}^{ie}_{am} - \hat{v}^{ei}_{am}\right) \\ & + \Lambda^a_i\left(2v^{be}_{jm} - v^{eb}_{jm}\right)\tilde{T}^{ij}_{ab} - \Lambda^e_i v^{bc}_{mk}\tilde{T}^{ki}_{cb} - \Lambda^a_m v^{ec}_{jk}\tilde{T}^{kj}_{ca}.\end{aligned} \tag{2.5}$$

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

with a "contravariation" operator,

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

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

$$\begin{aligned}D_i^j &= -2\Lambda_{ik}^{cd}T_{cd}^{jk},\\ D_a^b &= 2\Lambda_{kl}^{bc}T_{ac}^{kl},\\ D_i^a &= \Lambda_i^a,\\ D_a^i &= \Lambda_k^c\tilde{T}_{ac}^{ik}.\end{aligned} \tag{2.8}$$

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,

$$\begin{aligned}\hat{D}_i^j &= D_i^j - D_i^c T_c^j,\\ \hat{D}_a^b &= D_a^b + D_k^b T_a^k,\\ \hat{D}_i^a &= D_i^a,\\ \hat{D}_a^i &= D_a^i + 2T_a^i - D_a^c T_c^i + \hat{D}_k^i T_a^k.\end{aligned} \tag{2.9}$$

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

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

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

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

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

2.3 Perturbative triples for closed-shell CCSD

The perturbative triples equations for CCSD are given by

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

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

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

The (T) correction contains additionally the following terms,

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

In case of **ΛCCSD(T)** K_{ijk}^{abc} is different from K^{ijk}_{abc} 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

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

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

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

$$\begin{aligned} \mathcal{L}_{\alpha\beta} &= v_{k\bar{l}}^{c\bar{d}}T_{c\bar{d}}^{k\bar{l}} + \Lambda_{i\bar{j}}^{a\bar{b}}\left(\hat{v}_{k\bar{l}}^{i\bar{j}} + v_{k\bar{l}}^{c\bar{d}}T_{c\bar{d}}^{i\bar{j}}\right)T_{a\bar{b}}^{k\bar{l}} + \Lambda_{i\bar{j}}^{a\bar{b}}K_{p\bar{q}}^{i\bar{j}}\delta_a^p\delta_{\bar{b}}^{\bar{q}} \\ &+ \Lambda_{i\bar{j}}^{a\bar{b}}\left\{\hat{x}_a^c T_{c\bar{b}}^{i\bar{j}} + \hat{x}_{\bar{b}}^{\bar{d}}T_{a\bar{d}}^{i\bar{j}} - \hat{x}_k^i T_{ab}^{kj} - \hat{x}_{\bar{l}}^{\bar{j}}T_{a\bar{b}}^{i\bar{l}}\right. \\ &+ \left(\hat{v}_{al}^{id} - \hat{v}_{al}^{di} + x_{al}^{id} + \bar{x}_{al}^{id}\right)T_{d\bar{b}}^{l\bar{j}} + \left(\hat{v}_{\bar{b}\bar{l}}^{\bar{j}\bar{d}} - \hat{v}_{\bar{b}\bar{l}}^{\bar{d}\bar{j}} + 2x_{\bar{b}\bar{l}}^{\bar{j}\bar{d}}\right)T_{a\bar{d}}^{i\bar{l}} \\ &+ \left(\hat{v}_{a\bar{l}}^{i\bar{d}} + v_{k\bar{l}}^{c\bar{d}}T_{ac}^{ik}\right)T_{\bar{d}\bar{b}}^{\bar{l}\bar{j}} + \hat{v}_{l\bar{b}}^{d\bar{j}}T_{ad}^{il} - \hat{v}_{a\bar{k}}^{c\bar{j}}T_{c\bar{b}}^{i\bar{k}} - \left(\hat{v}_{k\bar{b}}^{i\bar{d}} - v_{k\bar{l}}^{c\bar{d}}T_{c\bar{b}}^{i\bar{l}}\right)T_{a\bar{d}}^{k\bar{j}} \\ &\left. - K_{p\bar{q}}^{i\bar{j}}\left(T_a^k\delta_k^p\delta_{\bar{b}}^{\bar{q}} + T_{\bar{b}}^{\bar{l}}\delta_a^q\delta_{\bar{l}}^{\bar{q}} - \delta_k^p\delta_{\bar{l}}^{\bar{q}}T_a^k T_{\bar{b}}^{\bar{l}}\right)\right\} \end{aligned} \tag{2.21}$$

