

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 , the occupied orbitals by i, j, k, \dots , the active (open-shell) orbitals by t, u, v, \dots , 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,

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

or for the normal-ordered Hamiltonian,

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

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:

$$\begin{aligned} \mathcal{P}(ab) X_{ab}^{ij} &= X_{ba}^{ij} \\ \mathcal{P}(ab \rightarrow ba) X_{ab}^{ij} &= X_{ba}^{ij} \end{aligned} \quad (1.3)$$

Symmetrization operators:

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

Antisymmetrization operators:

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

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 an interface to the `libcint`[2] library.

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

$$v_{pq}^{rs} \approx v_p^{rP} [v^{-1}]_{PQ} v_q^{sQ}, \quad (2.1)$$

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

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

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

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

The Coulomb metric matrix is decomposed using the Cholesky factorization,

$$v^{PQ} = \sum_L L_L^P L_L^Q, \quad (2.4)$$

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

$$L_{L'}^P C_P^L = \delta_{L'}^L, \quad (2.5)$$

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,

$$v_p^{rL} = v_p^{rP} C_P^L, \quad (2.6)$$

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

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

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,

$$\begin{aligned}\tilde{h}_p^q &= \tilde{f}_p^q - \sum_L \left(2v_p^{qL} v_i^{iL} - v_p^{iL} v_i^{qL} \right) \\ \tilde{E}_0 &= E_0 + h_i^i - \tilde{h}_i^i + \tilde{f}_I^I,\end{aligned}\tag{2.8}$$

where

$$\tilde{f}_p^q = h_p^q + \sum_{\tilde{L}} \left(2v_p^{q\tilde{L}} v_i^{\tilde{i}\tilde{L}} - v_p^{\tilde{i}\tilde{L}} v_i^{q\tilde{L}} \right),\tag{2.9}$$

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 *mpfit* 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,

$$\begin{aligned}\tilde{h}_p^q &= h_p^q + 2v_{pI}^{qI} - v_{pI}^{Iq} \\ \tilde{E}_0 &= E_0 + 2h_I^I + 2v_{IJ}^{IJ} - v_{IJ}^{JI},\end{aligned}\tag{2.10}$$

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

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

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

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

Alternatively, the v_μ^{iL} integrals can be precomputed and the Fock matrix can be calculated as

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

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

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

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

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

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

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

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 $\bar{C}_p^{\dagger\tilde{r}} C_{\tilde{r}}^p = \delta_p^r$.

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

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

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

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

where

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

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

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

4.2 MCSCF

The energy expectation value of the wavefunction is be given by

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

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

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

with \hat{e}_{qs}^{pr} as the 2-electron excitation operator $\sum_{\sigma\tau} \hat{a}_{p\sigma}^\dagger \hat{a}_{r\tau}^\dagger \hat{a}_{s\tau} \hat{a}_{q\sigma}$. 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

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

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 $[\mathbf{x}_t^j, \mathbf{x}_a^j, \mathbf{x}_t^u, \mathbf{x}_a^u]$.

Here, \mathbf{g} is calculated from

$$\begin{aligned} g_r^k &= \left(\frac{\partial E}{\partial x_r^k} \right)_{\mathbf{R}=\mathbf{0}} \\ &= \langle 0 | [\hat{H}, \hat{E}_r^k - \hat{E}_r^k] | 0 \rangle \\ &= [1 - \mathcal{P}(rk)] \langle 0 | [\hat{E}_r^k, h_{p'}^{q'} \hat{E}_{q'}^{p'} + \frac{1}{2} v_{p'r'}^{q's'} \hat{e}_{q's'}^{p'r'}] | 0 \rangle \\ &= [1 - \mathcal{P}(rk)] \langle 0 | h_r^{q'} \hat{E}_{q'}^k - h_{p'}^k \hat{E}_r^{p'} + v_{rr'}^{q's'} \hat{e}_{q's'}^{kr'} - v_{p'r'}^{ks'} \hat{e}_{rs'}^{p'r'} | 0 \rangle, \\ &= [1 - \mathcal{P}(rk)] (h_r^{q'} {}^1D_{q'}^k - h_{p'}^k {}^1D_r^{p'} + v_{rr'}^{q's'} {}^2D_{q's'}^{kr'} - v_{p'r'}^{ks'} {}^2D_{rs'}^{p'r'}) \end{aligned} \quad (4.7)$$

let

$$A_r^k = \frac{1}{2} (h_r^{q'} {}^1D_{q'}^k + h_{p'}^r {}^1D_k^{p'}) + \frac{1}{2} (v_{rr'}^{q's'} {}^2D_{q's'}^{kr'} + v_{p'r'}^{rs'} {}^2D_{ks'}^{p'r'}), \quad (4.8)$$

then

$$g_r^k = 2(A_r^k - A_k^r). \quad (4.9)$$

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

$$\begin{aligned} {}^1D_u^t &= \langle 0 | \hat{E}_u^t | 0 \rangle = c_I c_J \langle \Phi_I | \hat{E}_u^t | \Phi_J \rangle, \\ {}^2D_{uv}^{tv} &= \langle 0 | \hat{e}_{uv}^{tv} | 0 \rangle = c_I c_J \langle \Phi_I | \hat{e}_{uv}^{tv} | \Phi_J \rangle. \end{aligned} \quad (4.10)$$

In order to simplify the expression, the ${}^1D_v^u$ is written as D_v^u , and ${}^2D_{tv}^{uv}$ is written as D_{tv}^{uv} in follow.

Fock matrix can be generalizingly defined as

$$F_r^s = {}^cF_r^s + D_u^t [v_{rt}^{su} - \frac{1}{2} v_{rt}^{us}], \quad (4.11)$$

with

$${}^cF_r^s = h_r^s + (2v_{rj}^{sj} - v_{rj}^{js}) \quad (4.12)$$

defined as the closed shell part of Fock matrix.

\mathbf{A}_r^k can be calculated as

$$\begin{aligned}
 A_r^i &= \frac{1}{2}(h_r^{q'} D_{q'}^i + h_{p'}^r D_i^{p'}) + \frac{1}{2}(v_{rr'}^{q's'} D_{q's'}^{ir'} + v_{p'r'}^{rs'} D_{is'}^{p'r'}), \\
 &= \frac{1}{2}(h_r^i D_i^i + h_i^r D_i^i) + \frac{1}{2}(v_{rj}^{ij} D_{ij}^{ij} + v_{ij}^{rj} D_{ij}^{ij} + v_{rj}^{ji} D_{ji}^{ij} + v_{ji}^{rj} D_{ij}^{ji} \\
 &\quad + v_{rt}^{iu} D_{iu}^{it} + v_{iu}^{rt} D_{it}^{iu} + v_{rt}^{ui} D_{ui}^{it} + v_{ui}^{rt} D_{it}^{ui}) \\
 &= \frac{1}{2}(2h_r^i + 2h_i^r) + \frac{1}{2}(4v_{rj}^{ij} + 4v_{ij}^{rj} - 2v_{rj}^{ji} - 2v_{ji}^{rj} + 2v_{rt}^{iu} D_u^t + 2v_{iu}^{rt} D_t^u - v_{rt}^{ui} D_u^t - v_{ui}^{rt} D_t^u) \\
 &= \mathcal{S}(ri) (h_r^i + 2v_{rj}^{ij} - v_{rj}^{ji} + v_{rt}^{iu} D_u^t - \frac{1}{2}v_{rt}^{ui} D_u^t) \\
 &= \mathcal{S}(ri) F_r^i,
 \end{aligned} \tag{4.13}$$

$$\begin{aligned}
 A_r^u &= \frac{1}{2}(h_r^{q'} D_{q'}^u + h_{p'}^r D_u^{p'}) + \frac{1}{2}(v_{rr'}^{q's'} D_{q's'}^{ur'} + v_{p'r'}^{rs'} D_{us'}^{p'r'}) \\
 &= \frac{1}{2}(h_r^t D_t^u + h_t^r D_u^t) + \frac{1}{2}(v_{rj}^{tj} D_{tj}^{uj} + v_{tj}^{rj} D_{uj}^{tj} + v_{rw}^{tw} D_{tw}^{uw} + v_{tw}^{rw} D_{uw}^{tw} + v_{rj}^{jt} D_{jt}^{uj} + v_{jt}^{rj} D_{uj}^{jt}) \\
 &= \frac{1}{2}(h_r^t D_t^u + h_t^r D_u^t) + \frac{1}{2}(2v_{rj}^{tj} D_t^u + 2v_{tj}^{rj} D_u^t + v_{rw}^{tw} D_{tw}^{uw} + v_{tw}^{rw} D_{uw}^{tw} - v_{rj}^{jt} D_t^u - v_{jt}^{rj} D_u^t) \\
 &= \frac{1}{2}[(h_r^t + 2v_{rj}^{tj} - v_{rj}^{jt}) D_t^u + v_{rw}^{tw} D_{tw}^{uw}] + \frac{1}{2}[(h_t^r + 2v_{tj}^{rj} - v_{tj}^{jr}) D_u^t + v_{tw}^{rw} D_{uw}^{tw}] \\
 &= \frac{1}{2}({}^c F_r^t D_t^u + v_{rw}^{tw} D_{tw}^{uw}) + \frac{1}{2}({}^c F_t^r D_u^t + v_{tw}^{rw} D_{uw}^{tw}),
 \end{aligned} \tag{4.14}$$

$$A_r^a = 0. \tag{4.15}$$

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

$$E = {}^c F_t^u D_u^t + \frac{1}{2} v_{tw}^{uw} D_{uw}^{tw} + E_c, \tag{4.16}$$

with

$$E_c = h_j^j + {}^c F_j^j, \tag{4.17}$$

E_c is the closed shell electronic energy.

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

$$\begin{aligned}
 v_{tw}^{uw} &= v_t^{uL} v_v^{wL}, \\
 v_t^{uL} &= v_\mu^{\nu L} C_t^{\dagger \mu} C_\nu^u.
 \end{aligned} \tag{4.18}$$

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} [3]

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

in which

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

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

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

$$\lambda = \frac{(\|\mathbf{x}_{\text{small}\lambda}\| - \text{trust}) + (\text{trust} - \|\mathbf{x}_{\text{large}\lambda}\|)}{\|\mathbf{x}_{\text{small}\lambda}\| - \|\mathbf{x}_{\text{large}\lambda}\|}, \quad (4.22)$$

$$\lambda = \exp(\ln \text{small}\lambda + (\ln \text{big}\lambda - \ln \text{small}\lambda) * \text{bisecdamp}).$$

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[4], in which

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

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

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

More specifically,

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

4.4.2 Second Order Approximation

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

$$\begin{aligned}
 {}^{SO}H_{rs}^{kl} &= \left(\frac{\partial E}{\partial x_r^k \partial x_s^l} \right)_{\mathbf{R}=0} \\
 &= \frac{1}{2} \mathcal{S}(rs, kl) \langle 0 | [[\hat{H}, \hat{E}_r^k - \hat{E}_k^r], \hat{E}_s^l - \hat{E}_l^s] | 0 \rangle \\
 &= \frac{1}{2} \mathcal{S}(rs, kl) \mathcal{A}(rk; sl) \langle 0 | [[\hat{H}, \hat{E}_r^k], \hat{E}_s^l] | 0 \rangle \\
 &= \frac{1}{2} \mathcal{S}(rs, kl) \mathcal{A}(rk; sl) \langle 0 | [\hat{E}_s^l, [\hat{E}_r^k, h_{p'}^{q'} \hat{E}_{q'}^{p'} + \frac{1}{2} v_{p'r'}^{q's'} \hat{e}_{q's'}^{p'r'}]] | 0 \rangle \\
 &= \frac{1}{2} \mathcal{S}(rs, kl) \mathcal{A}(rk; sl) (-h_r^l D_s^k - h_s^k D_r^l + h_r^{q'} D_{q'}^l \delta_s^k + h_{p'}^k D_s^{p'} \delta_r^l \\
 &\quad + \delta_s^k v_{rr'}^{q's'} D_{q's'}^{lr'} + \delta_r^l v_{p'r'}^{ks'} D_{ss'}^{p'r'} - v_{rr'}^{ls'} D_{ss'}^{kr'} - v_{sr'}^{ks'} D_{rs'}^{lr'} \\
 &\quad + v_{rs}^{q's'} D_{q's'}^{kl} + v_{p'r'}^{kl} D_{rs}^{p'r'} - v_{rr'}^{q'l} D_{q's'}^{kr'} - v_{p's}^{ks'} D_{rs'}^{p'l}) \\
 &= \mathcal{A}(rk; sl) (-h_r^l D_s^k - h_s^k D_r^l - v_{rr'}^{ls'} D_{ss'}^{kr'} - v_{sr'}^{ks'} D_{rs'}^{lr'} + v_{rs}^{q's'} D_{q's'}^{kl} + v_{p'r'}^{kl} D_{rs}^{p'r'} - v_{rr'}^{q'l} D_{q's'}^{kr'} - v_{p's}^{ks'} D_{rs'}^{p'l}) \\
 &\quad + \frac{1}{2} \mathcal{S}(rs, kl) \mathcal{A}(rk; sl) \delta_s^k (h_r^{q'} D_{q'}^l + h_{p'}^r D_l^{p'} + v_{rr'}^{q's'} D_{q's'}^{lr'} + v_{p'r'}^{rs} D_{kl}^{p'r'} + v_{rr'}^{q's} D_{q'l}^{kr'} + v_{p's}^{rs'} D_{ks'}^{p'l}) \\
 &= \mathcal{A}(rk; sl) (h_r^s D_l^k + h_s^r D_k^l + v_{rr'}^{ss'} D_{ls'}^{kr'} + v_{sr'}^{rs'} D_{ks'}^{lr'} + v_{rs}^{q's'} D_{q's'}^{kl} + v_{p'r'}^{rs} D_{kl}^{p'r'} + v_{rr'}^{q's} D_{q'l}^{kr'} + v_{p's}^{rs'} D_{ks'}^{p'l}) \\
 &\quad + \mathcal{A}(rk; sl) (\delta_s^k A_r^l + \delta_r^l A_s^k) \\
 &= \mathcal{A}(rk; sl) [2G_{rs}^{kl} + \delta_s^k (A_r^l + A_l^r)] \\
 &= \mathcal{A}(rk; sl) [2G_{rs}^{kl} - \delta_l^k (A_r^s + A_s^r)],
 \end{aligned} \tag{4.27}$$

matrices \mathbf{G} are defined as

$$G_{rs}^{kl} = \frac{1}{2} (h_r^s D_l^k + h_s^r D_k^l + v_{rr'}^{ss'} D_{ls'}^{kr'} + v_{sr'}^{rs'} D_{ks'}^{lr'} + v_{rs}^{q's'} D_{q's'}^{kl} + v_{p'r'}^{rs} D_{kl}^{p'r'} + v_{rr'}^{q's} D_{q'l}^{kr'} + v_{p's}^{rs'} D_{ks'}^{p'l}) \tag{4.28}$$

$$G_{rs}^{ij} = \delta_i^j (F_s^r + F_r^s) + L_{rs}^{ij} + L_{ij}^{rs}, \tag{4.29}$$

$$G_{rs}^{tj} = \frac{1}{2} (D_u^t L_{rs}^{uj} + D_t^u L_{uj}^{rs}) = G_{sr}^{jt}, \tag{4.30}$$

$$G_{rs}^{tu} = \frac{1}{2} ({}^c F_r^s D_t^u + {}^c F_s^r D_u^t + v_{rv}^{sw} D_{uw}^{tv} + v_{sw}^{rv} D_{tv}^{uw}) + v_{rs}^{vw} D_{vw}^{tu} + v_{vw}^{rs} D_{tu}^{vw}, \tag{4.31}$$

where

$$L_{rs}^{pq} = 2v_{rs}^{pq} + 2v_{rq}^{ps} - v_{rq}^{sp} - v_{rs}^{qp}. \tag{4.32}$$

4.4.3 Combined Second-Order and Super-CI Hessian Approximation

By default, the SO-SCI Hessian matrix [5] 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. [6]. The closed-shell CCSD and DCSD Lagrangian is given by

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

The DCSD Lagrangian is obtained by removing terms in red.

