Equations and derivations for ElemCo.jl

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June 21, 2024

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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,

$$\hat{H} = E_0 + h_p^q \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} v_{pq}^{rs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r, \tag{1.1}$$

or for the normal-ordered Hamiltonian,

$$\hat{H}_N = f_p^q \left\{ \hat{a}_p^\dagger \hat{a}_q \right\}_N + \frac{1}{2} v_{pq}^{rs} \left\{ \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \right\}_N, \tag{1.2}$$

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

Permutation operators:

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

Symmetrization operators:

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

Antisymmetrization operators:

$$\begin{aligned} \mathcal{A}\,(ab)\, X_{ab}^{ij} &= X_{ab}^{ij} - X_{ba}^{ij} \\ \mathcal{A}\,(ab; ij)\, X_{ab}^{ij} &= X_{ab}^{ij} - X_{ab}^{ji} - X_{ba}^{ij} + X_{ba}^{ji} \end{aligned} \tag{1.5}$$

Chapter 2

Integrals

2.1 Density fitting and Cholesky decomposition

The electron-repulsion integrals in ElemCo.jl are obtained either from an external program through an FCIDUMP [1] interface, or are calculated using the density-fitting approximation using the `GaussianBasis.jl` interface[2] to the `libcint`[3] library.

In the density-fitting approximation, the electron-repulsion integrals are approximated by

$$v_{pq}^{rs} \approx v_p^{rP} \left[v^{-1}\right]_{PQ} v_q^{sQ}, \tag{2.1}$$

where v_p^{rP} and v_q^{sQ} are density-fitted 3-index integrals with auxiliary basis functions P, Q,

$$v_p^{rP} = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\phi_p^*(\mathbf{r}_1)\phi^r(\mathbf{r}_1)\phi^P(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{2.2}$$

and v^{PQ} is the Coulomb metric matrix,

$$v^{PQ} = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\phi^P(\mathbf{r}_1)\phi^Q(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{2.3}$$

The Coulomb metric matrix is decomposed using the Cholesky factorization,

$$v^{PQ} = \sum_L L_L^P L_L^Q, \tag{2.4}$$

where L_L^P is a lower triangular matrix. Thereafter, a non-symmetric square root of the inverse, C_P^L, is calculated by solving the equations

$$L_{L'}^P C_P^L = \delta_{L'}^L, \tag{2.5}$$

with δ_L^K being the Kronecker delta. If L_L^P is low-rank, the equation is solved using the QR decomposition, otherwise it can be solved by simple back-substitution.

The transformed density-fitted integrals which are used throughout ElemCo.jl are then calculated by multiplying the density-fitted 3-index integrals with the non-symmetric square root of the inverse,

$$v_p^{rL} = v_p^{rP} C_P^L, \tag{2.6}$$

and the density-fitted 4-index integrals can be calculated by

$$v_{pq}^{rs} \approx \sum_L v_p^{rL} v_q^{sL}. \tag{2.7}$$

If all integrals are calculated using the density-fitting approximation using *mp2fit* fitting basis in ElemCo.jl , the correction terms are added using the *jkfit* fitting basis to the one-body and zero-body terms of the Hamiltonian in order to ensure that the reference energy and the Fock matrix from DF-HF is not changed by the density-fitting approximation,

$$\begin{aligned} \tilde{h}^q_p &= \tilde{f}^q_p - \sum_L \left(2v^{qL}_p v^{iL}_i - v^{iL}_p v^{qL}_i \right) \\ \tilde{E}_0 &= E_0 + h^i_i - \tilde{h}^i_i + \tilde{f}^I_I, \end{aligned} \tag{2.8}$$

where

$$\tilde{f}^q_p = h^q_p + \sum_{\tilde{L}} \left(2v^{q\tilde{L}}_p v^{\tilde{i}\tilde{L}}_{\tilde{i}} - v^{\tilde{i}\tilde{L}}_p v^{q\tilde{L}}_{\tilde{i}} \right), \tag{2.9}$$

and I denotes the core orbitals (cf. Sec. 2.2), $\tilde{i}$ denote all occupied orbitals (including core) and other indices do not include the core orbitals. $\tilde{L}$ corresponds to the *jkfit* density-fitting basis functions, and L corresponds to the *mp2fit* density-fitting basis functions.

2.2 Frozen-core approximation

The frozen-core approximation is used to reduce the number of orbitals in the correlated calculation. The frozen-core approximation is implemented in ElemCo.jl by setting the corresponding integrals to zero and adding their contribution to the one-particle and zero-particle part of the Hamiltonian,

$$\begin{aligned} \tilde{h}^q_p &= h^q_p + 2v^{qI}_{pI} - v^{Iq}_{pI} \\ \tilde{E}_0 &= E_0 + 2h^I_I + 2v^{IJ}_{IJ} - v^{JI}_{IJ}, \end{aligned} \tag{2.10}$$

where I, J denote the core orbitals, and other indices do not include the core orbitals. For the UHF Hamiltonian, the frozen-core approximation is implemented as

$$\begin{aligned} \tilde{h}^q_p &= h^q_p + v^{qI}_{pI} + v^{q\bar{I}}_{p\bar{I}} - v^{Iq}_{pI} \\ \tilde{h}^{\bar{q}}_{\bar{p}} &= h^{\bar{q}}_{\bar{p}} + v^{\bar{q}\bar{I}}_{\bar{p}\bar{I}} + v^{\bar{q}I}_{\bar{p}I} - v^{\bar{I}\bar{q}}_{\bar{p}\bar{I}} \\ \tilde{E}_0 &= E_0 + h^I_I + h^{\bar{I}}_{\bar{I}} + \frac{1}{2}\left(v^{IJ}_{IJ} + v^{\bar{I}\bar{J}}_{\bar{I}\bar{J}} + 2v^{I\bar{J}}_{I\bar{J}} - v^{JI}_{IJ} - v^{\bar{J}\bar{I}}_{\bar{I}\bar{J}} \right). \end{aligned} \tag{2.11}$$

If the frozen-core approximation is used in combination with the density-fitting approximation, *jkfit* correction terms are added to the one-body and zero-body terms of the Hamiltonian in order to ensure that the reference energy and the Fock matrix from DF-HF is not changed by the frozen-core approximation, cf. Sec. 2.1.

Chapter 3

Hartree-Fock

3.1 Density-fitted Hartree-Fock

The density-fitted Hartree-Fock equations are given by

$$\begin{aligned} f_\mu^\nu C_\nu^p &= S_\mu^\nu C_\nu^p \epsilon_p \\ f_\mu^\nu &= h_\mu^\nu + 2\sum_L \left(v_{\mu'}^{iL} C_i^{\dagger\mu'}\right) C_P^L v_\mu^{\nu P} - v_\mu^{iL} v_{iL}^{\dagger\nu} \\ v_\mu^{iL} &= \left(v_\mu^{\nu P} C_\nu^i\right) C_P^L. \end{aligned} \tag{3.1}$$

Alternatively, the $v_\mu^{\nu L}$ integrals can be precomputed and the Fock matrix can be calculated as

$$\begin{aligned} f_\mu^\nu &= h_\mu^\nu + 2\sum_L \left(v_{\mu'}^{iL} C_i^{\dagger\mu'}\right) v_\mu^{\nu L} - v_\mu^{iL} v_{iL}^{\dagger\nu} \\ v_\mu^{iL} &= v_\mu^{\nu L} C_\nu^i. \end{aligned} \tag{3.2}$$

Note that our orbitals are real, and therefore $v_{iL}^{\dagger\mu} = v_\mu^{iL}$, and $C_i^{\dagger\mu} = C_\mu^i$.

The unrestricted Hartree-Fock equations are given (for α spin) by

$$\begin{aligned} {}^\alpha f_\mu^\nu C_\nu^p &= S_\mu^\nu C_\nu^p \epsilon_p \\ {}^\alpha f_\mu^\nu &= h_\mu^\nu + \sum_L \left(v_{\mu'}^{iL} C_i^{\dagger\mu'} + v_{\mu'}^{\bar{i}L} C_{\bar{i}}^{\dagger\mu'}\right) C_P^L v_\mu^{\nu P} - v_\mu^{iL} v_{iL}^{\dagger\nu} \\ v_\mu^{iL} &= \left(v_\mu^{\nu P} C_\nu^i\right) C_P^L, \end{aligned} \tag{3.3}$$

and equations for β spin can be obtained by swapping the spins.

The residual of the Hartree-Fock equations, which can be used in DIIS, is given by

$$\Delta f_\mu^\nu = S_\mu^{\nu'} D_{\nu'}^\rho f_\rho^\nu - f_\mu^{\nu'} D_{\nu'}^\rho S_\rho^\nu, \quad \text{with} \quad D_\mu^\nu = C_\mu^i C_i^{\dagger\nu}. \tag{3.4}$$

3.2 (Bi-orthogonal) Hartree-Fock

The closed-shell Hartree-Fock on top of the FCIDUMP integrals (including the case of similarity-transformed Hamiltonians) is given by

$$\begin{aligned} f_{\tilde{p}}^{\tilde{q}} C_{\tilde{q}}^p &= C_{\tilde{p}}^p \epsilon_p, \\ f_{\tilde{p}}^{\tilde{q}} &= h_{\tilde{p}}^{\tilde{q}} + \gamma_{\tilde{s}}^{\tilde{r}} \left(V_{\tilde{p}\tilde{r}}^{\tilde{q}\tilde{s}} - \frac{1}{2} V_{\tilde{p}\tilde{r}}^{\tilde{s}\tilde{q}}\right), \\ \gamma_{\tilde{s}}^{\tilde{r}} &= 2\sum_{i\in\mathrm{occ}} \bar{C}_i^{\dagger\tilde{r}} C_{\tilde{s}}^i, \end{aligned} \tag{3.5}$$

where tilde indices correspond to the original orbitals. If the FCIDUMP is similarity-transformed, $\bar{C}_p^{\dagger\tilde{r}} \neq C_{\tilde{r}}^p$, and $\bar{C}_p^{\dagger\tilde{r}}$ are obtained as an inverse of $C_{\tilde{r}}^p$ such that $\bar{C}_p^{\dagger\tilde{r}} C_{\tilde{r}}^r = \delta_p^r$.

The unrestricted Hartree-Fock equations are given (for α case) by

$$\begin{aligned} {}^{\alpha}f_{\tilde{p}}^{\tilde{q}} C_{\tilde{q}}^p &= C_{\tilde{p}}^p \epsilon_p, \\ {}^{\alpha}f_{\tilde{p}}^{\tilde{q}} &= h_{\tilde{p}}^{\tilde{q}} + \left({}^{\alpha}\gamma_{\tilde{s}}^{\tilde{r}} + {}^{\beta}\gamma_{\tilde{s}}^{\tilde{r}} \right) V_{\tilde{p}\tilde{r}}^{\tilde{q}\tilde{s}} - {}^{\alpha}\gamma_{\tilde{s}}^{\tilde{r}} V_{\tilde{p}\tilde{r}}^{\tilde{s}\tilde{q}}, \\ {}^{\alpha}\gamma_{\tilde{s}}^{\tilde{r}} &= \sum_{i \in \mathrm{occ}} \bar{C}_i^{\dagger\tilde{r}} C_{\tilde{s}}^i, \\ {}^{\beta}\gamma_{\tilde{s}}^{\tilde{r}} &= \sum_{\bar{i} \in \mathrm{occ}} \bar{C}_{\bar{i}}^{\dagger\tilde{r}} C_{\tilde{s}}^{\bar{i}}, \end{aligned} \tag{3.6}$$

and equations for β spin can be obtained by swapping the spins. Note that if the FCIDUMP is of UHF type, the original indices and integrals are spin-dependent, which has to be taken into account in the equations.

The residual of the Hartree-Fock equations, which can be used in DIIS, is equivalent to Eq. (3.4), with the overlap matrix S_μ^ν removed.

Chapter 4

Density-Fitted Multiconfigurational Self-Consistent Field

4.1 Orbital Rotation

The orbital transformed wavefunction can be expressed by

$$|\Psi\rangle = \exp(\hat{R})|0\rangle, \tag{4.1}$$

where

$$\begin{aligned} \exp(\hat{R}) &= 1 + \hat{R} + \frac{1}{2!}\hat{R}^2 + \cdots, \\ \hat{R} &= R_r^s \hat{E}_s^r, \end{aligned} \tag{4.2}$$

$\hat{E}_s^r$ is the singlet excitation operator $(\hat{a}_{r\alpha}^\dagger \hat{a}_{k\alpha} + \hat{a}_{r\beta}^\dagger \hat{a}_{k\beta})$. Mathemetically if $\mathbf{R}$ is anti-symmetric, $\exp(\hat{R})$ is an unitary transformation.

$$\begin{aligned} R_r^s &= -R_s^r, \\ \hat{R} &= [R_r^s(\hat{E}_s^r - \hat{E}_r^s)]_{r>s}, \end{aligned} \tag{4.3}$$

4.2 MCSCF

The energy expectation value of the wavefunction is be given by

$$\begin{aligned} E(\mathbf{R}) &= \langle\Psi|\hat{H}|\Psi\rangle \\ &= \langle 0|\exp(-\hat{R})\hat{H}\exp(\hat{R})|0\rangle \\ &= \langle 0|\hat{H}|0\rangle + \langle 0|[\hat{H},\hat{R}]|0\rangle + \frac{1}{2!}\langle 0|[[\hat{H},\hat{R}],\hat{R}]|0\rangle + \cdots \\ &= E_0 + \mathbf{g}^\mathbf{T}\mathbf{x} + \frac{\mathbf{1}}{\mathbf{2}}\mathbf{x}^\mathbf{T}\mathbf{h}\mathbf{x} + \cdots. \end{aligned} \tag{4.4}$$

In which Hamiltonian operator $\hat{H}$ is expressed as

$$\begin{aligned} \hat{H} &= E_0 + h_p^q \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} v_{pr}^{qs} \hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q \\ &= E_0 + h_p^q \hat{E}_q^p + \frac{1}{2} v_{pr}^{qs} \hat{e}_{qs}^{pr}, \end{aligned} \tag{4.5}$$

with $\hat{e}^{pr}_{qs}$ as the 2-electron excitation operator $\sum_{\sigma\tau}\hat{a}^{\dagger}_{p\sigma}\hat{a}^{\dagger}_{r\tau}\hat{a}_{s\tau}\hat{a}_{q\sigma}$. In the first expression, p,q,r,s denote the spin orbitals, and in the second expression, p,q,r,s denote spatial orbitals.

The orbital transformation parameters $\mathbf{R}$ is expressed as vector $\mathbf{x}$, the linear coefficients as gradient vector $\mathbf{g}$, the quadratic coefficients as matrix $\mathbf{h}$. When terms after the quadratic terms truncated, to minimize the energy expectation value, the Lagrangian equation as known as the Newton-Raphson equation is

$$\frac{\partial}{\partial \mathbf{x}}(\mathbf{g}^{\mathbf{T}}\mathbf{x}+\frac{\mathbf{1}}{\mathbf{2}}\mathbf{x}^{\mathbf{T}}\mathbf{h}\mathbf{x})=\mathbf{g}+\mathbf{h}\mathbf{x}=\mathbf{0}. \tag{4.6}$$

Since the internal rotation of each of doubly occupied orbitals and virtual orbitals don't change the wavefunction, vector $\mathbf{x}$ is consisted of 4 parts, can be expressed as $[\mathbf{x^j_t}, \mathbf{x^j_a}, \mathbf{x^u_t}, \mathbf{x^u_a}]$.

