From Canonical CCSD to Local CCSD

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1. Spin-adapted CC

The derivation of the spin-adapted CCSD uses Wick's theorem with the addition of the biorthogonal basis for the doubles residual. The expression given has been translated from the implementation of this method within PyCC.

Notation

The expressions are represented in physicist's notation. For Fock matrices that contain occupied and virtual indices such as f_{ia} will be written as f^i_a for clarity when comparing canonical and PNO forms of the CCSD. With the same reasoning, the single and double amplitudes are written as t^i_a and t^{ij}_{ab}. Other tensors with pair occupied indices will be written similarly to the double amplitudes. Intermediate terms such as F_{me}; however, are not written in that notation to differentiate itself from Fock matrices and such.

1.1 Singles residual

The singles residual is

$$\begin{aligned} R^i_a =& f^i_a + \sum_e t^i_e F_{ae} - \sum_m t^m_a F_{mi} + \sum_{me} \left(2t^{im}_{ae} - t^{im}_{ea}\right) F_{me} \\ &+ \sum_{nf} t^n_f L_{nafi} + \sum_{mef} \left(2t^{mi}_{ef} - t^{mi}_{fe}\right) K_{maef} - \sum_{mne} t^{mn}_{ae} L_{nmei} \end{aligned} \tag{1}$$

where K^{ij}_{ab} is the two-electron integral $\langle ij|ab\rangle$ and L^{ij}_{ab} is $2K^{ij}_{ab} - K^{ij}_{ba}$.

1.2 Doubles Residual

$$
\begin{aligned}
R_{ab}^{ij} =& \frac{1}{2}K_{ab}^{ij} + \sum_e t_{ae}^{ij}\left(F_{be} - \frac{1}{2}\sum_m t_b^m F_{me}\right) \\
&- \sum_m t_{ab}^{im}\left(F_{mj} + \frac{1}{2}\sum_e t_e^j F_{me}\right) \\
&+ \frac{1}{2}\sum_{mn}\tau_{ab}^{mn}W_{mnij} + \frac{1}{2}\sum_{ef}\tau_{ef}^{ij}K_{abef} \\
&- \sum_m t_a^m Z_{mbij} + \sum_{me}\left(t_{ae}^{im} - t_{ea}^{im}\right)W_{mbej} \\
&+ \sum_{me} t_{ae}^{im}\left(W_{mbej} + W_{mbje}^{*}\right) + \sum_{me} t_{ae}^{mj}W_{mbie} - \sum_{me} t_e^i t_a^m K_{mbej} \\
&- \sum_{me} t_e^i t_b^m K_{maje} + \sum_e t_e^i K_{abej} - \sum_m t_a^m K_{mbij}
\end{aligned} \tag{2}
$$

where τ is defined as, for example,

$$
\tau_{ab}^{mn} = t_{ab}^{mn} + t_a^m t_b^n. \tag{3}
$$

The asterisk on one of the terms indicates an index swap between j and e, W_{mbje}, when implemented in PyCC to match the shape of W_{mbej}. An additional set of the double residual expressions are evaluated, where there is a permutation between i and j as well as a and b, due to the use of the biorthogonal basis. For example, K_{ab}^{ij} becomes K_{ba}^{ji}.

1.3 Intermediates

One-Particle Intermediates

$$
F_{ae} = f_{ae} - \frac{1}{2}\sum_m f_e^m t_a^m + \sum_{mf} t_f^m L_{mafe} - \sum_{mnf}\tilde{\tau}_{af}^{mn}L_{ef}^{mn} \tag{4}
$$

$$
F_{mi} = f_{mi} + \frac{1}{2}\sum_e t_e^i f_e^m + \sum_{ne} t_e^n L_{mnie} + \sum_{nef}\tilde{\tau}_{ef}^{in}L_{ef}^{mn} \tag{5}
$$

$$
F_{me} = f_{me} + \sum_{nf} t_f^n L_{ef}^{mn} \tag{6}
$$

where $\tilde{\tau}$ is defined as, for example,

$$\tilde{\tau}_{af}^{mn} = t_{af}^{mn} + \frac{1}{2} t_a^m t_f^n. \tag{7}$$

Two-Particle Intermediates

$$W_{mnij} = K_{mnij} + \sum_e t_e^j K_{mnie} + \sum_e t_e^i K_{mnej} + \sum_{ef} \tau_{ef}^{ij} K_{ef}^{mn} \tag{8}$$

$$W_{mbej} = K_{mbej} + \sum_f t_f^j K_{mbef} - \sum_n t_b^n K_{mnej} - \sum_{nf} \bar{\tau}_{fb}^{jn} K_{ef}^{mn} + \frac{1}{2} \sum_{nf} t_{fb}^{nj} L_{ef}^{mn} \tag{9}$$

$$W_{mbje} = -K_{mbje} - \sum_f t_f^j K_{mbfe} + \sum_n t_b^n K_{mnje} + \sum_{nf} \bar{\tau}_{fb}^{jn} K_{fe}^{mn} \tag{10}$$

$$Z_{mbij} = \sum_{ef} K_{mbef} \tau_{ef}^{ij} \tag{11}$$

where $\bar{\tau}$ is defined as, for example,

$$\bar{\tau}_{fb}^{jn} = \frac{1}{2} t_{ab}^{mn} + t_a^m t_b^n \tag{12}$$

1.4 Energy

$$E_{ccsd} = 2 f_a^i t_a^i + \tau_{ab}^{ij} L_{ab}^{ij} \tag{13}$$

2. PNO form of CCSD

Notation

Within the local representation, the superscript indicate which pair occupied orbitals (ij) whereas the subscript with a bar, $\bar{a}_{ij}$, depicts the virtual subspace that originates from the pair occupied orbitals. For example, $K_{\bar{a}_{ij}\bar{b}_{ij}}^{ij}$ is the two-electron integral in the local representation.

Background

The diagonalization of the pair density, D^{ij}, (Eq. 14) yields $d^{ij}_{a\bar{a}_{ij}}$ which are MP2-PNOs expanded in terms of virtual MOs (Eq. 15) with corresponding $\bar{n}^{ij}$, known as the natural orbital occupation numbers:

$$D^{ij} d^{ij}_{a\bar{a}_{ij}} = n^{ij} d^{ij}_{a\bar{a}_{ij}} \tag{14}$$

and

$$|\bar{a}_{ij}\rangle = \sum_{a} d^{ij}_{a\bar{a}_{ij}} |a\rangle \,. \tag{15}$$

The MP2-PNOs are for a given occupied pair ij such that each pair are orthonormal but the PNOs of different pairs are not. The overlap between the PNOs of two different pairs is

$$\sum_{cd} \langle c| \, d^{ij}_{c\bar{a}_{ij}} d^{kl}_{e\bar{b}_{kl}} \, |e\rangle \equiv \langle \bar{a}_{ij} | \bar{b}_{kl} \rangle \equiv S^{ij,kl}_{\bar{a}_{ij}\bar{b}_{kl}}. \tag{16}$$

Though, the overlap terms appear due to the generalization of the derived spin-adapted CC expressions via Wick's Theorem such that the basis is nonorthogonal. Those terms are interpreted as a projections from one pair correlation space to another and can be better understood in the perspective of a matrix multiplication. Below are examples of transformation of spin-adapted CCSD terms to the local basis and the use of overlap terms (not written in an appropriate matrix notation). The singles amplitudes are expanded with PNOs of the diagonal pairs,

$$t^{i}_{\bar{a}_{ii}} = \sum_{a} d^{ii}_{a\bar{a}_{ii}} t^{i}_{a}, \tag{17}$$

hence the use of $d^{ii}_{a\bar{a}_{ii}}$ instead of $d^{ij}_{a\bar{a}_{ij}}$. Looking at the third term of the singles residual with the already transformed amplitude,

$$R^{i}_{\bar{a}_{ii}} \leftarrow \sum_{m} t^{m}_{\bar{a}_{mm}} F_{mi}, \tag{18}$$

there needs to be a projection of the virtual space of pair mm of the amplitude to the pair ii so that the contraction results to the correct target PNO virtual index, $\bar{a}_{ii}$. Therefore, with the use of the overlap terms, the expression leads to

$$R^{i}_{\bar{a}_{ii}} \leftarrow \sum_{m\bar{a}_{mm}} S^{ii,mm}_{\bar{a}_{ii}\bar{a}_{mm}} t^{m}_{\bar{a}_{mm}} F_{mi}. \tag{19}$$

In the case where the singles amplitudes are coupled to either the four-index terms (eg. fifth term) or one-particle intermediates (eg. second term), the resulting expressions are:

$$R^{i}_{\bar{a}_{ii}} \leftarrow \sum_{n\bar{f}_{nn}} t^{n}_{\bar{f}_{nn}} L_{n\bar{a}_{ii}\bar{f}_{nn}i}, \tag{20}$$

where the L term resulted from

$$\sum_{af} d^{ii}_{a\bar{a}_{ii}} d^{mn}_{f\bar{f}_{nn}} L_{nafi}, \tag{21}$$

and

$$R^{i}_{\bar{a}_{ii}} \leftarrow \sum_{\bar{e}_{ii}} t^{i}_{\bar{e}_{ii}} F_{\bar{a}_{ii}\bar{e}_{ii}} \tag{22}$$

where the transformation from canonical virtual a to the PNO basis $\bar{a}_{ii}$ is due to the target index $\bar{a}_{ii}$ of the singles residual while e to $\bar{e}_{ii}$ is due to its dependency of the amplitude and what the occupied index is which is i. The same reasoning applies to Eq. (20) and all the other integrals and intermediates. In Eq. (22), the one-particle intermediate, $F_{\bar{a}_{ii}\bar{e}_{ii}}$, is obtained through the transformation of its component to the appropriate PNO basis:

$$\begin{aligned} F_{\bar{a}_{ii}\bar{e}_{ii}} =& f_{\bar{a}_{ii}\bar{e}_{ii}} - \frac{1}{2}\sum_{m\bar{a}_{mm}} f^{m}_{\bar{e}_{ii}} t^{m}_{\bar{a}_{mm}} S^{mm,ii}_{\bar{a}_{mm}\bar{a}_{ii}} \\ &+ \sum_{m\bar{f}_{mm}} t^{m}_{\bar{f}_{mm}} L_{m\bar{a}_{ii}\bar{f}_{mm}\bar{e}_{ii}} - \sum_{mn\bar{f}_{mn}\bar{a}_{mn}} S^{ii,mn}_{\bar{a}_{ii}\bar{a}_{mn}} \tilde{\tau}^{mn}_{\bar{a}_{mn}\bar{f}_{mn}} L^{mn}_{\bar{e}_{ii}\bar{f}_{mn}} \end{aligned} \tag{23}$$

where

$$f_{\bar{a}_{ii}\bar{e}_{ii}} = \sum_{ae} d^{ii}_{a\bar{a}_{ii}} d^{ii}_{e\bar{e}_{ii}} f_{ae}, \tag{24}$$

$$f^m_{\bar{e}_{ii}} t^m_{\bar{a}_{mm}} = \sum_e d^{ii}_{e\bar{e}_{ii}} f^m_e \sum_a d^{mm}_{a\bar{a}_{mm}} t^m_a, \tag{25}$$

$$t^m_{\bar{f}_{mm}} L_{m\bar{a}_{ii}\bar{f}_{mm}\bar{e}_{ii}} = \sum_f d^{mm}_{f\bar{f}_{mm}} t^m_f \sum_{afe} d^{ii}_{a\bar{a}_{ii}} d^{mm}_{f\bar{f}_{mm}} d^{ii}_{e\bar{e}_{ii}} L_{mafe}, \tag{26}$$

and

$$\tilde{\tau}^{mn}_{\bar{a}_{mn}\bar{f}_{mn}} L^{mn}_{\bar{e}_{ii}\bar{f}_{mn}} = \tilde{\tau}^{mn}_{\bar{a}_{mn}\bar{f}_{mn}} \sum_{ef} d^{mn}_{f\bar{f}_{mn}} d^{ii}_{e\bar{e}_{ii}} L^{mn}_{ef} \tag{27}$$

such that

$$\begin{aligned}\tilde{\tau}^{mn}_{\bar{a}_{mn}\bar{f}_{mn}} =& \sum_{af} d^{mn}_{a\bar{a}_{mn}} d^{mn}_{f\bar{f}_{mn}} t^{mn}_{af} \\ &+ \frac{1}{2} \sum_{\bar{a}_{mm}\bar{f}_{nn}} S^{mn,mm}_{\bar{a}_{mn}\bar{a}_{mm}} t^m_{\bar{a}_{mm}} t^n_{\bar{f}_{nn}} S^{nn,mn}_{\bar{f}_{nn}\bar{f}_{mn}}\end{aligned} \tag{28}$$

Eq. 28 is an example of the doubles amplitudes expanded with the PNOs of pair mn. Looking at the doubles residual now, we notice that F_{be} intermediate is coupled to the doubles amplitudes,

$$R^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} \leftarrow \sum_{\bar{e}_{ij}} t^{ij}_{\bar{a}_{ij}\bar{e}_{ij}} F_{\bar{b}_{ij}\bar{e}_{ij}}, \tag{29}$$

which results to

$$\begin{aligned}F_{\bar{b}_{ij}\bar{e}_{ij}} =& f_{\bar{b}_{ij}\bar{e}_{ij}} - \frac{1}{2} \sum_{m\bar{b}_{mm}} f^m_{\bar{e}_{ij}} t^m_{\bar{b}_{mm}} S^{mm,ij}_{\bar{b}_{mm}\bar{b}_{ij}} \\ &+ \sum_{m\bar{f}_{mm}} t^m_{\bar{f}_{mm}} L_{m\bar{b}_{ij}\bar{f}_{mm}\bar{e}_{ij}} + \sum_{mn\bar{f}_{mm}\bar{b}_{mn}\bar{f}_{ij}} S^{ij,mn}_{\bar{b}_{ij}\bar{b}_{mn}} \tilde{\tau}^{mn}_{\bar{b}_{mn}\bar{f}_{mn}} L^{mn}_{\bar{e}_{ij}\bar{f}_{mn}}\end{aligned} \tag{30}$$

compared to F_{ae} intermediate coupling to the single amplitudes,

$$\begin{aligned}F_{\bar{a}_{ii}\bar{e}_{ii}} =& f_{\bar{a}_{ii}\bar{e}_{ii}} - \frac{1}{2} \sum_{m\bar{a}_{mm}} f^m_{\bar{e}_{ii}} t^m_{\bar{a}_{mm}} S^{mm,ii}_{\bar{a}_{mm}\bar{a}_{ii}} \\ &+ \sum_{m\bar{f}_{mm}} t^m_{\bar{f}_{mm}} L_{m\bar{a}_{ii}\bar{f}_{mm}\bar{e}_{ii}} - \sum_{mn\bar{f}_{mn}\bar{a}_{mn}} S^{ii,mn}_{\bar{a}_{ii}\bar{a}_{mn}} \tilde{\tau}^{mn}_{\bar{a}_{mn}\bar{f}_{mn}} L^{mn}_{\bar{e}_{ii}\bar{f}_{mn}}\end{aligned} \tag{31}$$

The last example is a doubles amplitude coupled with a two-particle intermediate such as W_{mbej}:

$$R^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} \leftarrow \sum_{m\bar{e}_{im}\bar{a}_{im}} t^{im}_{\bar{e}_{im}\bar{a}_{im}} S^{im,ij}_{\bar{a}_{im}\bar{a}_{ij}} W_{m\bar{b}_{ij}\bar{e}_{im}j} \tag{32}$$

where

$$\begin{aligned} W_{m\bar{b}_{ij}\bar{e}_{im}j} =& K_{m\bar{b}_{ij}\bar{e}_{im}j} + \sum_{\bar{f}_{jj}} t^{j}_{\bar{f}_{jj}} K_{m\bar{b}_{ij}\bar{e}_{im}\bar{f}_{jj}} - \sum_{n\bar{b}_{nn}} t^{n}_{\bar{b}_{nn}} S^{nn,ij}_{\bar{b}_{nn}\bar{b}_{ij}} K_{mn\bar{e}_{im}j} \\ & - \sum_{n\bar{f}_{jn}\bar{b}_{jn}} \bar{\tau}^{jn}_{\bar{f}_{jn}\bar{b}_{jn}} S^{jn,ij}_{\bar{b}_{jn}\bar{b}_{ij}} K^{mn}_{\bar{e}_{im}\bar{f}_{jn}} + \frac{1}{2} \sum_{n\bar{f}_{nj}} t^{nj}_{\bar{f}_{nj}\bar{b}_{nj}} S^{nj,ij}_{\bar{b}_{nj}\bar{b}_{ij}} L^{mn}_{\bar{e}_{im}\bar{f}_{nj}} \end{aligned} \tag{33}$$

Given the examples for transforming the spin-adapted CCSD to the PNO form, the next sections will just be expressions in terms of the PNO basis without the complete transformation procedure.