\tilde{T}_{ab}^{ij} are the contravariant amplitudes,

$$\tilde{T}_{ab}^{ij} = 2T_{ab}^{ij} - T_{ba}^{ij}. \tag{5.2}$$

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.,

$$\begin{aligned}
 \hat{v}_{kl}^{id} &= v_{kl}^{id} + v_{kl}^{cd} T_c^i \\
 \hat{v}_{al}^{cd} &= v_{al}^{cd} - v_{kl}^{cd} T_a^k \\
 \hat{f}_k^c &= h_k^c + 2\hat{v}_{kl}^{cl} - \hat{v}_{lk}^{cl} = f_k^c + (2v_{kl}^{cd} - v_{lk}^{cd}) T_d^l.
 \end{aligned} \tag{5.3}$$

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. [7] and is given by

$$\begin{aligned}
\mathcal{L} = & v_{kl}^{cd} \tilde{T}_{cd}^{kl} + \left(\hat{f}_k^c + f_k^c \right) T_c^k + \Lambda_{ij}^{ab} \left(\hat{v}_{kl}^{ij} + v_{kl}^{cd} T_{cd}^{ij} \right) T_{ab}^{kl} + \Lambda_{ij}^{ab} K_{pq}^{ij} \delta_a^p \delta_b^q \\
& + \Lambda_{ij}^{ab} v_{kl}^{cd} T_{ad}^{kj} T_{cb}^{il} \\
& + \Lambda_{ij}^{ab} \mathcal{S}(ab, ij) \left\{ \left(\hat{f}_a^c - 2 \times \frac{1}{2} v_{kl}^{cd} \tilde{T}_{ad}^{kl} \right) T_{cb}^{ij} - \left(\hat{f}_k^i + 2 \times \frac{1}{2} v_{kl}^{cd} \tilde{T}_{cd}^{il} \right) T_{ab}^{kj} \right. \\
& + \left(\hat{v}_{al}^{id} + \frac{1}{2} v_{kl}^{cd} \tilde{T}_{ac}^{ik} \right) \tilde{T}_{db}^{lj} - \hat{v}_{ka}^{ic} T_{cb}^{kj} - \hat{v}_{kb}^{ic} T_{ac}^{kj} - v_{kl}^{cd} T_{da}^{ki} \left(T_{cb}^{lj} - T_{bc}^{lj} \right) \\
& \left. - K_{pq}^{ij} \left(\delta_k^p \delta_b^q - \frac{1}{2} \delta_k^p \delta_l^q T_b^l \right) T_a^k \right\} + \Lambda_i^a K_{pq}^{ij} (2\delta_a^p \delta_j^q - \delta_j^p \delta_a^q) \\
& - \Lambda_i^a T_a^k K_{pq}^{ij} (2\delta_k^p \delta_j^q - \delta_j^p \delta_k^q) + \Lambda_i^a \hat{h}_a^i + \Lambda_i^a \hat{f}_j^b \tilde{T}_{ab}^{ij} - \Lambda_i^a \hat{v}_{jk}^{ic} \tilde{T}_{ca}^{kj},
\end{aligned} \tag{5.4}$$

where

$$K_{pq}^{ij} = v_{pq}^{rs} \left((T_{ab}^{ij} + T_a^i T_b^j) \delta_r^a \delta_s^b + \delta_r^i T_b^j \delta_s^b + T_a^i \delta_r^a \delta_s^j + \delta_r^i \delta_s^j \right) \tag{5.5}$$

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.,

$$\begin{aligned}
\frac{\partial \mathcal{L}}{\partial T_e^m} = & 2(2v_{jm}^{be} - v_{jm}^{eb}) T_b^j + 2f_m^e - \Lambda_{ij}^{eb} \hat{v}_{mb}^{ij} - \Lambda_{ij}^{ae} \hat{v}_{am}^{ij} + \Lambda_{mj}^{ab} \hat{v}_{ab}^{ej} + \Lambda_{im}^{ab} \hat{v}_{ab}^{ie} \\
& + \Lambda_{mj}^{ab} \hat{v}_{kl}^{ej} T_{ab}^{kl} + \Lambda_{im}^{ab} \hat{v}_{kl}^{ie} T_{ab}^{kl} - \Lambda_{ij}^{eb} \hat{v}_{mb}^{cd} T_{cd}^{ij} - \Lambda_{ij}^{ae} \hat{v}_{am}^{cd} T_{cd}^{ij} \\
& - \Lambda_{ij}^{eb} \hat{f}_m^d T_{db}^{ij} - \Lambda_{ij}^{ae} \hat{f}_m^d T_{ad}^{ij} - \Lambda_{mj}^{ab} \hat{f}_k^e T_{ab}^{kj} - \Lambda_{im}^{ab} \hat{f}_k^e T_{ab}^{ik} \\
& + \Lambda_{ij}^{ab} \mathcal{S}(ab, ij) \left\{ (2\hat{v}_{am}^{de} - \hat{v}_{am}^{ed}) T_{db}^{ij} - (2\hat{v}_{km}^{ie} - \hat{v}_{km}^{ei}) T_{ab}^{kj} \right\} \\
& - \Lambda_{ij}^{eb} \hat{v}_{ml}^{id} \tilde{T}_{db}^{lj} - \Lambda_{ij}^{ae} \hat{v}_{ml}^{jd} \tilde{T}_{ad}^{il} + \Lambda_{mj}^{ab} \hat{v}_{al}^{ed} \tilde{T}_{db}^{lj} + \Lambda_{im}^{ab} \hat{v}_{bl}^{ed} \tilde{T}_{ad}^{il} \\
& + \Lambda_{ij}^{eb} \hat{v}_{km}^{ic} T_{cb}^{kj} - \Lambda_{mj}^{ab} \hat{v}_{ka}^{ec} T_{cb}^{kj} + \Lambda_{ij}^{ae} \hat{v}_{km}^{jc} T_{ac}^{ik} - \Lambda_{im}^{ab} \hat{v}_{kb}^{ec} T_{ac}^{ik} \\
& + \Lambda_{ij}^{ae} \hat{v}_{km}^{ic} T_{ac}^{kj} - \Lambda_{mj}^{ab} \hat{v}_{kb}^{ec} T_{ac}^{kj} + \Lambda_{ij}^{eb} \hat{v}_{km}^{jc} T_{cb}^{ik} - \Lambda_{im}^{ab} \hat{v}_{ka}^{ec} T_{cb}^{ik} \\
& - \Lambda_i^e \hat{f}_m^i + \Lambda_m^a \hat{f}_a^e + \Lambda_i^a (2\hat{v}_{am}^{ie} - \hat{v}_{am}^{ei}) \\
& + \Lambda_i^a (2v_{jm}^{be} - v_{jm}^{eb}) \tilde{T}_{ab}^{ij} - \Lambda_i^e v_{mk}^{bc} \tilde{T}_{cb}^{ki} - \Lambda_m^a v_{jk}^{ec} \tilde{T}_{ca}^{kj}.
\end{aligned} \tag{5.6}$$

$$\begin{aligned}
\frac{\partial \mathcal{L}}{\partial T_{ef}^{mn}} = & \frac{1}{2} \mathcal{S}(ef, mn) \left[\tilde{v}_{mn}^{ef} + \Lambda_{ij}^{ef} \left(\hat{v}_{mn}^{ij} + v_{mn}^{cd} T_{cd}^{ij} \right) + \Lambda_{mn}^{ab} v_{kl}^{ef} T_{ab}^{kl} + \Lambda_{mn}^{ab} \hat{v}_{ab}^{ef} \right. \\
& + \Lambda_{in}^{eb} v_{ml}^{cf} T_{cb}^{il} + \Lambda_{mj}^{af} v_{kn}^{ed} T_{ad}^{kj} \\
& + \Lambda_{mn}^{af} \mathcal{S}(af, mn) \left(\hat{f}_a^e - 2 \times \frac{1}{2} v_{kl}^{ed} \tilde{T}_{ad}^{kl} \right) - \Lambda_{ij}^{eb} \mathcal{S}(eb, ij) 2 \times \frac{1}{2} \tilde{v}_{mn}^{cf} T_{cb}^{ij} \\
& - \Lambda_{in}^{ef} \mathcal{S}(ef, in) \left(\hat{f}_m^i + 2 \times \frac{1}{2} v_{ml}^{cd} \tilde{T}_{cd}^{il} \right) - \Lambda_{mj}^{ab} \mathcal{S}(ab, mj) 2 \times \frac{1}{2} \tilde{v}_{kn}^{ef} T_{ab}^{kj} \\
& + 2 \Lambda_{in}^{af} \mathcal{S}(af, in) \left(\hat{v}_{am}^{ie} + \frac{1}{2} v_{km}^{ce} \tilde{T}_{ac}^{ik} \right) - \Lambda_{im}^{af} \mathcal{S}(af, im) \left(\hat{v}_{an}^{ie} + \frac{1}{2} v_{kn}^{ce} \tilde{T}_{ac}^{ik} \right) \\
& + 2 \Lambda_{mj}^{eb} \mathcal{S}(eb, mj) \frac{1}{2} v_{nl}^{fd} \tilde{T}_{db}^{lj} - \Lambda_{nj}^{eb} \mathcal{S}(eb, nj) \frac{1}{2} v_{ml}^{fd} \tilde{T}_{db}^{lj} \\
& - \Lambda_{in}^{af} \mathcal{S}(af, in) \hat{v}_{ma}^{ie} - \Lambda_{in}^{eb} \mathcal{S}(eb, in) \hat{v}_{mb}^{if} \\
& - \Lambda_{nj}^{fb} \mathcal{S}(fb, nj) v_{ml}^{ce} \left(T_{cb}^{lj} - T_{bc}^{lj} \right) - \Lambda_{in}^{af} \mathcal{S}(af, in) v_{km}^{ed} T_{da}^{ki} \\
& + \Lambda_{in}^{ae} \mathcal{S}(ae, in) v_{km}^{fd} T_{da}^{ki} \\
& \left. + \mathcal{T}(mn) \left\{ \Lambda_m^e \hat{f}_n^f + \Lambda_n^a \hat{v}_{am}^{fe} - \Lambda_i^f \hat{v}_{nm}^{ie} \right\} \right], \quad (5.7)
\end{aligned}$$

with a “contravariation” operator,

$$\mathcal{T}(mn) X_{mn}^{ef} = 2X_{mn}^{ef} - X_{nm}^{ef}, \quad (5.8)$$

and

$$\tilde{v}_{mn}^{ef} = 2v_{mn}^{ef} - v_{nm}^{ef}. \quad (5.9)$$

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

$$\begin{aligned}
D_i^j &= -2\Lambda_{ik}^{cd} T_{cd}^{jk}, \\
D_a^b &= 2\Lambda_{kl}^{bc} T_{ac}^{kl}, \\
D_i^a &= \Lambda_i^a, \\
D_a^i &= \Lambda_k^c \tilde{T}_{ac}^{ik}.
\end{aligned} \quad (5.10)$$

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,

$$\begin{aligned}
\hat{D}_i^j &= D_i^j - D_i^c T_c^j, \\
\hat{D}_a^b &= D_a^b + D_k^b T_a^k, \\
\hat{D}_i^a &= D_i^a, \\
\hat{D}_a^i &= D_a^i + 2T_a^i - D_a^c T_c^i + \hat{D}_k^i T_a^k.
\end{aligned} \quad (5.11)$$

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

$$\begin{aligned}
D_{ij}^{kl} &= \Lambda_{ij}^{cd} T_{cd}^{kl} \\
D_{ib}^{aj} &= \Lambda_{ik}^{ac} \tilde{T}_{cb}^{kj} \\
\bar{D}_{ib}^{aj} &= \Lambda_{ik}^{ac} T_{cb}^{kj} + \Lambda_{ik}^{ca} T_{bc}^{kj}
\end{aligned} \quad (5.12)$$

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

$$\begin{aligned} K_{mn}^{rs} &= \hat{\Lambda}_{mn}^{pq} v_{pq}^{rs} \\ \hat{\Lambda}_{mn}^{pq} &= \Lambda_{mn}^{ab} \delta_a^p \delta_b^q - \Lambda_{mn}^{ab} T_a^i \delta_i^p \delta_b^q - \Lambda_{mn}^{ab} \delta_a^p T_b^j \delta_j^q + \Lambda_{mn}^{ab} T_a^i T_b^j \delta_i^p \delta_j^q \\ x_m^i &= \tilde{T}_{cd}^{il} v_{ml}^{cd} & x_a^e &= \tilde{T}_{ac}^{kl} v_{kl}^{ec} \end{aligned} \quad (5.13)$$