Here, $\mathbf{g}$ is calculated from

$$\begin{aligned} g^k_r &= (\frac{\partial E}{\partial x^k_r})_{\mathbf{R}=\mathbf{0}} \\ &= \langle 0|[\hat{H}, \hat{E}^r_k - \hat{E}^k_r]|0\rangle \\ &= [1-\mathcal{P}(rk)]\langle 0|[\hat{E}^k_r, h^{q'}_{p'}\hat{E}^{p'}_{q'} + \frac{1}{2}v^{q's'}_{p'r'}\hat{e}^{p'r'}_{q's'}]|0\rangle \\ &= [1-\mathcal{P}(rk)]\langle 0|h^{q'}_r\hat{E}^k_{q'} - h^k_{p'}\hat{E}^{p'}_r + v^{q's'}_{rr'}\hat{e}^{kr'}_{q's'} - v^{ks'}_{p'r'}\hat{e}^{p'r'}_{rs'}|0\rangle, \\ &= [1-\mathcal{P}(rk)](h^{q'}_r\,{}^1D^k_{q'} - h^k_{p'}\,{}^1D^{p'}_r + v^{q's'}_{rr'}\,{}^2D^{kr'}_{q's'} - v^{ks'}_{p'r'}\,{}^2D^{p'r'}_{rs'}) \end{aligned} \tag{4.7}$$

let

$$A^k_r = \frac{1}{2}(h^{q'}_r\,{}^1D^k_{q'} + h^r_{p'}\,{}^1D^{p'}_k) + \frac{1}{2}(v^{q's'}_{rr'}\,{}^2D^{kr'}_{q's'} + v^{rs'}_{p'r'}\,{}^2D^{p'r'}_{ks'}), \tag{4.8}$$

then

$$g^k_r = 2(A^k_r - A^r_k). \tag{4.9}$$

In which 1-particle density matrix $\mathbf{{}^1D}$ and 2-particle density matrix $\mathbf{{}^2D}$ are defined as

$$\begin{aligned} {}^1D^t_u &= \langle 0|\hat{E}^t_u|0\rangle = c_I c_J\langle\Phi_I|\hat{E}^t_u|\Phi_J\rangle, \\ {}^2D^{tv}_{uw} &= \langle 0|\hat{e}^{tv}_{uw}|0\rangle = c_I c_J\langle\Phi_I|\hat{e}^{tv}_{uw}|\Phi_J\rangle. \end{aligned} \tag{4.10}$$

In order to simplify the expression, the ${}^1D^u_v$ is written as D^u_v, and ${}^2D^{uw}_{tv}$ is written as D^{uw}_{tv} in follow.

Fock matrix can be generalizingly defined as

$$F^s_r = {}^cF^s_r + D^t_u[v^{su}_{rt} - \frac{1}{2}v^{us}_{rt}], \tag{4.11}$$

with

$${}^cF^s_r = h^s_r + (2v^{sj}_{rj} - v^{js}_{rj}) \tag{4.12}$$

defined as the closed shell part of Fock matrix.

$\mathbf{A^k_r}$ can be calculated as

$$\begin{aligned}
A^i_r =&\frac{1}{2}(h^{q'}_r D^i_{q'} + h^r_{p'} D^{p'}_i) + \frac{1}{2}(v^{q's'}_{rr'} D^{ir'}_{q's'} + v^{rs'}_{p'r'} D^{p'r'}_{is'}),\\
=&\frac{1}{2}(h^i_r D^i_i + h^r_i D^i_i) + \frac{1}{2}(v^{ij}_{rj} D^{ij}_{ij} + v^{rj}_{ij} D^{ij}_{ij} + v^{ji}_{rj} D^{ij}_{ji} + v^{rj}_{ji} D^{ji}_{ij}\\
&+ v^{iu}_{rt} D^{it}_{iu} + v^{rt}_{iu} D^{iu}_{it} + v^{ui}_{rt} D^{it}_{ui} + v^{rt}_{ui} D^{ui}_{it})\\
=&\frac{1}{2}(2h^i_r + 2h^r_i) + \frac{1}{2}(4v^{ij}_{rj} + 4v^{rj}_{ij} - 2v^{ji}_{rj} - 2v^{rj}_{ji} + 2v^{iu}_{rt} D^t_u + 2v^{rt}_{iu} D^u_t - v^{ui}_{rt} D^t_u - v^{rt}_{ui} D^u_t)\\
=&\mathcal{S}(ri)\,(h^i_r + 2v^{ij}_{rj} - v^{ji}_{rj} + v^{iu}_{rt} D^t_u - \frac{1}{2} v^{ui}_{rt} D^t_u)\\
=&\mathcal{S}(ri)\,F^i_r,
\end{aligned} \tag{4.13}$$

$$\begin{aligned}
A^u_r =&\frac{1}{2}(h^{q'}_r D^u_{q'} + h^r_{p'} D^{p'}_u) + \frac{1}{2}(v^{q's'}_{rr'} D^{ur'}_{q's'} + v^{rs'}_{p'r'} D^{p'r'}_{us'})\\
=&\frac{1}{2}(h^t_r D^u_t + h^r_t D^t_u) + \frac{1}{2}(v^{tj}_{rj} D^{uj}_{tj} + v^{rj}_{tj} D^{tj}_{uj} + v^{tv}_{rw} D^{uw}_{tv} + v^{rw}_{tv} D^{tv}_{uw} + v^{jt}_{rj} D^{uj}_{jt} + v^{rj}_{jt} D^{jt}_{uj})\\
=&\frac{1}{2}(h^t_r D^u_t + h^r_t D^t_u) + \frac{1}{2}(2v^{tj}_{rj} D^u_t + 2v^{rj}_{tj} D^t_u + v^{tv}_{rw} D^{uw}_{tv} + v^{rw}_{tv} D^{tv}_{uw} - v^{jt}_{rj} D^u_t - v^{rj}_{jt} D^t_u)\\
=&\frac{1}{2}[(h^t_r + 2v^{tj}_{rj} - v^{jt}_{rj}) D^u_t + v^{tv}_{rw} D^{uw}_{tv}] + \frac{1}{2}[(h^r_t + 2v^{rj}_{tj} - v^{jr}_{tj}) D^t_u + v^{rw}_{tv} D^{tv}_{uw}]\\
=&\frac{1}{2}({}^cF^t_r D^u_t + v^{tv}_{rw} D^{uw}_{tv}) + \frac{1}{2}({}^cF^r_t D^t_u + v^{rw}_{tv} D^{tv}_{uw}),
\end{aligned} \tag{4.14}$$

$$A^a_r = 0. \tag{4.15}$$

Electronic energy E after orbital transformation is calculated with transformed orbitals and active orbital 1- and 2-particle density matrices

$$E = {}^cF^u_t D^t_u + \frac{1}{2} v^{uw}_{tv} D^{tv}_{uw} + E_c, \tag{4.16}$$

with

$$E_c = h^j_j + {}^cF^j_j, \tag{4.17}$$

E_c is the closed shell electronic energy.

The 4-index integral v^{uw}_{tv} is calculated as the density fitted integrals, as mentioned in previous chapter,

$$\begin{aligned}
v^{uw}_{tv} =& v^{uL}_t v^{wL}_v,\\
v^{uL}_t =& v^{\nu L}_\mu C^{\dagger\mu}_t C^u_\nu.
\end{aligned} \tag{4.18}$$

Likewise, other four-index integrals in this chapter are calculated in the same way.

4.3 Augmented Hessian

In order to make the coefficients transforming step smaller and more robust, a level-shift ϵ is introduced to control the step $\mathbf{x}$ [4]

$$\mathbf{g} + (\mathbf{h} + \epsilon\mathbf{I})\mathbf{x} = \mathbf{0}, \tag{4.19}$$

in which

$$\epsilon = -\lambda^2 \mathbf{x}^\mathbf{T} \mathbf{g}, \tag{4.20}$$

$$\begin{pmatrix} 0 & \lambda \mathbf{g}^\mathbf{T} \\ \lambda \mathbf{g} & \mathbf{h} \end{pmatrix} \begin{pmatrix} \frac{1}{\lambda} \\ \mathbf{x} \end{pmatrix} = \nu \begin{pmatrix} \frac{1}{\lambda} \\ \mathbf{x} \end{pmatrix}. \tag{4.21}$$

We search for the value of λ with a combination method of linear search and logarithmic bisection search:

$$\begin{aligned} \lambda =& \frac{(\|\mathbf{x}_{\mathbf{small}\lambda}\| - trust) + (trust - \|\mathbf{x}_{\mathbf{large}\lambda}\|)}{\|\mathbf{x}_{\mathbf{small}\lambda}\| - \|\mathbf{x}_{\mathbf{large}\lambda}\|}, \\ \lambda =& \exp\left(\ln small\lambda + (\ln big\lambda - \ln small\lambda) * bisecdamp\right). \end{aligned} \tag{4.22}$$

If there are both tested smallest and biggest limits in one iteration search for λ, we adopt the linear search with the norm of both limit $\mathbf{x}$, otherwise, we use either the upper and lower boundaries value(by default set to be 1000 and 1) and the tested λ to do the logarithmic bisection search.

4.4 Hessian Approximation

4.4.1 First Order Approximation

We adopt the Super-CI optimization approximation[5], in which

$$\hat{H}^{eff} = \sum_{pq} F_p^q \hat{E}_p^q, \tag{4.23}$$

$$E^{(0)} = \langle 0 | \hat{H}^{eff} | 0 \rangle, \tag{4.24}$$

$${}^{SCI}H_{rs}^{kl} = 2\langle rk | \hat{H}^{eff} - E^{(0)} | sl \rangle. \tag{4.25}$$

More specifically,

$$\begin{aligned} {}^{SCI}H_{ab}^{ij} =& 4(\delta_i^j F_a^b - \delta_a^b F_i^j), \\ {}^{SCI}H_{ab}^{iu} =& -2\delta_a^b F_i^v D_v^u, \\ {}^{SCI}H_{au}^{ij} =& \delta_i^j (4F_a^u - 2F_a^v D_v^u), \\ {}^{SCI}H_{tb}^{iu} =& 0, \\ {}^{SCI}H_{tu}^{ij} =& (2D_t^u - 4\delta_t^u) F_i^j + 2\delta_i^j [2F_t^u - (D_{uw}^{tv} - D_u^t D_w^v) F_v^w - D_t^v F_v^u - F_t^v D_u^v], \\ {}^{SCI}H_{ab}^{tu} =& 2\delta_b^a (D_{uw}^{tv} - D_u^t D_w^v) F_v^w + 2D_u^t F_a^b. \end{aligned} \tag{4.26}$$

4.4.2 Second Order Approximation

In general, the second-order Hessian matrix elements are calculated as

$$
\begin{aligned}
{}^{SO}H^{kl}_{rs} =& (\frac{\partial E}{\partial x^k_r \partial x^l_s})_{\mathbf{R=0}} \\
=& \frac{1}{2}\mathcal{S}\left(rs,kl\right)\langle 0|[[\hat{H},\hat{E}^k_r-\hat{E}^r_k],\hat{E}^l_s-\hat{E}^s_l]|0\rangle \\
=& \frac{1}{2}\mathcal{S}\left(rs,kl\right)\mathcal{A}\left(rk;sl\right)\langle 0|[[\hat{H},\hat{E}^k_r],\hat{E}^l_s]|0\rangle \\
=& \frac{1}{2}\mathcal{S}\left(rs,kl\right)\mathcal{A}\left(rk;sl\right)\langle 0|[\hat{E}^l_s,[\hat{E}^k_r,h^{q'}_{p'}\hat{E}^{p'}_{q'}+\frac{1}{2}v^{q's'}_{p'r'}\hat{e}^{p'r'}_{q's'}]]|0\rangle \\
=& \frac{1}{2}\mathcal{S}\left(rs,kl\right)\mathcal{A}\left(rk;sl\right)(-h^l_r D^k_s - h^k_s D^l_r + h^{q'}_r D^l_{q'}\delta^k_s + h^k_{p'}D^{p'}_s\delta^l_r \\
&+ \delta^k_s v^{q's'}_{rr'}D^{lr'}_{q's'} + \delta^l_r v^{ks'}_{p'r'}D^{p'r'}_{ss'} - v^{ls'}_{rr'}D^{kr'}_{ss'} - v^{ks'}_{sr'}D^{lr'}_{rs'} \\
&+ v^{q's'}_{rs}D^{kl}_{q's'} + v^{kl}_{p'r'}D^{p'r'}_{rs} - v^{q'l}_{rr'}D^{kr'}_{q's} - v^{ks'}_{p's}D^{p'l}_{rs'}) \\
=& \mathcal{A}\left(rk;sl\right)(-h^l_r D^k_s - h^k_s D^l_r - v^{ls'}_{rr'}D^{kr'}_{ss'} - v^{ks'}_{sr'}D^{lr'}_{rs'} + v^{q's'}_{rs}D^{kl}_{q's'} + v^{kl}_{p'r'}D^{p'r'}_{rs} - v^{q'l}_{rr'}D^{kr'}_{q's} - v^{ks'}_{p's}D^{p'l}_{rs'}) \\
&+ \frac{1}{2}\mathcal{S}\left(rs,kl\right)\mathcal{A}\left(rk;sl\right)\delta^k_s(h^{q'}_r D^l_{q'} + h^r_{p'}D^{p'}_l + v^{q's'}_{rr'}D^{lr'}_{q's'} + v^{rs'}_{p'r'}D^{p'r'}_{ls'}) \\
=& \mathcal{A}\left(rk;sl\right)(h^s_r D^k_l + h^r_s D^l_k + v^{ss'}_{rr'}D^{kr'}_{ls'} + v^{rs'}_{sr'}D^{lr'}_{ks'} + v^{q's'}_{rs}D^{kl}_{q's'} + v^{rs}_{p'r'}D^{p'r'}_{kl} + v^{q's}_{rr'}D^{kr'}_{q'l} + v^{rs'}_{p's}D^{p'l}_{ks'}) \\
&+ \mathcal{A}\left(rk;sl\right)(\delta^k_s A^l_r + \delta^l_r A^k_s) \\
=& \mathcal{A}\left(rk;sl\right)[2G^{kl}_{rs} + \delta^k_s(A^l_r + A^r_l)] \\
=& \mathcal{A}\left(rk;sl\right)[2G^{kl}_{rs} - \delta^k_l(A^s_r + A^r_s)],
\end{aligned}
\tag{4.27}
$$

matrices $\mathbf{G}$ are defined as

$$
G^{kl}_{rs} = \frac{1}{2}(h^s_r D^k_l + h^r_s D^l_k + v^{ss'}_{rr'}D^{kr'}_{ls'} + v^{rs'}_{sr'}D^{lr'}_{ks'} + v^{q's'}_{rs}D^{kl}_{q's'} + v^{rs}_{p'r'}D^{p'r'}_{kl} + v^{q's}_{rr'}D^{kr'}_{q'l} + v^{rs'}_{p's}D^{p'l}_{ks'}) \tag{4.28}
$$

$$
G^{ij}_{rs} = \delta^j_i(F^r_s + F^s_r) + L^{ij}_{rs} + L^{rs}_{ij}, \tag{4.29}
$$

$$
G^{tj}_{rs} = \frac{1}{2}(D^t_u L^{uj}_{rs} + D^u_t L^{rs}_{uj}) = G^{jt}_{sr}, \tag{4.30}
$$

$$
G^{tu}_{rs} = \frac{1}{2}({}^cF^s_r D^u_t + {}^cF^r_s D^t_u + v^{sw}_{rv}D^{tv}_{uw} + v^{rv}_{sw}D^{uw}_{tv}) + v^{vw}_{rs}D^{tu}_{vw} + v^{rs}_{vw}D^{vw}_{tu}, \tag{4.31}
$$

where

$$
L^{pq}_{rs} = 2v^{pq}_{rs} + 2^{ps}_{rq} - v^{sp}_{rq} - v^{qp}_{rs}. \tag{4.32}
$$

4.4.3 Combined Second-Order and Super-CI Hessian Approximation

By default, the SO-SCI Hessian matrix [6] is approximated as below:

$$\begin{aligned}
{}^{SO-SCI}H_{ab}^{ij} &= {}^{SCI}H_{ab}^{ij}, \\
{}^{SO-SCI}H_{ab}^{iu} &= {}^{SCI}H_{ab}^{iu}, \\
{}^{SO-SCI}H_{au}^{ij} &= {}^{SCI}H_{au}^{ij}, \\
{}^{SO-SCI}H_{tb}^{iu} &= {}^{SO}H_{tb}^{iu}, \\
{}^{SO-SCI}H_{tu}^{ij} &= {}^{SO}H_{tu}^{ij}, \\
{}^{SO-SCI}H_{ab}^{tu} &= {}^{SO}H_{ab}^{tu}.
\end{aligned} \tag{4.33}$$

If the **SO_SCI_origin** option is set to be $false$,

$${}^{SO-SCI}H_{ab}^{tu} = {}^{SCI}H_{ab}^{tu}, \tag{4.34}$$

and the rest blocks of Hessian matrix remain the same.