2.1 Singles residual

$$\begin{aligned} R^{i}_{\bar{a}_{ii}} =& f^{i}_{\bar{a}_{ii}} + \sum_{\bar{e}_{ii}} t^{i}_{\bar{e}_{ii}} F_{\bar{a}_{ii}\bar{e}_{ii}} - \sum_{m\bar{a}_{mm}} S^{ii,mm}_{\bar{a}_{ii}\bar{a}_{mm}} t^{m}_{\bar{a}_{mm}} F_{mi} \\ & + \sum_{m\bar{e}_{im}\bar{a}_{im}} \left(2S^{ii,im}_{\bar{a}_{ii}\bar{a}_{im}} t^{im}_{\bar{a}_{im}\bar{e}_{im}} - t^{im}_{\bar{e}_{im}\bar{a}_{im}} S^{im,ii}_{\bar{a}_{im}\bar{a}_{ii}}\right) F_{m\bar{e}_{im}} \\ & + \sum_{n\bar{f}_{nn}} t^{n}_{\bar{f}_{nn}} L_{n\bar{a}_{ii}\bar{f}_{nn}i} \\ & + \sum_{m\bar{e}_{mi}\bar{f}_{mi}} \left(2t^{mi}_{\bar{e}_{mi}\bar{f}_{mi}} - t^{mi}_{\bar{f}_{mi}\bar{e}_{mi}}\right) K_{m\bar{a}_{ii}\bar{e}_{mi}\bar{f}_{mi}} \\ & - \sum_{mn\bar{e}_{mn}\bar{a}_{mn}} S^{ii,mn}_{\bar{a}_{ii}\bar{a}_{mn}} t^{mn}_{\bar{a}_{mn}\bar{e}_{mn}} L_{nm\bar{e}_{mn}i} \end{aligned} \tag{34}$$

2.2 Doubles Residual

$$\begin{aligned}
R^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} =&\frac{1}{2}K^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} + \sum_{\bar{e}_{ij}} t^{ij}_{\bar{a}_{ij}\bar{e}_{ij}} \left(F_{\bar{b}_{ij}\bar{e}_{ij}} - \frac{1}{2}\sum_{m\bar{b}_{mm}} S^{ij,mm}_{\bar{b}_{ij}\bar{b}_{mm}} t^{m}_{\bar{b}_{mm}} F_{m\bar{e}_{ij}} \right) \\
&- \sum_{m\bar{a}_{im}\bar{b}_{im}} S^{ij,im}_{\bar{a}_{ij}\bar{a}_{im}} t^{im}_{\bar{a}_{im}\bar{b}_{im}} S^{im,ij}_{\bar{b}_{im}\bar{b}_{ij}} \left(F_{mj} + \frac{1}{2}\sum_{\bar{e}_{jj}} t^{j}_{\bar{e}_{jj}} F_{m\bar{e}_{jj}} \right) \\
&+ \frac{1}{2}\sum_{mn\bar{a}_{mn}\bar{b}_{mn}} S^{ij,mn}_{\bar{a}_{ij}\bar{a}_{mn}} \tau^{mn}_{\bar{a}_{mn}\bar{b}_{mn}} S^{mn,ij}_{\bar{b}_{mn}\bar{b}_{ij}} W_{mnij} \\
&+ \frac{1}{2}\sum_{\bar{e}_{ij}\bar{f}_{ij}} \tau^{ij}_{\bar{e}_{ij}\bar{f}_{ij}} K_{\bar{a}_{ij}\bar{b}_{ij}\bar{e}_{ij}\bar{f}_{ij}} - \sum_{m\bar{a}_{mm}} S^{ij,mm}_{\bar{a}_{ij}\bar{a}_{mm}} t^{m}_{\bar{a}_{mm}} Z_{m\bar{b}_{ij}ij} \\
&+ \sum_{m\bar{e}_{im}\bar{a}_{im}} \left(S^{ij,im}_{\bar{a}_{ij}\bar{a}_{im}} t^{im}_{\bar{a}_{im}\bar{e}_{im}} - t^{im}_{\bar{e}_{im}\bar{a}_{im}} S^{im,ij}_{\bar{a}_{im}\bar{a}_{ij}} \right) W_{m\bar{b}_{ij}\bar{e}_{im}j} \\
&+ \sum_{m\bar{e}_{im}\bar{a}_{im}} S^{ij,im}_{\bar{a}_{ij}\bar{a}_{im}} t^{im}_{\bar{a}_{im}\bar{e}_{im}} \left(W_{m\bar{b}_{ij}\bar{e}_{im}j} + W^{*}_{m\bar{b}_{ij}j\bar{e}_{im}} \right) \\
&+ \sum_{m\bar{e}_{mj}\bar{a}_{mj}} S^{ij,mj}_{\bar{a}_{ij}\bar{a}_{mj}} t^{mj}_{\bar{a}_{mj}\bar{e}_{mj}} W_{m\bar{b}_{ij}i\bar{e}_{mj}} - \sum_{m\bar{e}_{ii}\bar{a}_{mm}} t^{i}_{\bar{e}_{ii}} S^{ij,mm}_{\bar{a}_{ij}\bar{a}_{mm}} t^{m}_{\bar{a}_{mm}} K_{m\bar{b}_{ij}\bar{e}_{ii}j} \\
&- \sum_{m\bar{e}_{ii}\bar{b}_{mm}} t^{i}_{\bar{e}_{ii}} S^{ij,mm}_{\bar{b}_{ij}\bar{b}_{mm}} t^{m}_{\bar{b}_{mm}} K_{m\bar{a}_{ij}j\bar{e}_{ii}} \\
&+ \sum_{\bar{e}_{ii}} t^{i}_{\bar{e}_{ii}} K_{\bar{a}_{ij}\bar{b}_{ij}\bar{e}_{ii}j} - \sum_{m\bar{a}_{mm}} S^{ij,mm}_{\bar{a}_{ij}\bar{a}_{mm}} t^{m}_{\bar{a}_{mm}} K_{m\bar{b}_{ij}ij}
\end{aligned} \tag{35}$$

2.3 Intermediates

One-Particle Intermediates for Singles Residual

$$\begin{aligned}
F_{\bar{a}_{ii}\bar{e}_{ii}} =&f_{\bar{a}_{ii}\bar{e}_{ii}} - \frac{1}{2}\sum_{m\bar{a}_{mm}} f^{m}_{\bar{e}_{ii}} t^{m}_{\bar{a}_{mm}} S^{mm,ii}_{\bar{a}_{mm}\bar{a}_{ii}} \\
&+ \sum_{m\bar{f}_{mm}} t^{m}_{\bar{f}_{mm}} L_{m\bar{a}_{ii}\bar{f}_{mm}\bar{e}_{ii}} - \sum_{mn\bar{f}_{mn}\bar{a}_{mn}} S^{ii,mn}_{\bar{a}_{ii}\bar{a}_{mn}} \tilde{\tau}^{mn}_{\bar{a}_{mn}\bar{f}_{mn}} L^{mn}_{\bar{e}_{ii}\bar{f}_{mn}}
\end{aligned} \tag{36}$$

$$F_{mi} = f_{mi} + \frac{1}{2}\sum_{\bar{e}_{ii}} t^{i}_{\bar{e}_{ii}} f^{m}_{\bar{e}_{ii}} + \sum_{n\bar{e}_{nn}} t^{n}_{\bar{e}_{nn}} L_{mni\bar{e}_{nn}} + \sum_{n\bar{e}_{in}\bar{f}_{in}} \tilde{\tau}^{in}_{\bar{e}_{in}\bar{f}_{in}} L^{mn}_{\bar{e}_{in}\bar{f}_{in}} \tag{37}$$

$$F_{m\bar{e}_{im}} = f_{m\bar{e}_{im}} + \sum_{n\bar{f}_{nn}} t^{n}_{\bar{f}_{nn}} L^{mn}_{\bar{e}_{im}\bar{f}_{nn}} \tag{38}$$

One-Particle Intermediates for Doubles Residual

$$\begin{aligned}F_{\bar{b}_{ij}\bar{e}_{ij}} =& f_{\bar{b}_{ij}\bar{e}_{ij}} - \frac{1}{2}\sum_{m\bar{b}_{mm}} f^{m}_{\bar{e}_{ij}} t^{m}_{\bar{b}_{mm}} S^{mm,ij}_{\bar{b}_{mm}\bar{b}_{ij}} \\ &+ \sum_{m\bar{f}_{mm}} t^{m}_{\bar{f}_{mm}} L_{m\bar{b}_{ij}\bar{f}_{mm}\bar{e}_{ij}} - \sum_{mn\bar{f}_{mm}\bar{b}_{mn}\bar{f}_{ij}} S^{ij,mn}_{\bar{b}_{ij}\bar{b}_{mn}} \tilde{\tau}^{mn}_{\bar{b}_{mn}\bar{f}_{mn}} L^{mn}_{\bar{e}_{ij}\bar{f}_{mn}}\end{aligned} \tag{39}$$

$$F_{mj} = f_{mj} + \frac{1}{2}\sum_{\bar{e}_{jj}} t^{j}_{\bar{e}_{jj}} f^{m}_{\bar{e}_{jj}} + \sum_{n\bar{e}_{nn}} t^{n}_{\bar{e}_{nn}} L_{mnj\bar{e}_{nn}} + \sum_{n\bar{e}_{jn}\bar{f}_{jn}} \tilde{\tau}^{jn}_{\bar{e}_{jn}\bar{f}_{jn}} L^{mn}_{\bar{e}_{jn}\bar{f}_{jn}} \tag{40}$$

$$F_{m\bar{e}_{ij}} = f_{m\bar{e}_{ij}} + \sum_{n\bar{f}_{nn}} t^{n}_{\bar{f}_{nn}} L^{mn}_{\bar{e}_{ij}\bar{f}_{nn}} \tag{41}$$

$$F_{m\bar{e}_{jj}} = f_{m\bar{e}_{jj}} + \sum_{n\bar{f}_{nn}} t^{n}_{\bar{f}_{nn}} L^{mn}_{\bar{e}_{jj}\bar{f}_{nn}} \tag{42}$$

Two-Particle Intermediates for Doubles Residual

$$W_{mnij} = K_{mnij} + \sum_{\bar{e}_{jj}} t^{j}_{\bar{e}_{jj}} K_{mni\bar{e}_{jj}} + \sum_{\bar{e}_{ii}} t^{i}_{\bar{e}_{ii}} K_{mn\bar{e}_{ii}j} + \sum_{\bar{e}_{ij}\bar{f}_{ij}} \tau^{ij}_{\bar{e}_{ij}\bar{f}_{ij}} K^{mn}_{\bar{e}_{ij}\bar{f}_{ij}} \tag{43}$$

$$\begin{aligned}W_{m\bar{b}_{ij}\bar{e}_{im}j} =& K_{m\bar{b}_{ij}\bar{e}_{im}j} + \sum_{\bar{f}_{jj}} t^{j}_{\bar{f}_{jj}} K_{m\bar{b}_{ij}\bar{e}_{im}\bar{f}_{jj}} - \sum_{n\bar{b}_{nn}} t^{n}_{\bar{b}_{nn}} S^{nn,ij}_{\bar{b}_{nn}\bar{b}_{ij}} K_{mn\bar{e}_{im}j} \\ &- \sum_{n\bar{f}_{jn}\bar{b}_{jn}} \bar{\tau}^{jn}_{\bar{f}_{jn}\bar{b}_{jn}} S^{jn,ij}_{\bar{b}_{jn}\bar{b}_{ij}} K^{mn}_{\bar{e}_{im}\bar{f}_{jn}} + \frac{1}{2}\sum_{n\bar{f}_{nj}\bar{b}_{nj}} t^{nj}_{\bar{f}_{nj}\bar{b}_{nj}} S^{nj,ij}_{\bar{b}_{nj}\bar{b}_{ij}} L^{mn}_{\bar{e}_{im}\bar{f}_{nj}}\end{aligned} \tag{44}$$

$$\begin{aligned}W_{m\bar{b}_{ij}j\bar{e}_{im}} =& - K_{m\bar{b}_{ij}j\bar{e}_{im}} - \sum_{\bar{f}_{jj}} t^{j}_{\bar{f}_{jj}} K_{m\bar{b}_{ij}\bar{f}_{jj}\bar{e}_{im}} \\ &+ \sum_{n\bar{b}_{nn}} S^{ij,nn}_{\bar{b}_{ij}\bar{b}_{nn}} t^{n}_{\bar{b}_{nn}} K_{mnj\bar{e}_{im}} + \sum_{n\bar{f}_{jn}\bar{b}_{jn}} \bar{\tau}^{jn}_{\bar{f}_{jn}\bar{b}_{jn}} S^{jn,ij}_{\bar{b}_{jn}\bar{b}_{ij}} K^{mn}_{\bar{f}_{jn}\bar{e}_{im}}\end{aligned} \tag{45}$$

$$\begin{aligned}W_{m\bar{b}_{ij}i\bar{e}_{mj}} =& - K_{m\bar{b}_{ij}i\bar{e}_{mj}} - \sum_{\bar{f}_{ii}} t^{i}_{\bar{f}_{ii}} K_{m\bar{b}_{ij}\bar{f}_{ii}\bar{e}_{mj}} \\ &+ \sum_{n\bar{b}_{nn}} S^{ij,nn}_{\bar{b}_{ij}\bar{b}_{nn}} t^{n}_{\bar{b}_{nn}} K_{mni\bar{e}_{mj}} + \sum_{n\bar{f}_{jn}\bar{b}_{jn}} \bar{\tau}^{in}_{\bar{f}_{in}\bar{b}_{in}} S^{in,ij}_{\bar{b}_{in}\bar{b}_{ij}} K^{mn}_{\bar{f}_{in}\bar{e}_{mj}}\end{aligned} \tag{46}$$

$$Z_{m\bar{b}_{ij}ij} = \sum_{\bar{e}_{ij}\bar{f}_{ij}} K_{m\bar{b}_{ij}\bar{e}_{ij}\bar{f}_{ij}} \tau^{ij}_{\bar{e}_{ij}\bar{f}_{ij}} \tag{47}$$

2.4 Energy

$$E_{ccsd} = 2f^{i}_{\bar{a}_{ii}} t^{i}_{\bar{a}_{ii}} + \tau^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} L^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} \tag{48}$$

3. Implementation

3.1 PNO-CCD

For the implementation of PNO-CCD, we keep the doubles residual containing only the doubles amplitudes,

$$\begin{aligned}
R^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} =& \frac{1}{2} K^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} + \sum_{\bar{e}_{ij}} t^{ij}_{\bar{a}_{ij}\bar{e}_{ij}} F_{\bar{b}_{ij}\bar{e}_{ij}} - \sum_{m\bar{a}_{im}\bar{b}_{im}} S^{ij,im}_{\bar{a}_{ij}\bar{a}_{im}} t^{im}_{\bar{a}_{im}\bar{b}_{im}} S^{im,ij}_{\bar{b}_{im}\bar{b}_{ij}} F_{mj} \\
&+ \frac{1}{2} \sum_{mn\bar{a}_{mn}\bar{b}_{mn}} S^{ij,mn}_{\bar{a}_{ij}\bar{a}_{mn}} t^{mn}_{\bar{a}_{mn}\bar{b}_{mn}} S^{mn,ij}_{\bar{b}_{mn}\bar{b}_{ij}} W_{mnij} + \frac{1}{2} \sum_{\bar{e}_{ij}\bar{f}_{ij}} t^{ij}_{\bar{e}_{ij}\bar{f}_{ij}} K_{\bar{a}_{ij}\bar{b}_{ij}\bar{e}_{ij}\bar{f}_{ij}} \\
&+ \sum_{m\bar{e}_{im}\bar{a}_{im}} \left(S^{ij,im}_{\bar{a}_{ij}\bar{a}_{im}} t^{im}_{\bar{a}_{im}\bar{e}_{im}} - t^{im}_{\bar{e}_{im}\bar{a}_{im}} S^{im,ij}_{\bar{a}_{im}\bar{a}_{ij}}\right) W_{m\bar{b}_{ij}\bar{e}_{im}j} \\
&+ \sum_{m\bar{e}_{im}\bar{a}_{im}} S^{ij,im}_{\bar{a}_{ij}\bar{a}_{im}} t^{im}_{\bar{a}_{im}\bar{e}_{im}} \left(W_{m\bar{b}_{ij}\bar{e}_{im}j} + W^{*}_{m\bar{b}_{ij}j\bar{e}_{im}}\right) \\
&+ \sum_{m\bar{e}_{mj}\bar{a}_{mj}} S^{ij,mj}_{\bar{a}_{ij}\bar{a}_{mj}} t^{mj}_{\bar{a}_{mj}\bar{e}_{mj}} W_{m\bar{b}_{ij}i\bar{e}_{mj}},
\end{aligned} \tag{49}$$

as well as the contraction of the doubles amplitudes to the L term (Eq. 50) for the energy,

$$E_{ccd} = t^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} L^{ij}_{\bar{a}_{ij}\bar{b}_{ij}}. \tag{50}$$

The intermediates needed for PNO-CCD are listed below:

$$F_{\bar{b}_{ij}\bar{e}_{ij}} = f_{\bar{b}_{ij}\bar{e}_{ij}} - \sum_{mn\bar{f}_{mm}\bar{b}_{mn}\bar{f}_{ij}} S^{ij,mn}_{\bar{b}_{ij}\bar{b}_{mn}} t^{mn}_{\bar{b}_{mn}\bar{f}_{mn}} L^{mn}_{\bar{e}_{ij}\bar{f}_{mn}} \tag{51}$$

$$F_{mj} = f_{mj} + \sum_{n\bar{e}_{jn}\bar{f}_{jn}} t^{jn}_{\bar{e}_{jn}\bar{f}_{jn}} L^{mn}_{\bar{e}_{jn}\bar{f}_{jn}} \tag{52}$$

$$W_{mnij} = K_{mnij} + \sum_{\bar{e}_{ij}\bar{f}_{ij}} t^{ij}_{\bar{e}_{ij}\bar{f}_{ij}} K^{mn}_{\bar{e}_{ij}\bar{f}_{ij}} \tag{53}$$

$$W_{m\bar{b}_{ij}\bar{e}_{im}j} = K_{m\bar{b}_{ij}\bar{e}_{im}j} - \frac{1}{2}\sum_{n\bar{f}_{jn}\bar{b}_{jn}} t^{jn}_{\bar{f}_{jn}\bar{b}_{jn}} S^{jn,ij}_{\bar{b}_{jn}\bar{b}_{ij}} K^{mn}_{\bar{e}_{im}\bar{f}_{jn}} + \frac{1}{2}\sum_{n\bar{f}_{nj}\bar{b}_{nj}} t^{nj}_{\bar{f}_{nj}\bar{b}_{nj}} S^{nj,ij}_{\bar{b}_{nj}\bar{b}_{ij}} L^{mn}_{\bar{e}_{im}\bar{f}_{nj}} \tag{54}$$

$$W_{m\bar{b}_{ij}j\bar{e}_{im}} = -K_{m\bar{b}_{ij}j\bar{e}_{im}} + \frac{1}{2}\sum_{n\bar{f}_{jn}\bar{b}_{jn}} t^{jn}_{\bar{f}_{jn}\bar{b}_{jn}} S^{jn,ij}_{\bar{b}_{jn}\bar{b}_{ij}} K^{mn}_{\bar{f}_{jn}\bar{e}_{im}} \tag{55}$$

$$W_{m\bar{b}_{ij}i\bar{e}_{mj}} = -K_{m\bar{b}_{ij}i\bar{e}_{mj}} + \frac{1}{2}\sum_{n\bar{f}_{jn}\bar{b}_{jn}} t^{in}_{\bar{f}_{in}\bar{b}_{in}} S^{in,ij}_{\bar{b}_{in}\bar{b}_{ij}} K^{mn}_{\bar{f}_{in}\bar{e}_{mj}} \tag{56}$$

The expression for the overlap terms is reformulated as

$$S^{ij,kl}_{\bar{a}_{ij}\bar{b}_{kl}} \equiv (Q^{ij}L^{ij})^T Q^{kl} L^{kl}, \tag{57}$$

where Q^{ij} is defined as $d^{ij}_{a\bar{a}_{ij}}$, such that the diagonalization of the pair density can be rewritten as

$$D^{ij}Q^{ij} = n^{ij}Q^{ij} \tag{58}$$

with a dimension of virtual molecular orbitals (vmos) by virtual natural orbitals (vnos) and L^{ij} is obtain through the diagonalization of the local Fock virtual space,

$$F^{ij}L^{ij} = \epsilon^{ij}L^{ij}, \tag{59}$$

with a dimension of vnos by semi-canonical vnos. The vmos are transformed to the semi-canonical vnos and are kept in that representation to avoid the additional cost of transforming them back and forth during the amplitude updates where the semi-canonical virtual pair energies, ϵ^{ij}, can be used for the energy denominator.