With these definitions, the Λ equations can be written as

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial T_e^m} &= (2v_{qm}^{pe} - v_{qm}^{ep}) \hat{D}_p^q + 2f_m^e - 2\Lambda_{ij}^{eb} \hat{v}_{mb}^{ij} + 2K_{mj}^{rs} \delta_r^e (\delta_s^j + \delta_s^b T_b^j) \\ &\quad + 2D_{mj}^{kl} \hat{v}_{kl}^{ej} - 2\Lambda_{ij}^{eb} (\hat{v}_{mb}^{cd} T_{cd}^{ij}) - D_d^e \hat{f}_m^d + D_m^k \hat{f}_k^e - 2D_{id}^{el} \hat{v}_{ml}^{id} + 2D_{md}^{al} \hat{v}_{al}^{ed} \\ &\quad + 2\bar{D}_{ic}^{ek} \hat{v}_{km}^{ic} - 2\bar{D}_{mc}^{ak} \hat{v}_{ka}^{ec} - \Lambda_i^e \hat{f}_m^i + \Lambda_m^a \hat{f}_a^e - \Lambda_i^e x_m^i - \Lambda_m^a x_a^e. \end{aligned} \quad (5.14)$$

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial T_{ef}^{mn}} &= \tilde{v}_{mn}^{ef} + \Lambda_{ij}^{ef} (\hat{v}_{mn}^{ij} + \textcolor{red}{v}_{mn}^{cd} T_{cd}^{ij}) + \textcolor{red}{D}_{mn}^{kl} v_{kl}^{ef} + K_{mn}^{rs} \delta_r^e \delta_s^f \\ &\quad + \mathcal{S}(ef, mn) \left\{ \Lambda_{mn}^{af} \left(\hat{f}_a^e - \textcolor{red}{2} \times \frac{1}{2} x_a^e \right) - \Lambda_{in}^{ef} \left(\hat{f}_m^i + \textcolor{red}{2} \times \frac{1}{2} x_m^i \right) \right. \\ &\quad + \mathcal{T}(mn) \left[\textcolor{red}{2} \times \frac{1}{4} v_{kn}^{ef} D_m^k - \textcolor{red}{2} \times \frac{1}{4} v_{mn}^{cf} D_c^e + \Lambda_{in}^{af} (\hat{v}_{am}^{ie} + v_{km}^{ce} \tilde{T}_{ac}^{ik}) \right. \\ &\quad \left. \left. + \frac{1}{2} (\Lambda_m^e \hat{f}_n^f + \Lambda_n^a \hat{v}_{am}^{fe} - \Lambda_i^f \hat{v}_{nm}^{ie}) \right] \right. \\ &\quad \left. - \Lambda_{in}^{af} \hat{v}_{ma}^{ie} - \Lambda_{in}^{eb} \hat{v}_{mb}^{if} - \textcolor{red}{D}_{nc}^{fl} v_{ml}^{ce} + \textcolor{red}{D}_{nd}^{ek} v_{km}^{fd} \right\}. \end{aligned} \quad (5.15)$$

5.3 Perturbative triples for closed-shell CCSD

The perturbative triples equations for CCSD are given by

$$\begin{aligned} E_{[T]} &= \sum_{i \leq j \leq k} p(i, j, k) K_{ijk}^{abc} X_{abc}^{ijk} \\ p(i, j, k) &= \begin{cases} 2 & i \neq j \neq k \\ 1 & i = j \oplus j = k \\ 0 & i = j = k \end{cases} \end{aligned} \quad (5.16)$$

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

$$\begin{aligned} K_{ijk}^{abc} &= K_{abc}^{ijk} = v_{bc}^{dk} T_{ad}^{ij} + v_{ac}^{dk} T_{db}^{ij} + v_{cb}^{dj} T_{ad}^{ik} + v_{ab}^{dj} T_{dc}^{ik} + v_{ca}^{di} T_{bd}^{jk} + v_{ba}^{di} T_{dc}^{jk} \\ &\quad - v_{lc}^{jk} T_{ba}^{li} - v_{lc}^{ik} T_{ab}^{lj} - v_{lb}^{kj} T_{ca}^{li} - v_{lb}^{ij} T_{ac}^{lk} - v_{la}^{ki} T_{cb}^{lj} - v_{la}^{ji} T_{bc}^{lk} \\ X_{abc}^{ijk} &= \frac{4K_{abc}^{ijk} - 2K_{acb}^{ijk} - 2K_{cba}^{ijk} - 2K_{bac}^{ijk} + K_{cab}^{ijk} + K_{bca}^{ijk}}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c} \end{aligned} \quad (5.17)$$

The (T) correction contains additionally the following terms,

$$\begin{aligned} E_{(T)} &= E_{[T]} + \sum_{i \leq j \leq k} p(i, j, k) \left[v_{jk}^{bc} X_{abc}^{ijk} T_i^{\dagger a} + v_{ik}^{ac} X_{abc}^{ijk} T_j^{\dagger b} + v_{ij}^{ab} X_{abc}^{ijk} T_k^{\dagger c} \right. \\ &\quad \left. + T_{jk}^{\dagger bc} X_{abc}^{ijk} f_i^a + T_{ik}^{\dagger ac} X_{abc}^{ijk} f_j^b + T_{ij}^{\dagger ab} X_{abc}^{ijk} f_k^c \right]. \end{aligned} \quad (5.18)$$

In case of $\Lambda\text{CCSD}(\mathbf{T})$ K_{ijk}^{abc} is different from K_{abc}^{ijk} and is calculated using the Lagrange multipliers,

$$K_{ijk}^{abc} = v_{dk}^{bc} \bar{\Lambda}_{ij}^{ad} + v_{dk}^{ac} \bar{\Lambda}_{ij}^{db} + v_{dj}^{cb} \bar{\Lambda}_{ik}^{ad} + v_{dj}^{ab} \bar{\Lambda}_{ik}^{dc} + v_{di}^{ca} \bar{\Lambda}_{jk}^{bd} + v_{di}^{ba} \bar{\Lambda}_{jk}^{dc} \\ - v_{jk}^{lc} \bar{\Lambda}_{li}^{ba} - v_{ik}^{lc} \bar{\Lambda}_{lj}^{ab} - v_{kj}^{lb} \bar{\Lambda}_{li}^{ca} - v_{ij}^{lb} \bar{\Lambda}_{lk}^{ac} - v_{ki}^{la} \bar{\Lambda}_{lj}^{cb} - v_{ji}^{la} \bar{\Lambda}_{lk}^{bc}, \quad (5.19)$$

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

$$\bar{\Lambda}_{ij}^{ab} = \frac{2}{3} \Lambda_{ij}^{ab} + \frac{1}{3} \Lambda_{ij}^{ba}. \quad (5.20)$$

Additionally, the conjugate-transposed amplitudes in Eq. (5.18) are replaced by the covariant Lagrange multipliers $\bar{\Lambda}_{ij}^{ab}$ and $\bar{\Lambda}_i^a = \frac{1}{2} \Lambda_i^a$.

5.4 Open-shell CCSD/DCSD 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

$$\mathcal{L} = \mathcal{L}_\alpha + \mathcal{L}_\beta + \mathcal{L}_{\alpha\beta}, \quad (5.21)$$

$$\mathcal{L}_\alpha = \frac{1}{2} \left[v_{kl}^{cd} T_{cd}^{kl} + \left(\hat{f}_k^c + f_k^c \right) T_c^k \right] + \frac{1}{4} \Lambda_{ij}^{ab} \left(\hat{v}_{ab}^{ij} - \hat{v}_{ab}^{ji} \right) + \frac{1}{4} \Lambda_{ij}^{ab} \left(\hat{v}_{kl}^{ij} + \frac{1}{2} v_{kl}^{cd} T_{cd}^{ij} \right) T_{ab}^{kl} \\ + \frac{1}{4} \Lambda_{ij}^{ab} \hat{v}_{ab}^{cd} T_{cd}^{ij} + \frac{1}{4} \Lambda_{ij}^{ab} \mathcal{S}(ab, ij) \left\{ \hat{x}_a^c T_{cb}^{ij} - \hat{x}_k^i T_{ab}^{kj} \right\} \\ + \frac{1}{4} \Lambda_{ij}^{ab} \mathcal{A}(ab; ij) \left\{ \left(\hat{v}_{al}^{id} - \hat{v}_{al}^{di} + \bar{x}_{al}^{id} \right) T_{db}^{lj} + \left(\hat{v}_{al}^{i\bar{d}} + x_{al}^{i\bar{d}} \right) T_{bd}^{j\bar{l}} \right\} \\ + \Lambda_i^a \hat{v}_{al}^{cd} T_{cd}^{il} + \Lambda_i^a \hat{v}_{al}^{c\bar{d}} T_{cd}^{i\bar{l}} - \Lambda_i^a \hat{v}_{jk}^{ic} T_{ac}^{jk} - \Lambda_i^a \hat{v}_{jk}^{i\bar{c}} T_{ac}^{j\bar{k}} \\ + \Lambda_i^a \hat{f}_a^i + \Lambda_i^a \hat{f}_j^b T_{ab}^{ij} + \Lambda_i^a \hat{f}_{\bar{j}}^{\bar{b}} T_{a\bar{b}}^{i\bar{j}}, \quad (5.22)$$

or using the cckext factorization,

$$\mathcal{L}_\alpha = \frac{1}{2} \left[v_{kl}^{cd} T_{cd}^{kl} + \left(\hat{f}_k^c + f_k^c \right) T_c^k \right] + \frac{1}{4} \Lambda_{ij}^{ab} \left(\hat{v}_{kl}^{ij} + \frac{1}{2} v_{kl}^{cd} T_{cd}^{ij} \right) T_{ab}^{kl} \\ + \frac{1}{4} \Lambda_{ij}^{ab} K_{pq}^{ij} \left(\delta_a^p - \delta_k^p T_a^k \right) \left(\delta_b^q - \delta_l^q T_b^l \right) + \frac{1}{4} \Lambda_{ij}^{ab} \mathcal{S}(ab, ij) \left\{ \hat{x}_a^c T_{cb}^{ij} - \hat{x}_k^i T_{ab}^{kj} \right\} \\ + \frac{1}{4} \Lambda_{ij}^{ab} \mathcal{A}(ab; ij) \left\{ \left(\hat{v}_{al}^{id} - \hat{v}_{al}^{di} + \bar{x}_{al}^{id} \right) T_{db}^{lj} + \left(\hat{v}_{al}^{i\bar{d}} + x_{al}^{i\bar{d}} \right) T_{bd}^{j\bar{l}} \right\} \\ + \Lambda_i^a \left(K_{pq}^{ij} \delta_j^q + K_{p\bar{q}}^{i\bar{j}} \delta_{\bar{j}}^{\bar{q}} \right) \left(\delta_a^p - \delta_k^p T_a^k \right) - \Lambda_i^a \hat{v}_{jk}^{ic} T_{ac}^{jk} - \Lambda_i^a \hat{v}_{jk}^{i\bar{c}} T_{a\bar{c}}^{j\bar{k}} \\ + \Lambda_i^a \hat{h}_a^i + \Lambda_i^a \hat{f}_j^b T_{ab}^{ij} + \Lambda_i^a \hat{f}_{\bar{j}}^{\bar{b}} T_{a\bar{b}}^{i\bar{j}}, \quad (5.23)$$

\mathcal{L}_β is obtained from \mathcal{L}_α by flipping the spins;

$$\mathcal{L}_{\alpha\beta} = v_{kl}^{c\bar{d}} T_{cd}^{k\bar{l}} + \Lambda_{ij}^{a\bar{b}} \hat{v}_{ab}^{i\bar{j}} + \Lambda_{ij}^{a\bar{b}} \left(\hat{v}_{kl}^{i\bar{j}} + v_{kl}^{c\bar{d}} T_{cd}^{i\bar{j}} \right) T_{ab}^{k\bar{l}} + \Lambda_{ij}^{a\bar{b}} \hat{v}_{ab}^{c\bar{d}} T_{cd}^{i\bar{j}} \\ + \Lambda_{ij}^{a\bar{b}} \left\{ \hat{x}_a^c T_{cb}^{i\bar{j}} + \hat{x}_b^{\bar{d}} T_{ad}^{i\bar{j}} - \hat{x}_k^i T_{ab}^{k\bar{j}} - \hat{x}_{\bar{l}}^{\bar{j}} T_{a\bar{b}}^{i\bar{l}} \right\} \\ + \Lambda_{ij}^{a\bar{b}} \left\{ \left(\hat{v}_{al}^{id} - \hat{v}_{al}^{di} + x_{al}^{id} + \bar{x}_{al}^{id} \right) T_{db}^{lj} + \left(\hat{v}_{bl}^{j\bar{d}} - \hat{v}_{bl}^{\bar{d}j} + 2x_{bl}^{j\bar{d}} \right) T_{ad}^{i\bar{l}} \right. \\ \left. + \left(\hat{v}_{al}^{i\bar{d}} + v_{kl}^{c\bar{d}} T_{ac}^{ik} \right) T_{db}^{l\bar{j}} + \hat{v}_{lb}^{d\bar{j}} T_{ad}^{i\bar{l}} - \hat{v}_{ak}^{c\bar{j}} T_{cb}^{i\bar{k}} - \left(\hat{v}_{kb}^{i\bar{d}} - v_{kl}^{c\bar{d}} T_{cb}^{i\bar{l}} \right) T_{ad}^{k\bar{j}} \right\}, \quad (5.24)$$

or using the `cckext` factorization,

$$\begin{aligned}
\mathcal{L}_{\alpha\beta} = & v_{kl}^{cd} T_{cd}^{kl} + \Lambda_{ij}^{ab} \left(\hat{v}_{kl}^{ij} + \textcolor{red}{v}_{kl}^{cd} \textcolor{red}{T}_{cd}^{ij} \right) T_{ab}^{kl} + \Lambda_{ij}^{ab} K_{pq}^{ij} \left(\delta_a^p - \delta_k^p T_a^k \right) \left(\delta_b^q - \delta_l^q T_b^l \right) \\
& + \Lambda_{ij}^{ab} \left\{ \hat{x}_a^c T_{cb}^{ij} + \hat{x}_b^d T_{ad}^{ij} - \hat{x}_k^i T_{ab}^{kj} - \hat{x}_l^j T_{ab}^{il} \right\} \\
& + \Lambda_{ij}^{ab} \left\{ \left(\hat{v}_{al}^{id} - \hat{v}_{al}^{di} + x_{al}^{id} + \bar{x}_{al}^{id} \right) T_{db}^{ij} + \left(\hat{v}_{bl}^{jd} - \hat{v}_{bl}^{dj} + 2x_{bl}^{jd} \right) T_{ad}^{ij} \right. \\
& \left. + \left(\hat{v}_{al}^{id} + v_{kl}^{cd} T_{ac}^{ik} \right) T_{db}^{ij} + \hat{v}_{lb}^{dj} T_{ad}^{il} - \hat{v}_{ak}^{cj} T_{cb}^{ik} - \left(\hat{v}_{kb}^{id} - \textcolor{red}{v}_{kl}^{cd} \textcolor{red}{T}_{cb}^{il} \right) T_{ad}^{kj} \right\}.
\end{aligned} \tag{5.25}$$

