

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, \dots and the occupied orbitals by i, j, k, \dots . The Einstein summation convention is used for repeated indices (repeated lower and upper indices are summed over).

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,

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

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

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

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

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.,

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

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

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

where

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

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.,

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

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

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

$$\begin{aligned}
D_i^j &= -2 \Lambda_{ik}^{cd} T_{cd}^{jk}, \\
D_a^b &= 2 \Lambda_{kl}^{bc} T_{ac}^{kl}, \\
D_i^a &= \Lambda_i^a, \\
D_a^i &= \Lambda_k^c \tilde{T}_{ac}^{ik}. \quad (2.7)
\end{aligned}$$

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,

$$\begin{aligned}
\hat{D}_i^j &= D_i^j - D_i^c T_c^j, \\
\hat{D}_a^b &= D_a^b + D_k^b T_a^k, \\
\hat{D}_i^a &= D_i^a, \\
\hat{D}_a^i &= D_a^i + 2 T_a^i - D_a^c T_c^i + \hat{D}_k^i T_a^k. \quad (2.8)
\end{aligned}$$

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

$$\begin{aligned}
D_{ij}^{kl} &= \Lambda_{ij}^{cd} T_{cd}^{kl} \\
D_{ib}^{aj} &= \Lambda_{ik}^{ac} \tilde{T}_{cb}^{kj} \\
\bar{D}_{ib}^{aj} &= \Lambda_{ik}^{ac} T_{cb}^{kj} + \Lambda_{ik}^{ca} T_{bc}^{kj} \quad (2.9)
\end{aligned}$$

Finally, we define the following quantities (which correspond to the `cckext` factorization

and a doubles-dressing of the Fock matrix) and a “contravariation” operator,

$$\begin{aligned}
K_{mn}^{rs} &= \hat{\Lambda}_{mn}^{pq} v_{pq}^{rs} \\
\hat{\Lambda}_{mn}^{pq} &= \Lambda_{mn}^{ab} \delta_a^p \delta_b^q - \Lambda_{mn}^{ab} T_a^i \delta_i^p \delta_b^q - \Lambda_{mn}^{ab} \delta_a^p T_b^j \delta_j^q + \Lambda_{mn}^{ab} T_a^i T_b^j \delta_i^p \delta_j^q \\
x_m^i &= \tilde{T}_{cd}^{il} v_{ml}^{cd} & x_a^e &= \tilde{T}_{ac}^{kl} v_{kl}^{ec} \\
\mathcal{T}(mn) X_{mn}^{ef} &= 2X_{mn}^{ef} - X_{nm}^{ef}
\end{aligned} \tag{2.10}$$

With these definitions, the Λ equations can be written as

$$\begin{aligned}
\frac{\partial \mathcal{L}}{\partial T_e^m} &= (2v_{qm}^{pe} - v_{qm}^{ep}) \hat{D}_p^q + 2f_m^e - 2\Lambda_{ij}^{eb} \hat{v}_{mb}^{ij} + 2K_{mj}^{rs} \delta_r^e (\delta_s^j + \delta_s^b T_b^j) \\
&+ 2D_{mj}^{kl} \hat{v}_{kl}^{ej} - 2\Lambda_{ij}^{eb} (\hat{v}_{mb}^{cd} T_{cd}^{ij}) - D_{df}^e \hat{f}_m^d + D_m^k \hat{f}_k^e - 2D_{id}^{el} \hat{v}_{ml}^{id} + 2D_{md}^{al} \hat{v}_{al}^{ed} \\
&+ 2\bar{D}_{ic}^{ek} \hat{v}_{km}^{ic} - 2\bar{D}_{mc}^{ak} \hat{v}_{ka}^{ec} - \Lambda_i^e \hat{f}_m^i + \Lambda_m^a \hat{f}_a^e - \Lambda_i^e x_m^i - \Lambda_m^a x_a^e.
\end{aligned} \tag{2.11}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}}{\partial T_{ef}^{mn}} &= \tilde{v}_{mn}^{ef} + \Lambda_{ij}^{ef} (\hat{v}_{mn}^{ij} + v_{mn}^{cd} T_{cd}^{ij}) + D_{mn}^{kl} v_{kl}^{ef} + K_{mn}^{rs} \delta_r^e \delta_s^f \\
&+ \mathcal{P}(em; fn) \left\{ \Lambda_{mn}^{af} \left(\hat{f}_a^e - 2 \times \frac{1}{2} x_a^e \right) - \Lambda_{in}^{ef} \left(\hat{f}_m^i + 2 \times \frac{1}{2} x_m^i \right) \right. \\
&+ \mathcal{T}(mn) \left[2 \times \frac{1}{4} v_{kn}^{ef} D_m^k - 2 \times \frac{1}{4} v_{mn}^{cf} D_c^e + \Lambda_{in}^{af} (\hat{v}_{am}^{ie} + v_{km}^{ce} \tilde{T}_{ac}^{ik}) \right. \\
&+ \frac{1}{2} (\Lambda_m^e \hat{f}_n^f + \Lambda_n^a \hat{v}_{am}^{fe} - \Lambda_i^f \hat{v}_{nm}^{ie}) \left. \right] \\
&\left. - \Lambda_{in}^{af} \hat{v}_{ma}^{ie} - \Lambda_{in}^{eb} \hat{v}_{mb}^{if} - D_{nc}^{fl} v_{ml}^{ce} + \bar{D}_{nd}^{ek} v_{km}^{fd} \right\}.
\end{aligned} \tag{2.12}$$