3.2 PNO-CCSD

With the inclusion of the singles residual and all the singles amplitudes from the doubles residual as well as the contraction of the singles amplitudes to the Fock matrices for the energy, different results may be obtained due to how τ is computed. For all the τ expressions, cautionary use of the overlap terms to project from one pair correlation domain to another is necessary to avoid projection errors. For example, if the second expression of the energy equation is computed like so

$$E_{ccsd} \leftarrow \tau^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} L^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} \tag{60}$$

where

$$\tau^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} = t^{ij}_{\bar{a}_{ij}b\bar{i}j} + \sum_{\bar{c}_{ii}\bar{d}_{jj}} S^{ij,ii}_{\bar{a}_{ij}\bar{c}_{ii}} t^{i}_{\bar{c}_{ii}} t^{j}_{\bar{d}_{jj}} S^{jj,ij}_{\bar{d}_{jj}\bar{b}_{ij}} \tag{61}$$

then the converged energy deviates at the sixth decimal places against the local filter code for a water molecule with cc-pvdz basis set and $1e-7$ truncation cutoff. If the expression is computed such that the product of the singles amplitudes are not projected,

$$E_{ccsd} \leftarrow t^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} L^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} + t^{i}_{\bar{a}_{ii}} t^{j}_{\bar{b}_{jj}} L^{ij}_{\bar{a}_{ii}\bar{b}_{jj}}, \tag{62}$$

then the converged energy matches exactly with the local filter code.

The PNO-CCSD equations are shown in Section 2, starting at Section 2.1 but is also shown below with modification of the τ terms.

Singles residual

$$\begin{aligned}
R^{i}_{\bar{a}_{ii}} = & f^{i}_{\bar{a}_{ii}} + \sum_{\bar{e}_{ii}} t^{i}_{\bar{e}_{ii}} F_{\bar{a}_{ii}\bar{e}_{ii}} - \sum_{m\bar{a}_{mm}} S^{ii,mm}_{\bar{a}_{ii}\bar{a}_{mm}} t^{m}_{\bar{a}_{mm}} F_{mi} \\
& + \sum_{m\bar{e}_{im}\bar{a}_{im}} \left(2S^{ii,im}_{\bar{a}_{ii}\bar{a}_{im}} t^{im}_{\bar{a}_{im}\bar{e}_{im}} - t^{im}_{\bar{e}_{im}\bar{a}_{im}} S^{im,ii}_{\bar{a}_{im}\bar{a}_{ii}}\right) F_{m\bar{e}_{im}} \\
& + \sum_{n\bar{f}_{nn}} t^{n}_{\bar{f}_{nn}} L_{n\bar{a}_{ii}\bar{f}_{nn}i} \\
& + \sum_{m\bar{e}_{mi}\bar{f}_{mi}} \left(2t^{mi}_{\bar{e}_{mi}\bar{f}_{mi}} - t^{mi}_{\bar{f}_{mi}\bar{e}_{mi}}\right) K_{m\bar{a}_{ii}\bar{e}_{mi}\bar{f}_{mi}} \\
& - \sum_{mn\bar{e}_{mn}\bar{a}_{mn}} S^{ii,mn}_{\bar{a}_{ii}\bar{a}_{mn}} t^{mn}_{\bar{a}_{mn}\bar{e}_{mn}} L_{nm\bar{e}_{mn}i}
\end{aligned} \tag{63}$$

Doubles Residual

$$
\begin{aligned}
R^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} =& \frac{1}{2}K^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} + \sum_{\bar{e}_{ij}} t^{ij}_{\bar{a}_{ij}\bar{e}_{ij}} \left(F_{\bar{b}_{ij}\bar{e}_{ij}} - \frac{1}{2} \sum_{m\bar{b}_{mm}} S^{ij,mm}_{\bar{b}_{ij}\bar{b}_{mm}} t^{m}_{\bar{b}_{mm}} F_{m\bar{e}_{ij}} \right) \\
& - \sum_{m\bar{a}_{im}\bar{b}_{im}} S^{ij,im}_{\bar{a}_{ij}\bar{a}_{im}} t^{im}_{\bar{a}_{im}\bar{b}_{im}} S^{im,ij}_{\bar{b}_{im}\bar{b}_{ij}} \left(F_{mj} + \frac{1}{2} \sum_{\bar{e}_{jj}} t^{j}_{\bar{e}_{jj}} F_{m\bar{e}_{jj}} \right) \\
& + \frac{1}{2} \sum_{mn\bar{a}_{mn}\bar{b}_{mn}} S^{ij,mn}_{\bar{a}_{ij}\bar{a}_{mn}} t^{mn}_{\bar{a}_{mn}\bar{b}_{mn}} S^{mn,ij}_{\bar{b}_{mn}\bar{b}_{ij}} W_{mnij} \\
& + \frac{1}{2} \sum_{mn\bar{a}_{mm}\bar{b}_{nn}} S^{ij,mm}_{\bar{a}_{ij}\bar{a}_{mm}} t^{m}_{\bar{a}_{mm}} t^{n}_{\bar{b}_{nn}} S^{nn,ij}_{\bar{b}_{nn}\bar{b}_{ij}} W_{mnij} \\
& + \frac{1}{2} \sum_{\bar{e}_{ij}\bar{f}_{ij}} \tau^{ij}_{\bar{e}_{ij}\bar{f}_{ij}} K_{\bar{a}_{ij}\bar{b}_{ij}\bar{e}_{ij}\bar{f}_{ij}} + \frac{1}{2} \sum_{\bar{e}_{ii}\bar{f}_{jj}} t^{i}_{\bar{e}_{ii}} t^{j}_{\bar{f}_{jj}} K_{\bar{a}_{ij}\bar{b}_{ij}\bar{e}_{jj}\bar{f}_{jj}} \\
& - \sum_{m\bar{a}_{mm}} S^{ij,mm}_{\bar{a}_{ij}\bar{a}_{mm}} t^{m}_{\bar{a}_{mm}} Z_{m\bar{b}_{ij}ij} + \sum_{m\bar{e}_{im}\bar{a}_{im}} \left(S^{ij,im}_{\bar{a}_{ij}\bar{a}_{im}} t^{im}_{\bar{a}_{im}\bar{e}_{im}} - t^{im}_{\bar{e}_{im}\bar{a}_{im}} S^{im,ij}_{\bar{a}_{im}\bar{a}_{ij}} \right) W_{m\bar{b}_{ij}\bar{e}_{im}j} \\
& + \sum_{m\bar{e}_{im}\bar{a}_{im}} S^{ij,im}_{\bar{a}_{ij}\bar{a}_{im}} t^{im}_{\bar{a}_{im}\bar{e}_{im}} \left(W_{m\bar{b}_{ij}\bar{e}_{im}j} + W^{*}_{m\bar{b}_{ij}j\bar{e}_{im}} \right) \\
& + \sum_{m\bar{e}_{mj}\bar{a}_{mj}} S^{ij,mj}_{\bar{a}_{ij}\bar{a}_{mj}} t^{mj}_{\bar{a}_{mj}\bar{e}_{mj}} W_{m\bar{b}_{ij}i\bar{e}_{mj}} - \sum_{m\bar{e}_{ii}\bar{a}_{mm}} t^{i}_{\bar{e}_{ii}} S^{ij,mm}_{\bar{a}_{ij}\bar{a}_{mm}} t^{m}_{\bar{a}_{mm}} K_{m\bar{b}_{ij}\bar{e}_{ii}j} \\
& - \sum_{m\bar{e}_{ii}\bar{b}_{mm}} t^{i}_{\bar{e}_{ii}} S^{ij,mm}_{\bar{b}_{ij}\bar{b}_{mm}} t^{m}_{\bar{b}_{mm}} K_{m\bar{a}_{ij}j\bar{e}_{ii}} \\
& + \sum_{\bar{e}_{ii}} t^{i}_{\bar{e}_{ii}} K_{\bar{a}_{ij}\bar{b}_{ij}\bar{e}_{ii}j} - \sum_{m\bar{a}_{mm}} S^{ij,mm}_{\bar{a}_{ij}\bar{a}_{mm}} t^{m}_{\bar{a}_{mm}} K_{m\bar{b}_{ij}ij}
\end{aligned} \tag{64}
$$

One-Particle Intermediates

$$
\begin{aligned}
F_{\bar{b}_{ij}\bar{e}_{ij}} =& f_{\bar{b}_{ij}\bar{e}_{ij}} - \frac{1}{2} \sum_{m\bar{b}_{mm}} f^{m}_{\bar{e}_{ij}} t^{m}_{\bar{b}_{mm}} S^{mm,ij}_{\bar{b}_{mm}\bar{b}_{ij}} \\
& + \sum_{m\bar{f}_{mm}} t^{m}_{\bar{f}_{mm}} L_{m\bar{b}_{ij}\bar{f}_{mm}\bar{e}_{ij}} - \sum_{mn\bar{f}_{mn}\bar{b}_{mn}} S^{ij,mn}_{\bar{b}_{ij}\bar{b}_{mn}} t^{mn}_{\bar{b}_{mn}\bar{f}_{mn}} L^{mn}_{\bar{e}_{ij}\bar{f}_{mn}} \\
& - \frac{1}{2} \sum_{mn\bar{f}_{nn}\bar{b}_{mm}} S^{ij,mn}_{\bar{b}_{ij}\bar{b}_{mm}} t^{m}_{\bar{b}_{mm}} t^{n}_{\bar{f}_{nn}} L^{mn}_{\bar{e}_{ij}\bar{f}_{nn}}
\end{aligned} \tag{65}
$$

$$
\begin{aligned}
F_{mi} =& f_{mi} + \frac{1}{2}\sum_{\bar{e}_{ii}} t^{i}_{\bar{e}_{ii}} f^{m}_{\bar{e}_{ii}} + \sum_{n\bar{e}_{nn}} t^{n}_{\bar{e}_{nn}} L_{mni\bar{e}_{nn}} \\
&+ \sum_{n\bar{e}_{in}\bar{f}_{in}} t^{in}_{\bar{e}_{in}\bar{f}_{in}} L^{mn}_{\bar{e}_{in}\bar{f}_{in}} + \frac{1}{2}\sum_{n\bar{e}_{ii}\bar{f}_{nn}} t^{i}_{\bar{e}_{ii}} t^{n}_{\bar{f}_{nn}} L^{mn}_{\bar{e}_{ii}\bar{f}_{nn}}
\end{aligned} \tag{66}
$$

$$
F_{m\bar{e}_{im}} = f_{m\bar{e}_{im}} + \sum_{n\bar{f}_{nn}} t^{n}_{\bar{f}_{nn}} L^{mn}_{\bar{e}_{im}\bar{f}_{nn}} \tag{67}
$$

$$
F_{m\bar{e}_{ij}} = f_{m\bar{e}_{ij}} + \sum_{n\bar{f}_{nn}} t^{n}_{\bar{f}_{nn}} L^{mn}_{\bar{e}_{ij}\bar{f}_{nn}} \tag{68}
$$

Two-Particle Intermediates

$$
\begin{aligned}
W_{mnij} =& K_{mnij} + \sum_{\bar{e}_{jj}} t^{j}_{\bar{e}_{jj}} K_{mni\bar{e}_{jj}} + \sum_{\bar{e}_{ii}} t^{i}_{\bar{e}_{ii}} K_{mn\bar{e}_{ii}j} \\
&+ \sum_{\bar{e}_{ij}\bar{f}_{ij}} t^{ij}_{\bar{e}_{ij}\bar{f}_{ij}} K^{mn}_{\bar{e}_{ij}\bar{f}_{ij}} + \sum_{\bar{e}_{ii}\bar{f}_{jj}} t^{i}_{\bar{e}_{ii}} t^{j}_{\bar{f}_{jj}} K^{mn}_{\bar{e}_{ii}\bar{f}_{jj}}
\end{aligned} \tag{69}
$$

$$
\begin{aligned}
W_{m\bar{b}_{ij}\bar{e}_{im}j} =& K_{m\bar{b}_{ij}\bar{e}_{im}j} + \sum_{\bar{f}_{jj}} t^{j}_{\bar{f}_{jj}} K_{m\bar{b}_{ij}\bar{e}_{im}\bar{f}_{jj}} - \sum_{n\bar{b}_{nn}} t^{n}_{\bar{b}_{nn}} S^{nn,ij}_{\bar{b}_{nn}\bar{b}_{ij}} K_{mn\bar{e}_{im}j} \\
&- \frac{1}{2}\sum_{n\bar{f}_{jn}\bar{b}_{jn}} t^{jn}_{\bar{f}_{jn}\bar{b}_{jn}} S^{jn,ij}_{\bar{b}_{jn}\bar{b}_{ij}} K^{mn}_{\bar{e}_{im}\bar{f}_{jn}} - \sum_{n\bar{f}_{jj}\bar{b}_{nn}} t^{j}_{\bar{f}_{jj}} t^{n}_{\bar{b}_{nn}} S^{nn,ij}_{\bar{b}_{nn}\bar{b}_{ij}} K^{mn}_{\bar{e}_{im}\bar{f}_{jj}} + \frac{1}{2}\sum_{n\bar{f}_{nj}\bar{b}_{nj}} t^{nj}_{\bar{f}_{nj}\bar{b}_{nj}} S^{nj,ij}_{\bar{b}_{nj}\bar{b}_{ij}} L^{mn}_{\bar{e}_{im}\bar{f}_{nj}}
\end{aligned} \tag{70}
$$

$$
\begin{aligned}
W_{m\bar{b}_{ij}j\bar{e}_{im}} =& - K_{m\bar{b}_{ij}j\bar{e}_{im}} - \sum_{\bar{f}_{jj}} t^{j}_{\bar{f}_{jj}} K_{m\bar{b}_{ij}\bar{f}_{jj}\bar{e}_{im}} \\
&+ \sum_{n\bar{b}_{nn}} S^{ij,nn}_{\bar{b}_{ij}\bar{b}_{nn}} t^{n}_{\bar{b}_{nn}} K_{mnj\bar{e}_{im}} + \frac{1}{2}\sum_{n\bar{f}_{jn}\bar{b}_{jn}} t^{jn}_{\bar{f}_{jn}\bar{b}_{jn}} S^{jn,ij}_{\bar{b}_{jn}\bar{b}_{ij}} K^{mn}_{\bar{f}_{jn}\bar{e}_{im}} + \sum_{n\bar{f}_{jj}\bar{b}_{nn}} t^{j}_{\bar{f}_{jj}} t^{n}_{\bar{b}_{nn}} S^{nn,ij}_{\bar{b}_{nn}\bar{b}_{ij}} K^{mn}_{\bar{f}_{jj}\bar{e}_{im}}
\end{aligned} \tag{71}
$$

$$W_{m\bar{b}_{ij}i\bar{e}_{mj}} = -K_{m\bar{b}_{ij}i\bar{e}_{mj}} - \sum_{\bar{f}_{ii}} t^{i}_{\bar{f}_{ii}} K_{m\bar{b}_{ij}\bar{f}_{ii}\bar{e}_{mj}}$$
$$+ \sum_{n\bar{b}_{nn}} S^{ij,nn}_{\bar{b}_{ij}\bar{b}_{nn}} t^{n}_{\bar{b}_{nn}} K_{mni\bar{e}_{mj}} + \frac{1}{2} \sum_{n\bar{f}_{in}\bar{b}_{in}} t^{in}_{\bar{f}_{in}\bar{b}_{in}} S^{in,ij}_{\bar{b}_{in}\bar{b}_{ij}} K^{mn}_{\bar{f}_{in}\bar{e}_{mj}} + \sum_{n\bar{f}_{ii}\bar{b}_{nn}} t^{i}_{\bar{f}_{ii}} t^{n}_{\bar{b}_{nn}} S^{mn,ij}_{\bar{b}_{nn}\bar{b}_{ij}} K^{mn}_{\bar{f}_{ii}\bar{e}_{mj}} \tag{72}$$

$$Z_{m\bar{b}_{ij}ij} = \sum_{\bar{e}_{ij}\bar{f}_{ij}} K_{m\bar{b}_{ij}\bar{e}_{ij}\bar{f}_{ij}} t^{ij}_{\bar{e}_{ij}\bar{f}_{ij}} + \sum_{\bar{e}_{ii}\bar{f}_{jj}} K_{m\bar{b}_{ij}\bar{e}_{ii}\bar{f}_{jj}} t^{ii}_{\bar{e}_{ii}} t^{j}_{\bar{f}_{jj}} \tag{73}$$

4. PNO Lambda CC

The approach to obtaining the PNO-CC lambda equations is no different to that of the PNO-CC amplitudes equations. The procedure starts from the canonical molecular orbital (CMO) based lambda equations and applying the PNO approximations. Briefly, the CC lambda equations are obtained by differentiating the CC Lagrangian with respect to the t-amplitudes, t_ν, and setting the derivative to zero,

$$\frac{\partial \mathscr{L}_{CC}}{\partial t_\nu} = \frac{\partial E_{CC}}{\partial t_\nu} + \frac{\partial \lambda_\nu r_\nu}{\partial t_\nu} = 0. \tag{74}$$

In Eq (74), λ_ν are the lagrange multipliers subject to the constraint of the CC residuals, r_ν where ν are levels of substitution. For CCSD, this will provide us the λ- singles, l^i_a, and doubles, l^{ij}_{ab}, residuals,

$$l^i_a = \frac{\partial \mathscr{L}_{CCSD}}{\partial t^i_a} = \langle 0| \big(1+\Lambda\big)\bar{H} \left|\phi^a_i\right\rangle = 0 \tag{75}$$

and

$$l^{ij}_{ab} = \frac{\partial \mathscr{L}_{CCSD}}{\partial t^{ij}_{ab}} = \langle 0| \big(1+\Lambda\big)\bar{H} \left|\phi^{ab}_{ij}\right\rangle = 0. \tag{76}$$

Our formulation starts with the construction of the similarity-transformed Hamiltonian $\bar{H}$, used as intermediates for solving the lambda equations After the construction of $\bar{H}$, the iterative process of converging the lambda equations starts. *Comments for myself $->$ add workflow figure

4.1 PNO Lambda CCD

4.2 PNO Lambda CCSD

The similarity-transformed Hamiltonian is denoted, for simplicity, as H without a bar to avoid confusion to the PNO indices. The implementation of these H intermediates will be discussed on the section Similarity-Transformed Hamiltonian.