The intermediate quantities are defined as follows,

$$\begin{aligned}
K_{pq}^{ij} &= v_{pq}^{rs} D_{rs}^{ij} & K_{pq}^{i\bar{j}} &= v_{pq}^{r\bar{s}} D_{rs}^{i\bar{j}} \\
D_{rs}^{ij} &= \left(T_{ab}^{ij} + T_a^i T_b^j - T_b^i T_a^j \right) \delta_r^a \delta_s^b + \mathcal{A}(ij; rs) \delta_r^i T_b^j \delta_s^b + \delta_r^i \delta_s^j - \delta_s^i \delta_r^j \\
D_{rs}^{i\bar{j}} &= \left(T_{ab}^{i\bar{j}} + T_a^i T_b^{\bar{j}} \right) \delta_r^a \delta_s^{\bar{b}} + \delta_r^i T_b^{\bar{j}} \delta_s^{\bar{b}} + T_a^i \delta_s^a \delta_s^{\bar{j}} + \delta_r^i \delta_s^{\bar{j}} \\
x_{al}^{id} &= \frac{1}{2} T_{ac}^{ik} \left(v_{kl}^{cd} - \textcolor{red}{v}_{kl}^{dc} \right) \\
\bar{x}_{al}^{id} &= x_{al}^{id} + T_{a\bar{c}}^{i\bar{k}} v_{l\bar{k}}^{d\bar{c}} \\
x_{al}^{i\bar{d}} &= \frac{1}{2} T_{a\bar{c}}^{i\bar{k}} \left(v_{kl}^{\bar{c}\bar{d}} - \textcolor{red}{v}_{kl}^{\bar{d}\bar{c}} \right) \\
\hat{x}_k^i &= \hat{f}_k^i + \textcolor{red}{2} \times \frac{1}{2} \left(v_{kl}^{cd} T_{cd}^{il} + v_{kl}^{cd} T_{cd}^{i\bar{l}} \right) \\
\hat{x}_a^c &= \hat{f}_a^c - \textcolor{red}{2} \times \frac{1}{2} \left(v_{kl}^{cd} T_{ad}^{kl} + v_{kl}^{cd} T_{ad}^{k\bar{l}} \right)
\end{aligned} \tag{5.26}$$

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. [8, 9]

In this section we use the following notation:

$$\begin{aligned}
\alpha\alpha T_{ab}^{ij} &= T_{ab}^{ij}, \\
\beta\beta T_{ab}^{ij} &= T_{ab}^{i\bar{j}}, \\
\alpha\beta T_{ab}^{ij} &= T_{ab}^{i\bar{j}},
\end{aligned} \tag{5.27}$$

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

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

$$\alpha\beta \bar{T}_{ab}^{ij} = \frac{1}{6} \left(\alpha\alpha T_{ab}^{ij} + \beta\beta T_{ab}^{ij} + 2 \alpha\beta T_{ab}^{ij} + \alpha\beta T_{ba}^{ij} + 2 \alpha\beta T_{ba}^{ji} + \alpha\beta T_{ab}^{ji} \right) \tag{5.28}$$

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

$$\begin{aligned}
\alpha\beta \bar{T}_{at}^{ij} &= \frac{1}{3} \left(\beta\beta T_{at}^{ij} + 2 \alpha\beta T_{at}^{ij} + \alpha\beta T_{at}^{ji} \right) \\
\alpha\beta \bar{T}_{ab}^{tj} &= \frac{1}{3} \left(\alpha\alpha T_{ab}^{tj} + 2 \alpha\beta T_{ab}^{tj} + \alpha\beta T_{ba}^{tj} \right) \\
\alpha\beta \bar{T}_{au}^{tj} &= \alpha\beta T_{au}^{tj} + \frac{\delta_u^t}{2m_s + 2} \left(\beta T_a^j - \alpha T_a^j - \alpha\beta T_{av}^{vj} \right)
\end{aligned} \tag{5.29}$$

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

$$\begin{aligned}\alpha\bar{T}_a^i &= \frac{1}{2} \left(\alpha T_a^i + \beta T_a^i - \alpha\beta\bar{T}_{av}^i \right), \\ \beta\bar{T}_a^i &= \frac{1}{2} \left(\alpha T_a^i + \beta T_a^i + \alpha\beta\bar{T}_{av}^i \right), \\ \alpha\bar{T}_a^t &= \alpha T_a^t \quad \text{and} \quad \beta\bar{T}_t^i = \beta T_t^i.\end{aligned}\tag{5.30}$$

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

$$\begin{aligned}\sigma\sigma\bar{T}_{ab}^{ij} &= \alpha\beta\bar{T}_{ab}^{ij} - \alpha\beta\bar{T}_{ba}^{ij}, \\ \alpha\alpha\bar{T}_{ab}^{tj} &= \alpha\alpha\bar{T}_{ba}^{tj} = \alpha\beta\bar{T}_{ab}^{tj} - \alpha\beta\bar{T}_{ba}^{tj}, \\ \beta\beta\bar{T}_{at}^{ij} &= \beta\beta\bar{T}_{ta}^{ji} = \alpha\beta\bar{T}_{at}^{ij} - \alpha\beta\bar{T}_{at}^{ji}, \\ \alpha\alpha\bar{T}_{ab}^{tu} &= \alpha\alpha T_{ab}^{tu} \quad \text{and} \quad \beta\beta\bar{T}_{tu}^{ij} = \beta\beta T_{tu}^{ij}.\end{aligned}\tag{5.31}$$

5.5 Open-shell CCSD/DSCD Lagrangian multiplier 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.

$$\begin{aligned}\frac{\partial\mathcal{L}_\alpha}{\partial T_e^m} &= (v_{km}^{ce} - v_{km}^{ec}) T_c^k + \frac{1}{2} v_{m\bar{k}}^{e\bar{c}} T_{\bar{c}}^{\bar{k}} + f_m^e - \Lambda_{ij}^{eb} \hat{v}_{mb}^{ij} + \Lambda_{mj}^{ab} \hat{v}_{ab}^{ej} + \frac{1}{4} \Lambda_{mj}^{ab} \hat{v}_{kl}^{ej} T_{ab}^{kl} \\ &+ \frac{1}{4} \Lambda_{im}^{ab} \hat{v}_{kl}^{ie} T_{ab}^{kl} - \frac{1}{4} \Lambda_{ij}^{eb} \hat{v}_{mb}^{cd} T_{cd}^{ij} - \frac{1}{4} \Lambda_{ij}^{ae} \hat{v}_{am}^{cd} T_{cd}^{ij} - \frac{1}{2} \Lambda_{ij}^{eb} \hat{f}_m^c T_{cb}^{ij} - \frac{1}{2} \Lambda_{mj}^{ab} \hat{f}_k^e T_{ab}^{kj} \\ &+ \frac{1}{2} \Lambda_{ij}^{ab} \left\{ (\hat{v}_{am}^{ce} - \hat{v}_{am}^{ec}) T_{cb}^{ij} - (\hat{v}_{km}^{ie} - \hat{v}_{mk}^{ie}) T_{ab}^{kj} \right\} \\ &- \Lambda_{ij}^{eb} \hat{v}_{ml}^{id} T_{db}^{lj} + \Lambda_{mj}^{ab} \hat{v}_{al}^{ed} T_{db}^{lj} + \Lambda_{ij}^{eb} \hat{v}_{ml}^{di} T_{db}^{lj} \\ &- \Lambda_{mj}^{ab} \hat{v}_{al}^{de} T_{db}^{lj} - \Lambda_{ij}^{eb} \hat{v}_{ml}^{i\bar{d}} T_{b\bar{d}}^{j\bar{l}} + \Lambda_{mj}^{ab} \hat{v}_{al}^{e\bar{d}} T_{b\bar{d}}^{j\bar{l}} \\ &- \Lambda_i^e \hat{v}_{ml}^{cd} T_{cd}^{i\bar{l}} - \Lambda_i^e \hat{v}_{ml}^{c\bar{d}} T_{cd}^{i\bar{l}} - \Lambda_m^a \hat{v}_{jk}^{ec} T_{ac}^{jk} - \Lambda_m^a \hat{v}_{jk}^{e\bar{c}} T_{a\bar{c}}^{j\bar{k}} \\ &- \Lambda_i^e \hat{f}_m^i + \Lambda_m^a \hat{f}_a^e + \Lambda_i^a (\hat{v}_{am}^{ie} - \hat{v}_{am}^{ei}) + \Lambda_i^a (v_{jm}^{be} - v_{jm}^{eb}) T_{ab}^{ij} + \Lambda_i^a v_{mj}^{e\bar{b}} T_{ab}^{i\bar{j}}\end{aligned}\tag{5.32}$$

$$\begin{aligned}\frac{\partial\mathcal{L}_\beta}{\partial T_e^m} &= \frac{1}{2} v_{m\bar{k}}^{e\bar{c}} T_{\bar{c}}^{\bar{k}} + \frac{1}{2} \Lambda_{ij}^{\bar{a}\bar{b}} \left\{ \hat{v}_{m\bar{a}}^{e\bar{c}} T_{\bar{c}\bar{b}}^{i\bar{j}} - \hat{v}_{m\bar{k}}^{e\bar{i}} T_{\bar{a}\bar{b}}^{k\bar{j}} \right\} \\ &+ \Lambda_{\bar{i}}^{\bar{a}} \hat{v}_{m\bar{a}}^{e\bar{i}} + \Lambda_{\bar{i}}^{\bar{a}} v_{m\bar{j}}^{e\bar{b}} T_{\bar{a}\bar{b}}^{i\bar{j}} + \Lambda_{\bar{i}}^{\bar{a}} (v_{mj}^{eb} - v_{mj}^{be}) T_{b\bar{a}}^{j\bar{i}},\end{aligned}\tag{5.33}$$

$$\begin{aligned}\frac{\partial\mathcal{L}_{\alpha\beta}}{\partial T_e^m} &= -\Lambda_{ij}^{\bar{e}\bar{b}} \hat{v}_{m\bar{b}}^{i\bar{j}} + \Lambda_{mj}^{\bar{a}\bar{b}} \hat{v}_{ab}^{e\bar{j}} + \Lambda_{mj}^{\bar{a}\bar{b}} \hat{v}_{kl}^{e\bar{j}} T_{ab}^{kl} - \Lambda_{ij}^{\bar{e}\bar{b}} \hat{v}_{mb}^{cd} T_{cd}^{i\bar{j}} \\ &- \Lambda_{ij}^{\bar{e}\bar{b}} \hat{f}_m^c T_{cb}^{i\bar{j}} - \Lambda_{mj}^{\bar{a}\bar{b}} \hat{f}_k^e T_{ab}^{k\bar{j}} \\ &+ \Lambda_{ij}^{\bar{a}\bar{b}} \left\{ (\hat{v}_{am}^{ce} - \hat{v}_{am}^{ec}) T_{cb}^{i\bar{j}} + \hat{v}_{mb}^{cd} T_{ad}^{i\bar{j}} - (\hat{v}_{km}^{ie} - \hat{v}_{mk}^{ie}) T_{ab}^{k\bar{j}} - \hat{v}_{ml}^{e\bar{j}} T_{a\bar{b}}^{l\bar{i}} \right\} \\ &- \Lambda_{ij}^{\bar{e}\bar{b}} \hat{v}_{ml}^{id} T_{db}^{l\bar{j}} + \Lambda_{mj}^{\bar{a}\bar{b}} \hat{v}_{al}^{ed} T_{db}^{l\bar{j}} + \Lambda_{ij}^{\bar{e}\bar{b}} \hat{v}_{ml}^{di} T_{db}^{l\bar{j}} - \Lambda_{mj}^{\bar{a}\bar{b}} \hat{v}_{al}^{de} T_{db}^{l\bar{j}} \\ &- \Lambda_{ij}^{\bar{e}\bar{b}} \hat{v}_{ml}^{i\bar{d}} T_{b\bar{d}}^{j\bar{l}} + \Lambda_{mj}^{\bar{a}\bar{b}} \hat{v}_{al}^{e\bar{d}} T_{b\bar{d}}^{j\bar{l}} + \Lambda_{ij}^{\bar{e}\bar{b}} \hat{v}_{mk}^{e\bar{j}} T_{cb}^{i\bar{k}} - \Lambda_{mj}^{\bar{a}\bar{b}} \hat{v}_{kb}^{e\bar{d}} T_{ad}^{k\bar{j}},\end{aligned}\tag{5.34}$$