Chapter 5

CCSD and DCSD amplitude and Λ equations

5.1 Closed-shell CCSD/DCSD Lagrangian

The singles-dressed factorization of the closed-shell CCSD and DCSD amplitude equations roughly follows the factorization from Ref. [7]. The closed-shell CCSD and DCSD Lagrangian is given by

$$\begin{aligned}
\mathcal{L} &= v_{kl}^{cd}\tilde{T}_{cd}^{kl} + \left(\hat{f}_k^c + f_k^c\right) T_c^k + \Lambda_{ij}^{ab}\hat{v}_{ab}^{ij} + \Lambda_{ij}^{ab}\left(\hat{v}_{kl}^{ij} + v_{kl}^{cd}T_{cd}^{ij}\right) T_{ab}^{kl} + \Lambda_{ij}^{ab}\hat{v}_{ab}^{cd}T_{cd}^{ij} \\
&+ \Lambda_{ij}^{ab}v_{kl}^{cd}T_{ad}^{kj}T_{cb}^{il} \\
&+ \Lambda_{ij}^{ab}\mathcal{S}\left(ab,ij\right)\left\{\left(\hat{f}_a^c - 2\times\frac{1}{2}v_{kl}^{cd}\tilde{T}_{ad}^{kl}\right)T_{cb}^{ij} - \left(\hat{f}_k^i + 2\times\frac{1}{2}v_{kl}^{cd}\tilde{T}_{cd}^{il}\right)T_{ab}^{kj}\right. \\
&+ \left.\left(\hat{v}_{al}^{id} + \frac{1}{2}v_{kl}^{cd}\tilde{T}_{ac}^{ik}\right)\tilde{T}_{db}^{lj} - \hat{v}_{ka}^{ic}T_{cb}^{kj} - \hat{v}_{kb}^{ic}T_{ac}^{kj} - v_{kl}^{cd}T_{da}^{ki}\left(T_{cb}^{lj} - T_{bc}^{lj}\right)\right\} \\
&+ \Lambda_i^a\hat{f}_a^i + \Lambda_i^a\hat{f}_j^b\tilde{T}_{ab}^{ij} + \Lambda_i^a\hat{v}_{ak}^{bc}\tilde{T}_{cb}^{ki} - \Lambda_i^a\hat{v}_{jk}^{ic}\tilde{T}_{ca}^{kj}.
\end{aligned} \tag{5.1}$$

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.,

$$\begin{aligned}
\hat{v}_{kl}^{id} &= v_{kl}^{id} + v_{kl}^{cd}T_c^i \\
\hat{v}_{al}^{ij} &= v_{al}^{ij} - v_{kl}^{ij}T_a^k \\
\hat{f}_k^c &= h_k^c + 2\hat{v}_{kl}^{cl} - \hat{v}_{lk}^{cl} = f_k^c + \left(2v_{kl}^{cd} - v_{lk}^{cd}\right)T_d^l.
\end{aligned} \tag{5.2}$$

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. [8] and is given by

$$\begin{aligned}
\mathcal{L} = & v_{kl}^{cd}\tilde{T}_{cd}^{kl} + \left(\hat{f}_k^c + f_k^c\right) T_c^k + \Lambda_{ij}^{ab}\left(\hat{v}_{kl}^{ij} + v_{kl}^{cd}T_{cd}^{ij}\right) T_{ab}^{kl} + \Lambda_{ij}^{ab}K_{pq}^{ij}\delta_a^p\delta_b^q \\
& + \Lambda_{ij}^{ab}v_{kl}^{cd}T_{ad}^{kj}T_{cb}^{il} \\
& + \Lambda_{ij}^{ab}\mathcal{S}\left(ab,ij\right)\left\{\left(\hat{f}_a^c - 2\times\frac{1}{2}v_{kl}^{cd}\tilde{T}_{ad}^{kl}\right) T_{cb}^{ij} - \left(\hat{f}_k^i + 2\times\frac{1}{2}v_{kl}^{cd}\tilde{T}_{cd}^{il}\right) T_{ab}^{kj}\right. \\
& + \left(\hat{v}_{al}^{id} + \frac{1}{2}v_{kl}^{cd}\tilde{T}_{ac}^{ik}\right)\tilde{T}_{db}^{lj} - \hat{v}_{ka}^{ic}T_{cb}^{kj} - \hat{v}_{kb}^{ic}T_{ac}^{kj} - v_{kl}^{cd}T_{da}^{ki}\left(T_{cb}^{lj} - T_{bc}^{lj}\right) \\
& \left. - K_{pq}^{ij}\left(\delta_k^p\delta_b^q - \frac{1}{2}\delta_k^p\delta_l^q T_b^l\right) T_a^k\right\} + \Lambda_i^a K_{pq}^{ij}\left(2\delta_a^p\delta_j^q - \delta_j^p\delta_a^q\right) \\
& - \Lambda_i^a T_a^k K_{pq}^{ij}\left(2\delta_k^p\delta_j^q - \delta_j^p\delta_k^q\right) + \Lambda_i^a\hat{h}_a^i + \Lambda_i^a\hat{f}_j^b\tilde{T}_{ab}^{ij} - \Lambda_i^a\hat{v}_{jk}^{ic}\tilde{T}_{ca}^{kj},
\end{aligned} \tag{5.3}$$

where

$$K_{pq}^{ij} = v_{pq}^{rs}\left(\left(T_{ab}^{ij} + T_a^iT_b^j\right)\delta_r^a\delta_s^b + \delta_r^iT_b^j\delta_s^b + T_a^i\delta_r^a\delta_s^j + \delta_r^i\delta_s^j\right) \tag{5.4}$$

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

5.2 Closed-shell CCSD/DSCD Lagrangian multipliers equations

The Λ equations are obtained by taking the derivative of the Lagrangian Eq. (5.1) with respect to the amplitudes and setting the result to zero, i.e.,

$$\begin{aligned}
\frac{\partial\mathcal{L}}{\partial T_e^m} = & 2\left(2v_{jm}^{be} - v_{jm}^{eb}\right)T_b^j + 2f_m^e - \Lambda_{ij}^{eb}\hat{v}_{mb}^{ij} - \Lambda_{ij}^{ae}\hat{v}_{am}^{ij} + \Lambda_{mj}^{ab}\hat{v}_{ab}^{ej} + \Lambda_{im}^{ab}\hat{v}_{ab}^{ie} \\
& + \Lambda_{mj}^{ab}\hat{v}_{kl}^{ej}T_{ab}^{kl} + \Lambda_{im}^{ab}\hat{v}_{kl}^{ie}T_{ab}^{kl} - \Lambda_{ij}^{eb}\hat{v}_{mb}^{cd}T_{cd}^{ij} - \Lambda_{ij}^{ae}\hat{v}_{am}^{cd}T_{cd}^{ij} \\
& - \Lambda_{ij}^{eb}\hat{f}_m^dT_{db}^{ij} - \Lambda_{ij}^{ae}\hat{f}_m^dT_{ad}^{ij} - \Lambda_{mj}^{ab}\hat{f}_k^eT_{ab}^{kj} - \Lambda_{im}^{ab}\hat{f}_k^eT_{ab}^{ik} \\
& + \Lambda_{ij}^{ab}\mathcal{S}\left(ab,ij\right)\left\{\left(2\hat{v}_{am}^{de} - \hat{v}_{am}^{ed}\right)T_{db}^{ij} - \left(2\hat{v}_{km}^{ie} - \hat{v}_{km}^{ei}\right)T_{ab}^{kj}\right\} \\
& - \Lambda_{ij}^{eb}\hat{v}_{ml}^{id}\tilde{T}_{db}^{lj} - \Lambda_{ij}^{ae}\hat{v}_{ml}^{jd}\tilde{T}_{ad}^{il} + \Lambda_{mj}^{ab}\hat{v}_{al}^{ed}\tilde{T}_{db}^{lj} + \Lambda_{im}^{ab}\hat{v}_{bl}^{ed}\tilde{T}_{ad}^{il} \\
& + \Lambda_{ij}^{eb}\hat{v}_{km}^{ic}T_{cb}^{kj} - \Lambda_{mj}^{ab}\hat{v}_{ka}^{ec}T_{cb}^{kj} + \Lambda_{ij}^{ae}\hat{v}_{km}^{jc}T_{ac}^{ik} - \Lambda_{im}^{ab}\hat{v}_{kb}^{ec}T_{ac}^{ik} \\
& + \Lambda_{ij}^{ae}\hat{v}_{km}^{ic}T_{ac}^{kj} - \Lambda_{mj}^{ab}\hat{v}_{kb}^{ec}T_{ac}^{kj} + \Lambda_{ij}^{eb}\hat{v}_{km}^{jc}T_{cb}^{ik} - \Lambda_{im}^{ab}\hat{v}_{ka}^{ec}T_{cb}^{ik} \\
& - \Lambda_i^e\hat{f}_m^i + \Lambda_m^a\hat{f}_a^e + \Lambda_i^a\left(2\hat{v}_{am}^{ie} - \hat{v}_{am}^{ei}\right) \\
& + \Lambda_i^a\left(2v_{jm}^{be} - v_{jm}^{eb}\right)\tilde{T}_{ab}^{ij} - \Lambda_i^ev_{mk}^{bc}\tilde{T}_{cb}^{ki} - \Lambda_m^av_{jk}^{ec}\tilde{T}_{ca}^{kj}.
\end{aligned} \tag{5.5}$$

$$
\begin{aligned}
\frac{\partial \mathcal{L}}{\partial T^{mn}_{ef}} = \frac{1}{2}\mathcal{S}\left(ef,mn\right)\Big[&\Lambda^{e}_{m}\hat{f}^{f}_{n}\tilde{v}^{ef}_{mn} + \Lambda^{ef}_{ij}\left(\hat{v}^{ij}_{mn} + v^{cd}_{mn}T^{ij}_{cd}\right) + \Lambda^{ab}_{mn}v^{ef}_{kl}T^{kl}_{ab} + \Lambda^{ab}_{mn}\hat{v}^{ef}_{ab} \\
&+ \Lambda^{eb}_{in}v^{cf}_{ml}T^{il}_{cb} + \Lambda^{af}_{mj}v^{ed}_{kn}T^{kj}_{ad} \\
&+ \Lambda^{af}_{mn}\mathcal{S}\left(af,mn\right)\left(\hat{f}^{e}_{a} - 2\times\frac{1}{2}v^{ed}_{kl}\tilde{T}^{kl}_{ad}\right) - \Lambda^{eb}_{ij}\mathcal{S}\left(eb,ij\right)2\times\frac{1}{2}\tilde{v}^{cf}_{mn}T^{ij}_{cb} \\
&- \Lambda^{ef}_{in}\mathcal{S}\left(ef,in\right)\left(\hat{f}^{i}_{m} + 2\times\frac{1}{2}v^{cd}_{ml}\tilde{T}^{il}_{cd}\right) - \Lambda^{ab}_{mj}\mathcal{S}\left(ab,mj\right)2\times\frac{1}{2}\tilde{v}^{ef}_{kn}T^{kj}_{ab} \\
&+ 2\Lambda^{af}_{in}\mathcal{S}\left(af,in\right)\left(\hat{v}^{ie}_{am} + \frac{1}{2}v^{ce}_{km}\tilde{T}^{ik}_{ac}\right) - \Lambda^{af}_{im}\mathcal{S}\left(af,im\right)\left(\hat{v}^{ie}_{an} + \frac{1}{2}v^{ce}_{kn}\tilde{T}^{ik}_{ac}\right) \\
&+ 2\Lambda^{eb}_{mj}\mathcal{S}\left(eb,mj\right)\frac{1}{2}v^{fd}_{nl}\tilde{T}^{lj}_{db} - \Lambda^{eb}_{nj}\mathcal{S}\left(eb,nj\right)\frac{1}{2}v^{fd}_{ml}\tilde{T}^{lj}_{db} \\
&- \Lambda^{af}_{in}\mathcal{S}\left(af,in\right)\hat{v}^{ie}_{ma} - \Lambda^{eb}_{in}\mathcal{S}\left(eb,in\right)\hat{v}^{if}_{mb} \\
&- \Lambda^{fb}_{nj}\mathcal{S}\left(fb,nj\right)v^{ce}_{ml}\left(T^{lj}_{cb} - T^{lj}_{bc}\right) - \Lambda^{af}_{in}\mathcal{S}\left(af,in\right)v^{ed}_{km}T^{ki}_{da} \\
&+ \Lambda^{ae}_{in}\mathcal{S}\left(ab,ij\right)v^{fd}_{km}T^{ki}_{da} \\
&+ \mathcal{T}(mn)\left\{\Lambda^{e}_{m}\hat{f}^{f}_{n} + \Lambda^{a}_{n}\hat{v}^{fe}_{am} - \Lambda^{f}_{i}\hat{v}^{ie}_{nm}\right\}\Big],
\end{aligned}
\tag{5.6}
$$

with a "contravariation" operator,

$$
\mathcal{T}(mn)X^{ef}_{mn} = 2X^{ef}_{mn} - X^{ef}_{nm}. \tag{5.7}
$$

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

$$
\begin{aligned}
D^{j}_{i} &= -2\Lambda^{cd}_{ik}T^{jk}_{cd}, \\
D^{b}_{a} &= 2\Lambda^{bc}_{kl}T^{kl}_{ac}, \\
D^{a}_{i} &= \Lambda^{a}_{i}, \\
D^{i}_{a} &= \Lambda^{c}_{k}\tilde{T}^{ik}_{ac}.
\end{aligned}
\tag{5.8}
$$

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,

$$
\begin{aligned}
\hat{D}^{j}_{i} &= D^{j}_{i} - D^{c}_{i}T^{j}_{c}, \\
\hat{D}^{b}_{a} &= D^{b}_{a} + D^{b}_{k}T^{k}_{a}, \\
\hat{D}^{a}_{i} &= D^{a}_{i}, \\
\hat{D}^{i}_{a} &= D^{i}_{a} + 2T^{i}_{a} - D^{c}_{a}T^{i}_{c} + \hat{D}^{i}_{k}T^{k}_{a}.
\end{aligned}
\tag{5.9}
$$

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

$$
\begin{aligned}
D^{kl}_{ij} &= \Lambda^{cd}_{ij}T^{kl}_{cd} \\
D^{aj}_{ib} &= \Lambda^{ac}_{ik}\tilde{T}^{kj}_{cb} \\
\bar{D}^{aj}_{ib} &= \Lambda^{ac}_{ik}T^{kj}_{cb} + \Lambda^{ca}_{ik}T^{kj}_{bc}
\end{aligned}
\tag{5.10}
$$