λ - Singles Residuals

$$\begin{aligned} l^{i}_{\bar{a}_{ii}} =& 2H_{i\bar{a}_{ii}} - l^{i}_{\bar{e}_{ii}} H_{\bar{e}_{ii}\bar{a}_{ii}} + l^{im}_{\bar{e}_{im}\bar{f}_{im}} H_{\bar{e}_{im}\bar{f}_{im}\bar{a}_{ii}m} \\ & - S_{\bar{a}_{ii}\bar{a}_{mn}} l^{mn}_{\bar{a}_{mn}\bar{e}_{mn}} H_{i\bar{e}_{mn}mn} + l^{m}_{\bar{e}_{mm}} \left(2H_{i\bar{e}_{mm}\bar{a}_{ii}m} - H^{*}_{i\bar{e}_{mm}m\bar{a}_{ii}}\right) \\ & - 2G_{\bar{e}_{mn}\bar{f}_{mn}} H_{\bar{e}_{mn}i\bar{f}_{mn}\bar{a}_{ii}} + 2G_{\bar{e}_{mn}\bar{f}_{mn}} H_{\bar{e}_{mn}i\bar{a}_{ii}\bar{f}_{mn}} \\ & - 2G_{mn}H_{min\bar{a}_{ii}} + G_{mn}H_{imn\bar{a}_{ii}} \end{aligned} \tag{77}$$

where

$$G_{\bar{e}_{mn}\bar{f}_{mn}} = -t^{mn}_{\bar{e}_{mn}\bar{b}_{mn}} l^{mn}_{\bar{f}_{mn}\bar{b}_{mn}} \tag{78}$$

and

$$G_{mn} = S_{\bar{a}_{ij}\bar{a}_{mj}} t^{mj}_{\bar{a}_{mj}\bar{b}_{mj}} S_{\bar{b}_{mj}\bar{b}_{ij}} l^{ij}_{\bar{a}_{ij}\bar{b}_{ij}}. \tag{79}$$

The arterisk on $H_{i\bar{e}_{mm}m\bar{a}_{ii}}$ indicates index swap between a and m when implemented to match the shape of the singles residuals.

λ -Double Residuals

$$
\begin{aligned}
l^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} =& L^{ij}_{\bar{a}_{ij}\bar{b}_{ij}} + 2S_{\bar{a}_{ij}\bar{a}_{ii}} l^{i}_{\bar{a}_{ii}} H_{j\bar{b}_{ij}} - S_{\bar{a}_{ij}\bar{a}_{jj}} l^{j}_{\bar{a}_{jj}} H_{i\bar{b}_{ij}} \\
&+ 2l^{i}_{\bar{e}_{ii}} H_{\bar{e}_{ii}j\bar{b}_{ij}\bar{a}_{ij}} - l^{i}_{\bar{e}_{ii}} H_{\bar{e}_{ii}j\bar{a}_{ij}\bar{b}_{ij}} \\
&- 2S_{\bar{b}_{ij}\bar{b}_{mm}} l^{m}_{\bar{b}_{mm}} H_{jim\bar{a}_{ij}} + 2S_{\bar{b}_{ij}\bar{b}_{mm}} l^{m}_{\bar{b}_{mm}} H_{ijm\bar{a}_{ij}} \\
&+ l^{ij}_{\bar{e}_{ij}\bar{b}_{ij}} H_{\bar{e}_{ij}\bar{a}_{ij}} - S_{\bar{a}_{ij}\bar{a}_{mj}} l^{mj}_{\bar{a}_{mj}\bar{b}_{mj}} S_{\bar{b}_{mj}\bar{b}_{ij}} H_{im} \\
&+ \frac{1}{2} S_{\bar{a}_{ij}\bar{a}_{mn}} l^{mn}_{\bar{a}_{mn}\bar{b}_{mn}} S_{\bar{b}_{mn}\bar{i}\bar{j}} H_{ijmn} + \frac{1}{2} l^{ij}_{\bar{e}_{ij}\bar{f}_{ij}} H_{\bar{e}_{ij}\bar{f}_{ij}\bar{a}_{ij}\bar{b}_{ij}} \\
&+ l^{mj}_{\bar{e}_{mj}\bar{b}_{mj}} S_{\bar{b}_{mj}\bar{b}_{ij}} \left(2H_{i\bar{e}_{mj}\bar{a}_{ij}m} - H_{i\bar{e}_{mj}m\bar{a}_{ij}}\right) - S_{\bar{b}_{ij}\bar{b}_{mi}} l^{mi}_{\bar{b}_{mi}\bar{e}_{mi}} H_{j\bar{e}_{mi}m\bar{a}_{ij}} \\
&- S_{\bar{b}_{ij}\bar{b}_{mi}} l^{mi}_{\bar{b}_{mi}\bar{e}_{mi}} H_{j\bar{e}_{mi}\bar{a}_{ij}m} + S_{\bar{a}_{ij}\bar{a}_{mn}} G_{\bar{a}_{mn}\bar{e}_{mn}} L^{ij}_{\bar{e}_{mn}\bar{b}_{ij}} - G_{mi} L^{mj}_{\bar{a}_{ij}\bar{b}_{ij}}
\end{aligned} \tag{80}
$$

Similarity-Transformed Hamiltonian

The similarity-transformed Hamiltonian, simply denoted as H, is constructed (non-iteratively) after the convergence of the t-amplitudes and used as intermediates to solve for lambda equations. Here we list all of H intermediates, commenting on redundant equations for optimizing the implementation process.

Taking a look at the first term of the singles residuals, $H_{i\bar{a}_{ii}}$, and the second and third term of the doubles residual, $H_{j\bar{b}_{ij}}$ and $H_{i\bar{b}_{ij}}$. These H intermediates have a structure of $H_{ov_{ij}}$ and are defined as

$$H_{i\bar{a}_{ii}} = F^{i}_{\bar{a}_{ii}} + t^{n}_{f} L^{in}_{\bar{a}_{ii}\bar{f}_{nn}}, \tag{81}$$

$$H_{i\bar{b}_{ij}} = F^{i}_{\bar{b}_{ij}} + t^{n}_{f} L^{in}_{\bar{b}_{ij}\bar{f}_{nn}}, \tag{82}$$

$$H_{j\bar{b}_{ij}} = F^{j}_{\bar{b}_{ij}} + t^{n}_{f} L^{jn}_{\bar{b}_{ij}\bar{f}_{nn}}. \tag{83}$$

These H intermediates can be consolidated and implemented as such

```
lHov = []
for ij in range(no*no):


    Hov = Fov[ij].copy()
```

```
    for n in range(no):
        nn = n*no + n

        tmp = contract('eE, mef-> mEf', QL[ij], L[o,n,v,v]
        tmp = contract('fF, mEf-> mEF', QL[nn], tmp)
        Hov = Hov + contract('F,mEF->mE',t1[n], tmp)
    lHov.append(Hov)
```

Keeping that in mind, here are the rest of the H intermediates:

The equations given are ordered based on their implementation within cchbar object of PyCC

$H_{v_{ij}v_{ij}}$ structure such as $H_{\bar{e}_{ii}\bar{a}_{ii}}$ and $H_{\bar{e}_{ij}\bar{a}_{ij}}$

$$\begin{aligned} H_{\bar{e}_{ij}\bar{a}_{ij}} =& F_{\bar{e}_{ij}\bar{a}_{ij}} - F^{m}_{\bar{a}_{ij}} t^{m}_{\bar{e}_{ij}} + t^{m}_{\bar{f}_{mm}} L_{\bar{e}_{ij}m\bar{a}_{ij}\bar{f}_{mm}} \\ & - t^{mn}_{\bar{f}_{mn}\bar{e}_{mn}} S_{\bar{e}_{mn}\bar{e}_{ij}} L^{mn}_{\bar{f}_{mn}\bar{a}_{ij}} - t^{m}_{\bar{f}_{mm}} t^{n}_{\bar{e}_{nn}} S_{\bar{e}_{nn}\bar{e}_{ij}} L^{mn}_{\bar{f}_{mn}\bar{a}_{ij}}. \end{aligned} \tag{84}$$

H_{oo} structure such as H_{im}

$$H_{im} = F_{im} + t^{m}_{\bar{e}_{mm}} F^{i}_{\bar{e}_{mm}} + t^{n}_{\bar{e}_{nn}} L_{inm\bar{e}_{nn}} + t^{mn}_{\bar{e}_{mn}\bar{f}_{mn}} L^{in}_{\bar{e}_{mn}\bar{f}_{mn}} + t^{m}_{\bar{e}_{mm}} t^{n}_{\bar{f}_{nn}} L^{in}_{\bar{e}_{mm}\bar{f}_{nn}}. \tag{85}$$

H_{oooo} structure such as H_{ijmn}

$$H_{ijmn} = K_{ijmn} + X_{ijmn} + X^{*}_{jinm} + t^{mn}_{\bar{e}_{mn}\bar{f}_{mn}} K_{ij\bar{e}_{mn}\bar{f}_{mn}} + t^{m}_{\bar{e}_{mm}} t^{n}_{\bar{f}_{nn}} K^{ij}_{\bar{e}_{mm}\bar{f}_{nn}} \tag{86}$$

where X_{ijmn} and X_{jinm} are defined as

$$X_{ijmn} = t^{n}_{\bar{e}_{nn}} K_{ijm\bar{e}_{nn}} \tag{87}$$

and

$$X_{jinm} = t^{m}_{\bar{e}_{mm}} K_{jin\bar{e}_{mm}}. \tag{88}$$

The asterisk on X_{jinm} denotes swapping indices to match the shape of H_{ijmn}

$H_{v_{im}v_{im}v_{ii}v_{im}}$ structure such as $H_{\bar{a}_{im}\bar{b}_{im}\bar{e}_{ii}\bar{f}_{im}}$

$$\begin{aligned} H_{\bar{a}_{im}\bar{b}_{im}\bar{e}_{ii}\bar{f}_{im}} =& K_{\bar{a}_{im}\bar{b}_{im}\bar{e}_{ii}\bar{f}_{im}} + X_{\bar{a}_{im}\bar{b}_{im}\bar{e}_{ii}\bar{f}_{im}} + X_{\bar{b}_{im}\bar{a}_{im}\bar{f}_{im}\bar{e}_{ii}} \\ &+ S_{\bar{a}_{im}\bar{a}_{mn}} t^{mn}_{\bar{a}_{mn}\bar{b}_{mn}} S_{\bar{f}_{mn}\bar{f}_{im}} K^{mn}_{\bar{e}_{ii}\bar{f}_{im}} + S_{\bar{a}_{im}\bar{a}_{mm}} t^{m}_{\bar{a}_{mm}} t^{n}_{\bar{b}_{nn}} S_{\bar{f}_{nn}\bar{f}_{im}} K^{mn}_{\bar{e}_{ii}\bar{f}_{im}} \end{aligned} \tag{89}$$

where $X_{\bar{a}_{im}\bar{b}_{im}\bar{e}_{ii}\bar{f}_{im}}$ and $X_{\bar{b}_{im}\bar{a}_{im}\bar{f}_{im}\bar{e}_{ii}}$ are defined as

$$X_{\bar{a}_{im}\bar{b}_{im}\bar{e}_{ii}\bar{f}_{im}} = S_{\bar{b}_{im}\bar{b}_{mm}} t^{m}_{\bar{b}_{mm}} K_{\bar{a}_{im}m\bar{e}_{ii}\bar{f}_{im}} \tag{90}$$

$$X_{\bar{b}_{im}\bar{a}_{im}\bar{f}_{im}\bar{e}_{ii}} = S_{\bar{a}_{im}\bar{a}_{mm}} t^{m}_{\bar{a}_{mm}} K_{\bar{b}_{im}m\bar{f}_{im}\bar{e}_{ii}} \tag{91}$$

$H_{v_{ij}v_{ij}v_{ij}v_{ij}}$ structure such as $H_{\bar{e}_{ij}\bar{f}_{ij}\bar{a}_{ij}\bar{b}_{ij}}$

$$\begin{aligned} H_{\bar{e}_{ij}\bar{f}_{ij}\bar{a}_{ij}\bar{b}_{ij}} =& K_{\bar{e}_{ij}\bar{f}_{ij}\bar{a}_{ij}\bar{b}_{ij}} + X_{\bar{e}_{ij}\bar{f}_{ij}\bar{a}_{ij}\bar{b}_{ij}} + X_{\bar{f}_{ij}\bar{e}_{ij}\bar{b}_{ij}\bar{a}_{ij}} \\ &+ S_{\bar{e}_{ij}\bar{e}_{mn}} t^{mn}_{\bar{e}_{mn}\bar{f}_{mn}} S_{\bar{f}_{mn}\bar{f}_{ij}} K^{mn}_{\bar{a}_{ij}\bar{b}_{ij}} + S_{\bar{e}_{ij}\bar{e}_{mm}} t^{m}_{\bar{e}_{mm}} t^{n}_{\bar{f}_{nn}} S_{\bar{f}_{nn}\bar{f}_{ij}} K^{mn}_{\bar{a}_{ij}\bar{b}_{ij}} \end{aligned} \tag{92}$$

where $X_{\bar{e}_{ij}\bar{f}_{ij}\bar{a}_{ij}\bar{b}_{ij}}$ and $X_{\bar{f}_{ij}\bar{e}_{ij}\bar{b}_{ij}\bar{a}_{ij}}$ are defined as

$$X_{\bar{e}_{ij}\bar{f}_{ij}\bar{a}_{ij}\bar{b}_{ij}} = S_{\bar{f}_{ij}\bar{f}_{mm}} t^{m}_{\bar{f}_{mm}} K_{\bar{e}_{ij}m\bar{a}_{ij}\bar{b}_{ij}} \tag{93}$$

$$X_{\bar{f}_{ij}\bar{e}_{ij}\bar{b}_{ij}\bar{a}_{ij}} = S_{\bar{e}_{ij}\bar{e}_{mm}} t^{m}_{\bar{e}_{mm}} K_{\bar{f}_{ij}m\bar{b}_{ij}\bar{a}_{ij}} \tag{94}$$

$H_{v_{mn}iv_{ii}v_{mn}}$ structure such as $H_{\bar{e}_{mn}i\bar{a}_{ii}\bar{f}_{mn}}$

$$H_{\bar{e}_{mn}i\bar{a}_{ii}\bar{f}_{mn}} = K_{\bar{e}_{mn}i\bar{a}_{ii}\bar{f}_{mn}} - S_{\bar{e}_{mn}\bar{e}_{nn}} t^{k}_{\bar{e}_{kk}} K^{kj}_{\bar{a}_{ii}\bar{f}_{mn}} \tag{95}$$

$H_{v_{mn}iv_{mn}v_{ii}}$ structure such as $H_{\bar{e}_{mn}i\bar{f}_{mn}\bar{a}_{ii}}$

$$H_{\bar{e}_{mn}i\bar{f}_{mn}\bar{a}_{ii}} = K_{\bar{e}_{mn}i\bar{f}_{mn}\bar{a}_{ii}} - S_{\bar{e}_{mn}\bar{e}_{nn}} t^{n}_{\bar{e}_{nn}} K^{nj}_{\bar{f}_{mn}\bar{a}_{ii}} \tag{96}$$

$H_{v_{ii}jv_{ij}v_{ij}}$ structure such as $H_{\bar{e}_{ii}j\bar{b}_{ij}\bar{a}_{ij}}$

$$H_{\bar{e}_{ii}j\bar{b}_{ij}\bar{a}_{ij}} = K_{\bar{e}_{ii}j\bar{b}_{ij}\bar{a}_{ij}} - S_{\bar{e}_{ii}\bar{e}_{nn}} t^{n}_{\bar{e}_{nn}} K^{nj}_{\bar{b}_{ij}\bar{a}_{ij}} \tag{97}$$

$H_{oiov_{ii}}$ structure such as $H_{min\bar{a}_{ii}}$

$$H_{min\bar{a}_{ii}} = K_{min\bar{a}_{ii}} + t^{n}_{\bar{f}_{nn}} K^{im}_{\bar{a}_{ij}\bar{f}_{nn}} \tag{98}$$

$H_{ioov_{ii}}$ structure such as $H_{imn\bar{a}_{ii}}$

$$H_{imn\bar{a}_{ii}} = K_{imn\bar{a}_{ii}} + t^{n}_{\bar{f}_{nn}} K^{mi}_{\bar{a}_{ij}\bar{f}_{nn}} \tag{99}$$

$H_{jiov_{ij}}$ structure such as $H_{jim\bar{a}_{ij}}$

$$H_{jim\bar{a}_{ij}} = K_{jim\bar{a}_{ij}} + t^{m}_{\bar{f}_{mm}} K^{ij}_{\bar{a}_{ij}\bar{f}_{mm}} \tag{100}$$

$H_{ijov_{ij}}$ structure such as $H_{ijm\bar{a}_{ij}}$

$$H_{ijm\bar{a}_{ij}} = K_{ijm\bar{a}_{ij}} + t^{m}_{\bar{f}_{mm}} K^{ji}_{\bar{a}_{ij}\bar{f}_{mm}} \tag{101}$$

$H_{iv_{mm}v_{ii}o}$ structure such as $H_{i\bar{e}_{mm}\bar{a}_{ii}m}$

$$\begin{aligned} H_{i\bar{e}_{mm}\bar{a}_{ii}m} =& K_{i\bar{e}_{mm}\bar{a}_{ii}m} + t^{m}_{\bar{f}_{mm}} K_{i\bar{e}_{mm}\bar{a}_{ii}\bar{f}_{mm}} \\ & - S_{\bar{e}_{mm}\bar{e}_{nn}} t^{n}_{\bar{e}_{nn}} K_{in\bar{a}_{ii}m} - t^{jn}_{\bar{f}_{jn}\bar{e}_{jn}} S_{\bar{e}_{jn}\bar{e}_{mm}} K_{in\bar{a}_{ii}\bar{f}_{jn}} \\ & - t^{j}_{\bar{f}_{jj}} t^{n}_{\bar{e}_{nn}} S_{\bar{e}_{nn}\bar{e}_{mm}} K_{in\bar{a}_{ii}\bar{f}_{jj}} + t^{nj}_{\bar{f}_{nj}\bar{e}_{nj}} S_{\bar{e}_{nj}\bar{e}_{mm}} L_{in\bar{a}_{ii}\bar{f}_{nj}} \end{aligned} \tag{102}$$

$H_{jv_{mi}v_{ij}o}$ structure such as $H_{j\bar{e}_{mi}\bar{a}_{ij}m}$

$$\begin{aligned} H_{j\bar{e}_{mi}\bar{a}_{ij}m} =& K_{j\bar{e}_{mi}\bar{a}_{ij}m} + t^{m}_{\bar{f}_{mm}} K_{j\bar{e}_{mi}\bar{a}_{ij}\bar{f}_{mm}} \\ & - S_{\bar{e}_{mi}\bar{e}_{nn}} t^{n}_{\bar{e}_{nn}} K_{jn\bar{a}_{ij}m} - t^{in}_{\bar{f}_{in}\bar{e}_{in}} S_{\bar{e}_{in}\bar{e}_{mi}} K_{jn\bar{a}_{ij}\bar{f}_{in}} \\ & - t^{i}_{\bar{f}_{ii}} t^{n}_{\bar{e}_{nn}} S_{\bar{e}_{nn}\bar{e}_{mi}} K_{jn\bar{a}_{ij}\bar{f}_{ii}} + t^{ni}_{\bar{f}_{ni}\bar{e}_{ni}} S_{\bar{e}_{ni}\bar{e}_{mi}} L_{jn\bar{a}_{ij}\bar{f}_{ni}} \end{aligned} \tag{103}$$