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

$$4 \frac{\partial \mathcal{L}_\alpha}{\partial T_{ef}^{mn}} = \mathcal{A}(ef; mn) \left[\frac{1}{2} v_{mn}^{ef} + \frac{1}{4} \Lambda_{ij}^{ef} \left(\hat{v}_{mn}^{ij} + \frac{1}{2} v_{mn}^{cd} T_{cd}^{ij} \right) + \frac{1}{8} \Lambda_{mn}^{ab} v_{kl}^{ef} T_{ab}^{kl} \right. \\ + \frac{1}{4} \Lambda_{mn}^{ab} \hat{v}_{ab}^{ef} + \frac{1}{2} \Lambda_{mn}^{af} \hat{x}_a^e - \frac{1}{2} \Lambda_{in}^{ef} \hat{x}_m^i - 2 \times \frac{1}{4} \Lambda_{ij}^{eb} v_{mn}^{cf} T_{cb}^{ij} - 2 \times \frac{1}{4} \Lambda_{mj}^{ab} v_{kn}^{ef} T_{ab}^{kj} \\ + \Lambda_{in}^{af} (\hat{v}_{am}^{ie} - \hat{v}_{am}^{ei} + \bar{x}_{am}^{ie}) + \frac{1}{2} \Lambda_{mj}^{eb} (v_{nl}^{fd} - v_{nl}^{df}) T_{db}^{lj} \\ \left. + \Lambda_m^a \hat{v}_{an}^{ef} - \Lambda_i^e \hat{v}_{mn}^{if} + \Lambda_m^e \hat{f}_n^f \right], \quad (5.35)$$

$$\frac{\partial \mathcal{L}_\beta}{\partial T_{ef}^{mn}} = 0, \quad (5.36)$$

$$4 \frac{\partial \mathcal{L}_{\alpha\beta}}{\partial T_{ef}^{mn}} = \mathcal{A}(ef; mn) \left[-2 \times \frac{1}{2} \Lambda_{ij}^{e\bar{b}} v_{mn}^{cf} T_{cb}^{i\bar{j}} - 2 \times \frac{1}{2} \Lambda_{mj}^{a\bar{b}} v_{kn}^{ef} T_{ab}^{k\bar{j}} \right. \\ \left. + \Lambda_{m\bar{j}}^{e\bar{b}} (v_{nl}^{fd} - v_{nl}^{df}) T_{db}^{l\bar{j}} + \Lambda_{m\bar{j}}^{e\bar{b}} v_{nl}^{f\bar{d}} T_{db}^{l\bar{j}} + \Lambda_{m\bar{j}}^{e\bar{b}} \hat{v}_{n\bar{b}}^{f\bar{j}} \right], \quad (5.37)$$

$$\frac{\partial \mathcal{L}_\alpha}{\partial T_{ef}^{m\bar{n}}} = -2 \times \frac{1}{4} \Lambda_{ij}^{eb} v_{m\bar{n}}^{cf} T_{cb}^{ij} - 2 \times \frac{1}{4} \Lambda_{mj}^{ab} v_{k\bar{n}}^{ef} T_{ab}^{kj} \\ + \Lambda_{mj}^{eb} v_{l\bar{n}}^{df} T_{db}^{lj} + \Lambda_{im}^{ae} (\hat{v}_{a\bar{n}}^{i\bar{f}} + x_{a\bar{n}}^{i\bar{f}}) + \frac{1}{2} \Lambda_{mj}^{eb} (v_{n\bar{l}}^{f\bar{d}} - v_{n\bar{l}}^{d\bar{f}}) T_{bd}^{j\bar{l}} \\ + \Lambda_m^a \hat{v}_{a\bar{n}}^{e\bar{f}} - \Lambda_i^e \hat{v}_{m\bar{n}}^{i\bar{f}} + \Lambda_m^e \hat{f}_{\bar{n}}^f, \quad (5.38)$$

$$\frac{\partial \mathcal{L}_\beta}{\partial T_{ef}^{m\bar{n}}} = -2 \times \frac{1}{4} \Lambda_{ij}^{f\bar{b}} v_{m\bar{n}}^{e\bar{c}} T_{cb}^{i\bar{j}} - 2 \times \frac{1}{4} \Lambda_{n\bar{j}}^{a\bar{b}} v_{m\bar{k}}^{ef} T_{ab}^{k\bar{j}} \\ + \Lambda_{n\bar{j}}^{f\bar{b}} v_{m\bar{l}}^{e\bar{d}} T_{db}^{l\bar{j}} + \Lambda_{i\bar{n}}^{a\bar{f}} (\hat{v}_{m\bar{a}}^{e\bar{i}} + x_{a\bar{m}}^{i\bar{e}}) + \frac{1}{2} \Lambda_{n\bar{j}}^{f\bar{b}} (v_{m\bar{l}}^{ed} - v_{m\bar{l}}^{de}) T_{db}^{l\bar{j}} \\ + \Lambda_{n\bar{j}}^{a\bar{f}} \hat{v}_{a\bar{m}}^{f\bar{e}} - \Lambda_{i\bar{n}}^{f\bar{b}} \hat{v}_{n\bar{m}}^{i\bar{e}} + \Lambda_{n\bar{j}}^{f\bar{b}} \hat{f}_m^e, \quad (5.39)$$

$$\frac{\partial \mathcal{L}_{\alpha\beta}}{\partial T_{ef}^{m\bar{n}}} = v_{m\bar{n}}^{e\bar{f}} + \Lambda_{ij}^{e\bar{f}} \left(\hat{v}_{m\bar{n}}^{ij} + v_{m\bar{n}}^{cd} T_{cd}^{ij} \right) + \Lambda_{m\bar{n}}^{ab} v_{kl}^{ef} T_{ab}^{kl} + \Lambda_{m\bar{n}}^{ab} \hat{v}_{ab}^{ef} \\ + \Lambda_{m\bar{n}}^{a\bar{f}} \hat{x}_a^e - 2 \times \frac{1}{2} \Lambda_{ij}^{e\bar{b}} v_{m\bar{n}}^{cf} T_{cb}^{i\bar{j}} + \Lambda_{m\bar{n}}^{e\bar{b}} \hat{x}_b^{\bar{f}} - 2 \times \frac{1}{2} \Lambda_{ij}^{a\bar{f}} v_{m\bar{n}}^{ed} T_{ad}^{i\bar{j}} \\ - \Lambda_{i\bar{n}}^{ef} \hat{x}_m^i - 2 \times \frac{1}{2} \Lambda_{mj}^{a\bar{b}} v_{k\bar{n}}^{ef} T_{ab}^{kj} - \Lambda_{mj}^{e\bar{f}} \hat{x}_{\bar{n}}^{\bar{j}} - 2 \times \frac{1}{2} \Lambda_{i\bar{n}}^{a\bar{b}} v_{m\bar{l}}^{ef} T_{ab}^{i\bar{l}} \\ + \Lambda_{i\bar{n}}^{a\bar{f}} (\hat{v}_{am}^{ie} - \hat{v}_{am}^{ei} + x_{am}^{ie} + \bar{x}_{am}^{ie}) + \Lambda_{m\bar{j}}^{e\bar{b}} v_{l\bar{n}}^{df} T_{db}^{l\bar{j}} + \Lambda_{m\bar{j}}^{e\bar{b}} (\hat{v}_{b\bar{n}}^{j\bar{f}} - \hat{v}_{b\bar{n}}^{f\bar{j}} + 2x_{b\bar{n}}^{j\bar{f}}) \\ - \Lambda_{m\bar{j}}^{a\bar{f}} \hat{v}_{a\bar{n}}^{e\bar{j}} - \Lambda_{i\bar{n}}^{e\bar{b}} (\hat{v}_{m\bar{b}}^{i\bar{f}} - v_{m\bar{l}}^{cf} T_{cb}^{i\bar{l}}) + \Lambda_{m\bar{j}}^{a\bar{f}} v_{k\bar{n}}^{ed} T_{ad}^{kj}, \quad (5.40)$$

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

$$D_i^j = -\frac{1}{2} \Lambda_{ik}^{cd} T_{cd}^{jk} - \Lambda_{ik}^{c\bar{d}} T_{c\bar{d}}^{j\bar{k}} \\ D_a^b = \frac{1}{2} \Lambda_{kl}^{bc} T_{ac}^{kl} + \Lambda_{kl}^{b\bar{c}} T_{a\bar{c}}^{k\bar{l}} \\ D_i^a = \Lambda_i^a \\ D_a^i = \Lambda_k^c T_{ac}^{ik} + \Lambda_k^{\bar{c}} T_{a\bar{c}}^{i\bar{k}} \quad (5.41)$$

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

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

$$\begin{aligned}\hat{D}_i^j &= D_i^j - D_i^c T_c^j, \\ \hat{D}_a^b &= D_a^b + D_k^b T_a^k, \\ \hat{D}_i^a &= D_i^a, \\ \hat{D}_a^i &= D_a^i + T_a^i - D_a^c T_c^i + \hat{D}_k^i T_a^k.\end{aligned}\tag{5.42}$$

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

$$\begin{aligned}D_{ij}^{kl} &= \frac{1}{2} \Lambda_{ij}^{cd} T_{cd}^{kl} \\ D_{i\bar{j}}^{k\bar{l}} &= \Lambda_{i\bar{j}}^{cd} T_{cd}^{k\bar{l}} \\ D_{ib}^{aj} &= \Lambda_{ik}^{ac} T_{bc}^{jk} + \Lambda_{ik}^{a\bar{c}} T_{b\bar{c}}^{j\bar{k}} \\ \bar{D}_{i\bar{b}}^{a\bar{j}} &= \Lambda_{ik}^{ac} T_{c\bar{b}}^{k\bar{j}} + \Lambda_{ik}^{a\bar{c}} T_{b\bar{c}}^{j\bar{k}}\end{aligned}\tag{5.43}$$

and doubles-dressed Fock matrix,

$$\begin{aligned}x_k^i &= v_{kl}^{cd} T_{cd}^{il} + v_{k\bar{l}}^{cd} T_{cd}^{i\bar{l}} \\ x_a^c &= v_{kl}^{cd} T_{ad}^{kl} + v_{k\bar{l}}^{cd} T_{a\bar{d}}^{kl}.\end{aligned}\tag{5.44}$$

The intermediates for the `cckext` factorization are given by

$$\begin{aligned}K_{mn}^{rs} &= \hat{\Lambda}_{mn}^{pq} v_{pq}^{rs} \\ \hat{\Lambda}_{mn}^{pq} &= \Lambda_{mn}^{ab} \delta_a^p \delta_b^q - \Lambda_{mn}^{ab} T_a^i \delta_i^p \delta_b^q - \Lambda_{mn}^{ab} \delta_a^p T_b^j \delta_j^q + \Lambda_{mn}^{ab} T_a^i T_b^j \delta_i^p \delta_j^q.\end{aligned}\tag{5.45}$$

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

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

$$\begin{aligned}\hat{y}_{am}^{ie} &= \hat{v}_{am}^{ie} - \hat{v}_{am}^{ei} + \bar{x}_{am}^{ie} + x_{am}^{ie} \\ \hat{y}_{\bar{b}n}^{\bar{j}f} &= v_{n\bar{l}}^{f\bar{d}} T_{\bar{d}\bar{b}}^{\bar{l}j} + \hat{v}_{n\bar{b}}^{f\bar{j}} + 2x_{\bar{b}n}^{\bar{j}f}\end{aligned}\tag{5.46}$$

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

$$\begin{aligned}\frac{\partial \mathcal{L}}{\partial T_e^m} &= (v_{pm}^{qe} - v_{pm}^{eq}) \hat{D}_q^p + v_{m\bar{p}}^{e\bar{q}} \hat{D}_{\bar{q}}^{\bar{p}} + f_m^e - \Lambda_{ij}^{eb} \hat{v}_{mb}^{ij} - \Lambda_{ij}^{e\bar{b}} \hat{v}_{m\bar{b}}^{i\bar{j}} \\ &+ K_{mj}^{rs} \delta_r^e (\delta_s^j + \delta_s^b T_b^j) + K_{m\bar{j}}^{r\bar{s}} \delta_r^e (\delta_{\bar{s}}^{\bar{j}} + \delta_{\bar{s}}^{\bar{b}} T_{\bar{b}}^{\bar{j}}) + D_{mj}^{kl} \hat{v}_{kl}^{ej} + D_{m\bar{j}}^{k\bar{l}} \hat{v}_{k\bar{l}}^{e\bar{j}} \\ &- \frac{1}{2} \Lambda_{ij}^{eb} (\hat{v}_{mb}^{cd} T_{cd}^{ij}) - \Lambda_{i\bar{j}}^{e\bar{b}} (\hat{v}_{m\bar{b}}^{cd} T_{cd}^{i\bar{j}}) - D_c^e \hat{f}_m^c + D_m^k \hat{f}_k^e \\ &+ D_{id}^{el} (\hat{v}_{ml}^{di} - \hat{v}_{lm}^{di}) + D_{md}^{al} (\hat{v}_{al}^{ed} - \hat{v}_{al}^{de}) - \bar{D}_{i\bar{d}}^{e\bar{l}} \hat{v}_{m\bar{l}}^{i\bar{d}} + \bar{D}_{m\bar{d}}^{a\bar{l}} \hat{v}_{a\bar{l}}^{e\bar{d}} \\ &+ \Lambda_{i\bar{j}}^{e\bar{b}} \hat{v}_{m\bar{k}}^{c\bar{j}} T_{c\bar{b}}^{i\bar{k}} - \Lambda_{m\bar{j}}^{a\bar{b}} \hat{v}_{k\bar{b}}^{ed} T_{a\bar{d}}^{k\bar{j}} \\ &- \Lambda_i^e \hat{f}_m^i + \Lambda_m^a \hat{f}_a^e - \Lambda_i^e x_m^i - \Lambda_m^a x_a^e\end{aligned}\tag{5.47}$$

$$\begin{aligned}
4 \frac{\partial \mathcal{L}}{\partial T_{ef}^{mn}} = & v_{mn}^{ef} - v_{nm}^{ef} + \Lambda_{ij}^{ef} \left(\hat{v}_{mn}^{ij} + \frac{1}{2} v_{mn}^{cd} T_{cd}^{ij} \right) + D_{mn}^{kl} v_{kl}^{ef} + K_{mn}^{rs} \delta_r^e \delta_s^f \\
& + \mathcal{S}(ef, mn) \left\{ \Lambda_{mn}^{af} \hat{x}_a^e - \Lambda_{in}^{ef} \hat{x}_m^i \right\} \\
& + \mathcal{A}(ef; mn) \left\{ 2 \times \frac{1}{2} D_m^k v_{kn}^{ef} - 2 \times \frac{1}{2} D_c^e v_{mn}^{cf} + \Lambda_{in}^{af} \hat{y}_{am}^{ie} + \Lambda_{mj}^{e\bar{b}} \hat{y}_{bn}^{\bar{j}f} \right. \\
& \left. + \Lambda_m^a \hat{v}_{an}^{ef} - \Lambda_i^e \hat{v}_{mn}^{if} + \Lambda_m^e \hat{f}_n^f \right\}
\end{aligned} \tag{5.48}$$