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

$$\begin{aligned} K^{rs}_{mn} &= \hat{\Lambda}^{pq}_{mn} v^{rs}_{pq} \\ \hat{\Lambda}^{pq}_{mn} &= \Lambda^{ab}_{mn}\delta^p_a\delta^q_b - \Lambda^{ab}_{mn}T^i_a\delta^p_i\delta^q_b - \Lambda^{ab}_{mn}\delta^p_a T^j_b\delta^q_j + \Lambda^{ab}_{mn}T^i_a T^j_b\delta^p_i\delta^q_j \\ x^i_m &= \tilde{T}^{il}_{cd}v^{cd}_{ml} \qquad\qquad x^e_a = \tilde{T}^{kl}_{ac}v^{ec}_{kl} \end{aligned} \tag{5.11}$$

With these definitions, the Λ equations can be written as

$$\begin{aligned} \frac{\partial\mathcal{L}}{\partial T^m_e} &= \left(2v^{pe}_{qm} - v^{ep}_{qm}\right)\hat{D}^q_p + 2f^e_m - 2\Lambda^{eb}_{ij}\hat{v}^{ij}_{mb} + 2K^{rs}_{mj}\delta^e_r\left(\delta^j_s + \delta^b_s T^j_b\right) \\ &+ 2D^{kl}_{mj}\hat{v}^{ej}_{kl} - 2\Lambda^{eb}_{ij}\left(\hat{v}^{cd}_{mb}T^{ij}_{cd}\right) - D^e_d\hat{f}^d_m + D^k_m\hat{f}^e_k - 2D^{el}_{id}\hat{v}^{id}_{ml} + 2D^{al}_{md}\hat{v}^{ed}_{al} \\ &+ 2\bar{D}^{ek}_{ic}\hat{v}^{ic}_{km} - 2\bar{D}^{ak}_{mc}\hat{v}^{ec}_{ka} - \Lambda^e_i\hat{f}^i_m + \Lambda^a_m\hat{f}^e_a - \Lambda^e_i x^i_m - \Lambda^a_m x^e_a. \end{aligned} \tag{5.12}$$

$$\begin{aligned} \frac{\partial\mathcal{L}}{\partial T^{mn}_{ef}} &= \tilde{v}^{ef}_{mn} + \Lambda^{ef}_{ij}\left(\hat{v}^{ij}_{mn} + v^{cd}_{mn}T^{ij}_{cd}\right) + D^{kl}_{mn}v^{ef}_{kl} + K^{rs}_{mn}\delta^e_r\delta^f_s \\ &+ \mathcal{S}\left(ef,mn\right)\left\{\Lambda^{af}_{mn}\left(\hat{f}^e_a - 2\times\frac{1}{2}x^e_a\right) - \Lambda^{ef}_{in}\left(\hat{f}^i_m + 2\times\frac{1}{2}x^i_m\right)\right. \\ &+ \mathcal{T}(mn)\left[2\times\frac{1}{4}v^{ef}_{kn}D^k_m - 2\times\frac{1}{4}v^{cf}_{mn}D^e_c + \Lambda^{af}_{in}\left(\hat{v}^{ie}_{am} + v^{ce}_{km}\tilde{T}^{ik}_{ac}\right)\right. \\ &\left.\left.+\frac{1}{2}\left(\Lambda^e_m\hat{f}^f_n + \Lambda^a_n\hat{v}^{fe}_{am} - \Lambda^f_i\hat{v}^{ie}_{nm}\right)\right] \right. \\ &\left. -\Lambda^{af}_{in}\hat{v}^{ie}_{ma} - \Lambda^{eb}_{in}\hat{v}^{if}_{mb} - D^{fl}_{nc}v^{ce}_{ml} + \bar{D}^{ek}_{nd}v^{fd}_{km}\right\}. \end{aligned} \tag{5.13}$$

5.3 Perturbative triples for closed-shell CCSD

The perturbative triples equations for CCSD are given by

$$\begin{aligned} E_{[T]} &= \sum_{i\le j\le k} p(i,j,k)K^{abc}_{ijk}X^{ijk}_{abc} \\ p(i,j,k) &= \begin{cases} 2 & i\neq j\neq k \\ 1 & i = j\oplus j = k \\ 0 & i = j = k \end{cases} \end{aligned} \tag{5.14}$$

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

$$\begin{aligned} K^{abc}_{ijk} = K^{ijk}_{abc} &= v^{dk}_{bc}T^{ij}_{ad} + v^{dk}_{ac}T^{ij}_{db} + v^{dj}_{cb}T^{ik}_{ad} + v^{dj}_{ab}T^{ik}_{dc} + v^{di}_{ca}T^{jk}_{bd} + v^{di}_{ba}T^{jk}_{dc} \\ &- v^{jk}_{lc}T^{li}_{ba} - v^{ik}_{lc}T^{lj}_{ab} - v^{kj}_{lb}T^{li}_{ca} - v^{ij}_{lb}T^{lk}_{ac} - v^{ki}_{la}T^{lj}_{cb} - v^{ji}_{la}T^{lk}_{bc} \\ X^{ijk}_{abc} &= \frac{4K^{ijk}_{abc} - 2K^{ijk}_{acb} - 2K^{ijk}_{cba} - 2K^{ijk}_{bac} + K^{ijk}_{cab} + K^{ijk}_{bca}}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c} \end{aligned} \tag{5.15}$$

The (T) correction contains additionally the following terms,

$$\begin{aligned} E_{(T)} = E_{[T]} + \sum_{i\le j\le k} p(i,j,k)\left[v^{bc}_{jk}X^{ijk}_{abc}T^{\dagger a}_i + v^{ac}_{ik}X^{ijk}_{abc}T^{\dagger b}_j + v^{ab}_{ij}X^{ijk}_{abc}T^{\dagger c}_k\right. \\ \left. + T^{\dagger bc}_{jk}X^{ijk}_{abc}f^a_i + T^{\dagger ac}_{ik}X^{ijk}_{abc}f^b_j + T^{\dagger ab}_{ij}X^{ijk}_{abc}f^c_k\right]. \end{aligned} \tag{5.16}$$

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

$$\begin{aligned} K^{abc}_{ijk} = {} & v^{bc}_{dk}\bar{\Lambda}^{ad}_{ij} + v^{ac}_{dk}\bar{\Lambda}^{db}_{ij} + v^{cb}_{dj}\bar{\Lambda}^{ad}_{ik} + v^{ab}_{dj}\bar{\Lambda}^{dc}_{ik} + v^{ca}_{di}\bar{\Lambda}^{bd}_{jk} + v^{ba}_{di}\bar{\Lambda}^{dc}_{jk} \\ & - v^{lc}_{jk}\bar{\Lambda}^{ba}_{li} - v^{lc}_{ik}\bar{\Lambda}^{ab}_{lj} - v^{lb}_{kj}\bar{\Lambda}^{ca}_{li} - v^{lb}_{ij}\bar{\Lambda}^{ac}_{lk} - v^{la}_{ki}\bar{\Lambda}^{cb}_{lj} - v^{la}_{ji}\bar{\Lambda}^{bc}_{lk}, \end{aligned} \tag{5.17}$$

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

$$\bar{\Lambda}^{ab}_{ij} = \frac{2}{3}\Lambda^{ab}_{ij} + \frac{1}{3}\Lambda^{ba}_{ij}. \tag{5.18}$$

Additionally, the conjugate-transposed amplitudes in Eq. (5.16) are replaced by the covariant Lagrange multipliers $\bar{\Lambda}^{ab}_{ij}$ and $\bar{\Lambda}^{a}_{i} = \frac{1}{2}\Lambda^{a}_{i}$.

5.4 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. 5.1. The open-shell CCSD and DCSD Lagrangian – i.e., spin dependent – is given by

$$\mathcal{L} = \mathcal{L}_\alpha + \mathcal{L}_\beta + \mathcal{L}_{\alpha\beta}, \tag{5.19}$$

$$\begin{aligned} \mathcal{L}_\alpha = {} & \frac{1}{2}\left[v^{cd}_{kl}T^{kl}_{cd} + \left(\hat{f}^c_k + f^c_k\right)T^k_c\right] + \frac{1}{4}\Lambda^{ab}_{ij}\left(\hat{v}^{ij}_{ab} - \hat{v}^{ji}_{ab}\right) + \frac{1}{4}\Lambda^{ab}_{ij}\left(\hat{v}^{ij}_{kl} + \frac{1}{2}v^{cd}_{kl}T^{ij}_{cd}\right)T^{kl}_{ab} \\ & + \frac{1}{4}\Lambda^{ab}_{ij}\hat{v}^{cd}_{ab}T^{ij}_{cd} + \frac{1}{4}\Lambda^{ab}_{ij}\mathcal{S}\left(ab,ij\right)\left\{\hat{x}^c_a T^{ij}_{cb} - \hat{x}^i_k T^{kj}_{ab}\right\} \\ & + \frac{1}{4}\Lambda^{ab}_{ij}\mathcal{A}\left(ab;ij\right)\left\{\left(\hat{v}^{id}_{al} - \hat{v}^{di}_{al} + \bar{x}^{id}_{al}\right)T^{lj}_{db} + \left(\hat{v}^{i\bar{d}}_{a\bar{l}} + x^{i\bar{d}}_{a\bar{l}}\right)T^{j\bar{l}}_{b\bar{d}}\right\} \\ & + \Lambda^a_i\hat{v}^{cd}_{al}T^{il}_{cd} + \Lambda^a_i\hat{v}^{c\bar{d}}_{a\bar{l}}T^{i\bar{l}}_{c\bar{d}} - \Lambda^a_i\hat{v}^{ic}_{jk}T^{jk}_{ac} - \Lambda^a_i\hat{v}^{i\bar{c}}_{j\bar{k}}T^{j\bar{k}}_{a\bar{c}} \\ & + \Lambda^a_i\hat{f}^i_a + \Lambda^a_i\hat{f}^b_j T^{ij}_{ab} + \Lambda^a_i\hat{f}^{\bar{b}}_{\bar{j}}T^{i\bar{j}}_{a\bar{b}}, \end{aligned} \tag{5.20}$$

or using the cckext factorization,

$$\begin{aligned} \mathcal{L}_\alpha = {} & \frac{1}{2}\left[v^{cd}_{kl}T^{kl}_{cd} + \left(\hat{f}^c_k + f^c_k\right)T^k_c\right] + \frac{1}{4}\Lambda^{ab}_{ij}\left(\hat{v}^{ij}_{kl} + \frac{1}{2}v^{cd}_{kl}T^{ij}_{cd}\right)T^{kl}_{ab} \\ & + \frac{1}{4}\Lambda^{ab}_{ij}K^{ij}_{pq}\left(\delta^p_a - \delta^p_k T^k_a\right)\left(\delta^q_b - \delta^q_l T^l_b\right) + \frac{1}{4}\Lambda^{ab}_{ij}\mathcal{S}\left(ab,ij\right)\left\{\hat{x}^c_a T^{ij}_{cb} - \hat{x}^i_k T^{kj}_{ab}\right\} \\ & + \frac{1}{4}\Lambda^{ab}_{ij}\mathcal{A}\left(ab;ij\right)\left\{\left(\hat{v}^{id}_{al} - \hat{v}^{di}_{al} + \bar{x}^{id}_{al}\right)T^{lj}_{db} + \left(\hat{v}^{i\bar{d}}_{a\bar{l}} + x^{i\bar{d}}_{a\bar{l}}\right)T^{j\bar{l}}_{b\bar{d}}\right\} \\ & + \Lambda^a_i\left(K^{ij}_{pq}\delta^q_j + K^{i\bar{j}}_{pq}\delta^{\bar{q}}_{\bar{j}}\right)\left(\delta^p_a - \delta^p_k T^k_a\right) - \Lambda^a_i\hat{v}^{ic}_{jk}T^{jk}_{ac} - \Lambda^a_i\hat{v}^{i\bar{c}}_{j\bar{k}}T^{j\bar{k}}_{a\bar{c}} \\ & + \Lambda^a_i\hat{h}^i_a + \Lambda^a_i\hat{f}^b_j T^{ij}_{ab} + \Lambda^a_i\hat{f}^{\bar{b}}_{\bar{j}}T^{i\bar{j}}_{a\bar{b}}; \end{aligned} \tag{5.21}$$

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

$$\begin{aligned} \mathcal{L}_{\alpha\beta} = {} & v^{c\bar{d}}_{k\bar{l}}T^{k\bar{l}}_{c\bar{d}} + \Lambda^{a\bar{b}}_{i\bar{j}}\hat{v}^{i\bar{j}}_{ab} + \Lambda^{a\bar{b}}_{i\bar{j}}\left(\hat{v}^{i\bar{j}}_{k\bar{l}} + v^{c\bar{d}}_{k\bar{l}}T^{i\bar{j}}_{c\bar{d}}\right)T^{k\bar{l}}_{a\bar{b}} + \Lambda^{a\bar{b}}_{i\bar{j}}\hat{v}^{c\bar{d}}_{a\bar{b}}T^{i\bar{j}}_{c\bar{d}} \\ & + \Lambda^{a\bar{b}}_{i\bar{j}}\left\{\hat{x}^c_a T^{i\bar{j}}_{c\bar{b}} + \hat{x}^{\bar{d}}_{\bar{b}}T^{i\bar{j}}_{a\bar{d}} - \hat{x}^i_k T^{kj}_{ab} - \hat{x}^{\bar{j}}_{\bar{l}}T^{i\bar{l}}_{a\bar{b}}\right\} \\ & + \Lambda^{a\bar{b}}_{i\bar{j}}\left\{\left(\hat{v}^{id}_{al} - \hat{v}^{di}_{al} + x^{id}_{al} + \bar{x}^{id}_{al}\right)T^{l\bar{j}}_{d\bar{b}} + \left(\hat{v}^{\bar{j}\bar{d}}_{\bar{b}\bar{l}} - \hat{v}^{\bar{d}\bar{j}}_{\bar{b}\bar{l}} + 2x^{\bar{j}\bar{d}}_{\bar{b}\bar{l}}\right)T^{i\bar{l}}_{a\bar{d}}\right. \\ & \left. + \left(\hat{v}^{i\bar{d}}_{a\bar{l}} + v^{c\bar{d}}_{k\bar{l}}T^{ik}_{ac}\right)T^{\bar{l}\bar{j}}_{\bar{d}\bar{b}} + \hat{v}^{d\bar{j}}_{l\bar{b}}T^{il}_{ad} - \hat{v}^{c\bar{j}}_{a\bar{k}}T^{i\bar{k}}_{c\bar{b}} - \left(\hat{v}^{i\bar{d}}_{k\bar{b}} - v^{c\bar{d}}_{k\bar{l}}T^{i\bar{l}}_{c\bar{b}}\right)T^{k\bar{j}}_{a\bar{d}}\right\}, \end{aligned} \tag{5.22}$$

or using the cckext factorization,

$$\begin{aligned}\mathcal{L}_{\alpha\beta} = {} & v^{c\bar{d}}_{k\bar{l}} T^{k\bar{l}}_{c\bar{d}} + \Lambda^{a\bar{b}}_{i\bar{j}} \left(\hat{v}^{i\bar{j}}_{k\bar{l}} + v^{c\bar{d}}_{k\bar{l}} T^{i\bar{j}}_{c\bar{d}} \right) T^{k\bar{l}}_{a\bar{b}} + \Lambda^{a\bar{b}}_{i\bar{j}} K^{i\bar{j}}_{p\bar{q}} \left(\delta^p_a - \delta^p_k T^k_a \right) \left(\delta^{\bar{q}}_{\bar{b}} - \delta^{\bar{q}}_{\bar{l}} T^{\bar{l}}_{\bar{b}} \right) \\ & + \Lambda^{a\bar{b}}_{i\bar{j}} \left\{ \hat{x}^c_a T^{i\bar{j}}_{c\bar{b}} + \hat{x}^{\bar{d}}_{\bar{b}} T^{i\bar{j}}_{a\bar{d}} - \hat{x}^i_k T^{k\bar{j}}_{a\bar{b}} - \hat{x}^{\bar{j}}_{\bar{l}} T^{i\bar{l}}_{a\bar{b}} \right\} \\ & + \Lambda^{a\bar{b}}_{i\bar{j}} \left\{ \left(\hat{v}^{id}_{al} - \hat{v}^{di}_{al} + x^{id}_{al} + \bar{x}^{id}_{al} \right) T^{l\bar{j}}_{d\bar{b}} + \left(\hat{v}^{\bar{j}\bar{d}}_{\bar{b}\bar{l}} - \hat{v}^{\bar{d}\bar{j}}_{\bar{b}\bar{l}} + 2 x^{\bar{j}\bar{d}}_{\bar{b}\bar{l}} \right) T^{i\bar{l}}_{a\bar{d}} \right. \\ & \left. + \left(\hat{v}^{i\bar{d}}_{a\bar{l}} + v^{c\bar{d}}_{k\bar{l}} T^{ik}_{ac} \right) T^{\bar{l}\bar{j}}_{\bar{d}\bar{b}} + \hat{v}^{\bar{d}\bar{j}}_{l\bar{b}} T^{il}_{ad} - \hat{v}^{c\bar{j}}_{a\bar{k}} T^{i\bar{k}}_{c\bar{b}} - \left(\hat{v}^{i\bar{d}}_{k\bar{b}} - v^{c\bar{d}}_{k\bar{l}} T^{i\bar{l}}_{c\bar{b}} \right) T^{k\bar{j}}_{a\bar{d}} \right\}.\end{aligned} \tag{5.23}$$