$H_{iv_{mj}v_{ij}o}$ structure such as $H_{i\bar{e}_{mj}\bar{a}_{ij}m}$

$$\begin{aligned} H_{i\bar{e}_{mj}\bar{a}_{ij}m} =& K_{i\bar{e}_{mj}\bar{a}_{ij}m} + t^{m}_{\bar{f}_{mm}} K_{i\bar{e}_{mj}\bar{a}_{ij}\bar{f}_{mm}} \\ & - S_{\bar{e}_{mj}\bar{e}_{nn}} t^{n}_{\bar{e}_{nn}} K_{in\bar{a}_{ij}m} - t^{jn}_{\bar{f}_{jn}\bar{e}_{jn}} S_{\bar{e}_{jn}\bar{e}_{mj}} K_{in\bar{a}_{ij}\bar{f}_{jn}} \\ & - t^{j}_{\bar{f}_{jj}} t^{n}_{\bar{e}_{nn}} S_{\bar{e}_{nn}\bar{e}_{mj}} K_{in\bar{a}_{ij}\bar{f}_{jj}} + t^{nj}_{\bar{f}_{nj}\bar{e}_{nj}} S_{\bar{e}_{nj}\bar{e}_{mj}} L_{in\bar{a}_{ij}\bar{f}_{nj}} \end{aligned} \tag{104}$$

$H_{iv_{mm}ov_{ii}}$ structure such as $H_{i\bar{e}_{mm}m\bar{a}_{ii}}$

$$\begin{aligned}H_{i\bar{e}_{mm}m\bar{a}_{ii}} =& K_{i\bar{e}_{mm}m\bar{a}_{ii}} + t^{m}_{\bar{f}_{mm}} K_{\bar{e}_{mm}i\bar{a}_{ii}\bar{f}_{mm}} \\ & - S_{\bar{e}_{mm}\bar{e}_{nn}} t^{n}_{\bar{e}_{nn}} K_{inm\bar{a}_{ii}} - t^{mn}_{\bar{f}_{mn}\bar{e}_{mn}} S_{\bar{e}_{mn}\bar{e}_{mm}} K^{ni}_{\bar{a}_{ii}\bar{f}_{mn}} \\ & - t^{m}_{\bar{f}_{mm}} t^{n}_{\bar{e}_{nn}} S_{\bar{e}_{nn}\bar{e}_{mm}} K^{ni}_{\bar{a}_{ii}\bar{f}_{mm}}\end{aligned} \tag{105}$$

$H_{iv_{mj}ov_{ij}}$ structure such as $H_{i\bar{e}_{mj}m\bar{a}_{ij}}$

$$\begin{aligned}H_{i\bar{e}_{mj}m\bar{a}_{ij}} =& K_{i\bar{e}_{mj}m\bar{a}_{ij}} + t^{m}_{\bar{f}_{mm}} K_{\bar{e}_{mj}i\bar{a}_{ij}\bar{f}_{mm}} \\ & - S_{\bar{e}_{mj}\bar{e}_{nn}} t^{n}_{\bar{e}_{nn}} K_{inm\bar{a}_{ij}} - t^{mn}_{\bar{f}_{mn}\bar{e}_{mn}} S_{\bar{e}_{mn}\bar{e}_{mj}} K^{ni}_{\bar{a}_{ij}\bar{f}_{mn}} \\ & - t^{m}_{\bar{f}_{mm}} t^{n}_{\bar{e}_{nn}} S_{\bar{e}_{nn}\bar{e}_{mj}} K^{ni}_{\bar{a}_{ij}\bar{f}_{mm}}\end{aligned} \tag{106}$$

$H_{jv_{mi}ov_{ij}}$ such as $H_{j\bar{e}_{mi}m\bar{a}_{ij}}$

$$\begin{aligned}H_{j\bar{e}_{mi}m\bar{a}_{ij}} =& K_{j\bar{e}_{mi}m\bar{a}_{ij}} + t^{m}_{\bar{f}_{mm}} K_{\bar{e}_{mi}j\bar{a}_{ij}\bar{f}_{mm}} \\ & - S_{\bar{e}_{mi}\bar{e}_{nn}} t^{n}_{\bar{e}_{nn}} K_{jnm\bar{a}_{ij}} - t^{mn}_{\bar{f}_{mn}\bar{e}_{mn}} S_{\bar{e}_{mn}\bar{e}_{mi}} K^{nj}_{\bar{a}_{ij}\bar{f}_{mn}} \\ & - t^{m}_{\bar{f}_{mm}} t^{n}_{\bar{e}_{nn}} S_{\bar{e}_{nn}\bar{e}_{mi}} K^{nj}_{\bar{a}_{ij}\bar{f}_{mm}}\end{aligned} \tag{107}$$

$H_{v_{im}v_{im}v_{ii}o}$ structure such as $H_{\bar{e}_{im}\bar{f}_{im}\bar{a}_{ii}m}$

$$\begin{aligned}H_{\bar{e}_{im}\bar{f}_{im}\bar{a}_{ii}m} =& K_{\bar{e}_{im}\bar{f}_{im}\bar{a}_{ii}m} - H_{n\bar{a}_{ii}} S_{\bar{e}_{im}\bar{e}_{nm}} t^{nm}_{\bar{e}_{nm}\bar{f}_{nm}} \\ & + t^{m}_{\bar{c}_{mm}} H_{\bar{e}_{im}\bar{f}_{im}\bar{a}_{ii}\bar{c}_{mm}} + S_{\bar{e}_{im}\bar{e}_{kn}} t^{kn}_{\bar{e}_{kn}\bar{f}_{kn}} S_{\bar{f}_{kn}\bar{f}_{im}} K_{kn\bar{a}_{ii}m} \\ & + t^{k}_{\bar{e}_{kk}} S_{\bar{e}_{kk}\bar{e}_{im}} t^{n}_{\bar{f}_{nn}} S_{\bar{f}_{nn}\bar{f}_{im}} K_{kn\bar{a}_{ii}m} - t^{mk}_{\bar{c}_{mk}\bar{e}_{mk}} S_{\bar{e}_{mk}\bar{e}_{im}} K_{\bar{f}_{im}m\bar{c}_{mk}\bar{a}_{ii}} \\ & - t^{mk}_{\bar{c}_{mk}\bar{f}_{mk}} S_{\bar{f}_{mk}\bar{f}_{im}} K_{\bar{e}_{im}k\bar{a}_{ii}\bar{c}_{mk}} + t^{km}_{\bar{c}_{mk}\bar{f}_{mk}} S_{\bar{f}_{mk}\bar{f}_{im}} L_{\bar{e}_{im}k\bar{a}_{ii}\bar{c}_{mk}} \\ & - t^{k}_{\bar{f}_{kk}} S_{\bar{f}_{kk}\bar{f}_{im}} X_{\bar{e}_{im}k\bar{a}_{ii}m} - t^{k}_{\bar{e}_{kk}} S_{\bar{e}_{kk}\bar{e}_{im}} X_{\bar{f}_{im}km\bar{a}_{ii}}\end{aligned} \tag{108}$$

where

$$X_{\bar{e}_{im}k\bar{a}_{ii}m} = K_{\bar{e}_{im}k\bar{a}_{ii}m} - t^{mn}_{\bar{f}_{mn}\bar{e}_{mn}} S_{\bar{e}_{mn}\bar{e}_{im}} K^{kn}_{\bar{f}_{mn}\bar{a}_{ii}} \tag{109}$$

and

$$X_{\bar{f}_{im}km\bar{a}_{ii}} = K_{\bar{f}_{im}km\bar{a}_{ii}} - t^{mn}_{\bar{c}_{mn}\bar{f}_{mn}} S_{\bar{f}_{mn}\bar{f}_{im}} K^{kn}_{\bar{a}_{ii}\bar{c}_{mn}} + t^{nm}_{\bar{c}_{nm}\bar{f}_{nm}} S_{\bar{f}_{nm}\bar{f}_{im}} K^{kn}_{\bar{a}_{ii}\bar{c}_{nm}} \tag{110}$$

$H_{iv_{mn}oo}$ structure such as $H_{i\bar{e}_{mn}mn}$

$$\begin{aligned} H_{i\bar{e}_{mn}mn} =& K_{i\bar{e}_{mn}mn} + H_{i\bar{c}_{mn}} t^{mn}_{\bar{c}_{mn}\bar{e}_{mn}} \\ & - t^{k}_{\bar{e}_{kk}} S_{\bar{e}_{kk}\bar{e}_{mn}} H_{ikmn} + t^{mn}_{\bar{c}_{mn}\bar{f}_{mn}} K_{i\bar{e}_{mn}\bar{c}_{mn}\bar{f}_{mn}} \\ & + t^{m}_{\bar{c}_{mm}} t^{n}_{\bar{f}_{nn}} K_{i\bar{e}_{mn}\bar{c}_{mm}\bar{f}_{nn}} - t^{mk}_{\bar{c}_{mk}\bar{e}_{mk}} S_{\bar{e}_{mk}\bar{e}_{mn}} K_{kin\bar{c}_{mk}} \\ & - t^{nk}_{\bar{c}_{nk}\bar{e}_{nk}} S_{\bar{e}_{nk}\bar{e}_{mn}} K_{ikm\bar{c}_{nk}} + t^{kn}_{\bar{c}_{kn}\bar{e}_{kn}} S_{\bar{e}_{kn}\bar{e}_{mn}} L_{ikm\bar{c}_{kn}} \\ & + t^{n}_{\bar{c}_{nn}} X_{i\bar{e}_{mn}m\bar{c}_{nn}} + t^{m}_{\bar{c}_{mm}} X_{\bar{e}_{mn}in\bar{c}_{mm}} \end{aligned} \tag{111}$$

where

$$X_{i\bar{e}_{mn}m\bar{c}_{nn}} = K_{i\bar{e}_{mn}m\bar{c}_{nn}} - t^{mk}_{\bar{f}_{mk}\bar{e}_{mk}} S_{\bar{e}_{mk}\bar{e}_{mn}} K^{ik}_{\bar{f}_{mk}\bar{c}_{nn}} \tag{112}$$

and

$$X_{\bar{e}_{mn}in\bar{c}_{mm}} = K_{\bar{e}_{mn}in\bar{c}_{mm}} - t^{nk}_{\bar{f}_{nk}\bar{e}_{nk}} S_{\bar{e}_{nk}\bar{e}_{mn}} K^{ik}_{\bar{c}_{mm}\bar{f}_{nk}} + t^{kn}_{\bar{f}_{kn}\bar{e}_{kn}} S_{\bar{e}_{kn}\bar{e}_{mn}} L^{ik}_{\bar{c}_{mm}\bar{f}_{kn}} \tag{113}$$

Noting apart from the target indices of the residuals, i and a for R^i_a and ij and ab for R^{ij}_{ab}, the rest of the occupied orbital indices and virtual orbital indices are dummy variables and can be carefully rename as needed to implement like-terms for the H intermediates.

Implementation

Below are just miscellaneous notes. No need to read further.

3.2 Infrastructure of local CC

Here is the infrastructure of local CC:

(1) SCF to obtain the reference wave function using Psi4

(2) localized internal (occupied) MO basis using Pipek-Mizey

(3) generate and store MO transformations of the Fock matrix and integrals

(4) localized external (unoccupied) MO basis using PNO

(5) transform and store the MO Fock matrix and integrals into the PNO basis for each given pair ij

---

```
def transform_integral(self,o,v):

    Q = self.Local.Q
    L = self.Local.L

    #contraction notation i,j,a,b typically MO; A,B,C,D virtual PNO; Z,X,Y
        virtual semicanonical PNO

    Fov_ij = []
    Fvv_ij = []

    ERIoovo_ij = []
    ERIooov_ij = []
    ERIovvv_ij = []
    ERIvvvv_ij = []
    ERIoovv_ij = []
    ERIovvo_ij = []
    ERIvvvo_ij = []
    ERIovov_ij = []
```

```
ERIovoo_ij = []

Loovv_ij = []
Lovvv_ij = []
Looov_ij = []
Loovo_ij = []
Lovvo_ij = []

for ij in range(self.no*self.no):
    i = ij // self.no
    j = ij % self.no

    Fov_ij.append(self.H.F[o,v] @ Q[ij] @ L[ij])
    Fvv_ij.append(L[ij].T @ Q[ij].T @ self.H.F[v,v] @ Q[ij] @ L[ij])

    ERIoovo_ij.append(contract('ijak,aA,AZ->ijZk',
        self.H.ERI[o,o,v,o],Q[ij],L[ij]))
    ERIooov_ij.append(contract('ijka,aA,AZ->ijkZ',
        self.H.ERI[o,o,o,v],Q[ij],L[ij]))
    ERIoovv_ij.append(contract('ijab,aA,AZ,bB,BY->ijZY',
        self.H.ERI[o,o,v,v],Q[ij],L[ij],Q[ij],L[ij]))
    tmp = contract('iabc,aA,AZ->iZbc',self.H.ERI[o,v,v,v], Q[ij], L[ij])
    tmp1 = contract('iZbc,bB,BY->iZYc',tmp, Q[ij],L[ij])
    ERIovvv_ij.append(contract('iZYc,cC,CX->iZYX',tmp1, Q[ij], L[ij]))
    tmp2 = contract('abcd,aA,AZ->Zbcd',self.H.ERI[v,v,v,v], Q[ij], L[ij])
    tmp3 = contract('Zbcd,bB,BY->ZYcd',tmp2, Q[ij], L[ij])
    tmp4 = contract('ZYcd,cC,CX->ZYXd',tmp3, Q[ij], L[ij])
    ERIvvvv_ij.append(contract('ZYXd,dD,DW->ZYXW',tmp4, Q[ij], L[ij]))
    tmp5 = contract('iabj,aA,AZ->iZbj',self.H.ERI[o,v,v,o], Q[ij],L[ij])
```

```
    ERIovvo_ij.append(contract('iZbj,bB,BY->iZYj',tmp5,Q[ij], L[ij]))
    tmp6 = contract('abci,aA,AZ->Zbci',self.H.ERI[v,v,v,o], Q[ij], L[ij])
    tmp7 = contract('Zbci,bB,BY->ZYci',tmp6, Q[ij], L[ij])
    ERIvvvo_ij.append(contract('ZYci,cC,CX->ZYXi',tmp7, Q[ij], L[ij]))
    tmp8 = contract('iajb,aA,AZ->iZjb',self.H.ERI[o,v,o,v], Q[ij], L[ij])
    ERIovov_ij.append(contract('iZjb,bB,BY->iZjY', tmp8, Q[ij], L[ij]))
    ERIovoo_ij.append(contract('iajk,aA,AZ->iZjk', self.H.ERI[o,v,o,o],
        Q[ij], L[ij]))

    Loovo_ij.append(contract('ijak,aA,AZ->ijZk',
        self.H.L[o,o,v,o],Q[ij],L[ij]))
    Loovv_ij.append(contract('ijab,aA,AZ,bB,BY->ijZY',
        self.H.L[o,o,v,v],Q[ij],L[ij],Q[ij],L[ij]))
    tmp9 = contract('iabc,aA,AZ->iZbc',self.H.L[o,v,v,v], Q[ij], L[ij])
    tmp10 = contract('iZbc,bB,BY->iZYc',tmp, Q[ij],L[ij])
    Lovvv_ij.append(contract('iZYc,cC,CX->iZYX',tmp1, Q[ij], L[ij]))
    Looov_ij.append(contract('ijka,aA,AZ->ijkZ',self.H.L[o,o,o,v],
        Q[ij],L[ij]))
    Lovvo_ij.append(contract('iabj,aA,AZ,bB,BY->iZYj',
        self.H.L[o,v,v,o],Q[ij],L[ij],Q[ij],L[ij]))

self.Fov_ij = Fov_ij
self.Fvv_ij = Fvv_ij

self.ERIoovo_ij = ERIoovo_ij
self.ERIooov_ij = ERIooov_ij
self.ERIovvv_ij = ERIovvv_ij
self.ERIvvvv_ij = ERIvvvv_ij
self.ERIoovv_ij = ERIoovv_ij
```

```
        self.ERIovvo_ij = ERIovvo_ij
        self.ERIvvvo_ij = ERIvvvo_ij
        self.ERIovov_ij = ERIovov_ij
        self.ERIovoo_ij = ERIovoo_ij

        self.Loovv_ij = Loovv_ij
        self.Lovvv_ij = Lovvv_ij
        self.Looov_ij = Looov_ij
        self.Loovo_ij = Loovo_ij
        self.Lovvo_ij = Lovvo_ij
```

(6) transform and store the t1 and t2 amplitudes as well

```
        if local is not None:
            t1_ii = []
            t2_ij = []

            for i in range(self.no):
                ii = i*self.no + i

                X = self.Local.Q[ii].T @ self.t1[i]
                t1_ii.append(self.Local.L[ii].T @ X)

                for j in range(self.no):
                    ij = i*self.no+ j

                    X = self.Local.L[ij].T @ self.Local.Q[ij].T @
                        self.H.ERI[i,j,v,v] @ self.Local.Q[ij] @ self.Local.L[ij]
                    t2_ij.append( -1*X/ (self.Local.eps[ij].reshape(1,-1) +
```

```
                self.Local.eps[ij].reshape(-1,1) - self.H.F[i,i] -
                self.H.F[j,j]))

        self.t1_ii = t1_ii
        self.t2_ij = t2_ij
```

(7) calculate local MP2 using initial t2 guess amplitude and compare against 0th iteration of CC iterative process

```
    for ij in range(self.no*self.no):
        i = ij // self.no
        j = ij % self.no

        L_ij = 2.0 * self.t2_ij[ij] - self.t2_ij[ij].T
        mp2_ij = np.sum(np.multiply(self.ERIoovv_ij[ij][i,j], L_ij))
        emp2 += mp2_ij

    print(emp2)

    ecc = self.lcc_energy(self.Fov_ij,self.Loovv_ij,self.t1_ii,self.t2_ij)

def lcc_energy(self,Fov_ij,Loovv_ij,t1_ii,t2_ij):
    ecc_ij = 0
    ecc_ii = 0
    ecc = 0

    for i in range(self.no):
        ii = i*self.no + i
```

```
        ecc_ii = 2*np.sum(np.multiply(Fov_ij[ii][i],t1_ii[i]))
        ecc += ecc_ii

        for j in range(self.no):
            ij = i*self.no + j

            ltau = self.build_ltau(ij,t1_ii,t2_ij)
            ecc_ij = np.sum(np.multiply(ltau,Loovv_ij[ij][i,j]))
            ecc += ecc_ij

    return ecc
```

Within the CC iterative procedure,

(8) calculate the single and double residuals

(9) update t1 and t2 amplitudes

```
        r1_ii, r2_ij = self.local_residuals(self.t1_ii, self.t2_ij)

        rms = 0

        for i in range(self.no):
            ii = i*self.no + i

            for a in range(self.Local.dim[ii]):
                self.t1_ii[i][a] += r1_ii[i][a]/(self.H.F[i,i] -
                    self.Local.eps[ii][a])

            rms += contract('Z,Z->',r1_ii[i], r1_ii[i])
```

```
            for j in range(self.no):
                ij = i*self.no + j

                self.t2_ij[ij] -= r2_ij[ij]/(self.Local.eps[ij].reshape(1,-1)
                    + self.Local.eps[ij].reshape(-1,1) - self.H.F[i,i] -
                    self.H.F[j,j])
                rms += contract('ZY,ZY->',r2_ij[ij],r2_ij[ij])

        rms = np.sqrt(rms)
```

(10) repeat 8 and 9 until thresholds are met

For step 5 and 6, the transformation is to the semi-canonical PNO basis which is beneficial for the amplitude update (step 8) since we can utilize the quasicanonical virtual Fock matrix in the energy denominator.