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

$$\begin{aligned}
\frac{\partial \mathcal{L}}{\partial T_{ef}^{m\bar{n}}} = & v_{m\bar{n}}^{e\bar{f}} + \Lambda_{ij}^{e\bar{f}} \left(\hat{v}_{m\bar{n}}^{i\bar{j}} + v_{m\bar{n}}^{c\bar{d}} T_{c\bar{d}}^{i\bar{j}} \right) + D_{m\bar{n}}^{k\bar{l}} v_{k\bar{l}}^{e\bar{f}} + K_{m\bar{n}}^{r\bar{s}} \delta_r^e \delta_{\bar{s}}^{\bar{f}} \\
& + \Lambda_{m\bar{n}}^{a\bar{f}} \hat{x}_a^e + \Lambda_{m\bar{n}}^{e\bar{b}} \hat{x}_{\bar{b}}^{\bar{f}} - \Lambda_{i\bar{n}}^{e\bar{f}} \hat{x}_m^i - \Lambda_{m\bar{j}}^{e\bar{f}} \hat{x}_{\bar{n}}^{\bar{j}} \\
& + 2 \times \frac{1}{2} \left(D_m^k v_{k\bar{n}}^{e\bar{f}} + D_{\bar{n}}^{\bar{k}} v_{m\bar{k}}^{e\bar{f}} - D_c^e v_{m\bar{n}}^{c\bar{f}} - D_{\bar{c}}^{\bar{e}} v_{m\bar{n}}^{e\bar{c}} \right) \\
& + \Lambda_{i\bar{n}}^{a\bar{f}} \hat{y}_{am}^{ie} + \Lambda_{m\bar{j}}^{e\bar{b}} \hat{y}_{b\bar{n}}^{\bar{j}f} + \Lambda_{im}^{ae} \hat{y}_{a\bar{n}}^{i\bar{f}} + \Lambda_{i\bar{n}}^{a\bar{f}} \hat{y}_{am}^{ie} \\
& - \Lambda_{m\bar{j}}^{a\bar{f}} \left(\hat{v}_{a\bar{n}}^{e\bar{j}} - v_{k\bar{n}}^{e\bar{d}} T_{a\bar{d}}^{k\bar{j}} \right) - \Lambda_{i\bar{n}}^{e\bar{b}} \left(\hat{v}_{m\bar{b}}^{i\bar{f}} - v_{m\bar{l}}^{c\bar{f}} T_{c\bar{b}}^{i\bar{l}} \right) \\
& + \Lambda_m^a \hat{v}_{a\bar{n}}^{e\bar{f}} - \Lambda_i^e \hat{v}_{m\bar{n}}^{i\bar{f}} + \Lambda_m^e \hat{f}_{\bar{n}}^{\bar{f}} + \Lambda_{\bar{n}}^{\bar{a}} \hat{v}_{am}^{\bar{f}e} - \Lambda_i^{\bar{e}} \hat{v}_{\bar{n}m}^{\bar{e}e} + \Lambda_{\bar{n}}^{\bar{f}} \hat{f}_m^e.
\end{aligned} \tag{5.49}$$

5.6 Perturbative triples for unrestricted CCSD

The perturbative triples equations for unrestricted CCSD are given by

$$E_{[T]} = \frac{1}{6} \sum_{i < j < k} K_{ijk}^{abc} T_{abc}^{ijk} + \frac{1}{6} \sum_{\bar{i} < \bar{j} < \bar{k}} K_{i\bar{j}\bar{k}}^{\bar{a}\bar{b}\bar{c}} T_{\bar{a}\bar{b}\bar{c}}^{\bar{i}\bar{j}\bar{k}} + \frac{1}{2} \sum_{i < j; \bar{k}} K_{ijk}^{ab\bar{c}} X_{ab\bar{c}}^{ijk} + \frac{1}{2} \sum_{\bar{i} < \bar{j}; k} K_{i\bar{j}k}^{\bar{a}\bar{b}c} X_{\bar{a}\bar{b}c}^{\bar{i}\bar{j}k}. \tag{5.50}$$

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

$$\begin{aligned}
K_{ijk}^{abc} = K_{abc}^{ijk} = & \mathcal{A}(abc) \left\{ v_{bc}^{dk} T_{ad}^{ij} + v_{cb}^{dj} T_{ad}^{ik} + v_{ba}^{di} T_{dc}^{jk} - \frac{1}{2} \left(\bar{v}_{cl}^{kj} T_{ab}^{il} + \bar{v}_{cl}^{ki} T_{ab}^{lj} + \bar{v}_{al}^{ij} T_{cb}^{kl} \right) \right\}, \\
\bar{v}_{al}^{ij} = & v_{al}^{ij} - v_{al}^j, \\
T_{abc}^{ijk} = & \frac{K_{abc}^{ijk}}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}
\end{aligned} \tag{5.51}$$

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

$$\begin{aligned}
K_{i\bar{j}\bar{k}}^{\bar{a}\bar{b}\bar{c}} = K_{\bar{a}\bar{b}\bar{c}}^{i\bar{j}\bar{k}} = & \mathcal{A}(ab) \left\{ v_{\bar{b}\bar{c}}^{d\bar{k}} T_{ad}^{i\bar{j}} + v_{ba}^{di} T_{d\bar{c}}^{j\bar{k}} + v_{ab}^{dj} T_{d\bar{c}}^{i\bar{k}} + v_{a\bar{c}}^{i\bar{d}} T_{b\bar{d}}^{j\bar{k}} + v_{b\bar{c}}^{j\bar{d}} T_{ad}^{i\bar{k}} - \bar{v}_{al}^{ij} T_{b\bar{c}}^{kl} \right. \\
& \left. - v_{b\bar{l}}^{j\bar{k}} T_{a\bar{c}}^{i\bar{l}} - v_{a\bar{l}}^{i\bar{k}} T_{b\bar{c}}^{j\bar{l}} \right\} - v_{l\bar{c}}^{j\bar{k}} T_{ab}^{il} - v_{l\bar{c}}^{i\bar{k}} T_{ab}^{lj}, \\
T_{\bar{a}\bar{b}\bar{c}}^{i\bar{j}\bar{k}} = & \frac{K_{\bar{a}\bar{b}\bar{c}}^{i\bar{j}\bar{k}}}{\epsilon_i + \epsilon_j + \epsilon_{\bar{k}} - \epsilon_a - \epsilon_b - \epsilon_{\bar{c}}}
\end{aligned} \tag{5.52}$$

The (T) correction contains additionally the following terms,

$$\begin{aligned}
E_{(T)} = E_{[T]} &+ \sum_{i < j < k} \left[v_{jk}^{bc} T_{abc}^{ijk} T_i^{\dagger a} + v_{ik}^{ac} T_{abc}^{ijk} T_j^{\dagger b} + v_{ij}^{ab} T_{abc}^{ijk} T_k^{\dagger c} \right. \\
&+ \frac{1}{2} \left(T_{jk}^{\dagger bc} T_{abc}^{ijk} f_i^a + T_{ik}^{\dagger ac} T_{abc}^{ijk} f_j^b + T_{ij}^{\dagger ab} T_{abc}^{ijk} f_k^c \right) \Big] \\
&+ \sum_{i < j; \bar{k}} \left[v_{j\bar{k}}^{b\bar{c}} T_{ab\bar{c}}^{ij\bar{k}} T_i^{\dagger a} + v_{i\bar{k}}^{a\bar{c}} T_{ab\bar{c}}^{ij\bar{k}} T_j^{\dagger b} + v_{ij}^{ab} T_{ab\bar{c}}^{ij\bar{k}} T_{\bar{k}}^{\dagger \bar{c}} \right. \\
&+ T_{j\bar{k}}^{\dagger b\bar{c}} T_{ab\bar{c}}^{ij\bar{k}} f_i^a + T_{i\bar{k}}^{\dagger a\bar{c}} T_{ab\bar{c}}^{ij\bar{k}} f_j^b + \frac{1}{2} T_{ij}^{\dagger ab} T_{ab\bar{c}}^{ij\bar{k}} f_{\bar{k}}^{\bar{c}} \Big] \\
&+ \text{spin-flipped terms.}
\end{aligned} \tag{5.53}$$

In case of $\Lambda\text{UCCSD}(\mathbf{T})$, 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,

$$\begin{aligned}
K_{ijk}^{abc} &= \mathcal{A}(abc) \left\{ v_{dk}^{bc} \Lambda_{ij}^{ad} + v_{dj}^{cb} \Lambda_{ik}^{ad} + v_{di}^{ba} \Lambda_{jk}^{dc} - \frac{1}{2} (\bar{v}_{kj}^{cl} \Lambda_{il}^{ab} + \bar{v}_{ki}^{cl} \Lambda_{lj}^{ab} + \bar{v}_{ij}^{al} \Lambda_{kl}^{cb}) \right\}, \\
K_{ij\bar{k}}^{ab\bar{c}} &= \mathcal{A}(ab) \left\{ v_{d\bar{k}}^{b\bar{c}} \Lambda_{ij}^{ad} + v_{di}^{ba} \Lambda_{j\bar{k}}^{d\bar{c}} + v_{dj}^{ab} \Lambda_{i\bar{k}}^{d\bar{c}} + v_{id}^{a\bar{c}} \Lambda_{j\bar{k}}^{b\bar{d}} + v_{jd}^{b\bar{c}} \Lambda_{i\bar{k}}^{a\bar{d}} - \bar{v}_{ij}^{al} \Lambda_{l\bar{k}}^{b\bar{c}} \right. \\
&\quad \left. - v_{j\bar{k}}^{b\bar{l}} \Lambda_{i\bar{l}}^{a\bar{c}} - v_{i\bar{k}}^{a\bar{l}} \Lambda_{j\bar{l}}^{b\bar{c}} \right\} - v_{j\bar{k}}^{l\bar{c}} \Lambda_{il}^{ab} - v_{i\bar{k}}^{l\bar{c}} \Lambda_{lj}^{ab},
\end{aligned} \tag{5.54}$$

and the conjugate-transpose of the amplitudes in Eq. (5.53) 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, \dots) and virtual (a, b, \dots) spaces do not contain the active orbitals. The equations follow the equations presented in Ref.[10]. 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.[10] are coloured [magenta](#). Terms we have added to ensure proper antisymmetry and which are not explicitly listed in Ref.[10] are coloured [green](#). IAS terms, which are terms including the all internal singles, are coloured [brown](#).

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

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

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

$$\tau_a^i = T_a^i - \bar{T}_{\bar{a}}^i, \quad (6.3)$$

$$\bar{\tau}_{\bar{a}}^i = \bar{T}_{\bar{a}}^i - T_a^i, \quad (6.4)$$

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

The singles M tensor is built as follows,

$$M_u^i = T_{ut}^{\bar{i}}, \quad (6.6)$$

$$M_u^i = T_u^t T_{\bar{t}}^{\bar{i}}, \quad (6.7)$$

$$M_a^t = -T_{u\bar{a}}^{t\bar{u}}, \quad (6.8)$$

$$M_a^t = -T_u^t T_{\bar{a}}^{\bar{u}}, \quad (6.9)$$

$$M_a^i = T_{\bar{a}}^{\bar{u}} T_{ut}^{\bar{i}} + T_{\bar{t}}^{\bar{i}} T_{u\bar{a}}^{t\bar{u}}, \quad (6.10)$$

$$M_a^i = T_u^t T_{\bar{a}\bar{t}}^{\bar{u}\bar{i}}, \quad (6.11)$$

$$M_a^i = T_u^t T_{\bar{a}}^{\bar{u}} T_{\bar{t}}^{\bar{i}}, \quad (6.12)$$

$$M_u^t = T_u^t. \quad (6.13)$$

$$M_{\bar{t}}^{\bar{i}} = T_{ut}^{i\bar{u}}, \quad (6.14)$$

$$M_{\bar{t}}^{\bar{i}} = T_{\bar{t}}^{\bar{u}} T_u^i, \quad (6.15)$$

$$M_{\bar{a}}^{\bar{u}} = -T_{a\bar{t}}^{t\bar{u}}, \quad (6.16)$$

$$M_{\bar{a}}^{\bar{u}} = -T_{\bar{t}}^{\bar{u}} T_a^t, \quad (6.17)$$

$$M_{\bar{a}}^{\bar{i}} = T_a^t T_{ut}^{i\bar{u}} + T_u^i T_{a\bar{t}}^{t\bar{u}}, \quad (6.18)$$

$$M_{\bar{a}}^{\bar{i}} = T_{\bar{t}}^{\bar{u}} T_{au}^{ti}, \quad (6.19)$$

$$M_{\bar{a}}^{\bar{i}} = T_{\bar{t}}^{\bar{u}} T_a^t T_u^i, \quad (6.20)$$

$$M_{\bar{t}}^{\bar{u}} = T_{\bar{t}}^{\bar{u}}. \quad (6.21)$$

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

$$M_{ua}^{ij} = \mathcal{A}(ij) \tau_a^i T_{ut}^{t\bar{j}} + \mathcal{A}(ij) T_t^{\bar{i}} T_{u\bar{a}}^{t\bar{j}}, \quad (6.22)$$

$$M_{ua}^{ij} = T_u^t T_{t\bar{a}}^{\bar{i}\bar{j}}, \quad (6.23)$$

$$M_{au}^{ij} = -\mathcal{A}(ij) \tau_a^i T_{ut}^{t\bar{j}} - \mathcal{A}(ij) T_t^{\bar{i}} T_{u\bar{a}}^{t\bar{j}}, \quad (6.24)$$

$$M_{au}^{ij} = -T_u^t T_{t\bar{a}}^{\bar{i}\bar{j}}, \quad (6.25)$$

$$M_{ab}^{ti} = \mathcal{A}(ab) \tau_b^i T_{u\bar{a}}^{t\bar{u}} + \mathcal{A}(ab) T_b^{\bar{u}} T_{u\bar{a}}^{t\bar{i}}, \quad (6.26)$$

$$M_{ab}^{ti} = T_u^t T_{b\bar{a}}^{\bar{u}\bar{i}}, \quad (6.27)$$

$$M_{ab}^{it} = -\mathcal{A}(ab) \tau_b^i T_{u\bar{a}}^{t\bar{u}} - \mathcal{A}(ab) T_b^{\bar{u}} T_{u\bar{a}}^{t\bar{i}}, \quad (6.28)$$