$$
\begin{aligned}
K^{ij}_{pq} &= v^{rs}_{pq} D^{ij}_{rs} \qquad\qquad K^{i\bar{j}}_{p\bar{q}} = v^{r\bar{s}}_{p\bar{q}} D^{i\bar{j}}_{r\bar{s}} \\
D^{ij}_{rs} &= \left(T^{ij}_{ab} + T^{i}_{a} T^{j}_{b} - T^{i}_{b} T^{j}_{a}\right) \delta^{a}_{r} \delta^{b}_{s} + \mathcal{A}\left(ij; rs\right) \delta^{i}_{r} T^{j}_{b} \delta^{b}_{s} + \delta^{i}_{r} \delta^{j}_{s} - \delta^{i}_{s} \delta^{j}_{r} \\
D^{i\bar{j}}_{r\bar{s}} &= \left(T^{i\bar{j}}_{a\bar{b}} + T^{i}_{a} T^{\bar{j}}_{\bar{b}}\right) \delta^{a}_{r} \delta^{\bar{b}}_{\bar{s}} + \delta^{i}_{r} T^{\bar{j}}_{\bar{b}} \delta^{\bar{b}}_{\bar{s}} + T^{i}_{a} \delta^{a}_{s} \delta^{\bar{j}}_{\bar{s}} + \delta^{i}_{r} \delta^{\bar{j}}_{\bar{s}} \\
x^{id}_{al} &= \frac{1}{2} T^{ik}_{ac} \left(v^{cd}_{kl} - v^{dc}_{kl}\right) \\
\bar{x}^{id}_{al} &= x^{id}_{al} + T^{i\bar{k}}_{a\bar{c}} v^{d\bar{c}}_{l\bar{k}} \\
x^{i\bar{d}}_{a\bar{l}} &= \frac{1}{2} T^{i\bar{k}}_{a\bar{c}} \left(v^{\bar{c}\bar{d}}_{\bar{k}\bar{l}} - v^{\bar{d}\bar{c}}_{\bar{k}\bar{l}}\right) \\
\hat{x}^{i}_{k} &= \hat{f}^{i}_{k} + 2\times\frac{1}{2} \left(v^{cd}_{kl} T^{il}_{cd} + v^{c\bar{d}}_{k\bar{l}} T^{i\bar{l}}_{c\bar{d}}\right) \\
\hat{x}^{c}_{a} &= \hat{f}^{c}_{a} - 2\times\frac{1}{2} \left(v^{cd}_{kl} T^{kl}_{ad} + v^{c\bar{d}}_{k\bar{l}} T^{k\bar{l}}_{a\bar{d}}\right)
\end{aligned}
\tag{2.22}
$$

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.[3]. 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.[3] are coloured magenta. Terms we have added to ensure proper antisymmetry and which are not explicitly listed in Ref.[3] are coloured green.

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

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

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,

$$M_u^i = T_{u\bar{t}}^{t\bar{i}}, \tag{3.6}$$
$$M_a^t = -T_{u\bar{a}}^{t\bar{u}}, \tag{3.7}$$
$$M_a^i = T_{\bar{a}}^{\bar{u}} T_{u\bar{t}}^{t\bar{i}} + T_{\bar{t}}^{\bar{i}} T_{u\bar{a}}^{t\bar{u}}. \tag{3.8}$$

$$M_{\bar{t}}^{\bar{i}} = T_{u\bar{t}}^{i\bar{u}}, \tag{3.9}$$
$$M_{\bar{a}}^{\bar{u}} = -T_{a\bar{t}}^{t\bar{u}}, \tag{3.10}$$
$$M_{\bar{a}}^{\bar{i}} = T_a^t T_{u\bar{t}}^{i\bar{u}} + T_u^i T_{a\bar{t}}^{t\bar{u}}. \tag{3.11}$$