There are some local integrals that require "on the fly" generations since they are not restricted to pair ij such as $L^{mn}_{\bar{e}_{ij}\bar{f}_{mn}}$. To demonstrate, if we were to project the $\bar{f}_{ij}$ to $\bar{f}_{mn}$ using the overlap term, $S^{ij,mn}_{\bar{f}_{ij}\bar{f}_{mn}}$, to obtain $L^{mn}_{\bar{e}_{ij}\bar{f}_{mn}}$ from $L^{mn}_{\bar{e}_{ij}\bar{f}_{ij}}$ then for a specific $m,n(0,1)$ the matrix block is

```
L01vv
[[-1.71270255e-02 -9.77405084e-03 -3.24042754e-14 1.06679742e-02
   2.66127288e-02]
[-4.52954652e-14 1.60787643e-14 7.53484309e-03 -2.52278673e-14
   1.54662632e-14]
[ 1.88986958e-02 -5.96108354e-03 1.96559542e-14 -2.62044608e-03
  -3.29947473e-02]
```

```
[-3.61508108e-02 1.68085356e-02 5.44704636e-14 -4.40568444e-02
   7.27566180e-03]]
```

while if its generated on the fly to the appropriate pair then the matrix block is

```
L01vv
[[-1.30324130e-02 -1.45252595e-02 -1.83595016e-14 6.06347708e-03
   3.03845128e-02]
[-4.62469207e-14 1.67479723e-14 7.53484309e-03 -2.56733226e-14
   1.58082407e-14]
[ 1.21775404e-02 -2.10039664e-03 1.90324772e-15 3.70451948e-03
  -3.80909045e-02]
[-3.68097327e-02 1.71331313e-02 5.52728188e-14 -4.39741543e-02
   7.19688660e-03]]
```

There are also some intermediates that contains two different pair correlation spaces such as $W_{m\bar{b}_{ij}j\bar{e}_{im}}$ which can be stored as a list with a compound index of ijm. Here is a code block that illustrates how it is done,

Concerns

For some intermediates that has different pairs due to their corresponding t amplitudes, for example $F_{m\bar{e}_{ij}}$ and $F_{m\bar{e}_{im}}$, is it appropriate to just generate the pair ij with the understanding that the pair im is just dummy indices? Follow up to the same question, for 4-index intermediates that have different pairs associated to virtual indexes such as $W_{m\bar{b}_{ij}j\bar{e}_{im}}$ and $W_{m\bar{b}_{ij}i\bar{e}_{mj}}$, this cannot be understood as dummy variables because pair im and mj is not accounting for the same pair external correlation space. To showcase, here is an example code:

```
no = 5
for ij in range(no*no):
```

```
    i = ij // no
    j = ij % no
    for m in range(no):
        im = i*no + m
        mj = m*no + j
        print(im, mj)
```

such that the output for pair ij equal 0, resulting pair im and mj are

```
0 0
1 5
2 10
3 15
4 20
```

Another complication is the permutation of i and j for these intermediates, which affect the position at which these pair external correlation space is placed within the tensor as well as other components: amplitudes, integrals, etc. Therefore, it deems necessary to generate both.

3.3 Suggestion for efficiency

Once a rough code is implemented, some things to look out for in terms of efficiency are the balance between generation and storage of integrals. Some if not most of my contraction can be factorized further to reduce the scaling of term calculated.

Miscellaneous

Now, in the case where the single amplitudes are coupled to either the four-index terms (eg. fifth term) or one-particle intermediates (eg. second term), the resulting expression are:

$$R^{i}_{\bar{a}_{ii}} \leftarrow \sum_{n\bar{f}_{nn}} t^{n}_{\bar{f}_{nn}} L_{n\bar{a}_{ii}\bar{f}_{ii}i} S^{ii,nn}_{\bar{f}_{ii}\bar{f}_{nn}} \tag{114}$$

In Eq. (20), the virtual space of L term is transformed to the diagonal pair ii (ante),

$$L_{n\bar{a}_{ii}\bar{f}_{ii}i} = \sum_{af} d^{ii}_{a\bar{a}_{ii}} d^{ii}_{f\bar{f}_{ii}} L_{nafi} \tag{115}$$

then use the overlap term to project the virtual space f of pair ii to the corresponding pair of the single amplitudes which in this case pair nn. The reason behind the pre-transformed L term is thinking ahead of the implementation such that these transformed integrals are stored prior to the calculation of the residuals and only requires the projection and not the whole construction of these integrals in the PNO basis "on the fly". **Therefore, keep in mind that all integrals are transformed into pair ii or pair ij prior to the expressions within the singles and doubles residuals**.

An idea ... do I only need to store the diagonal pair ii meaning only i =j in a list and generate my own pair ii in range(amount of diagonal pairs) ... do it like the filteramps() so need two types of storage for integrals (for Fae, such that its for i in range(no) when coupled with single amplitudes while for the double amplitudes uses for ij in range(no*no)

for tau such as eq 27, looks like i have to do for a specific mn m, n, mm, nn Smn,mm and Smn,nn

for t im ae, can trasnform the slice im a*e matrix into a 4 rank tensor i,m,a,e -¿ is there a better way?

Appendix

1. Spin-adapted CCSD

With prior knowledge of CC and second quantization, we start by defining the components of the normal ordered Hamiltonian operator, F_n and W_n, using single-excitation unitary group generators:

$$F_n = f^p_q\{E^q_p\} \tag{116}$$

and

$$W_n = \frac{1}{2} g^{pq}_{rs}\{E^{rs}_{pq}\}. \tag{117}$$

Taking into account the similarity-transformed normal-Hamiltonian acting on a reference wave function,

$$e^{-\hat{T}}\hat{H}_n e^{\hat{T}} |0\rangle , \tag{118}$$

we can left project with the reference wave function $\langle 0|$, singles manifold $\langle \phi^a_i|$, and doubles manifold $\left\langle \phi^{ab}_{ij} \right|$ to obtain the coupled cluster energy, singles and doubles amplitudes, respectively. The similarity-transformed normal-ordered Hamiltonian can be expressed in terms of commutators:

$$\begin{aligned} e^{-T}\hat{H}_n e^{T} =& \hat{H}_n + \left[\hat{H}_n, \hat{T}\right] + \frac{1}{2!}\left[\left[\hat{H}_n, \hat{T}\right], \hat{T}\right] \\ &+ \frac{1}{3!}\left[\left[\left[\hat{H}_n, \hat{T}, \right]\hat{T}\right], \hat{T}\right] + \frac{1}{4!}\left[\left[\left[\left[\hat{H}_n, \hat{T}\right], \hat{T}\right], \hat{T}\right], \hat{T}\right] + ... \end{aligned} \tag{119}$$

For clarity, here are the non-zero commutators of the Hamiltonian with the single-excitation unitary group generators acting on a reference determinant:

$$
\begin{aligned}
\left[\hat{H}_n, \{E_{ai}\}\right]|0\rangle =&\Bigg(2f_{ia} + \sum_{b} f_{ba}\{E_{bi}\} - \sum_{j} f_{ij}\{E_{aj}\} + \sum_{bj} L_{bija}\{E_{bj}\} \\
&+ \sum_{cbj} \langle cb|ja\rangle \{E_{cj}E_{bi}\} - \sum_{bkj} \langle bi|kj\rangle \{E_{bk}E_{aj}\}\Bigg)|0\rangle
\end{aligned} \tag{120}
$$

$$
\begin{aligned}
\left[\left[\hat{H}_n, \{E_{ai}\}\right], \{E_{bj}\}\right]|0\rangle =&P_{ab}^{ij}\Bigg[L_{ijab} - f_{ja}\{E_{bi}\} - \sum_{k} L_{ijak}\{E_{bk}\} + \sum_{c} L_{cjab}\{E_{ci}\} \\
&- \sum_{ck}(\langle jc|ka\rangle \{E_{bk}E_{ci}\} + \langle cj|ka\rangle \{E_{ck}E_{bi}\}) \\
&+ \frac{1}{2}\sum_{cd} \langle cd|ab\rangle \{E_{ci}E_{dj}\} + \frac{1}{2}\sum_{kl} \langle ij|kl\rangle \{E_{ak}E_{bl}\}\Bigg]|0\rangle
\end{aligned} \tag{121}
$$

$$
\left[\left[\left[\hat{H}_n, \{E_{ai}\}\right], \{E_{bj}\}\right], \{E_{ck}\}\right]|0\rangle =P_{abc}^{ijk}\Bigg[- L_{ijac}\{E_{bk}\} - \sum_{d} \langle kd|ab\rangle \{E_{dj}E_{ci}\} + \sum_{l} \langle kj|al\rangle \{E_{bl}E_{ci}\}\Bigg]|0\rangle\,, \tag{122}
$$

and

$$
\left[\left[\left[\left[\hat{H}_n, \{E_{ai}\}\right], \{E_{bj}\}\right], \{E_{ck}\}\right], \{E_{dl}\}\right]|0\rangle =\frac{1}{2}P_{abcd}^{ijkl}[\langle kl|ab\rangle \{E_{dj}E_{ci}\}]|0\rangle\,. \tag{123}
$$

To solve the projected coupled-cluster equations for the CCSD wave function, the second-quantized operators acting on the ket state are

$$
E_{ai}|\Phi_0\rangle = |\phi_i^a\rangle \tag{124}
$$

$$
E_{ai}E_{bj}|\Phi_0\rangle = \left|\phi_{ij}^{ab}\right\rangle \tag{125}
$$

such that a projection of a singles or doubles bra state onto these ket states result to

$$\langle \phi_i^a | \phi_k^c \rangle = 2\delta_{ai,ck} \tag{126}$$

$$\begin{aligned} \left\langle \phi_{ij}^{ab} \middle| \phi_{kl}^{cd} \right\rangle &= 4\delta_{ac}\delta_{bd}\delta_{jl}\delta_{ik} + 4\delta_{bc}\delta_{ad}\delta_{jk}\delta_{il} - 2\delta_{ac}\delta_{bd}\delta_{il}\delta_{jk} - 2\delta_{bc}\delta_{ad}\delta_{jl}\delta_{ik} \\ &= 2P_{ij}^{ab}(2\delta_{aibj,ckdl} - \delta_{ajbi,ckdl}) = 2P_{kl}^{cd}(2\delta_{aibj,ckdl} - \delta_{ajbi,ckdl}). \end{aligned} \tag{127}$$

However, with the use of the biorthogonal basis, it is convenient to construct the projections of the bra states onto the ket states as

$$\langle \phi_i^{\bar{a}} | \phi_k^c \rangle = \delta_{ai,ck} \tag{128}$$

and

$$\left\langle \phi_{ij}^{\bar{a}\bar{b}} \middle| \phi_{kl}^{cd} \right\rangle = P_{ij}^{ab}\delta_{aibj,ckdl} = P_{kl}^{cd}\delta_{aibj,ckdl}. \tag{129}$$

The bar over a, b indicate that the projection space can be nonorthogonal. For the sake of future derivations, the notation of the projection will not have the bar over it just for cleanliness.

The permutation terms, P_{ij}^{ab} and P_{ijk}^{abc}, are carried out in the following manner:

$$P_{ij}^{ab}A_{ab}^{ij} = A_{ab}^{ij} + A_{ba}^{ji}, \tag{130}$$

$$P_{ijk}^{abc}A_{abc}^{ijk} = A_{abc}^{ijk} + A_{acb}^{ikj} + A_{bac}^{jik} + A_{bca}^{jki} + A_{cab}^{kij} + A_{cba}^{kji} \tag{131}$$

and so forth.

1.1 Energy

$$E = \langle 0| \hat{H}_n |0\rangle = \langle 0| \left[\hat{H}_n, \hat{T}_1\right] + \frac{1}{2}\left[\hat{H}_n, \hat{T}_1, \hat{T}_1\right] + \left[\hat{H}_n, \hat{T}_2\right] |0\rangle \tag{132}$$

where Term 1.1

$$\langle 0| \left[\hat{H}_n, \hat{T}_1\right] |0\rangle = 2f_a^i t_a^i, \tag{133}$$

Term 1.2

$$\frac{1}{2}\left[\hat{H}_n, \hat{T}_1, \hat{T}_1\right] = \frac{1}{2} P_{ab}^{ij} t_a^i t_b^j L_{ijab} = t_a^i t_b^j L_{ijab}, \tag{134}$$

and Term 1.3

$$\langle 0| \left[\hat{H}_n, \hat{T}_2\right] |0\rangle = \frac{1}{2} P_{ab}^{ij} t_{ab}^{ij} L_{ijab} = t_{ab}^{ij} L_{ijab}. \tag{135}$$

The evaluation of the energy expression results to

$$E = 2f_a^i + t_a^i t_b^j L_{ijab} + t_{ab}^{ij} L_{ijab} = 2f_a^i + \tau_{ab}^{ij} L_{ijab} \tag{136}$$

1.2 Singles residual

$$\begin{aligned}
R_a^i =& f_a^i + \sum_e t_e^i f_{ae} - \frac{1}{2} \sum_{me} t_e^i f_e^m t_a^m + \sum_{emf} t_e^i t_f^m L_{mafe} \\
& - \sum_{emnf} t_e^i t_{af}^{mn} L_{ef}^{mn} + \sum_{emnf} \frac{1}{2} t_e^i t_a^m t_f^n L_{ef}^{mn} - \sum_m t_a^m f_{mi} \\
& + \frac{1}{2} \sum_{me} t_a^m t_e^i f_e^m + \sum_{mne} t_a^m t_e^n L_{mnie} + \sum_{mnef} t_a^m t_{ef}^{in} L_{ef}^{mn} + \sum_{mnef} \frac{1}{2} t_a^m t_e^i t_f^n L_{ef}^{mn} \\
& + \sum_{me} 2 t_{ae}^{im} f_{me} - \sum_{me} t_{ea}^{im} f_{me} + \sum_{menf} 2 t_{ae}^{im} t_f^n L_{ef}^{mn} - \sum_{menf} t_{ea}^{im} t_f^n L_{ef}^{mn} \\
& + \sum_{nf} t_f^n L_{nafi} + \sum_{mef} 2 t_{ef}^{mi} K_{maef} - t_{fe}^{mi} K_{maef} - \sum_{mne} t_{ae}^{mn} L_{nmei}
\end{aligned} \tag{137}$$

$$\begin{aligned}
0 = & \langle \phi_i^a | \hat{H} |\Phi_0\rangle + \langle \phi_i^a | \left[\hat{H}, \hat{T}\right] |\Phi_0\rangle + \frac{1}{2!} \langle \phi_i^a | \left[\left[\hat{H}, \hat{T}\right], \hat{T}\right] |\Phi_0\rangle \\
& + \frac{1}{3!} \langle \phi_i^a | \left[\left[\left[\hat{H}, \hat{T}\right], \hat{T}\right], \hat{T}\right] |\Phi_0\rangle
\end{aligned} \tag{138}$$

- Term 1

$$
\begin{aligned}
\langle \phi_i^a | \hat{H} | \Phi_0 \rangle &= \sum_{pq} f_{pq} \langle \Phi_0 | E_a^i E_p^q | \Phi_0 \rangle + \frac{1}{2} \sum_{pqrs} g_{rs}^{pq} \langle \Phi_0 | E_a^i E_{rs}^{pq} | \Phi_0 \rangle \\
&= \sum_{pq} f_q^p \delta_p^i \delta_q^a \\
&= f_a^i
\end{aligned} \tag{139}
$$

$$
\begin{aligned}
R_a^i =& f_a^i + \sum_e t_e^i f_{ae} - \frac{1}{2} \sum_{me} t_e^i f_e^m t_a^m + \sum_{emf} t_e^i t_f^m L_{mafe} \\
& - \sum_{emnf} t_e^i t_{af}^{mn} L_{ef}^{mn} + \sum_{emnf} \frac{1}{2} t_e^i t_a^m t_f^n L_{ef}^{mn} - \sum_m t_a^m f_{mi} \\
& + \frac{1}{2} \sum_{me} t_a^m t_e^i f_e^m + \sum_{mne} t_a^m t_e^n L_{mnie} + \sum_{mnef} t_a^m t_{ef}^{in} L_{ef}^{mn} + \sum_{mnef} \frac{1}{2} t_a^m t_e^i t_f^n L_{ef}^{mn} \\
& + \sum_{me} 2 t_{ae}^{im} f_{me} - \sum_{me} t_{ea}^{im} f_{me} + \sum_{menf} 2 t_{ae}^{im} t_f^n L_{ef}^{mn} - \sum_{menf} t_{ea}^{im} t_f^n L_{ef}^{mn} \\
& + \sum_{nf} t_f^n L_{nafi} + \sum_{mef} 2 t_{ef}^{mi} K_{maef} - t_{fe}^{mi} K_{maef} - \sum_{mne} t_{ae}^{mn} L_{nmei}
\end{aligned} \tag{140}
$$