$$M_{ab}^{it} = -T_u^t T_{b\bar{a}}^{\bar{u}\bar{i}}, \quad (6.29)$$

$$\begin{aligned} M_{ab}^{ij} = & -\mathcal{A}(ij; ab) \tau_b^j \left(T_{\bar{a}}^{\bar{u}} T_{ut}^{t\bar{i}} + T_t^{\bar{i}} T_{u\bar{a}}^{t\bar{u}} \right) - \mathcal{A}(\bar{i}\bar{j}; \bar{a}\bar{b}) \left(T_{t\bar{a}}^{\bar{u}\bar{i}} T_{ub}^{t\bar{j}} \right) \\ & - \mathcal{A}(\bar{i}\bar{j}) T_{\bar{a}\bar{b}}^{\bar{u}\bar{i}} T_{ut}^{t\bar{j}} - \mathcal{A}(ab) T_{t\bar{a}}^{\bar{i}\bar{j}} T_{ub}^{t\bar{u}} - \mathcal{A}(\bar{i}\bar{j}; \bar{a}\bar{b}) T_{\bar{a}}^{\bar{u}} T_t^{\bar{j}} T_{ub}^{t\bar{i}}, \end{aligned} \quad (6.30)$$

$$\begin{aligned} M_{ab}^{ij} = & -\mathcal{A}(\bar{i}\bar{j}; \bar{a}\bar{b}) \tau_{\bar{a}}^{\bar{i}} \left(T_{\bar{t}}^{\bar{u}} T_{ub}^{t\bar{j}} + T_u^t T_{t\bar{b}}^{\bar{u}\bar{j}} \right) \\ & - \mathcal{A}(\bar{i}\bar{j}) T_u^t T_{\bar{t}}^{\bar{j}} T_{\bar{a}\bar{b}}^{\bar{u}\bar{i}} - \mathcal{A}(\bar{a}\bar{b}) T_u^t T_{\bar{b}}^{\bar{u}} T_{t\bar{a}}^{\bar{i}\bar{j}}, \end{aligned} \quad (6.31)$$

$$M_{au}^{it} = -T_{u\bar{a}}^{t\bar{i}}, \quad (6.32)$$

$$M_{au}^{ti} = T_{u\bar{a}}^{t\bar{i}}, \quad (6.33)$$

$$M_{ua}^{it} = T_{u\bar{a}}^{t\bar{i}}, \quad (6.34)$$

$$M_{ua}^{ti} = -T_{u\bar{a}}^{t\bar{i}}, \quad (6.35)$$

$$M_{au}^{it} = -\tau_{\bar{a}}^{\bar{i}} T_u^t, \quad (6.36)$$

$$M_{ua}^{it} = +\tau_{\bar{a}}^{\bar{i}} T_u^t, \quad (6.37)$$

$$M_{au}^{ti} = +\tau_{\bar{a}}^{\bar{i}} T_u^t, \quad (6.38)$$

$$M_{ua}^{ti} = -\tau_{\bar{a}}^{\bar{i}} T_u^t. \quad (6.39)$$

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,

$$M_{u\bar{a}}^{i\bar{j}} = -\tau_{\bar{a}}^{\bar{j}} T_{u\bar{t}}^{t\bar{i}} - T_u^j T_{a\bar{t}}^{t\bar{i}} - T_a^t \tau_{u\bar{t}}^{j\bar{i}} - T_{\bar{t}}^{\bar{i}} T_{a\bar{u}}^{tj}, \quad (6.40)$$

$$M_{u\bar{a}}^{i\bar{j}} = T_u^t T_{a\bar{t}}^{j\bar{i}}, \quad (6.41)$$

$$M_{a\bar{t}}^{j\bar{i}} = -\tau_a^j T_{u\bar{t}}^{i\bar{u}} - T_{\bar{t}}^{\bar{j}} T_{u\bar{a}}^{i\bar{u}} - T_{\bar{a}}^{\bar{u}} \tau_{u\bar{t}}^{j\bar{i}} - T_u^i T_{\bar{t}\bar{a}}^{j\bar{u}}, \quad (6.42)$$

$$M_{a\bar{t}}^{j\bar{i}} = T_{\bar{t}}^{\bar{u}} T_{u\bar{a}}^{i\bar{j}}, \quad (6.43)$$

$$M_{a\bar{b}}^{t\bar{i}} = \tau_{\bar{b}}^{\bar{i}} T_{u\bar{a}}^{t\bar{u}} + T_b^t T_{u\bar{a}}^{i\bar{u}} + T_u^i \tau_{b\bar{a}}^{t\bar{u}} + T_{\bar{a}}^{\bar{u}} T_{ub}^{it}, \quad (6.44)$$

$$M_{a\bar{b}}^{t\bar{i}} = -T_u^t T_{b\bar{a}}^{i\bar{u}}, \quad (6.45)$$

$$M_{b\bar{a}}^{i\bar{u}} = \tau_b^i T_{a\bar{t}}^{t\bar{u}} + T_b^{\bar{u}} T_{a\bar{t}}^{t\bar{i}} + T_{\bar{t}}^{\bar{i}} \tau_{a\bar{b}}^{t\bar{u}} + T_a^t T_{\bar{t}\bar{b}}^{i\bar{u}}, \quad (6.46)$$

$$M_{b\bar{a}}^{i\bar{u}} = -T_{\bar{t}}^{\bar{u}} T_{a\bar{b}}^{t\bar{i}}, \quad (6.47)$$

$$\begin{aligned} M_{a\bar{b}}^{i\bar{j}} = & -\tau_{\bar{b}}^{\bar{j}} (T_{\bar{a}}^{\bar{u}} T_{u\bar{t}}^{t\bar{i}} + T_{\bar{t}}^{\bar{i}} T_{u\bar{a}}^{t\bar{u}}) - \tau_a^i (T_{u\bar{t}}^{j\bar{u}} T_b^t + T_{b\bar{t}}^{t\bar{u}} T_u^j) \\ & + T_{\bar{t}}^{\bar{i}} T_{\bar{a}}^{\bar{u}} T_{ub}^{tj} + T_b^t T_u^j T_{\bar{t}\bar{a}}^{i\bar{u}} - T_u^j T_{\bar{a}}^{\bar{u}} T_{b\bar{t}}^{t\bar{i}} - T_b^t T_{\bar{t}}^{\bar{i}} T_{u\bar{a}}^{j\bar{u}} \\ & - \tau_{u\bar{t}}^{j\bar{i}} T_{b\bar{a}}^{t\bar{u}} + T_{u\bar{t}}^{j\bar{u}} T_{b\bar{a}}^{t\bar{i}} + T_{u\bar{t}}^{t\bar{i}} T_{b\bar{a}}^{j\bar{u}} + T_{b\bar{t}}^{t\bar{u}} T_{u\bar{a}}^{j\bar{i}} \\ & + T_{u\bar{a}}^{t\bar{u}} T_{b\bar{t}}^{j\bar{i}} - T_{ub}^{tj} T_{\bar{t}\bar{a}}^{i\bar{u}} - T_{u\bar{a}}^{t\bar{i}} T_{b\bar{t}}^{j\bar{u}} - T_{u\bar{a}}^{j\bar{u}} T_{b\bar{t}}^{t\bar{i}}, \end{aligned} \quad (6.48)$$

$$\begin{aligned} M_{a\bar{b}}^{i\bar{j}} = & -\tau_{\bar{b}}^{\bar{j}} T_u^t T_{a\bar{t}}^{i\bar{u}} - \tau_a^i T_{\bar{t}}^{\bar{u}} T_{ub}^{jt} + T_u^t T_{\bar{t}}^{\bar{i}} T_{b\bar{a}}^{j\bar{u}} + T_u^t T_{\bar{a}}^{\bar{u}} T_{b\bar{t}}^{j\bar{i}} \\ & + T_{\bar{t}}^{\bar{u}} T_b^t T_{u\bar{a}}^{j\bar{i}} + T_{\bar{t}}^{\bar{i}} T_u^t T_{b\bar{a}}^{t\bar{i}}, \end{aligned} \quad (6.49)$$

$$M_{u\bar{t}}^{t\bar{i}} = T_u^i, \quad (6.50)$$

$$M_{u\bar{t}}^{i\bar{u}} = T_{\bar{t}}^{\bar{i}}, \quad (6.51)$$

$$M_{u\bar{a}}^{t\bar{i}} = \tau_{ua}^{it}, \quad (6.52)$$

$$M_{a\bar{t}}^{i\bar{u}} = \tau_{\bar{t}\bar{a}}^{i\bar{u}}, \quad (6.53)$$

$$M_{a\bar{t}}^{t\bar{i}} = \tau_{u\bar{a}}^{i\bar{u}}, \quad (6.54)$$

$$M_{u\bar{a}}^{i\bar{u}} = \tau_{a\bar{t}}^{t\bar{i}}, \quad (6.55)$$

$$M_{u\bar{a}}^{t\bar{u}} = -T_a^t, \quad (6.56)$$

$$M_{a\bar{t}}^{t\bar{u}} = -T_{\bar{a}}^{\bar{u}}, \quad (6.57)$$

$$M_{u\bar{t}}^{i\bar{j}} = -\tau_{u\bar{t}}^{j\bar{i}}, \quad (6.58)$$

$$M_{a\bar{b}}^{t\bar{u}} = -\tau_{b\bar{a}}^{t\bar{u}}. \quad (6.59)$$

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

$$W = R_{u\bar{t}}^{t\bar{u}}. \quad (6.60)$$

The all internal 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.

IAS contribution to the energy,

$$\Delta E_{\text{IAS}} = -W_{u\bar{t}}^{t\bar{u}} T_u^t T_{\bar{t}}^{\bar{u}}. \quad (6.61)$$

Chapter 7

Full Configuration Interaction and Selected CI Methods

7.1 Introduction

Full Configuration Interaction (FCI) provides the exact solution to the time-independent Schrödinger equation within a given orbital basis set. While FCI is the ultimate benchmark for quantum chemistry calculations, its exponential scaling with system size limits its applicability to small systems. This chapter describes the implementation of FCI and selected CI methods in `ElemCo.jl`, including Heat-bath CI (HCI), multi-state calculations, P-space enhanced Davidson solver, and reduced density matrix calculations.

7.2 Full Configuration Interaction

7.2.1 Determinantal Representation

A Slater determinant $|\Phi_I\rangle$ is specified by occupation numbers for each spin-orbital. In the Knowles-Handy algorithm[11], determinants are represented separately for α and β spins:

$$|\Phi^I\rangle = |\alpha^I\rangle \otimes |\beta^I\rangle \quad (7.1)$$

where $|\alpha^I\rangle$ and $|\beta^I\rangle$ are strings of occupied spin-orbitals.

The FCI wave function is expanded as:

$$|\Psi\rangle = \sum_I c_I |\Phi^I\rangle \quad (7.2)$$

where c_I are the CI coefficients to be determined.

7.2.2 Slater-Condon Rules

Matrix elements $\langle \Phi_I | \hat{H} | \Phi_J \rangle$ can be evaluated using Slater-Condon rules:

Identical determinants ($|\Phi^I\rangle = |\Phi^J\rangle$):

$$\langle \Phi_I | \hat{H} | \Phi^I \rangle = \sum_{i \in I} h_i^i + \frac{1}{2} \sum_{i,j \in I} [v_{ij}^{ij} - v_{ij}^{ji}] \quad (7.3)$$

Single excitation ($|\Phi^J\rangle = \hat{a}_a^\dagger \hat{a}_i |\Phi^I\rangle$):

$$\langle \Phi_I | \hat{H} | \Phi^J \rangle = \text{sgn}_{ia} \left[h_a^i + \sum_{j \in I} [v_{aj}^{ij} - v_{aj}^{ji}] \right] \quad (7.4)$$

where sgn_{ia} is the fermionic phase factor from orbital reordering.

Double excitation ($|\Phi^J\rangle = \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i |\Phi^I\rangle$):

$$\langle \Phi_I | \hat{H} | \Phi^J \rangle = \text{sgn}_{iajb} [v_{ab}^{ij} - v_{ba}^{ij}] \quad (7.5)$$

Higher excitations: Matrix elements vanish for determinants differing by more than two orbitals.

7.2.3 String-Based Algorithm

The Knowles-Handy algorithm[11] evaluates the matrix-vector product $\mathbf{v}_{\text{out}} = \hat{H} \mathbf{c}_{\text{in}}$ efficiently using string-based techniques and resolution of identity:

$$v_I = H_I^J c_J = \langle \alpha_I \beta_I | \hat{H} | \alpha^J \beta^J \rangle c_J \quad (7.6)$$

For the two-electron part of the Hamiltonian, we have:

$$\langle I | \frac{1}{2} v_{pq}^{rs} \left(\hat{E}_r^p \hat{E}_s^q - \hat{E}_s^p \hat{E}_r^q \right) | J \rangle c_J = \frac{1}{2} v_{pq}^{rs} \langle I | \hat{E}_r^p | K \rangle \langle K | \hat{E}_s^q | J \rangle c_J - \dots, \quad (7.7)$$

The Hamiltonian is decomposed into one-electron and two-electron parts:

$$\hat{H} = \hat{H}_1^{(\alpha)} + \hat{H}_1^{(\beta)} + \hat{H}_2^{(\alpha\alpha)} + \hat{H}_2^{(\beta\beta)} + \hat{H}_2^{(\alpha\beta)} \quad (7.8)$$

The one-electron part is absorbed into the two-electron integrals. For remaining components, string substitutions are performed:

- **Same-spin two-electron:** Substitution in one string, sum over other string
- **Opposite-spin two-electron:** Substitution in both strings simultaneously

7.3 Davidson Iterative Diagonalization

7.3.1 Davidson Algorithm

The Davidson method finds the lowest eigenvalues of large matrices without explicit matrix construction. Given initial guess vectors $\{\mathbf{u}^1, \dots, \mathbf{u}^k\}$, the algorithm iteratively builds a subspace and solves:

$$\mathbf{H}_{\text{sub}} \mathbf{c} = E \mathbf{c}, \quad (7.9)$$

where $[\mathbf{H}_{\text{sub}}]_i^j = \langle \mathbf{u}_i | \hat{H} | \mathbf{u}^j \rangle$.