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

$$
\begin{aligned}
M^{ij}_{ua} =& \mathcal{A}\,(ij)\,\tau^{i}_{a}T^{t\bar{j}}_{u\bar{t}} + \mathcal{A}\,(ij)\,T^{\bar{i}}_{\bar{t}}T^{t\bar{j}}_{u\bar{a}}, && (3.12)\\
M^{ij}_{au} =& -\mathcal{A}\,(ij)\,\tau^{i}_{a}T^{t\bar{j}}_{u\bar{t}} - \mathcal{A}\,(ij)\,T^{\bar{i}}_{\bar{t}}T^{t\bar{j}}_{u\bar{a}}, && (3.13)\\
M^{ti}_{ab} =& \mathcal{A}\,(ab)\,\tau^{i}_{b}T^{t\bar{u}}_{u\bar{a}} + \mathcal{A}\,(ab)\,T^{\bar{u}}_{\bar{b}}T^{t\bar{i}}_{u\bar{a}}, && (3.14)\\
M^{it}_{ab} =& -\mathcal{A}\,(ab)\,\tau^{i}_{b}T^{t\bar{u}}_{u\bar{a}} - \mathcal{A}\,(ab)\,T^{\bar{u}}_{\bar{b}}T^{t\bar{i}}_{u\bar{a}}, && (3.15)\\
M^{ij}_{ab} =& -\mathcal{A}\,(ij;ab)\,\tau^{j}_{b}\left(T^{\bar{u}}_{\bar{a}}T^{t\bar{i}}_{u\bar{t}} + T^{\bar{i}}_{\bar{t}}T^{t\bar{u}}_{u\bar{a}}\right) - \mathcal{A}\left(\bar{i}\bar{j};\bar{a}\bar{b}\right)\left(\tau^{\bar{u}\bar{i}}_{\bar{t}\bar{a}}T^{t\bar{j}}_{u\bar{b}}\right)\\
&- \mathcal{A}\,(ij)\,T^{\bar{u}\bar{i}}_{\bar{a}\bar{b}}T^{t\bar{j}}_{u\bar{t}} - \mathcal{A}\,(ab)\,T^{\bar{i}\bar{j}}_{\bar{t}\bar{a}}T^{t\bar{u}}_{u\bar{b}}, && (3.16)\\
M^{it}_{au} =& -T^{t\bar{i}}_{u\bar{a}}, && (3.17)\\
M^{ti}_{au} =& T^{t\bar{i}}_{u\bar{a}}, && (3.18)\\
M^{it}_{ua} =& T^{t\bar{i}}_{u\bar{a}}, && (3.19)\\
M^{ti}_{ua} =& -T^{t\bar{i}}_{u\bar{a}}. && (3.20)
\end{aligned}
$$

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,

$$
\begin{aligned}
M^{i\bar{j}}_{u\bar{a}} =& -\tau^{\bar{j}}_{\bar{a}}T^{t\bar{i}}_{u\bar{t}} - 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}, && (3.21)\\
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}}, && (3.22)\\
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}, && (3.23)\\
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}}, && (3.24)\\
M^{i\bar{j}}_{a\bar{b}} =& -\tau^{\bar{j}}_{\bar{b}}(T^{\bar{u}}_{\bar{a}}T^{t\bar{i}}_{u\bar{t}} + T^{\bar{i}}_{\bar{t}}T^{t\bar{u}}_{u\bar{a}}) - \tau^{i}_{a}(T^{j\bar{u}}_{u\bar{t}}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}}_{u\bar{t}}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}}, && (3.25)\\
M^{t\bar{i}}_{u\bar{t}} =& T^{i}_{u}, && (3.26)\\
M^{i\bar{u}}_{u\bar{t}} =& T^{\bar{i}}_{\bar{t}}, && (3.27)\\
M^{t\bar{i}}_{u\bar{a}} =& \tau^{it}_{ua}, && (3.28)\\
M^{i\bar{u}}_{a\bar{t}} =& \tau^{\bar{i}\bar{u}}_{\bar{t}\bar{a}}, && (3.29)\\
M^{t\bar{i}}_{a\bar{t}} =& \tau^{i\bar{u}}_{u\bar{a}}, && (3.30)\\
M^{i\bar{u}}_{u\bar{a}} =& \tau^{t\bar{i}}_{a\bar{t}}, && (3.31)\\
M^{t\bar{u}}_{u\bar{a}} =& -T^{t}_{a}, && (3.32)\\
M^{t\bar{u}}_{a\bar{t}} =& -T^{\bar{u}}_{\bar{a}}, && (3.33)\\
M^{i\bar{j}}_{u\bar{t}} =& -\tau^{j\bar{i}}_{u\bar{t}}, && (3.34)\\
M^{t\bar{u}}_{a\bar{b}} =& -\tau^{t\bar{u}}_{b\bar{a}}. && (3.35)
\end{aligned}
$$

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

$$W = R^{t\bar{u}}_{u\bar{t}}. \qquad (3.36)$$

The all internal singles T_u^t, $T_{\bar{t}}^{\bar{u}}$ and doubles $T_{u\bar{t}}^{t\bar{u}}$ coupled cluster amplitude is set to zero at the beginning of every iteration. At the end of every iteration the all internal doubles residuum $R_{u\bar{t}}^{t\bar{u}}$ is set to zero, but *not* the singles residuum.

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