The intermediate quantities are defined as follows,

$$\begin{aligned} K^{ij}_{pq} &= v^{rs}_{pq} D^{ij}_{rs} \qquad\qquad K^{i\bar{j}}_{p\bar{q}} = v^{r\bar{s}}_{p\bar{q}} D^{i\bar{j}}_{r\bar{s}} \\ D^{ij}_{rs} &= \left(T^{ij}_{ab} + T^i_a T^j_b - T^i_b T^j_a \right) \delta^a_r \delta^b_s + \mathcal{A}\left(ij;rs\right) \delta^i_r T^j_b \delta^b_s + \delta^i_r \delta^j_s - \delta^i_s \delta^j_r \\ D^{i\bar{j}}_{r\bar{s}} &= \left(T^{i\bar{j}}_{a\bar{b}} + T^i_a T^{\bar{j}}_{\bar{b}} \right) \delta^a_r \delta^{\bar{b}}_{\bar{s}} + \delta^i_r T^{\bar{j}}_{\bar{b}} \delta^{\bar{b}}_{\bar{s}} + T^i_a \delta^a_s \delta^{\bar{j}}_{\bar{s}} + \delta^i_r \delta^{\bar{j}}_{\bar{s}} \\ x^{id}_{al} &= \frac{1}{2} T^{ik}_{ac} \left(v^{cd}_{kl} - v^{dc}_{kl} \right) \\ \bar{x}^{id}_{al} &= x^{id}_{al} + T^{i\bar{k}}_{a\bar{c}} v^{d\bar{c}}_{l\bar{k}} \\ x^{i\bar{d}}_{al} &= \frac{1}{2} T^{i\bar{k}}_{a\bar{c}} \left(v^{c\bar{d}}_{k\bar{l}} - v^{\bar{d}\bar{c}}_{k\bar{l}} \right) \\ \hat{x}^i_k &= \hat{f}^i_k + 2\times \frac{1}{2} \left(v^{cd}_{kl} T^{il}_{cd} + v^{c\bar{d}}_{k\bar{l}} T^{i\bar{l}}_{c\bar{d}} \right) \\ \hat{x}^c_a &= \hat{f}^c_a - 2\times \frac{1}{2} \left(v^{cd}_{kl} T^{kl}_{ad} + v^{c\bar{d}}_{k\bar{l}} T^{k\bar{l}}_{a\bar{d}} \right) \end{aligned} \tag{5.24}$$

5.4.1 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. [9, 10]

In this section we use the following notation:

$$\begin{aligned} {}^{\alpha\alpha}T^{ij}_{ab} &= T^{ij}_{ab}, \\ {}^{\beta\beta}T^{ij}_{ab} &= T^{\bar{i}\bar{j}}_{\bar{a}\bar{b}}, \\ {}^{\alpha\beta}T^{ij}_{ab} &= T^{i\bar{j}}_{a\bar{b}}, \end{aligned} \tag{5.25}$$

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

$${}^{\alpha\beta}\bar{T}^{ij}_{ab} = \frac{1}{6}\left({}^{\alpha\alpha}T^{ij}_{ab} + {}^{\beta\beta}T^{ij}_{ab} + 2\,{}^{\alpha\beta}T^{ij}_{ab} + {}^{\alpha\beta}T^{ij}_{ba} + 2\,{}^{\alpha\beta}T^{ji}_{ba} + {}^{\alpha\beta}T^{ji}_{ab} \right) \tag{5.26}$$

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

$$\begin{aligned} {}^{\alpha\beta}\bar{T}^{ij}_{at} &= \frac{1}{3}\left({}^{\beta\beta}T^{ij}_{at} + 2\,{}^{\alpha\beta}T^{ij}_{at} + {}^{\alpha\beta}T^{ji}_{at} \right) \\ {}^{\alpha\beta}\bar{T}^{tj}_{ab} &= \frac{1}{3}\left({}^{\alpha\alpha}T^{tj}_{ab} + 2\,{}^{\alpha\beta}T^{tj}_{ab} + {}^{\alpha\beta}T^{tj}_{ba} \right) \\ {}^{\alpha\beta}\bar{T}^{tj}_{au} &= {}^{\alpha\beta}T^{tj}_{au} + \frac{\delta^t_u}{2m_s+2}\left({}^{\beta}T^j_a - {}^{\alpha}T^j_a - {}^{\alpha\beta}T^{vj}_{av} \right) \end{aligned} \tag{5.27}$$

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

$$\begin{aligned}
{}^{\alpha}\bar{T}^{i}_{a} &= \frac{1}{2}\left({}^{\alpha}T^{i}_{a} + {}^{\beta}T^{i}_{a} - {}^{\alpha\beta}\bar{T}^{vi}_{av}\right), \\
{}^{\beta}\bar{T}^{i}_{a} &= \frac{1}{2}\left({}^{\alpha}T^{i}_{a} + {}^{\beta}T^{i}_{a} + {}^{\alpha\beta}\bar{T}^{vi}_{av}\right), \\
{}^{\alpha}\bar{T}^{t}_{a} &= {}^{\alpha}T^{t}_{a} \qquad \text{and} \qquad {}^{\beta}\bar{T}^{i}_{t} = {}^{\beta}T^{i}_{t}.
\end{aligned} \tag{5.28}$$

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

$$\begin{aligned}
{}^{\sigma\sigma}\bar{T}^{ij}_{ab} &= {}^{\alpha\beta}\bar{T}^{ij}_{ab} - {}^{\alpha\beta}\bar{T}^{ij}_{ba}, \\
{}^{\alpha\alpha}\bar{T}^{tj}_{ab} &= {}^{\alpha\alpha}\bar{T}^{jt}_{ba} = {}^{\alpha\beta}\bar{T}^{tj}_{ab} - {}^{\alpha\beta}\bar{T}^{tj}_{ba}, \\
{}^{\beta\beta}\bar{T}^{ij}_{at} &= {}^{\beta\beta}\bar{T}^{ji}_{ta} = {}^{\alpha\beta}\bar{T}^{ij}_{at} - {}^{\alpha\beta}\bar{T}^{ji}_{at}, \\
{}^{\alpha\alpha}\bar{T}^{tu}_{ab} &= {}^{\alpha\alpha}T^{tu}_{ab} \qquad \text{and} \qquad {}^{\beta\beta}\bar{T}^{ij}_{tu} = {}^{\beta\beta}T^{ij}_{tu}.
\end{aligned} \tag{5.29}$$

5.5 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.

$$\begin{aligned}
\frac{\partial \mathcal{L}_{\alpha}}{\partial T^{m}_{e}} &= \left(v^{ce}_{km} - v^{ec}_{km}\right) T^{k}_{c} + \frac{1}{2} v^{e\bar{c}}_{m\bar{k}} T^{\bar{k}}_{\bar{c}} + f^{e}_{m} - \Lambda^{eb}_{ij}\hat{v}^{ij}_{mb} + \Lambda^{ab}_{mj}\hat{v}^{ej}_{ab} + \frac{1}{4}\Lambda^{ab}_{mj}\hat{v}^{ej}_{kl}T^{kl}_{ab} \\
&+ \frac{1}{4}\Lambda^{ab}_{im}\hat{v}^{ie}_{kl}T^{kl}_{ab} - \frac{1}{4}\Lambda^{eb}_{ij}\hat{v}^{cd}_{mb}T^{ij}_{cd} - \frac{1}{4}\Lambda^{ae}_{ij}\hat{v}^{cd}_{am}T^{ij}_{cd} - \frac{1}{2}\Lambda^{eb}_{ij}\hat{f}^{c}_{m}T^{ij}_{cb} - \frac{1}{2}\Lambda^{ab}_{mj}\hat{f}^{e}_{k}T^{kj}_{ab} \\
&+ \frac{1}{2}\Lambda^{ab}_{ij}\left\{\left(\hat{v}^{ce}_{am} - \hat{v}^{ec}_{am}\right)T^{ij}_{cb} - \left(\hat{v}^{ie}_{km} - \hat{v}^{ie}_{mk}\right)T^{kj}_{ab}\right\} \\
&- \Lambda^{eb}_{ij}\hat{v}^{id}_{ml}T^{lj}_{db} + \Lambda^{ab}_{mj}\hat{v}^{ed}_{al}T^{lj}_{db} + \Lambda^{eb}_{ij}\hat{v}^{di}_{ml}T^{lj}_{db} \\
&- \Lambda^{ab}_{mj}\hat{v}^{de}_{al}T^{lj}_{db} - \Lambda^{eb}_{ij}\hat{v}^{i\bar{d}}_{m\bar{l}}T^{j\bar{l}}_{b\bar{d}} + \Lambda^{ab}_{mj}\hat{v}^{e\bar{d}}_{a\bar{l}}T^{j\bar{l}}_{b\bar{d}} \\
&- \Lambda^{e}_{i}v^{cd}_{ml}T^{il}_{cd} - \Lambda^{e}_{i}v^{c\bar{d}}_{m\bar{l}}T^{i\bar{l}}_{c\bar{d}} - \Lambda^{a}_{m}\hat{v}^{ec}_{jk}T^{jk}_{ac} - \Lambda^{a}_{m}\hat{v}^{e\bar{c}}_{j\bar{k}}T^{j\bar{k}}_{a\bar{c}} \\
&- \Lambda^{e}_{i}\hat{f}^{i}_{m} + \Lambda^{a}_{m}\hat{f}^{e}_{a} + \Lambda^{a}_{i}\left(\hat{v}^{ie}_{am} - \hat{v}^{ei}_{am}\right) + \Lambda^{a}_{i}\left(v^{be}_{jm} - v^{eb}_{jm}\right)T^{ij}_{ab} + \Lambda^{a}_{i}v^{e\bar{b}}_{m\bar{j}}T^{i\bar{j}}_{a\bar{b}}
\end{aligned} \tag{5.30}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}_{\beta}}{\partial T^{m}_{e}} &= \frac{1}{2} v^{e\bar{c}}_{m\bar{k}} T^{\bar{k}}_{\bar{c}} + \frac{1}{2}\Lambda^{\bar{a}\bar{b}}_{\bar{i}\bar{j}}\left\{\hat{v}^{e\bar{c}}_{m\bar{a}}T^{\bar{i}\bar{j}}_{\bar{c}\bar{b}} - \hat{v}^{e\bar{i}}_{m\bar{k}}T^{\bar{k}\bar{j}}_{\bar{a}\bar{b}}\right\} \\
&+ \Lambda^{\bar{a}}_{\bar{i}}\hat{v}^{e\bar{i}}_{m\bar{a}} + \Lambda^{\bar{a}}_{\bar{i}}v^{e\bar{b}}_{m\bar{j}}T^{\bar{i}\bar{j}}_{\bar{a}\bar{b}} + \Lambda^{\bar{a}}_{\bar{i}}\left(v^{eb}_{mj} - v^{be}_{mj}\right)T^{j\bar{i}}_{b\bar{a}},
\end{aligned} \tag{5.31}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}_{\alpha\beta}}{\partial T^{m}_{e}} &= -\Lambda^{e\bar{b}}_{i\bar{j}}\hat{v}^{i\bar{j}}_{m\bar{b}} + \Lambda^{a\bar{b}}_{m\bar{j}}\hat{v}^{e\bar{j}}_{a\bar{b}} + \Lambda^{a\bar{b}}_{m\bar{j}}\hat{v}^{e\bar{j}}_{k\bar{l}}T^{k\bar{l}}_{a\bar{b}} - \Lambda^{e\bar{b}}_{i\bar{j}}\hat{v}^{c\bar{d}}_{m\bar{b}}T^{i\bar{j}}_{c\bar{d}} \\
&- \Lambda^{e\bar{b}}_{i\bar{j}}\hat{f}^{c}_{m}T^{i\bar{j}}_{c\bar{b}} - \Lambda^{a\bar{b}}_{m\bar{j}}\hat{f}^{e}_{k}T^{k\bar{j}}_{a\bar{b}} \\
&+ \Lambda^{a\bar{b}}_{i\bar{j}}\left\{\left(\hat{v}^{ce}_{am} - \hat{v}^{ec}_{am}\right)T^{i\bar{j}}_{c\bar{b}} + \hat{v}^{e\bar{d}}_{m\bar{b}}T^{i\bar{j}}_{a\bar{d}} - \left(\hat{v}^{ie}_{km} - \hat{v}^{ie}_{mk}\right)T^{k\bar{j}}_{a\bar{b}} - \hat{v}^{e\bar{j}}_{m\bar{l}}T^{i\bar{l}}_{a\bar{b}}\right\} \\
&- \Lambda^{e\bar{b}}_{i\bar{j}}\hat{v}^{id}_{ml}T^{l\bar{j}}_{d\bar{b}} + \Lambda^{a\bar{b}}_{m\bar{j}}\hat{v}^{ed}_{al}T^{l\bar{j}}_{d\bar{b}} + \Lambda^{e\bar{b}}_{i\bar{j}}\hat{v}^{di}_{ml}T^{l\bar{j}}_{d\bar{b}} - \Lambda^{a\bar{b}}_{m\bar{j}}\hat{v}^{de}_{al}T^{l\bar{j}}_{d\bar{b}} \\
&- \Lambda^{e\bar{b}}_{i\bar{j}}\hat{v}^{i\bar{d}}_{ml}T^{\bar{l}\bar{j}}_{d\bar{b}} + \Lambda^{a\bar{b}}_{m\bar{j}}\hat{v}^{e\bar{d}}_{a\bar{l}}T^{\bar{l}\bar{j}}_{d\bar{b}} + \Lambda^{e\bar{b}}_{i\bar{j}}\hat{v}^{c\bar{j}}_{m\bar{k}}T^{i\bar{k}}_{c\bar{b}} - \Lambda^{a\bar{b}}_{m\bar{j}}\hat{v}^{e\bar{d}}_{k\bar{b}}T^{k\bar{j}}_{a\bar{d}},
\end{aligned} \tag{5.32}$$