7.3.2 Subspace Expansion

The residual vector for eigenstate \mathbf{n} is:

$$\mathbf{r}^{\mathbf{n}} = \mathbf{H}\mathbf{x}^{\mathbf{n}} - E^{\mathbf{n}}\mathbf{x}^{\mathbf{n}}, \quad (7.10)$$

where $\mathbf{x}^{\mathbf{n}} = c_i^{\mathbf{n}}\mathbf{u}^i$ is the approximate eigenvector.

A correction vector $\mathbf{u}^{\mathbf{n}} \rightarrow \mathbf{u}^{k+1}$ is computed and added to the subspace. In ElemCo.jl, we use either the diagonal preconditioner,

$$u_I^{\mathbf{n}} = \frac{r_I^{\mathbf{n}}}{E^{\mathbf{n}} - H_I^I}, \quad (7.11)$$

or the P-space enhanced preconditioner (see Sec. 7.3.3 and Sec. 7.3.5).

7.3.3 Jacobi-Davidson Preconditioner

For improved convergence, especially for excited states, we implement the Jacobi-Davidson correction. The correction vector $\mathbf{u}^{\mathbf{n}}$ solves:

$$(\mathbf{I} - \mathbf{x}^{\mathbf{n}}\mathbf{x}_{\mathbf{n}}^{\dagger})(\mathbf{H} - E^{\mathbf{n}})(\mathbf{I} - \mathbf{x}^{\mathbf{n}}\mathbf{x}_{\mathbf{n}}^{\dagger})\mathbf{u}^{\mathbf{n}} = -\mathbf{r}^{\mathbf{n}\perp}, \quad (7.12)$$

where $\mathbf{x}^{\mathbf{n}}$ is the normalized Ritz vector and $\mathbf{r}^{\mathbf{n}\perp}$ is the residual orthogonalized to $\mathbf{x}^{\mathbf{n}}$.

In our implementation, we use a P-Q space decomposition where P is a selected subspace of important determinants and Q is its complement. For the Q space we use the simple diagonal preconditioner, Eq. (7.11), while for the P space we solve the Jacobi-Davidson equation exactly, including the coupling to Q space. The correction equation becomes:

$$\left[(\mathbf{I}_{\{P\}} - \mathbf{x}_{\{P\}}^{\mathbf{n}}\mathbf{x}_{\mathbf{n}\{P\}}^{\dagger})(\mathbf{H}_{\{P\}} - E^{\mathbf{n}})(\mathbf{I}_{\{P\}} - \mathbf{x}_{\{P\}}^{\mathbf{n}}\mathbf{x}_{\mathbf{n}\{P\}}^{\dagger}) + \alpha\mathbf{x}_{\{P\}}^{\mathbf{n}}\mathbf{x}_{\mathbf{n}\{P\}}^{\dagger} \right] \mathbf{u}_{\{P\}}^{\mathbf{n}} = -\mathbf{r}_{\{P\}}^{\mathbf{n}\perp} + \mathbf{s}_{\{P\}}, \quad (7.13)$$

with coupling terms:

$$\alpha = \mathbf{x}_{\mathbf{n}\{Q\}}^{\dagger}(\mathbf{H}_{\{Q\}} - E^{\mathbf{n}})\mathbf{x}_{\{Q\}}^{\mathbf{n}} \quad (7.14)$$

$$\mathbf{s}_{\{P\}}^{\mathbf{n}} = (\mathbf{I}_{\{P\}} - \mathbf{x}_{\{P\}}^{\mathbf{n}}\mathbf{x}_{\mathbf{n}\{P\}}^{\dagger})(\mathbf{H}_{\{P\}} - E^{\mathbf{n}})\mathbf{x}_{\{P\}}^{\mathbf{n}}(\mathbf{x}_{\mathbf{n}\{Q\}}^{\dagger}\mathbf{u}_{\{Q\}}^{\mathbf{n}}) + \beta\mathbf{x}_{\{P\}}^{\mathbf{n}} \quad (7.15)$$

$$\beta = \mathbf{x}_{\mathbf{n}\{Q\}}^{\dagger}(\mathbf{H}_{\{Q\}} - E^{\mathbf{n}})(\mathbf{I}_{\{Q\}} - \mathbf{x}_{\{Q\}}^{\mathbf{n}}\mathbf{x}_{\mathbf{n}\{Q\}}^{\dagger})\mathbf{u}_{\{Q\}}^{\mathbf{n}}. \quad (7.16)$$

Since \mathbf{H}_Q is diagonal, α and β are computed efficiently using only diagonal elements.

The equation is solved using a direct linear solver (LU or QR decomposition) since the P space is small.

7.3.4 Multi-State Davidson

For computing multiple states simultaneously, the algorithm is extended to maintain orthogonality between states. The subspace is expanded for all states:

$$\mathbf{H}_{\text{sub}}\mathbf{C} = \mathbf{C}\mathbf{E}, \quad (7.17)$$

where $\mathbf{E} = \text{diag}(E^1, E^2, \dots, E^{\mathbf{n}})$ and columns of \mathbf{C} contain eigenvector coefficients.

Dual convergence criteria: Both energy convergence ($|\Delta E^{\mathbf{n}}| < \epsilon_E$) and residual convergence ($\|\mathbf{r}^{\mathbf{n}}\| < \epsilon_R$) must be satisfied for all states to ensure correct excited state energies.

7.3.5 P-Space Selection

The P-space is a subset of important determinants used to generate high-quality initial guess vectors and preconditioners. Determinants are selected by:

Excitation level: Include all determinants up to n -fold excitations from the Hartree-Fock reference.

Energy criterion: Select determinants with diagonal elements satisfying:

$$H_I^I - E_{\text{HF}} < \Delta E_{\text{threshold}} \quad (7.18)$$

Hybrid selection: Combine excitation level and energy criteria.

HCI-based selection: Use Heat-bath CI (see Sec. 7.4) to select the most important determinants.

7.4 Heat-bath Configuration Interaction (HCI)/CIPSI

7.4.1 Algorithm Overview

Heat-bath CI (HCI)[12] is a selected CI method that efficiently selects important determinants using selection inspired by heat-bath sampling. An extension towards CIPSI[13] is also implemented.

The algorithm consists of three phases plus an extension towards CIPSI:

Phase I (Setup): Pre-compute sorted lists of double excitation matrix elements:

$$\text{For each } (p, q) : \quad \{(r, s, H_{rs \leftarrow pq})\} \text{ sorted by } |H_{rs \leftarrow pq}| \text{ (decreasing)} \quad (7.19)$$

Phase II: Variational calculation in the current selected space:

$$\mathbf{H}_{\text{sel}} \mathbf{c} = E_{\text{var}} \mathbf{c} \quad (7.20)$$

Phase III (Heat-Bath Selection): Generate candidate determinants connected to the variational space by $|H_J^I c_I| > \epsilon_h$:

For each determinant $|\Phi_I\rangle$ in the variational space:

- Generate single excitations with $|f_i^a c_I| > \epsilon_h$
- Use pre-sorted lists to generate only double excitations with $|v_{ij}^{ab} c_I| > \epsilon_h$
- Adaptive threshold: $\epsilon_{\text{adaptive}} = \epsilon_h / |c_I|$

Phase IV (Perturbative selection à la CIPSI): Select determinants corresponding to highest perturbative amplitudes:

$$pert_{C_J}^2 \approx \frac{\left| \sum_{I \in \{|H_J^I c_I| > \epsilon_h\}} H_J^I c_I \right|^2}{(E_{\text{var}} - H_J^J)^2} > \epsilon_p^2 \quad (7.21)$$

The sum runs only over determinants that have a large contribution to the J determinant according to the heat-bath criterion, and therefore can be calculated during the Phase III, essentially at no extra cost.

Note that in Phase III, the candidates are generated only for the new determinants, however, the $H_J^I c_I$ values are accumulated for all determinants in the variational space.

7.4.2 Efficient Excitation Generation

The key to HCI performance is the setup phase, which pre-computes and sorts excitation lists. For restricted Hartree-Fock (RHF), store:

$$\text{double_excitations}[(p, q)] = \{(r, s, H_{rs \leftarrow pq})\}_{\text{sorted}}, \quad (7.22)$$

where $H_{rs \leftarrow pq} = v_{pq}^{rs} - v_{pq}^{sr}$ is the antisymmetrized matrix element, and $H_{rs \leftarrow pq} = v_{pq}^{rs}$ for p, q of opposite spin.

For unrestricted Hartree-Fock (UHF), store separately:

- α - α excitations: $v_{pq}^{rs} - v_{pq}^{sr}$
- β - β excitations: $v_{pq}^{rs} - v_{pq}^{sr}$
- α - β mixed excitations: v_{pq}^{rs}

7.4.3 Multi-State HCI/CIPSI

For multi-state calculations, use **state-maximum selection**:

$$pert, max c_J^2 = \max_{n=1, \dots, N_{\text{states}}} \left[\frac{|\sum_{I \in \text{var}_{\epsilon_h}} H_J^I c_I^n|^2}{(E_{\text{var}}^n - H_J^J)^2} \right] \quad (7.23)$$

This ensures determinants important for *any* state are included, preventing bias toward the ground state.

The initial guess is generated by diagonalizing a small-space Hamiltonian:

$$N_{\text{small}} = \max \left(100, \sqrt{N_{\text{target}}}, 5N_{\text{states}} \right) \quad (7.24)$$

with determinants selected using hybrid method (energy + excitation level), and diagonalized to get initial eigenvectors for all states. This prevents missing excited states due to poor initialization.

7.4.4 Hamiltonian Matrix Construction

The Hamiltonian matrix in the selected space is constructed using the Slater-Condon rules (see Sec. 7.2) and stored in a sparse format (for each row, store only non-zero elements and their column indices).

The connections between determinants are identified using three helper lists (similar to Ref. [14]):

- **Same alpha list:** For each alpha string, store all indices of determinants sharing that alpha string. This list is used to find beta single and double excitations efficiently.
- **Same beta list:** For each beta string, store all indices of determinants sharing that beta string. This list is used to find alpha single and double excitations efficiently.
- **Single alpha excitation list:** For each alpha string, store all alpha strings reachable by a single excitation. This list is used to find mixed alpha-beta double excitations efficiently.

Using these lists, a list of connected determinants i for each determinant j is generated (for $i < j$) and used to compute and store the Hamiltonian matrix elements.

7.4.5 Second-Order Energy Correction

The PT2 correction recovers dynamical correlation from determinants outside the variational space[12]:

$$\Delta E_{\text{PT2}} = \sum_{K \notin \text{var}} \frac{(\sum_{I \in \text{var}} H_K^I c_I)^2}{E_{\text{var}} - H_K^K}, \quad (7.25)$$

where K runs over all determinants connected to the variational space but not included in it.

To compute PT2 efficiently, adaptive thresholding is employed. For each variational determinant $|\Phi^I\rangle$,

$$\epsilon_{\text{adaptive}} = \frac{\epsilon_{\text{pt2}}}{|c_I|}, \quad (7.26)$$

and only excitations are generated with $|H_K^I| > \epsilon_{\text{adaptive}}$ using pre-sorted lists from setup.

In order to reduce memory usage, an additional layer of thresholding is applied during PT2 calculation. This involves discarding excitations with small contributions before they are fully generated. For this purpose, the instantaneous PT2 amplitudes are calculated as $H_K^I c_I / (E_{\text{var}} - H_K^K)$, and excitations with amplitudes below a second threshold ϵ_{pt2}^c are not added to the list of candidates for PT2 correction. If the K determinant is already present in the list, its amplitude is updated accordingly, otherwise an energy contribution of this instantaneous excitation is added to the PT2 energy directly and also to the uncertainty estimate of the PT2 energy.

In practice, the calculation corresponds to the Phase III + Phase IV of the HCI selection with a different (tight) threshold ϵ_{pt2} .

7.5 Reduced Density Matrices

7.5.1 One-Particle Density Matrix

The one-particle reduced spin-resolved density matrix (1-RDM) is:

$$\gamma_q^p = \langle \Psi | \hat{a}_p^\dagger \hat{a}_q | \Psi \rangle = c^{I*} c_J \langle \Phi_I | \hat{a}_p^\dagger \hat{a}_q | \Phi_J \rangle \quad (7.27)$$

For separate spin components (p, q and \bar{p}, \bar{q} correspond to α and β orbitals, respectively):

$$\begin{aligned} \gamma_q^p &= c^{I*} c_J \langle \alpha_I \beta_I | \hat{a}_p^\dagger \hat{a}_q | \alpha^J \beta^J \rangle \\ \gamma_{\bar{q}}^{\bar{p}} &= c^{I*} c_J \langle \alpha_I \beta_I | \hat{a}_{\bar{p}}^\dagger \hat{a}_{\bar{q}} | \alpha^J \beta^J \rangle \end{aligned} \quad (7.28)$$

Properties:

- Trace: $\text{tr}(\gamma^{(\alpha)}) = N_\alpha$, $\text{tr}(\gamma^{(\beta)}) = N_\beta$
- Hermitian: $\gamma_{pq} = \gamma_{qp}^*$
- Eigenvalues: Natural orbital occupations $0 \leq n_i \leq 2$

7.5.2 Transition Density Matrix

For different states $|\Psi_m\rangle$ and $|\Psi_n\rangle$:

$${}^n_m\gamma_q^p = \langle \Psi_m | \hat{a}_p^\dagger \hat{a}_q | \Psi_n \rangle \quad (7.29)$$

Used for computing transition properties (e.g., oscillator strengths, transition dipole moments).

7.5.3 Two-Particle Density Matrix

The two-particle reduced (spin-resolved) density matrix (2-RDM) is:

$$\Gamma_{rs}^{pq} = \langle \Psi | \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r | \Psi \rangle \quad (7.30)$$

Energy verification:

$$E = h_p^q \gamma_q^p + \frac{1}{2} v_{pq}^{rs} \Gamma_{rs}^{pq} + E_{\text{nuc}} \quad (7.31)$$

7.5.4 Natural Orbitals

Diagonalize the 1-RDM:

$$\gamma \phi_i = n_i \phi_i \quad (7.32)$$

Natural orbital occupations n_i indicate importance of orbitals. Used for:

- Active space selection
- Identifying multireference character

Chapter 8

Automatically generated UCCSDT and UDC-CCSDT

Unrestricted implementations of CCSDT and DC-CCSDT[15, 16, 17] were generated with version 1.0.1 of the Quantwo program[18]. 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.jlis located in the src/algo directory.

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