- Term 2

$$
\langle \phi_i^a | \left[\hat{H}, \hat{T} \right] | \Phi_0 \rangle = \langle 0 | E_a^i \left[\hat{H}_n, \hat{T}_1 \right] + E_a^i \left[\hat{H}_n, \hat{T}_2 \right] | 0 \rangle \tag{141}
$$

where

$$
\begin{aligned}
\langle 0 | E_a^i \left[\hat{H}_n, \hat{T}_1 \right] | 0 \rangle &= \langle 0 | E_a^i \sum_{ck} t_c^k \big(\sum_b f_{bc} E_k^b - \sum_j f_{kj} E_j^c + \sum_{bj} L_{bkjc} E_j^b \big) | 0 \rangle \\
&= \sum_{ck} t_c^k \big(\sum_b f_{bc} \langle \phi_i^a | \phi_k^b \rangle - \sum_j f_{kj} \langle \phi_i^a | \phi_j^c \rangle + \sum_{bj} L_{bkjc} \langle \phi_i^a | \phi_j^b \rangle \big) \\
&= \sum_{ck} t_c^k \left(\sum_b f_{bc} (\delta_{ai,bk}) - \sum_j f_{kj} (\delta_{ai,cj}) + \sum_{bj} L_{bkjc} (\delta_{ai,bj}) \right) \\
&= \sum_c f_{ac} t_c^i - \sum_k f_{ki} t_a^k + \sum_{ck} L_{akic} t_c^k = 0
\end{aligned} \tag{142}
$$

$$
\begin{aligned}
R_a^i =& f_a^i + \sum_e t_e^i f_{ae} - \frac{1}{2}\sum_{me} t_e^i f_e^m t_a^m + \sum_{emf} t_e^i t_f^m L_{mafe} \\
& - \sum_{emnf} t_e^i t_{af}^{mn} L_{ef}^{mn} + \sum_{emnf} \frac{1}{2} t_e^i t_a^m t_f^n L_{ef}^{mn} - \sum_m t_a^m f_{mi} \\
& + \frac{1}{2}\sum_{me} t_a^m t_e^i f_e^m + \sum_{mne} t_a^m t_e^n L_{mnie} + \sum_{mnef} t_a^m t_{ef}^{in} L_{ef}^{mn} + \sum_{mnef} \frac{1}{2} t_a^m t_e^i t_f^n L_{ef}^{mn} \\
& + \sum_{me} 2t_{ae}^{im} f_{me} - \sum_{me} t_{ea}^{im} f_{me} + \sum_{menf} 2t_{ae}^{im} t_f^n L_{ef}^{mn} - \sum_{menf} t_{ea}^{im} t_f^n L_{ef}^{mn} \\
& + \sum_{nf} t_f^n L_{nafi} + \sum_{mef} 2t_{ef}^{mi} K_{maef} - t_{fe}^{mi} K_{maef} - \sum_{mne} t_{ae}^{mn} L_{nmei}
\end{aligned}
\tag{143}
$$

and

$$
\begin{aligned}
\langle 0| E_a^i \big[\hat{H}_n, \hat{T}_2\big] |0\rangle =& \frac{1}{2}\sum_{cdkl} t_{cd}^{kl} \Big(\langle 0| E_a^i \big[\big[\hat{H}_n, E_{ck}\big], E_{dl}\big] |0\rangle \\
& + \langle 0| E_a^i E_l^d \big[\hat{H}_n, E_{ck}\big] |0\rangle + \langle 0| E_a^i E_k^c \big[\hat{H}_n, E_{dl}\big] |0\rangle \Big)
\end{aligned}
\tag{144}
$$

such that the first term is

$$
\begin{aligned}
\frac{1}{2}\sum_{cdkl} t_{cd}^{kl} \langle 0| E_a^i \big[\big[\hat{H}_n, E_{ck}\big], E_{dl}\big] |0\rangle &= \frac{1}{2}\sum_{cdkl} t_{cd}^{kl} \langle 0| E_a^i \Big(- f_{lc} E_{dk} - \sum_m L_{klcm} E_{dm} + \sum_e L_{elcd} E_{ek} \Big) |0\rangle \\
&= \frac{1}{2}\sum_{cdkl} t_{cd}^{kl} \Big(- f_{lc} \langle 0| E_a^i E_{dk} |0\rangle - \sum_m L_{klcm} \langle 0| E_a^i E_{dm} |0\rangle \\
&+ \sum_e L_{elcd} \langle 0| E_a^i E_{ek} |0\rangle \Big) \\
&= \frac{1}{2}\sum_{cdkl} t_{cd}^{kl} \Big(- f_{lc} \big\langle \phi_i^a \big| \phi_k^d \big\rangle - \sum_m L_{klcm} \big\langle \phi_i^a \big| \phi_m^d \big\rangle + \sum_e L_{elcd} \big\langle \phi_i^a \big| \phi_k^e \big\rangle \Big) \\
&= \frac{1}{2}\sum_{cdkl} t_{cd}^{kl} \Big(- f_{lc} (2\delta_{ai,dk}) - \sum_m L_{klcm} (2\delta_{ai,dm}) + \sum_e L_{elcd} (2\delta_{ai,ek}) \Big) \\
&= - \sum_{cl} t_{ca}^{il} f_{lc} - \sum_{ckl} t_{ca}^{kl} L_{klci} + \sum_{cdl} t_{cd}^{il} L_{alcd} = 0
\end{aligned}
\tag{145}
$$

$$
\begin{aligned}
R_a^i =& f_a^i + \sum_e t_e^i f_{ae} - \frac{1}{2}\sum_{me} t_e^i f_e^m t_a^m + \sum_{emf} t_e^i t_f^m L_{mafe} \\
& - \sum_{emnf} t_e^i t_{af}^{mn} L_{ef}^{mn} + \sum_{emnf} \frac{1}{2} t_e^i t_a^m t_f^n L_{ef}^{mn} - \sum_m t_a^m f_{mi} \\
& + \frac{1}{2}\sum_{me} t_a^m t_e^i f_e^m + \sum_{mne} t_a^m t_e^n L_{mnie} + \sum_{mnef} t_a^m t_{ef}^{in} L_{ef}^{mn} + \sum_{mnef} \frac{1}{2} t_a^m t_e^i t_f^n L_{ef}^{mn} \\
& + \sum_{me} 2t_{ae}^{im} f_{me} - \sum_{me} t_{ea}^{im} f_{me} + \sum_{menf} 2t_{ae}^{im} t_f^n L_{ef}^{mn} - \sum_{menf} t_{ea}^{im} t_f^n L_{ef}^{mn} \\
& + \sum_{nf} t_f^n L_{nafi} + \sum_{mef} 2t_{ef}^{mi} K_{maef} - t_{fe}^{mi} K_{maef} - \sum_{mne} t_{ae}^{mn} L_{nmei}
\end{aligned} \tag{146}
$$

with an additional set of expressions resulting from the P_{cd}^{kl} (would this just cause the whole expression to just have a factor of 2?). The other two terms are

$$
\begin{aligned}
\frac{1}{2}\sum_{cdkl} t_{cd}^{kl} \langle 0| E_a^i E_l^d \left[\hat{H}_n, E_{ck}\right] |0\rangle &= \langle 0| E_a^i \frac{1}{2}\sum_{cdkl} t_{cd}^{kl} 2 f_{kc} |0\rangle \\
&= \frac{1}{2}\sum_{cdkl} t_{cd}^{kl} 2 f_{kc} \langle 0| E_a^i E_{dl} |0\rangle \\
&= \frac{1}{2}\sum_{cdkl} t_{cd}^{kl} 2 f_{kc} \left\langle \phi_i^a \middle| \phi_l^d \right\rangle \\
&= \frac{1}{2}\sum_{cdkl} t_{cd}^{kl} 2 f_{kc} (2\delta_{ai,dl}) \\
&= \sum_{ck} 2t_{ca}^{ki} f_{kc} = 0
\end{aligned} \tag{147}
$$

and

$$
\begin{aligned}
\langle 0| E_a^i E_k^c \left[\hat{H}_n, E_{dl}\right] |0\rangle &= \langle 0| E_a^i \sum_{cdkl} t_{cd}^{kl} 2 f_{ld} |0\rangle \\
&= \sum_{cdkl} t_{cd}^{kl} 2 f_{ld} \langle 0| E_a^i E_{ck} |0\rangle \\
&= \sum_{cdkl} t_{cd}^{kl} 2 f_{ld} \langle \phi_i^a | \phi_k^c \rangle \\
&= \sum_{cdkl} t_{cd}^{kl} 2 f_{ld} (2\delta_{ai,ck}) \\
&= \sum_{dl} 2 t_{ad}^{il} f_{ld} = 0
\end{aligned} \tag{148}
$$

$$
\begin{aligned}
R_a^i =& f_a^i + \sum_e t_e^i f_{ae} - \frac{1}{2} \sum_{me} t_e^i f_e^m t_a^m + \sum_{emf} t_e^i t_f^m L_{mafe} \\
& - \sum_{emnf} t_e^i t_{af}^{mn} L_{ef}^{mn} + \sum_{emnf} \frac{1}{2} t_e^i t_a^m t_f^n L_{ef}^{mn} - \sum_m t_a^m f_{mi} \\
& + \frac{1}{2} \sum_{me} t_a^m t_e^i f_e^m + \sum_{mne} t_a^m t_e^n L_{mnie} + \sum_{mnef} t_a^m t_{ef}^{in} L_{ef}^{mn} + \sum_{mnef} \frac{1}{2} t_a^m t_e^i t_f^n L_{ef}^{mn} \\
& + \sum_{me} 2 t_{ae}^{im} f_{me} - \sum_{me} t_{ea}^{im} f_{me} + \sum_{menf} 2 t_{ae}^{im} t_f^n L_{ef}^{mn} - \sum_{menf} t_{ea}^{im} t_f^n L_{ef}^{mn} \\
& + \sum_{nf} t_f^n L_{nafi} + \sum_{mef} 2 t_{ef}^{mi} K_{maef} - t_{fe}^{mi} K_{maef} - \sum_{mne} t_{ae}^{mn} L_{nmei}
\end{aligned} \tag{149}
$$

- Term 3

$$
\begin{aligned}
\frac{1}{2!} \langle \phi_i^a | \left[\left[\hat{H}, \hat{T}\right], \hat{T}\right] |\Phi_0\rangle =& \frac{1}{2} \langle \phi_i^a | \left[\left[\hat{H}, \hat{T}_1\right], \hat{T}_1\right] |\Phi_0\rangle + \frac{1}{2} \langle \phi_i^a | \left[\left[\hat{H}, \hat{T}_2\right], \hat{T}_1\right] |\Phi_0\rangle \\
& + \frac{1}{2} \langle \phi_i^a | \left[\left[\hat{H}, \hat{T}_1\right], \hat{T}_2\right] |\Phi_0\rangle + \frac{1}{2} \langle \phi_i^a | \left[\left[\hat{H}, \hat{T}_2\right], \hat{T}_2\right] |\Phi_0\rangle
\end{aligned} \tag{150}
$$

where term 3.1 is

$$
\begin{aligned}
\frac{1}{2}\langle\phi_i^a|\Big[\Big[\hat{H},\hat{T}_1\Big],\hat{T}_1\Big]|\Phi_0\rangle &= \frac{1}{2}\sum_{cdkl} t_c^k t_d^l \langle 0| E_a^i \big[\big[\hat{H}_n, E_{ck}\big], E_{dl}\big]|0\rangle \\
&= \frac{1}{2}\sum_{cdkl} t_c^k t_d^l \langle 0| E_a^i \Big(-f_{lc}E_{dk} - \sum_m L_{klcm}E_{dm} + \sum_e L_{elcd}E_{ek}\Big)|0\rangle \\
&= \frac{1}{2}\sum_{cdkl} t_c^k t_d^l \Big(-f_{lc}\langle 0| E_a^i E_{dk}|0\rangle - \sum_m L_{klcm}\langle 0| E_a^i E_{dm}|0\rangle \\
&+ \sum_e L_{elcd}\langle 0| E_a^i E_{ek}|0\rangle\Big) \\
&= \frac{1}{2}\sum_{cdkl} t_c^k t_d^l \Big(-f_{lc}\langle\phi_i^a|\phi_k^d\rangle - \sum_m L_{klcm}\langle\phi_i^a|\phi_m^d\rangle + \sum_e L_{elcd}\langle\phi_i^a|\phi_k^e\rangle\Big) \\
&= \frac{1}{2}\sum_{cdkl} t_c^k t_d^l \Big(-f_{lc}(2\delta_{ai,dk}) - \sum_m L_{klcm}(2\delta_{ai,dm}) + \sum_e L_{elcd}(2\delta_{ai,ek})\Big) \\
&= -\sum_{cl} t_c^i t_a^l f_{lc} - \sum_{ckl} t_c^k t_a^l L_{klci} + \sum_{cdl} t_c^i t_d^l L_{alcd} = 0
\end{aligned}
\tag{151}
$$

with an additional set of expressions from P_{kl}^{cd} or just a factor of 2.

$$
\begin{aligned}
R_a^i =& f_a^i + \sum_e t_e^i f_{ae} - \frac{1}{2}\sum_{me} t_e^i f_e^m t_a^m + \sum_{emf} t_e^i t_f^m L_{mafe} \\
& - \sum_{emnf} t_e^i t_{af}^{mn} L_{ef}^{mn} + \sum_{emnf} \frac{1}{2} t_e^i t_a^m t_f^n L_{ef}^{mn} - \sum_m t_a^m f_{mi} \\
& -\frac{1}{2}\sum_{me} t_a^m t_e^i f_e^m - \sum_{mne} t_a^m t_e^n L_{mnie} - \sum_{mnef} t_a^m t_{ef}^{in} L_{ef}^{mn} - \sum_{mnef} \frac{1}{2} t_a^m t_e^i t_f^n L_{ef}^{mn} \\
& + \sum_{me} 2t_{ae}^{im} f_{me} - \sum_{me} t_{ea}^{im} f_{me} + \sum_{menf} 2t_{ae}^{im} t_f^n L_{ef}^{mn} - \sum_{menf} t_{ea}^{im} t_f^n L_{ef}^{mn} \\
& + \sum_{nf} t_f^n L_{nafi} + \sum_{mef} 2t_{ef}^{mi} K_{maef} - t_{fe}^{mi} K_{maef} - \sum_{mne} t_{ae}^{mn} L_{nmei}
\end{aligned}
\tag{152}
$$

Term 3.2 is

$$\frac{1}{2}\langle\phi_i^a|\Big[\Big[\hat{H},\hat{T}_1\Big],\hat{T}_2\Big]|\Phi_0\rangle = \frac{1}{2}\sum_{cdeklm} t_c^k t_{de}^{lm}\Big(\langle 0|E_a^i\big[\big[\big[\hat{H}_n,\{E_{ck}\}\big],\{E_{dl}\}\big],\{E_{em}\}\big]|0\rangle$$
$$+\langle 0|E_a^i E_{em}\big[\big[\hat{H}_n,\{E_{ck}\}\big],\{E_{dl}\}\big]|0\rangle + \langle 0|E_a^i E_{dl}\big[\big[\hat{H}_n,\{E_{ck}\}\big],\{E_{em}\}\big]|0\rangle\Big) \tag{153}$$

such that first term is

$$\begin{aligned}
&\frac{1}{2}\sum_{cdeklm} t_c^k t_{de}^{lm}\langle 0|E_a^i\big[\big[\big[\hat{H}_n,\{E_{ck}\}\big],\{E_{dl}\}\big],\{E_{em}\}\big]|0\rangle \\
&= -\frac{1}{2}\sum_{cdeklm} t_c^k t_{de}^{lm}\langle 0|E_a^i P_{cde}^{klm} L_{klce} E_m^d|0\rangle \\
&= -\frac{1}{2}\sum_{cdeklm} t_c^k t_{de}^{lm}\langle 0|E_a^i\Big(L_{klce}E_m^d|0\rangle + L_{kmcd}E_l^e|0\rangle \\
&\quad + L_{lkde}E_m^c|0\rangle + L_{lmdc}E_k^e|0\rangle + L_{mked}E_l^c|0\rangle + L_{mlec}E_k^d|0\rangle\Big) \\
&= -\frac{1}{2}\Big(\sum_{cdeklm} t_c^k t_{de}^{lm} L_{klce}\langle 0|E_a^i E_m^d|0\rangle + \sum_{cdeklm} t_c^k t_{de}^{lm} L_{kmcd}\langle 0|E_a^i E_l^e|0\rangle \\
&\quad + \sum_{cdeklm} t_c^k t_{de}^{lm} L_{lkde}\langle 0|E_a^i E_m^c|0\rangle + \sum_{cdeklm} t_c^k t_{de}^{lm} L_{lmdc}\langle 0|E_a^i E_k^e|0\rangle \\
&\quad + \sum_{cdeklm} t_c^k t_{de}^{lm} L_{mked}\langle 0|E_a^i E_l^c|0\rangle + \sum_{cdeklm} t_c^k t_{de}^{lm} L_{mlec}\langle 0|E_a^i E_k^d|0\rangle\Big) \qquad (154) \\
&= -\frac{1}{2}\Big(\sum_{cdeklm} t_c^k t_{de}^{lm} L_{klce}\delta_{ai,dm} + \sum_{cdeklm} t_c^k t_{de}^{lm} L_{kmcd}\delta_{ai,el} \\
&\quad + \sum_{cdeklm} t_c^k t_{de}^{lm} L_{lkde}\delta_{ai,cm} + \sum_{cdeklm} t_c^k t_{de}^{lm} L_{lmdc}\delta_{ai,ek} \\
&\quad + \sum_{cdeklm} t_c^k t_{de}^{lm} L_{mked}\delta_{ai,cl} + \sum_{cdeklm} t_c^k t_{de}^{lm} L_{mlec}\delta_{ai,dk}\Big) \\
&= -\frac{1}{2}\Big(\sum_{cekl} t_c^k t_{ae}^{li} L_{klce} + \sum_{cdkm} t_c^k t_{da}^{im} L_{kmcd} \\
&\quad + \sum_{dekl} t_a^k t_{de}^{li} L_{lkde} + \sum_{cdlm} t_c^i t_{da}^{lm} L_{lmdc} \\
&\quad + \sum_{dekm} t_a^k t_{de}^{im} L_{mked} + \sum_{celm} t_c^i t_{ae}^{lm} L_{mlec}\Big)
\end{aligned}$$

$$
\begin{aligned}
R_a^i =& f_a^i + \sum_e t_e^i f_{ae} - \frac{1}{2}\sum_{me} t_e^i f_e^m t_a^m + \sum_{emf} t_e^i t_f^m L_{mafe} \\
& - \sum_{emnf} t_e^i t_{af}^{mn} L_{ef}^{mn} + \sum_{emnf} \frac{1}{2} t_e^i t_a^m t_f^n L_{ef}^{mn} - \sum_m t_a^m f_{mi} \\
& - \frac{1}{2}\sum_{me} t_a^m t_e^i f_e^m - \sum_{mne} t_a^m t_e^n L_{mnie} - \sum_{mnef} t_a^m t_{ef}^{in} L_{ef}^{mn} - \sum_{mnef} \frac{1}{2} t_a^m t_e^i t_f^n L_{ef}^{mn} \\
& + \sum_{me} 2t_{ae}^{im} f_{me} - \sum_{me} t_{ea}^{im} f_{me} + \sum_{menf} 2t_{ae}^{im} t_f^n L_{ef}^{mn} - \sum_{menf} t_{ea}^{im} t_f^n L_{ef}^{mn} \\
& + \sum_{nf} t_f^n L_{nafi} + \sum_{mef} 2t_{ef}^{mi} K_{maef} - t_{fe}^{mi} K_{maef} - \sum_{mne} t_{ae}^{mn} L_{nmei}
\end{aligned} \tag{155}
$$

The second term is

$$
\begin{aligned}
\frac{1}{2}\langle 0| E_a^i E_{em}\big[\big[\hat{H}_n, \{E_{ck}\}\big], \{E_{dl}\}\big]|0\rangle &= \frac{1}{4}\sum_{cdeklm} t_c^k t_{de}^{lm} \langle 0| E_a^i E_{em} P_{cd}^{kl} L_{klcd}|0\rangle \\
&= \frac{1}{4}\sum_{cdeklm} t_c^k t_{de}^{lm} P_{cd}^{kl} L_{klcd} \langle \phi_i^a | \phi_m^e \rangle \\
&= \frac{1}{4}\sum_{cdeklm} t_c^k t_{de}^{lm} P_{cd}^{kl} L_{klcd} (2\delta_{ai,em}) \\
&= \frac{1}{2}\sum_{cdkl} t_c^k t_{da}^{li} P_{cd}^{kl} L_{klcd} \\
&= \sum_{cdkl} t_c^k t_{da}^{li} L_{klcd}
\end{aligned} \tag{156}
$$

while the third term is

$$
\begin{aligned}
\frac{1}{2}\langle 0|\, E^i_a E_{dl}\big[\big[\hat{H}_n,\{E_{ck}\}\big],\{E_{em}\}\big]\,|0\rangle &= \frac{1}{4}\sum_{cdeklm} t^k_c t^{lm}_{de}\,\langle 0|\, E^i_a E_{dl} P^{km}_{ce} L_{klce}\,|0\rangle \\
&= \frac{1}{4}\sum_{cdeklm} t^k_c t^{lm}_{de} P^{km}_{ce} L_{klce}\left\langle \phi^a_i \middle| \phi^d_l \right\rangle \\
&= \frac{1}{4}\sum_{cdeklm} t^k_c t^{lm}_{de} P^{km}_{ce} L_{klce}(2\delta_{ai,dl}) \\
&= \frac{1}{2}\sum_{cdkl} t^k_c t^{im}_{ae} P^{km}_{ce} L_{klce} \\
&= \sum_{cdkl} t^k_c t^{li}_{da} L_{klcd}
\end{aligned}
\tag{157}
$$

$$
\begin{aligned}
R^i_a =& f^i_a + \sum_e t^i_e f_{ae} - \frac{1}{2}\sum_{me} t^i_e f^m_e t^m_a + \sum_{emf} t^i_e t^m_f L_{mafe} \\
& - \sum_{emnf} t^i_e t^{mn}_{af} L^{mn}_{ef} + \sum_{emnf} \frac{1}{2} t^i_e t^m_a t^n_f L^{mn}_{ef} - \sum_m t^m_a f_{mi} \\
& - \frac{1}{2}\sum_{me} t^m_a t^i_e f^m_e - \sum_{mne} t^m_a t^n_e L_{mnie} - \sum_{mnef} t^m_a t^{in}_{ef} L^{mn}_{ef} - \sum_{mnef} \frac{1}{2} t^m_a t^i_e t^n_f L^{mn}_{ef} \\
& + \sum_{me} 2t^{im}_{ae} f_{me} - \sum_{me} t^{im}_{ea} f_{me} + \sum_{menf} 2t^{im}_{ae} t^n_f L^{mn}_{ef} - \sum_{menf} t^{im}_{ea} t^n_f L^{mn}_{ef} \\
& + \sum_{nf} t^n_f L_{nafi} + \sum_{mef} 2t^{mi}_{ef} K_{maef} - t^{mi}_{fe} K_{maef} - \sum_{mne} t^{mn}_{ae} L_{nmei}
\end{aligned}
\tag{158}
$$

The prefactor is incorrect but is accounted for in term 3.3 which equates to the same expression as term 3.2 since the $\hat{T}$ commutes which resolves the factor of 2 in the singles residual.