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

$$\begin{aligned}
4\frac{\partial \mathcal{L}_\alpha}{\partial T^{mn}_{ef}} &= \mathcal{A}(ef;mn)\left[\frac{1}{2}v^{ef}_{mn} + \frac{1}{4}\Lambda^{ef}_{ij}\left(\hat{v}^{ij}_{mn} + \frac{1}{2}v^{cd}_{mn}T^{ij}_{cd}\right) + \frac{1}{8}\Lambda^{ab}_{mn}v^{ef}_{kl}T^{kl}_{ab}\right.\\
&+ \frac{1}{4}\Lambda^{ab}_{mn}\hat{v}^{ef}_{ab} + \frac{1}{2}\Lambda^{af}_{mn}\hat{x}^{e}_{a} - \frac{1}{2}\Lambda^{ef}_{in}\hat{x}^{i}_{m} - 2\times\frac{1}{4}\Lambda^{eb}_{ij}v^{cf}_{mn}T^{ij}_{cb} - 2\times\frac{1}{4}\Lambda^{ab}_{mj}v^{ef}_{kn}T^{kj}_{ab}\\
&+ \Lambda^{af}_{in}\left(\hat{v}^{ie}_{am} - \hat{v}^{ei}_{am} + \bar{x}^{ie}_{am}\right) + \frac{1}{2}\Lambda^{eb}_{mj}\left(v^{fd}_{nl} - v^{df}_{nl}\right)T^{lj}_{db}\\
&\left.+\Lambda^{a}_{m}\hat{v}^{ef}_{an} - \Lambda^{e}_{i}\hat{v}^{if}_{mn} + \Lambda^{e}_{m}\hat{f}^{f}_{n}\right],
\end{aligned} \tag{5.33}$$

$$\frac{\partial \mathcal{L}_\beta}{\partial T^{mn}_{ef}} = 0, \tag{5.34}$$

$$\begin{aligned}
4\frac{\partial \mathcal{L}_{\alpha\beta}}{\partial T^{mn}_{ef}} &= \mathcal{A}(ef;mn)\left[-2\times\frac{1}{2}\Lambda^{e\bar{b}}_{i\bar{j}}v^{cf}_{mn}T^{i\bar{j}}_{c\bar{b}} - 2\times\frac{1}{2}\Lambda^{a\bar{b}}_{m\bar{j}}v^{ef}_{kn}T^{k\bar{j}}_{a\bar{b}}\right.\\
&\left.+\Lambda^{e\bar{b}}_{m\bar{j}}\left(v^{fd}_{nl} - v^{df}_{nl}\right)T^{l\bar{j}}_{d\bar{b}} + \Lambda^{e\bar{b}}_{m\bar{j}}v^{f\bar{d}}_{nl}T^{\bar{l}\bar{j}}_{\bar{d}\bar{b}} + \Lambda^{e\bar{b}}_{m\bar{j}}\hat{v}^{f\bar{j}}_{n\bar{b}}\right],
\end{aligned} \tag{5.35}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}_\alpha}{\partial T^{m\bar{n}}_{e\bar{f}}} &= -2\times\frac{1}{4}\Lambda^{eb}_{ij}v^{c\bar{f}}_{m\bar{n}}T^{ij}_{cb} - 2\times\frac{1}{4}\Lambda^{ab}_{mj}v^{e\bar{f}}_{k\bar{n}}T^{kj}_{ab}\\
&+ \Lambda^{eb}_{mj}v^{d\bar{f}}_{l\bar{n}}T^{lj}_{db} + \Lambda^{ae}_{im}\left(\hat{v}^{i\bar{f}}_{a\bar{n}} + x^{i\bar{f}}_{a\bar{n}}\right) + \frac{1}{2}\Lambda^{eb}_{mj}\left(v^{\bar{f}\bar{d}}_{\bar{n}\bar{l}} - v^{\bar{d}\bar{f}}_{\bar{n}\bar{l}}\right)T^{j\bar{l}}_{b\bar{d}}\\
&+ \Lambda^{a}_{m}\hat{v}^{e\bar{f}}_{a\bar{n}} - \Lambda^{e}_{i}\hat{v}^{i\bar{f}}_{m\bar{n}} + \Lambda^{e}_{m}\hat{f}^{\bar{f}}_{\bar{n}},
\end{aligned} \tag{5.36}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}_\beta}{\partial T^{m\bar{n}}_{e\bar{f}}} &= -2\times\frac{1}{4}\Lambda^{\bar{f}b}_{\bar{i}j}v^{e\bar{c}}_{m\bar{n}}T^{\bar{i}j}_{\bar{c}b} - 2\times\frac{1}{4}\Lambda^{\bar{a}\bar{b}}_{\bar{n}\bar{j}}v^{e\bar{f}}_{m\bar{k}}T^{\bar{k}\bar{j}}_{\bar{a}\bar{b}}\\
&+ \Lambda^{\bar{f}\bar{b}}_{\bar{n}\bar{j}}v^{e\bar{d}}_{m\bar{l}}T^{\bar{l}\bar{j}}_{\bar{d}\bar{b}} + \Lambda^{\bar{a}\bar{f}}_{\bar{i}\bar{n}}\left(\hat{v}^{e\bar{i}}_{m\bar{a}} + x^{\bar{i}e}_{\bar{a}m}\right) + \frac{1}{2}\Lambda^{\bar{f}\bar{b}}_{\bar{n}\bar{j}}\left(v^{ed}_{ml} - v^{de}_{ml}\right)T^{l\bar{j}}_{d\bar{b}}\\
&+ \Lambda^{\bar{a}}_{\bar{n}}\hat{v}^{\bar{f}e}_{\bar{a}m} - \Lambda^{\bar{f}}_{\bar{i}}\hat{v}^{\bar{i}e}_{\bar{n}m} + \Lambda^{\bar{f}}_{\bar{n}}\hat{f}^{e}_{m},
\end{aligned} \tag{5.37}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}_{\alpha\beta}}{\partial T^{m\bar{n}}_{e\bar{f}}} &= v^{e\bar{f}}_{m\bar{n}} + \Lambda^{e\bar{f}}_{i\bar{j}}\left(\hat{v}^{i\bar{j}}_{m\bar{n}} + v^{c\bar{d}}_{m\bar{n}}T^{i\bar{j}}_{c\bar{d}}\right) + \Lambda^{a\bar{b}}_{m\bar{n}}v^{e\bar{f}}_{k\bar{l}}T^{k\bar{l}}_{a\bar{b}} + \Lambda^{a\bar{b}}_{m\bar{n}}\hat{v}^{e\bar{f}}_{a\bar{b}}\\
&+ \Lambda^{a\bar{f}}_{m\bar{n}}\hat{x}^{e}_{a} - 2\times\frac{1}{2}\Lambda^{e\bar{b}}_{i\bar{j}}v^{c\bar{f}}_{m\bar{n}}T^{i\bar{j}}_{cb} + \Lambda^{e\bar{b}}_{m\bar{n}}\hat{x}^{\bar{f}}_{\bar{b}} - 2\times\frac{1}{2}\Lambda^{a\bar{f}}_{i\bar{j}}v^{e\bar{d}}_{m\bar{n}}T^{i\bar{j}}_{ad}\\
&- \Lambda^{e\bar{f}}_{i\bar{n}}\hat{x}^{i}_{m} - 2\times\frac{1}{2}\Lambda^{a\bar{b}}_{m\bar{j}}v^{e\bar{f}}_{k\bar{n}}T^{k\bar{j}}_{a\bar{b}} - \Lambda^{e\bar{f}}_{m\bar{j}}\hat{x}^{\bar{j}}_{\bar{n}} - 2\times\frac{1}{2}\Lambda^{a\bar{b}}_{i\bar{n}}v^{e\bar{f}}_{m\bar{l}}T^{i\bar{l}}_{a\bar{b}}\\
&+ \Lambda^{a\bar{f}}_{i\bar{n}}\left(\hat{v}^{ie}_{am} - \hat{v}^{ei}_{am} + x^{ie}_{am} + \bar{x}^{ie}_{am}\right) + \Lambda^{e\bar{b}}_{m\bar{j}}v^{d\bar{f}}_{l\bar{n}}T^{l\bar{j}}_{d\bar{b}} + \Lambda^{e\bar{b}}_{m\bar{j}}\left(\hat{v}^{\bar{j}\bar{f}}_{\bar{b}\bar{n}} - \hat{v}^{\bar{f}\bar{j}}_{\bar{b}\bar{n}} + 2x^{\bar{j}\bar{f}}_{\bar{b}\bar{n}}\right)\\
&- \Lambda^{a\bar{f}}_{m\bar{j}}\hat{v}^{e\bar{j}}_{a\bar{n}} - \Lambda^{e\bar{b}}_{i\bar{n}}\left(\hat{v}^{i\bar{f}}_{m\bar{b}} - v^{c\bar{f}}_{m\bar{l}}T^{i\bar{l}}_{c\bar{b}}\right) + \Lambda^{a\bar{f}}_{m\bar{j}}v^{e\bar{d}}_{k\bar{n}}T^{k\bar{j}}_{ad},
\end{aligned} \tag{5.38}$$

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

$$\begin{aligned}
D^{j}_{i} &= -\frac{1}{2}\Lambda^{cd}_{ik}T^{jk}_{cd} - \Lambda^{c\bar{d}}_{i\bar{k}}T^{j\bar{k}}_{c\bar{d}}\\
D^{b}_{a} &= \frac{1}{2}\Lambda^{bc}_{kl}T^{kl}_{ac} + \Lambda^{b\bar{c}}_{k\bar{l}}T^{k\bar{l}}_{a\bar{c}}\\
D^{a}_{i} &= \Lambda^{a}_{i}\\
D^{i}_{a} &= \Lambda^{c}_{k}T^{ik}_{ac} + \Lambda^{\bar{c}}_{\bar{k}}T^{i\bar{k}}_{a\bar{c}}
\end{aligned} \tag{5.39}$$

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

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

$$\begin{aligned}
\hat{D}_i^j &= D_i^j - D_i^c T_c^j, \\
\hat{D}_a^b &= D_a^b + D_k^b T_a^k, \\
\hat{D}_i^a &= D_i^a, \\
\hat{D}_a^i &= D_a^i + T_a^i - D_a^c T_c^i + \hat{D}_k^i T_a^k.
\end{aligned} \tag{5.40}$$

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

$$\begin{aligned}
D_{ij}^{kl} &= \frac{1}{2}\Lambda_{ij}^{cd} T_{cd}^{kl} \\
D_{i\bar{j}}^{k\bar{l}} &= \Lambda_{i\bar{j}}^{c\bar{d}} T_{c\bar{d}}^{k\bar{l}} \\
D_{ib}^{aj} &= \Lambda_{ik}^{ac} T_{bc}^{jk} + \Lambda_{i\bar{k}}^{a\bar{c}} T_{b\bar{c}}^{j\bar{k}} \\
\bar{D}_{i\bar{b}}^{a\bar{j}} &= \Lambda_{ik}^{ac} T_{c\bar{b}}^{k\bar{j}} + \Lambda_{i\bar{k}}^{a\bar{c}} T_{\bar{b}\bar{c}}^{\bar{j}\bar{k}}
\end{aligned} \tag{5.41}$$

and doubles-dressed Fock matrix,

$$\begin{aligned}
x_k^i &= v_{kl}^{cd} T_{cd}^{il} + v_{k\bar{l}}^{c\bar{d}} T_{c\bar{d}}^{i\bar{l}} \\
x_a^c &= v_{kl}^{cd} T_{ad}^{kl} + v_{k\bar{l}}^{c\bar{d}} T_{a\bar{d}}^{k\bar{l}}.
\end{aligned} \tag{5.42}$$

The intermediates for the cckext factorization are given by

$$\begin{aligned}
K_{mn}^{rs} &= \hat{\Lambda}_{mn}^{pq} v_{pq}^{rs} \\
\hat{\Lambda}_{mn}^{pq} &= \Lambda_{mn}^{ab} \delta_a^p \delta_b^q - \Lambda_{mn}^{ab} T_a^i \delta_i^p \delta_b^q - \Lambda_{mn}^{ab} \delta_a^p T_b^j \delta_j^q + \Lambda_{mn}^{ab} T_a^i T_b^j \delta_i^p \delta_j^q.
\end{aligned} \tag{5.43}$$

$K_{m\bar{n}}^{r\bar{s}}$ 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,

$$\begin{aligned}
\hat{y}_{am}^{ie} &= \hat{v}_{am}^{ie} - \hat{v}_{am}^{ei} + \bar{x}_{am}^{ie} + x_{am}^{ie} \\
\hat{y}_{\bar{b}n}^{\bar{j}f} &= v_{n\bar{l}}^{f\bar{d}} T_{d\bar{b}}^{\bar{l}\bar{j}} + \hat{v}_{n\bar{b}}^{f\bar{j}} + 2x_{\bar{b}n}^{\bar{j}f}
\end{aligned} \tag{5.44}$$

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

$$\begin{aligned}
\frac{\partial \mathcal{L}}{\partial T_e^m} &= \left(v_{pm}^{qe} - v_{pm}^{eq}\right) \hat{D}_q^p + v_{m\bar{p}}^{e\bar{q}} \hat{D}_{\bar{q}}^{\bar{p}} + f_m^e - \Lambda_{ij}^{eb} \hat{v}_{mb}^{ij} - \Lambda_{i\bar{j}}^{e\bar{b}} \hat{v}_{m\bar{b}}^{i\bar{j}} \\
&\quad + K_{mj}^{rs} \delta_r^e \left(\delta_s^j + \delta_s^b T_b^j\right) + K_{m\bar{j}}^{r\bar{s}} \delta_r^e \left(\delta_{\bar{s}}^{\bar{j}} + \delta_{\bar{s}}^{\bar{b}} T_{\bar{b}}^{\bar{j}}\right) + D_{mj}^{kl} \hat{v}_{kl}^{ej} + D_{m\bar{j}}^{k\bar{l}} \hat{v}_{k\bar{l}}^{e\bar{j}} \\
&\quad - \frac{1}{2}\Lambda_{ij}^{eb} \left(\hat{v}_{mb}^{cd} T_{cd}^{ij}\right) - \Lambda_{i\bar{j}}^{e\bar{b}} \left(\hat{v}_{m\bar{b}}^{c\bar{d}} T_{c\bar{d}}^{i\bar{j}}\right) - D_c^e \hat{f}_m^c + D_m^k \hat{f}_k^e \\
&\quad + D_{id}^{el} \left(\hat{v}_{ml}^{di} - \hat{v}_{lm}^{di}\right) + D_{md}^{al} \left(\hat{v}_{al}^{ed} - \hat{v}_{al}^{de}\right) - \bar{D}_{i\bar{d}}^{e\bar{l}} \hat{v}_{m\bar{l}}^{i\bar{d}} + \bar{D}_{m\bar{d}}^{a\bar{l}} \hat{v}_{a\bar{l}}^{e\bar{d}} \\
&\quad + \Lambda_{i\bar{j}}^{e\bar{b}} \hat{v}_{m\bar{k}}^{c\bar{j}} T_{c\bar{b}}^{i\bar{k}} - \Lambda_{m\bar{j}}^{a\bar{b}} \hat{v}_{k\bar{b}}^{e\bar{d}} T_{a\bar{d}}^{k\bar{j}} \\
&\quad - \Lambda_i^e \hat{f}_m^i + \Lambda_m^a \hat{f}_a^e - \Lambda_i^e x_m^i - \Lambda_m^a x_a^e
\end{aligned} \tag{5.45}$$

$$
\begin{aligned}
4\frac{\partial \mathcal{L}}{\partial T^{mn}_{ef}} &= v^{ef}_{mn} - v^{ef}_{nm} + \Lambda^{ef}_{ij}\left(\hat{v}^{ij}_{mn} + \frac{1}{2} v^{cd}_{mn} T^{ij}_{cd}\right) + D^{kl}_{mn} v^{ef}_{kl} + K^{rs}_{mn}\delta^e_r \delta^f_s \\
&+ \mathcal{S}\left(ef, mn\right)\left\{\Lambda^{af}_{mn}\hat{x}^e_a - \Lambda^{ef}_{in}\hat{x}^i_m\right\} \\
&+ \mathcal{A}\left(ef; mn\right)\left\{2\times\frac{1}{2} D^k_m v^{ef}_{kn} - 2\times\frac{1}{2} D^e_c v^{cf}_{mn} + \Lambda^{af}_{in}\hat{y}^{ie}_{am} + \Lambda^{e\bar{b}}_{m\bar{j}}\hat{y}^{\bar{j}f}_{\bar{b}n}\right. \\
&\left. + \Lambda^a_m \hat{v}^{ef}_{an} - \Lambda^e_i \hat{v}^{if}_{mn} + \Lambda^e_m \hat{f}^f_n\right\}
\end{aligned}
\tag{5.46}
$$