2.3 Perturbative triples for closed-shell CCSD

The perturbative triples equations for CCSD are given by

$$\begin{aligned}
E_{[T]} &= \sum_{i \leq j \leq k} p(i, j, k) K_{ijk}^{abc} X_{abc}^{ijk} \\
p(i, j, k) &= \begin{cases} 2 & i \neq j \neq k \\ 1 & i = j \oplus j = k \\ 0 & i = j = k \end{cases}
\end{aligned} \tag{2.13}$$

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

$$\begin{aligned}
K_{ijk}^{abc} &= K_{abc}^{ijk} = v_{bc}^{dk} T_{ad}^{ij} + v_{ac}^{dk} T_{db}^{ij} + v_{cb}^{dj} T_{ad}^{ik} + v_{ab}^{dj} T_{dc}^{ik} + v_{ca}^{di} T_{bd}^{jk} + v_{ba}^{di} T_{dc}^{jk} \\
&- v_{lc}^{jk} T_{ba}^{li} - v_{lc}^{ik} T_{ab}^{lj} - v_{lb}^{kj} T_{ca}^{li} - v_{lb}^{ij} T_{ac}^{lk} - v_{la}^{ki} T_{cb}^{lj} - v_{la}^{ji} T_{bc}^{lk} \\
X_{abc}^{ijk} &= \frac{4K_{abc}^{ijk} - 2K_{acb}^{ijk} - 2K_{cba}^{ijk} - 2K_{bac}^{ijk} + K_{cab}^{ijk} + K_{bca}^{ijk}}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}
\end{aligned} \tag{2.14}$$

The (T) correction contains additionally the following terms,

$$\begin{aligned}
E_{(T)} &= E_{[T]} + \sum_{i \leq j \leq k} p(i, j, k) \left[v_{jk}^{bc} X_{abc}^{ijk} T_i^{\dagger a} + v_{ik}^{ac} X_{abc}^{ijk} T_j^{\dagger b} + v_{ij}^{ab} X_{abc}^{ijk} T_k^{\dagger c} \right. \\
&\left. + T_{jk}^{\dagger bc} X_{abc}^{ijk} f_i^a + T_{ik}^{\dagger ac} X_{abc}^{ijk} f_j^b + T_{ij}^{\dagger ab} X_{abc}^{ijk} f_k^c \right].
\end{aligned} \tag{2.15}$$

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

$$\begin{aligned} K_{ijk}^{abc} = & v_{dk}^{bc} \bar{\Lambda}_{ij}^{ad} + v_{dk}^{ac} \bar{\Lambda}_{ij}^{db} + v_{dj}^{cb} \bar{\Lambda}_{ik}^{ad} + v_{dj}^{ab} \bar{\Lambda}_{ik}^{dc} + v_{di}^{ca} \bar{\Lambda}_{jk}^{bd} + v_{di}^{ba} \bar{\Lambda}_{jk}^{dc} \\ & - v_{jk}^{lc} \bar{\Lambda}_{li}^{ba} - v_{ik}^{lc} \bar{\Lambda}_{lj}^{ab} - v_{kj}^{lb} \bar{\Lambda}_{li}^{ca} - v_{ij}^{lb} \bar{\Lambda}_{lk}^{ac} - v_{ki}^{la} \bar{\Lambda}_{lj}^{cb} - v_{ji}^{la} \bar{\Lambda}_{lk}^{bc}, \end{aligned} \quad (2.16)$$

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

$$\bar{\Lambda}_{ij}^{ab} = \frac{2}{3} \Lambda_{ij}^{ab} + \frac{1}{3} \Lambda_{ij}^{ba}. \quad (2.17)$$

Additionally, the conjugate-transposed amplitudes in Eq. (2.15) are replaced by the covariant Lagrange multipliers $\bar{\Lambda}_{ij}^{ab}$ and $\bar{\Lambda}_i^a = \frac{1}{2} \Lambda_i^a$.

Bibliography

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