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

$$
\begin{aligned}
\frac{\partial \mathcal{L}}{\partial T^{m\bar{n}}_{e\bar{f}}} &= v^{e\bar{f}}_{m\bar{n}} + \Lambda^{e\bar{f}}_{i\bar{j}}\left(\hat{v}^{i\bar{j}}_{m\bar{n}} + v^{c\bar{d}}_{m\bar{n}} T^{i\bar{j}}_{c\bar{d}}\right) + D^{k\bar{l}}_{m\bar{n}} v^{e\bar{f}}_{k\bar{l}} + K^{r\bar{s}}_{m\bar{n}}\delta^e_r\delta^{\bar{f}}_{\bar{s}} \\
&+ \Lambda^{a\bar{f}}_{m\bar{n}}\hat{x}^e_a + \Lambda^{e\bar{b}}_{m\bar{n}}\hat{x}^{\bar{f}}_{\bar{b}} - \Lambda^{e\bar{f}}_{i\bar{n}}\hat{x}^i_m - \Lambda^{e\bar{f}}_{m\bar{j}}\hat{x}^{\bar{j}}_{\bar{n}} \\
&+ 2\times\frac{1}{2}\left(D^k_m v^{e\bar{f}}_{k\bar{n}} + D^{\bar{k}}_{\bar{n}} v^{e\bar{f}}_{m\bar{k}} - D^e_c v^{c\bar{f}}_{m\bar{n}} - D^{\bar{f}}_{\bar{c}} v^{e\bar{c}}_{m\bar{n}}\right) \\
&+ \Lambda^{a\bar{f}}_{i\bar{n}}\hat{y}^{ie}_{am} + \Lambda^{e\bar{b}}_{m\bar{j}}\hat{y}^{\bar{j}\bar{f}}_{\bar{b}\bar{n}} + \Lambda^{ae}_{im}\hat{y}^{i\bar{f}}_{a\bar{n}} + \Lambda^{\bar{a}\bar{f}}_{\bar{i}\bar{n}}\hat{y}^{\bar{i}e}_{\bar{a}m} \\
&- \Lambda^{a\bar{f}}_{m\bar{j}}\left(\hat{v}^{e\bar{j}}_{a\bar{n}} - v^{e\bar{d}}_{k\bar{n}} T^{k\bar{j}}_{a\bar{d}}\right) - \Lambda^{e\bar{b}}_{i\bar{n}}\left(\hat{v}^{i\bar{f}}_{m\bar{b}} - v^{c\bar{f}}_{m\bar{l}} T^{i\bar{l}}_{c\bar{b}}\right) \\
&+ \Lambda^a_m \hat{v}^{e\bar{f}}_{a\bar{n}} - \Lambda^e_i \hat{v}^{i\bar{f}}_{m\bar{n}} + \Lambda^e_m \hat{f}^{\bar{f}}_{\bar{n}} + \Lambda^{\bar{a}}_{\bar{n}}\hat{v}^{\bar{f}e}_{\bar{a}m} - \Lambda^{\bar{f}}_{\bar{i}}\hat{v}^{\bar{i}e}_{\bar{n}m} + \Lambda^{\bar{f}}_{\bar{n}}\hat{f}^e_m.
\end{aligned}
\tag{5.47}
$$

5.6 Perturbative triples for unrestricted CCSD

The perturbative triples equations for unrestricted CCSD are given by

$$
E_{[T]} = \frac{1}{6}\sum_{i<j<k} K^{abc}_{ijk} T^{ijk}_{abc} + \frac{1}{6}\sum_{\bar{i}<\bar{j}<\bar{k}} K^{\bar{a}\bar{b}\bar{c}}_{\bar{i}\bar{j}\bar{k}} T^{\bar{i}\bar{j}\bar{k}}_{\bar{a}\bar{b}\bar{c}} + \frac{1}{2}\sum_{i<j;\bar{k}} K^{ab\bar{c}}_{ij\bar{k}} X^{ij\bar{k}}_{ab\bar{c}} + \frac{1}{2}\sum_{\bar{i}<\bar{j};k} K^{\bar{a}\bar{b}c}_{\bar{i}\bar{j}k} X^{\bar{i}\bar{j}k}_{\bar{a}\bar{b}c}. \tag{5.48}
$$

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

$$
\begin{aligned}
K^{abc}_{ijk} &= K^{ijk}_{abc} = \mathcal{A}\left(abc\right)\left\{v^{dk}_{bc} T^{ij}_{ad} + v^{dj}_{cb} T^{ik}_{ad} + v^{di}_{ba} T^{jk}_{dc} - \frac{1}{2}\left(\bar{v}^{kj}_{cl} T^{il}_{ab} + \bar{v}^{ki}_{cl} T^{lj}_{ab} + \bar{v}^{ij}_{al} T^{kl}_{cb}\right)\right\}, \\
\bar{v}^{ij}_{al} &= v^{ij}_{al} - v^{ji}_{al}, \\
T^{ijk}_{abc} &= \frac{K^{ijk}_{abc}}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}
\end{aligned}
\tag{5.49}
$$

$K^{ab\bar{c}}_{ij\bar{k}}$ 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 $j = 2:n_\alpha$),

$$
\begin{aligned}
K^{ab\bar{c}}_{ij\bar{k}} &= K^{ij\bar{k}}_{ab\bar{c}} = \mathcal{A}\left(ab\right)\left\{v^{d\bar{k}}_{b\bar{c}} T^{ij}_{ad} + v^{di}_{ba} T^{j\bar{k}}_{d\bar{c}} + v^{dj}_{ab} T^{i\bar{k}}_{d\bar{c}} + v^{i\bar{d}}_{a\bar{c}} T^{j\bar{k}}_{b\bar{d}} + v^{j\bar{d}}_{b\bar{c}} T^{i\bar{k}}_{a\bar{d}} - \bar{v}^{ij}_{al} T^{l\bar{k}}_{b\bar{c}}\right. \\
&\left. - v^{j\bar{k}}_{b\bar{l}} T^{i\bar{l}}_{a\bar{c}} - v^{i\bar{k}}_{a\bar{l}} T^{j\bar{l}}_{b\bar{c}}\right\} - v^{j\bar{k}}_{l\bar{c}} T^{il}_{ab} - v^{i\bar{k}}_{l\bar{c}} T^{lj}_{ab}, \\
T^{ij\bar{k}}_{ab\bar{c}} &= \frac{K^{ij\bar{k}}_{ab\bar{c}}}{\epsilon_i + \epsilon_j + \epsilon_{\bar{k}} - \epsilon_a - \epsilon_b - \epsilon_{\bar{c}}}
\end{aligned}
\tag{5.50}
$$

The (T) correction contains additionally the following terms,

$$\begin{aligned} E_{(T)} = E_{[T]} + \sum_{i<j<k} \Big[& v_{jk}^{bc} T_{abc}^{ijk} T_i^{\dagger a} + v_{ik}^{ac} T_{abc}^{ijk} T_j^{\dagger b} + v_{ij}^{ab} T_{abc}^{ijk} T_k^{\dagger c} \\ & + \frac{1}{2} \left(T_{jk}^{\dagger bc} T_{abc}^{ijk} f_i^a + T_{ik}^{\dagger ac} T_{abc}^{ijk} f_j^b + T_{ij}^{\dagger ab} T_{abc}^{ijk} f_k^c \right) \Big] \\ & + \sum_{i<j;\bar{k}} \Big[v_{j\bar{k}}^{b\bar{c}} T_{ab\bar{c}}^{ij\bar{k}} T_i^{\dagger a} + v_{i\bar{k}}^{a\bar{c}} T_{ab\bar{c}}^{ij\bar{k}} T_j^{\dagger b} + v_{ij}^{ab} T_{ab\bar{c}}^{ij\bar{k}} T_{\bar{k}}^{\dagger \bar{c}} \\ & + T_{j\bar{k}}^{\dagger b\bar{c}} T_{ab\bar{c}}^{ij\bar{k}} f_i^a + T_{i\bar{k}}^{\dagger a\bar{c}} T_{ab\bar{c}}^{ij\bar{k}} f_j^b + \frac{1}{2} T_{ij}^{\dagger ab} T_{ab\bar{c}}^{ij\bar{k}} f_{\bar{k}}^{\bar{c}} \Big] \\ & + \text{spin-flipped terms.} \end{aligned} \tag{5.51}$$

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,

$$\begin{aligned} K_{ijk}^{abc} &= \mathcal{A}(abc) \left\{ v_{dk}^{bc} \Lambda_{ij}^{ad} + v_{dj}^{cb} \Lambda_{ik}^{ad} + v_{di}^{ba} \Lambda_{jk}^{dc} - \frac{1}{2} \left(\bar{v}_{kj}^{cl} \Lambda_{il}^{ab} + \bar{v}_{ki}^{cl} \Lambda_{lj}^{ab} + \bar{v}_{ij}^{al} \Lambda_{kl}^{cb} \right) \right\}, \\ K_{ij\bar{k}}^{ab\bar{c}} &= \mathcal{A}(ab) \Big\{ v_{d\bar{k}}^{b\bar{c}} \Lambda_{ij}^{ad} + v_{di}^{ba} \Lambda_{j\bar{k}}^{d\bar{c}} + v_{dj}^{ab} \Lambda_{i\bar{k}}^{d\bar{c}} + v_{i\bar{d}}^{a\bar{c}} \Lambda_{j\bar{k}}^{b\bar{d}} + v_{j\bar{d}}^{b\bar{c}} \Lambda_{i\bar{k}}^{a\bar{d}} - \bar{v}_{ij}^{al} \Lambda_{l\bar{k}}^{b\bar{c}} \\ &\quad - v_{j\bar{k}}^{b\bar{l}} \Lambda_{i\bar{l}}^{a\bar{c}} - v_{i\bar{k}}^{a\bar{l}} \Lambda_{j\bar{l}}^{b\bar{c}} \Big\} - v_{j\bar{k}}^{l\bar{c}} \Lambda_{il}^{ab} - v_{i\bar{k}}^{l\bar{c}} \Lambda_{lj}^{ab}, \end{aligned} \tag{5.52}$$

and the conjugate-transpose of the amplitudes in Eq. (5.51) are replaced with the Lagrange multipliers.

Chapter 6

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.[11]. 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.[11] are coloured magenta. Terms we have added to ensure proper antisymmetry and which are not explicitly listed in Ref.[11] are coloured green. IAS terms, which are terms including the all internal singles, are coloured brown.

$$\begin{aligned} R_a^i &= \langle {}^A\Phi_a^i | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle_C - \left(\langle {}^A\Phi_a^i | e^{\hat{T}_B} | {}^B\Phi \rangle \langle {}^B\Phi | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle \right)_C \\ &\equiv \langle {}^A\Phi_a^i | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle_C + M_a^i W = 0, \end{aligned} \tag{6.1}$$

$$\begin{aligned} R_{ab}^{ij} &= \langle {}^A\Phi_{ab}^{ij} | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle_C - \left(\langle {}^A\Phi_{ab}^{ij} | e^{\hat{T}_B} | {}^B\Phi \rangle \langle {}^B\Phi | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle \right)_C \\ &- \mathcal{A}(ij; ab) \left[\langle {}^A\Phi_a^i | e^{\hat{T}_A} | {}^A\Phi \rangle \left(\langle {}^A\Phi_b^j | e^{\hat{T}_B} | {}^B\Phi \rangle \langle {}^B\Phi | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle \right)_C \right. \\ &\left. - \hat{R}(ia) \langle {}^B\Phi_a^i | e^{\hat{T}_B} | {}^B\Phi \rangle \left(\langle {}^A\Phi_b^j | e^{\hat{T}_B} | {}^B\Phi \rangle \langle {}^B\Phi | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle \right)_C \right] \\ &\equiv \langle {}^A\Phi_{ab}^{ij} | \hat{H}_N e^{\hat{T}_A} | {}^A\Phi \rangle_C + M_{ab}^{ij} W = 0, \end{aligned} \tag{6.2}$$

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

$$\tau_a^i = T_a^i - T_{\bar{a}}^{\bar{i}}, \tag{6.3}$$

$$\tau_{\bar{a}}^{\bar{i}} = T_{\bar{a}}^{\bar{i}} - T_a^i, \tag{6.4}$$

$$\tau_{ab}^{ij} = T_{ab}^{ij} + T_a^i T_b^j. \tag{6.5}$$

The singles M tensor is built as follows,

$$M^i_u = T^{t\bar{i}}_{u\bar{t}}, \tag{6.6}$$
$$M^i_u = T^t_u T^{\bar{i}}_{\bar{t}}, \tag{6.7}$$
$$M^t_a = -T^{t\bar{u}}_{u\bar{a}}, \tag{6.8}$$
$$M^t_a = -T^t_u T^{\bar{u}}_{\bar{a}}, \tag{6.9}$$
$$M^i_a = T^{\bar{u}}_{\bar{a}} T^{t\bar{i}}_{u\bar{t}} + T^{\bar{i}}_{\bar{t}} T^{t\bar{u}}_{u\bar{a}}, \tag{6.10}$$
$$M^i_a = T^t_u T^{\bar{u}\bar{i}}_{\bar{a}\bar{t}}, \tag{6.11}$$
$$M^i_a = T^t_u T^{\bar{u}}_{\bar{a}} T^{\bar{i}}_{\bar{t}}, \tag{6.12}$$
$$M^t_u = T^t_u. \tag{6.13}$$

$$M^{\bar{i}}_{\bar{t}} = T^{i\bar{u}}_{u\bar{t}}, \tag{6.14}$$
$$M^{\bar{i}}_{\bar{t}} = T^{\bar{u}}_{\bar{t}} T^i_u, \tag{6.15}$$
$$M^{\bar{u}}_{\bar{a}} = -T^{t\bar{u}}_{a\bar{t}}, \tag{6.16}$$
$$M^{\bar{u}}_{\bar{a}} = -T^{\bar{u}}_{\bar{t}} T^t_a, \tag{6.17}$$
$$M^{\bar{i}}_{\bar{a}} = T^t_a T^{i\bar{u}}_{u\bar{t}} + T^i_u T^{t\bar{u}}_{a\bar{t}}, \tag{6.18}$$
$$M^{\bar{i}}_{\bar{a}} = T^{\bar{u}}_{\bar{t}} T^{ti}_{au}, \tag{6.19}$$
$$M^{\bar{i}}_{\bar{a}} = T^{\bar{u}}_{\bar{t}} T^t_a T^i_u, \tag{6.20}$$
$$M^{\bar{u}}_{\bar{t}} = T^{\bar{u}}_{\bar{t}}. \tag{6.21}$$

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

$$M^{ij}_{ua} = \mathcal{A}(ij)\,\tau^{i}_{a} T^{t\bar{j}}_{u\bar{t}} + \mathcal{A}(ij)\,T^{\bar{i}}_{\bar{t}} T^{t\bar{j}}_{u\bar{a}}, \tag{6.22}$$

$$M^{ij}_{ua} = T^{t}_{u} T^{\bar{i}\bar{j}}_{\bar{t}\bar{a}}, \tag{6.23}$$

$$M^{ij}_{au} = -\mathcal{A}(ij)\,\tau^{i}_{a} T^{t\bar{j}}_{u\bar{t}} - \mathcal{A}(ij)\,T^{\bar{i}}_{\bar{t}} T^{t\bar{j}}_{u\bar{a}}, \tag{6.24}$$

$$M^{ij}_{au} = -T^{t}_{u} T^{\bar{i}\bar{j}}_{\bar{t}\bar{a}}, \tag{6.25}$$

$$M^{ti}_{ab} = \mathcal{A}(ab)\,\tau^{i}_{b} T^{t\bar{u}}_{u\bar{a}} + \mathcal{A}(ab)\,T^{\bar{u}}_{\bar{b}} T^{t\bar{i}}_{u\bar{a}}, \tag{6.26}$$

$$M^{ti}_{ab} = T^{t}_{u} T^{\bar{u}\bar{i}}_{\bar{b}\bar{a}}, \tag{6.27}$$

$$M^{it}_{ab} = -\mathcal{A}(ab)\,\tau^{i}_{b} T^{t\bar{u}}_{u\bar{a}} - \mathcal{A}(ab)\,T^{\bar{u}}_{\bar{b}} T^{t\bar{i}}_{u\bar{a}}, \tag{6.28}$$

$$M^{it}_{ab} = -T^{t}_{u} T^{\bar{u}\bar{i}}_{\bar{b}\bar{a}}, \tag{6.29}$$

$$\begin{aligned} M^{ij}_{ab} = &- \mathcal{A}(ij;ab)\,\tau^{j}_{b}\left(T^{\bar{u}}_{\bar{a}} T^{t\bar{i}}_{u\bar{t}} + T^{\bar{i}}_{\bar{t}} T^{t\bar{u}}_{u\bar{a}}\right) - \mathcal{A}\left(\bar{i}\bar{j};\bar{a}\bar{b}\right)\left(T^{\bar{u}\bar{i}}_{\bar{t}\bar{a}} T^{t\bar{j}}_{u\bar{b}}\right) \\ &- \mathcal{A}\left(\bar{i}\bar{j}\right) T^{\bar{u}\bar{i}}_{\bar{a}\bar{b}} T^{t\bar{j}}_{u\bar{t}} - \mathcal{A}(ab)\,T^{\bar{i}\bar{j}}_{\bar{t}\bar{a}} T^{t\bar{u}}_{u\bar{b}} - \mathcal{A}\left(\bar{i}\bar{j};\bar{a}\bar{b}\right) T^{\bar{u}}_{\bar{a}} T^{\bar{j}}_{\bar{t}} T^{t\bar{i}}_{u\bar{b}}, \end{aligned} \tag{6.30}$$

$$\begin{aligned} M^{ij}_{ab} = &-\mathcal{A}\left(\bar{i}\bar{j};\bar{a}\bar{b}\right)\tau^{\bar{i}}_{\bar{a}}\left(T^{\bar{u}}_{\bar{t}} T^{t\bar{j}}_{u\bar{b}} + T^{t}_{u} T^{\bar{u}\bar{j}}_{\bar{t}\bar{b}}\right) \\ &-\mathcal{A}\left(\bar{i}\bar{j}\right) T^{t}_{u} T^{\bar{j}}_{\bar{t}} T^{\bar{u}\bar{i}}_{\bar{a}\bar{b}} - \mathcal{A}\left(\bar{a}\bar{b}\right) T^{t}_{u} T^{\bar{u}}_{\bar{b}} T^{\bar{i}\bar{j}}_{\bar{t}\bar{a}}, \end{aligned} \tag{6.31}$$

$$M^{it}_{au} = -T^{t\bar{i}}_{u\bar{a}}, \tag{6.32}$$

$$M^{ti}_{au} = T^{t\bar{i}}_{u\bar{a}}, \tag{6.33}$$

$$M^{it}_{ua} = T^{t\bar{i}}_{u\bar{a}}, \tag{6.34}$$

$$M^{ti}_{ua} = -T^{t\bar{i}}_{u\bar{a}}, \tag{6.35}$$

$$M^{it}_{au} = -\tau^{\bar{i}}_{\bar{a}} T^{t}_{u}, \tag{6.36}$$

$$M^{it}_{ua} = +\tau^{\bar{i}}_{\bar{a}} T^{t}_{u}, \tag{6.37}$$

$$M^{ti}_{au} = +\tau^{\bar{i}}_{\bar{a}} T^{t}_{u}, \tag{6.38}$$

$$M^{ti}_{ua} = -\tau^{\bar{i}}_{\bar{a}} T^{t}_{u}. \tag{6.39}$$

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,

$$M^{i\bar{j}}_{u\bar{a}} = -\tau^{\bar{j}}_{\bar{a}} T^{t\bar{i}}_{ut} - T^{j}_{u} T^{t\bar{i}}_{a\bar{t}} - T^{t}_{a} \tau^{j\bar{i}}_{u\bar{t}} - T^{\bar{i}}_{\bar{t}} T^{tj}_{au}, \tag{6.40}$$

$$M^{i\bar{j}}_{u\bar{a}} = T^{t}_{u} T^{j\bar{i}}_{a\bar{t}}, \tag{6.41}$$

$$M^{j\bar{i}}_{a\bar{t}} = -\tau^{j}_{a} T^{i\bar{u}}_{u\bar{t}} - T^{\bar{j}}_{\bar{t}} T^{i\bar{u}}_{u\bar{a}} - T^{\bar{u}}_{\bar{a}} \tau^{i\bar{j}}_{u\bar{t}} - T^{i}_{u} T^{\bar{j}\bar{u}}_{\bar{t}\bar{a}}, \tag{6.42}$$

$$M^{j\bar{i}}_{a\bar{t}} = T^{\bar{u}}_{\bar{t}} T^{i\bar{j}}_{u\bar{a}}, \tag{6.43}$$

$$M^{t\bar{i}}_{a\bar{b}} = \tau^{\bar{i}}_{\bar{b}} T^{t\bar{u}}_{u\bar{a}} + T^{t}_{b} T^{i\bar{u}}_{u\bar{a}} + T^{i}_{u} \tau^{t\bar{u}}_{b\bar{a}} + T^{\bar{u}}_{\bar{a}} T^{it}_{ub}, \tag{6.44}$$

$$M^{t\bar{i}}_{a\bar{b}} = -T^{t}_{u} T^{i\bar{u}}_{b\bar{a}}, \tag{6.45}$$

$$M^{i\bar{u}}_{b\bar{a}} = \tau^{i}_{b} T^{t\bar{u}}_{a\bar{t}} + T^{\bar{u}}_{\bar{b}} T^{t\bar{i}}_{a\bar{t}} + T^{\bar{i}}_{\bar{t}} \tau^{t\bar{u}}_{a\bar{b}} + T^{t}_{a} T^{\bar{i}\bar{u}}_{\bar{t}\bar{b}}, \tag{6.46}$$

$$M^{i\bar{u}}_{b\bar{a}} = -T^{\bar{u}}_{\bar{t}} T^{t\bar{i}}_{a\bar{b}}, \tag{6.47}$$

$$\begin{aligned} M^{i\bar{j}}_{a\bar{b}} = &- \tau^{\bar{j}}_{\bar{b}} (T^{\bar{u}}_{\bar{a}} T^{t\bar{i}}_{ut} + T^{\bar{i}}_{\bar{t}} T^{t\bar{u}}_{u\bar{a}}) - \tau^{i}_{a} (T^{j\bar{u}}_{ut} T^{t}_{b} + T^{t\bar{u}}_{b\bar{t}} T^{j}_{u}) \\ &+ T^{\bar{i}}_{\bar{t}} T^{\bar{u}}_{\bar{a}} T^{tj}_{ub} + T^{t}_{b} T^{j}_{u} T^{\bar{u}\bar{i}}_{\bar{t}\bar{a}} - T^{j}_{u} T^{\bar{u}}_{\bar{a}} T^{t\bar{i}}_{b\bar{t}} - T^{t}_{b} T^{\bar{i}}_{\bar{t}} T^{j\bar{u}}_{u\bar{a}} \\ &- \tau^{j\bar{i}}_{u\bar{t}} \tau^{t\bar{u}}_{b\bar{a}} + T^{j\bar{u}}_{ut} T^{t\bar{i}}_{b\bar{a}} + T^{t\bar{i}}_{u\bar{t}} T^{j\bar{u}}_{b\bar{a}} + T^{t\bar{u}}_{b\bar{t}} T^{j\bar{i}}_{u\bar{a}} \\ &+ T^{t\bar{u}}_{u\bar{a}} T^{j\bar{i}}_{b\bar{t}} - T^{tj}_{ub} T^{\bar{u}\bar{i}}_{\bar{t}\bar{a}} - T^{t\bar{i}}_{u\bar{a}} T^{j\bar{u}}_{b\bar{t}} - T^{j\bar{u}}_{u\bar{a}} T^{t\bar{i}}_{b\bar{t}}, \end{aligned} \tag{6.48}$$

$$\begin{aligned} M^{i\bar{j}}_{a\bar{b}} = &- \tau^{\bar{j}}_{\bar{b}} T^{t}_{u} T^{\bar{u}\bar{i}}_{\bar{a}\bar{t}} - \tau^{i}_{a} T^{\bar{u}}_{\bar{t}} T^{jt}_{ub} + T^{t}_{u} T^{\bar{i}}_{\bar{t}} T^{j\bar{u}}_{b\bar{a}} + T^{t}_{u} T^{\bar{u}}_{\bar{a}} T^{j\bar{i}}_{b\bar{t}} \\ &+ T^{\bar{u}}_{\bar{t}} T^{t}_{b} T^{j\bar{i}}_{u\bar{a}} + T^{\bar{u}}_{\bar{t}} T^{j}_{u} T^{t\bar{i}}_{b\bar{a}}, \end{aligned} \tag{6.49}$$

$$M^{t\bar{i}}_{ut} = T^{i}_{u}, \tag{6.50}$$

$$M^{i\bar{u}}_{ut} = T^{\bar{i}}_{\bar{t}}, \tag{6.51}$$

$$M^{t\bar{i}}_{u\bar{a}} = \tau^{it}_{ua}, \tag{6.52}$$

$$M^{i\bar{u}}_{a\bar{t}} = \tau^{\bar{i}\bar{u}}_{\bar{t}\bar{a}}, \tag{6.53}$$

$$M^{t\bar{i}}_{a\bar{t}} = \tau^{i\bar{u}}_{u\bar{a}}, \tag{6.54}$$

$$M^{i\bar{u}}_{u\bar{a}} = \tau^{t\bar{i}}_{a\bar{t}}, \tag{6.55}$$

$$M^{t\bar{u}}_{u\bar{a}} = -T^{t}_{a}, \tag{6.56}$$

$$M^{t\bar{u}}_{a\bar{t}} = -T^{\bar{u}}_{\bar{a}}, \tag{6.57}$$

$$M^{i\bar{j}}_{ut} = -\tau^{j\bar{i}}_{ut}, \tag{6.58}$$

$$M^{t\bar{u}}_{a\bar{b}} = -\tau^{t\bar{u}}_{b\bar{a}}. \tag{6.59}$$

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

$$W = R^{t\bar{u}}_{ut}. \tag{6.60}$$

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,

$$\Delta E_{\mathrm{IAS}} = -W^{t\bar{u}}_{ut} T^{t}_{u} T^{\bar{u}}_{\bar{t}}. \tag{6.61}$$

Chapter 7

Automatically generated UCCSDT and UDC-CCSDT

Unrestricted implementations of CCSDT and DC-CCSDT[12, 13, 14] were generated with version 1.0.1 of the Quantwo program[15]. The Quantwo inputs are listed below.

- UCCSDT Quantwo input file:

```
prog,spinintegr=0,nobrafac=1,explspin=1,algo=2
output,level=1,maxlenline=70

\beq
<\Phi^{a}_{i}| \op H (1 + \op T_2 + \op T_3) |0>_C
\eeq
\beq
<\Phi^{ab}_{ij}| \op H (1 + \op T_2 + \half \op T_2 \op T_2 + \op T_3) |0>_C
\eeq
\beq
<\Phi^{abc}_{ijk}| \op H (\op T_2 + \op T_3 + \half \op T_2 \op T_2 + \op T_2 \op T_3) |0>_C
\eeq
```

- UDC-CCSDT Quantwo input file:

```
%singles and doubles amplitude equations from UCCSDT
%we only modify the triples amplitude equation

prog,spinintegr=0,nobrafac=1,explspin=1,algo=2
output,level=1,maxlenline=70

\beq
<\Phi^{abc}_{ijk}| \op H (\op T_2 + \op T_3 + \frac{1}{2} \op T_2 \op T_2
+ \op T_2 \op T_3) |0>_C
+ (1 - \Perm{IJ}{JI} - \Perm{IK}{KI})(1 - \Perm{AB}{BA} - \Perm{AC}{CA})
(\sum_{LMDE} \tnsr \intg{LE}{MD} \tnsr T^{IL}_{AD} \tnsr T^{MJK}_{EBC})
- \frac{1}{2}(1 - \Perm{KI}{IK} - \Perm{KJ}{JK})
\sum_{LMDE} \tnsr \intg{LD}{ME} \tnsr T^{IJ}_{DE} \tnsr T^{LMK}_{ABC}
- \frac{1}{2}(1 - \Perm{CA}{AC} - \Perm{CB}{BC})
\sum_{LMDE} \tnsr \intg{LD}{ME} \tnsr T^{LM}_{AB} \tnsr T^{IJK}_{DEC}
+ \frac{1}{2}(1 - \Perm{IJ}{JI} - \Perm{IK}{KI})
\sum_{LMDE} \tnsr \intg{LD}{ME} \tnsr T^{LI}_{DE} \tnsr T^{MJK}_{ABC}
+ \frac{1}{2}(1 - \Perm{AB}{BA} - \Perm{AC}{CA})
\sum_{LMDE} \tnsr \intg{LD}{ME} \tnsr T^{LM}_{DA} \tnsr T^{IJK}_{EBC}
+ \frac{1}{2}(1 - \Perm{KI}{IK} - \Perm{KJ}{JK})(1 - \Perm{AB}{BA} - \Perm{AC}{CA})
\sum_{LMDE} \tnsr \intg{LD}{ME} \tnsr T^{IJ}_{AD} \tnsr T^{LMK}_{BEC}
+ \frac{1}{2}(1 - \Perm{IJ}{JI} - \Perm{IK}{KI})(1 - \Perm{CA}{AC} - \Perm{CB}{BC})
\sum_{LMDE} \tnsr \intg{LD}{ME} \tnsr T^{IL}_{AB} \tnsr T^{JMK}_{DEC}
\eeq
```

The program generates TensorOperations code. The generated code used by ElemCo.jl is located in the `src/algo` directory.

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