- Term 4

$$
\frac{1}{3!}\langle \phi^a_i|\left[\left[\left[\hat{H},\hat{T}\right],\hat{T}\right],\hat{T}\right]|\Phi_0\rangle = \frac{1}{6}\langle \phi^a_i|\left[\left[\left[\hat{H},\hat{T}_1\right],\hat{T}_1\right],\hat{T}_1\right]|\Phi_0\rangle \tag{159}
$$

Term 4.1 is

$$\frac{1}{6}\langle\phi_i^a|\Big[\Big[\Big[\hat{H},\hat{T}_1\Big],\hat{T}_1\Big],\hat{T}_1\Big]|\Phi_0\rangle = \frac{1}{6}\sum_{cdeklm} t_c^k t_d^l t_e^m \langle 0| E_a^i \big[\big[\big[\hat{H}_n,\{E_{ck}\}\big],\{E_{dl}\}\big],\{E_{em}\}\big]|0\rangle \tag{160}$$

such that the term goes to

$$\begin{aligned}
\frac{1}{6}\sum_{cdeklm} t_c^k t_d^l t_e^m \langle 0| E_a^i \big[\big[\big[\hat{H}_n,\{E_{ck}\}\big],\{E_{dl}\}\big],\{E_{em}\}\big]|0\rangle \\
= -\frac{1}{6}\sum_{cdeklm} t_c^k t_d^l t_e^m \langle 0| E_a^i P_{cde}^{klm} L_{klce} E_m^d |0\rangle \\
= -\frac{1}{6}\sum_{cdeklm} t_c^k t_d^l t_e^m \Big(L_{klce} E_m^d |0\rangle + L_{kmcd} E_l^e |0\rangle \\
+ L_{lkde} E_m^c |0\rangle + L_{lmdc} E_k^e |0\rangle + L_{mked} E_l^c |0\rangle + L_{mlec} E_k^d |0\rangle \Big) \\
= -\frac{1}{6}\Big(\sum_{cdeklm} t_c^k t_d^l t_e^m L_{klce} \langle 0| E_a^i E_m^d |0\rangle + \sum_{cdeklm} t_c^k t_d^l t_e^m L_{kmcd} \langle 0| E_a^i E_l^e |0\rangle \\
+ \sum_{cdeklm} t_c^k t_d^l t_e^m L_{lkde} \langle 0| E_a^i E_m^c |0\rangle + \sum_{cdeklm} t_c^k t_d^l t_e^m L_{lmdc} \langle 0| E_a^i E_k^e |0\rangle \\
+ \sum_{cdeklm} t_c^k t_d^l t_e^m L_{mked} \langle 0| E_a^i E_l^c |0\rangle + \sum_{cdeklm} t_c^k t_d^l t_e^m L_{mlec} \langle 0| E_a^i E_k^d |0\rangle \Big) \\
= -\frac{1}{6}\Big(\sum_{cdeklm} t_c^k t_d^l t_e^m L_{klce}\delta_{ai,dm} + \sum_{cdeklm} t_c^k t_d^l t_e^m L_{kmcd}\delta_{ai,el} \\
+ \sum_{cdeklm} t_c^k t_d^l t_e^m L_{lkde}\delta_{ai,cm} + \sum_{cdeklm} t_c^k t_d^l t_e^m L_{lmdc}\delta_{ai,ek} \\
+ \sum_{cdeklm} t_c^k t_d^l t_e^m L_{mked}\delta_{ai,cl} + \sum_{cdeklm} t_c^k t_d^l t_e^m L_{mlec}\delta_{ai,dk} \Big) \\
= -\frac{1}{6}\Big(\sum_{cekl} t_c^k t_e^i t_e^i L_{klce} + \sum_{cdkm} t_c^k t_d^i t_a^m L_{kmcd} \\
+ \sum_{dekl} t_a^k t_d^l t_e^i L_{lkde} + \sum_{cdlm} t_c^i t_d^l t_a^m L_{lmdc} \\
+ \sum_{dekm} t_a^k t_d^i t_e^m L_{mked} + \sum_{celm} t_c^i t_a^l t_e^m L_{mlec} \Big)
\end{aligned} \tag{161}$$

$$
\begin{aligned}
R_a^i = & f_a^i + \sum_e t_e^i f_{ae} - \frac{1}{2}\sum_{me} t_e^i f_e^m t_a^m + \sum_{emf} t_e^i t_f^m L_{mafe} \\
& - \sum_{emnf} t_e^i t_{af}^{mn} L_{ef}^{mn} - \sum_{emnf} \frac{1}{2} t_e^i t_a^m t_f^n L_{ef}^{mn} - \sum_m t_a^m f_{mi} \\
& - \frac{1}{2}\sum_{me} t_a^m t_e^i f_e^m - \sum_{mne} t_a^m t_e^n L_{mnie} - \sum_{mnef} t_a^m t_{ef}^{in} L_{ef}^{mn} - \sum_{mnef} \frac{1}{2} t_a^m t_e^i t_f^n L_{ef}^{mn} \\
& + \sum_{me} 2 t_{ae}^{im} f_{me} - \sum_{me} t_{ea}^{im} f_{me} + \sum_{menf} 2 t_{ae}^{im} t_f^n L_{ef}^{mn} - \sum_{menf} t_{ea}^{im} t_f^n L_{ef}^{mn} \\
& + \sum_{nf} t_f^n L_{nafi} + \sum_{mef} 2 t_{ef}^{mi} K_{maef} - t_{fe}^{mi} K_{maef} - \sum_{mne} t_{ae}^{mn} L_{nmei}
\end{aligned}
\tag{162}
$$

1.3 Doubles residual

$$
\begin{aligned}
R^{ij}_{ab} =& \frac{1}{2} K^{ij}_{ab} + \sum_{e} t^{ij}_{ae} f_{be} - \frac{1}{2} \sum_{em} t^{ij}_{ae} f^{m}_{e} t^{m}_{b} \\
&+ \sum_{emf} t^{ij}_{ae} t^{m}_{f} L_{mbfe} - \sum_{emnf} t^{ij}_{ae} t^{mn}_{bf} - \frac{1}{2} \sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
&- \frac{1}{2} \sum_{em} t^{ij}_{ae} t^{m}_{b} f_{me} - \frac{1}{2} \sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
&- \sum_{m} t^{im}_{ab} f_{mj} - \frac{1}{2} \sum_{me} t^{im}_{ab} t^{j}_{e} f^{m}_{e} - \sum_{mne} t^{im}_{ab} t^{n}_{e} L_{mnje} - \sum_{mnef} t^{im}_{ab} t^{jn}_{ef} L_{mnje} \\
&- \frac{1}{2} \sum_{mnef} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} - \frac{1}{2} \sum_{me} t^{im}_{ab} t^{j}_{e} f_{me} - \frac{1}{2} \sum_{menf} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} \\
&+ \frac{1}{2} \sum_{mn} t^{mn}_{ab} K_{mnij} + \frac{1}{2} \sum_{mne} t^{mn}_{ab} t^{j}_{e} K_{mnie} + \frac{1}{2} \sum_{mne} t^{mn}_{ab} t^{i}_{e} K_{mnej} \\
&+ \frac{1}{2} \sum_{mnef} t^{mn}_{ab} t^{ij}_{ef} K^{mn}_{ef} + \frac{1}{2} \sum_{mnef} t^{mn}_{ab} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2} \sum_{mn} t^{m}_{a} t^{n}_{b} K_{mnij} \\
&+ \frac{1}{2} \sum_{mne} t^{m}_{a} t^{n}_{b} t^{j}_{e} K_{mnie} + \frac{1}{2} \sum_{mne} t^{m}_{a} t^{n}_{b} t^{i}_{e} K_{mnej} + \frac{1}{2} \sum_{mnef} t^{m}_{a} t^{n}_{b} t^{ij}_{ef} K^{mn}_{ef} \\
&+ \frac{1}{2} \sum_{mnef} t^{m}_{a} t^{n}_{b} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2} \sum_{ef} t^{ij}_{ef} K_{abef} + \frac{1}{2} \sum_{ef} t^{i}_{e} t^{j}_{f} K_{abef} \\
&- \sum_{mef} t^{m}_{a} K_{mbef} t^{ij}_{ef} - \sum_{mef} t^{m}_{a} K_{mbef} t^{i}_{e} t^{j}_{f} \\
&+ \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
&- \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2} \sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ea} K_{mbej} - \sum_{mef} t^{im}_{ea} t^{j}_{f} K_{mbef} \\
&+ \sum_{men} t^{im}_{ea} t^{n}_{b} K_{mnej} + \sum_{menf} \frac{1}{2} t^{im}_{ea} t^{jn}_{fb} K^{mn}_{ef} + \sum_{menf} t^{im}_{ea} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} - \frac{1}{2} \sum_{menf} t^{im}_{ea} t^{nj}_{fb} L^{mn}_{ef} \\
&+ \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
&- \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2} \sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ae} K_{mbje} - \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbfe} \\
&+ \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnje} + \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{fe} + \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{fe} \\
&- \sum_{me} t^{mj}_{ae} K_{mbie} - \sum_{mef} t^{mj}_{ae} t^{i}_{f} K_{mbfe} + \sum_{men} t^{mj}_{ae} t^{n}_{b} K_{mnie} + \sum_{menf} \frac{1}{2} t^{mj}_{ae} t^{in}_{fb} K^{mn}_{fe} + \sum_{menf} t^{mj}_{ae} t^{i}_{f} t^{n}_{b} K^{mn}_{fe} \\
&- \sum_{me} t^{i}_{e} t^{m}_{a} K_{mbej} + \sum_{me} t^{i}_{e} t^{m}_{b} K_{maje} + \sum_{e} t^{i}_{e} K_{abej} - \sum_{m} t^{m}_{a} K_{mbij}
\end{aligned}
\tag{163}
$$

$$
\begin{aligned}
0 =& \left\langle \phi_{ij}^{ab} \right| \hat{H} \left| \Phi_0 \right\rangle + \left\langle \phi_{ij}^{ab} \right| \left[\hat{H}, \hat{T} \right] \left| \Phi_0 \right\rangle + \frac{1}{2!} \left\langle \phi_{ij}^{ab} \right| \left[\left[\hat{H}, \hat{T} \right], \hat{T} \right] \left| \Phi_0 \right\rangle \\
&+ \frac{1}{3!} \left\langle \phi_{ij}^{ab} \right| \left[\left[\left[\hat{H}, \hat{T} \right], \hat{T} \right], \hat{T} \right] \left| \Phi_0 \right\rangle + \frac{1}{4!} \left\langle \phi_{ij}^{ab} \right| \left[\left[\left[\left[\hat{H}, \hat{T} \right], \hat{T} \right], \hat{T} \right], \hat{T} \right] \left| \Phi_0 \right\rangle
\end{aligned} \tag{164}
$$

-Term 1

$$
\begin{aligned}
\left\langle \phi_{ij}^{ab} \right| \hat{H} \left| \Phi_0 \right\rangle &= \sum_{pq} f_{pq} \left\langle \Phi_0 \right| E_a^i E_b^j E_p^q \left| \Phi_0 \right\rangle + \frac{1}{2} \sum_{pqrs} g_{rs}^{pq} \left\langle \Phi_0 \right| E_a^i E_b^j E_{rs}^{pq} \left| \Phi_0 \right\rangle \\
&= \frac{1}{2} \sum_{pqrs} g_{rs}^{pq} \left\langle \Phi_0 \right| E_a^i E_b^j E_{rs}^{pq} \left| \Phi_0 \right\rangle \\
&= \frac{1}{2} \sum_{pqrs} g_{rs}^{pq} \left\langle \phi_{ab}^{ij} \middle| \phi_{rs}^{pq} \right\rangle \\
&= \frac{1}{2} \sum_{pqrs} g_{rs}^{pq} 2 P_{ij}^{ab} (2\delta_{aibj,rpsq} - \delta_{ajbi,rqsp}) \\
&= \sum_{ijab} P_{ij}^{ab} g_{ab}^{ij}
\end{aligned} \tag{165}
$$

$$
\begin{aligned}
R^{ij}_{ab} =& \frac{1}{2} K^{ij}_{ab} + \sum_{e} t^{ij}_{ae} f_{be} - \frac{1}{2} \sum_{em} t^{ij}_{ae} f^{m}_{e} t^{m}_{b} \\
& + \sum_{emf} t^{ij}_{ae} t^{m}_{f} L_{mbfe} - \sum_{emnf} t^{ij}_{ae} t^{mn}_{bf} - \frac{1}{2} \sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
& - \frac{1}{2} \sum_{em} t^{ij}_{ae} t^{m}_{b} f_{me} - \frac{1}{2} \sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
& - \sum_{m} t^{im}_{ab} f_{mj} - \frac{1}{2} \sum_{me} t^{im}_{ab} t^{j}_{e} f^{m}_{e} - \sum_{mne} t^{im}_{ab} t^{n}_{e} L_{mnje} - \sum_{mnef} t^{im}_{ab} t^{jn}_{ef} L_{mnje} \\
& - \frac{1}{2} \sum_{mnef} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} - \frac{1}{2} \sum_{me} t^{im}_{ab} t^{j}_{e} f_{me} - \frac{1}{2} \sum_{menf} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} \\
& + \frac{1}{2} \sum_{mn} t^{mn}_{ab} K_{mnij} + \frac{1}{2} \sum_{mne} t^{mn}_{ab} t^{j}_{e} K_{mnie} + \frac{1}{2} \sum_{mne} t^{mn}_{ab} t^{i}_{e} K_{mnej} \\
& + \frac{1}{2} \sum_{mnef} t^{mn}_{ab} t^{ij}_{ef} K^{mn}_{ef} + \frac{1}{2} \sum_{mnef} t^{mn}_{ab} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2} \sum_{mn} t^{m}_{a} t^{n}_{b} K_{mnij} \\
& + \frac{1}{2} \sum_{mne} t^{m}_{a} t^{n}_{b} t^{j}_{e} K_{mnie} + \frac{1}{2} \sum_{mne} t^{m}_{a} t^{n}_{b} t^{i}_{e} K_{mnej} + \frac{1}{2} \sum_{mnef} t^{m}_{a} t^{n}_{b} t^{ij}_{ef} K^{mn}_{ef} \\
& + \frac{1}{2} \sum_{mnef} t^{m}_{a} t^{n}_{b} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2} \sum_{ef} t^{ij}_{ef} K_{abef} + \frac{1}{2} \sum_{ef} t^{i}_{e} t^{j}_{f} K_{abef} \\
& - \sum_{mef} t^{m}_{a} K_{mbef} t^{ij}_{ef} - \sum_{mef} t^{m}_{a} K_{mbef} t^{i}_{e} t^{j}_{f} \\
& + \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
& - \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2} \sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ea} K_{mbej} - \sum_{mef} t^{im}_{ea} t^{j}_{f} K_{mbef} \\
& + \sum_{men} t^{im}_{ea} t^{n}_{b} K_{mnej} + \sum_{menf} \frac{1}{2} t^{im}_{ea} t^{jn}_{fb} K^{mn}_{ef} + \sum_{menf} t^{im}_{ea} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} - \frac{1}{2} \sum_{menf} t^{im}_{ea} t^{nj}_{fb} L^{mn}_{ef} \\
& + \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
& - \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2} \sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ae} K_{mbje} - \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbfe} \\
& + \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnje} + \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{fe} + \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{fe} \\
& - \sum_{me} t^{mj}_{ae} K_{mbie} - \sum_{mef} t^{mj}_{ae} t^{i}_{f} K_{mbfe} + \sum_{men} t^{mj}_{ae} t^{n}_{b} K_{mnie} + \sum_{menf} \frac{1}{2} t^{mj}_{ae} t^{in}_{fb} K^{mn}_{fe} + \sum_{menf} t^{mj}_{ae} t^{i}_{f} t^{n}_{b} K^{mn}_{fe} \\
& - \sum_{me} t^{i}_{e} t^{m}_{a} K_{mbej} + \sum_{me} t^{i}_{e} t^{m}_{b} K_{maje} + \sum_{e} t^{i}_{e} K_{abej} - \sum_{m} t^{m}_{a} K_{mbij}
\end{aligned}
\tag{166}
$$

- Term 2

$$\left\langle \phi_{ij}^{ab} \right| \left[\hat{H}, \hat{T} \right] \left| \Phi_0 \right\rangle = \langle 0 | E_a^i E_b^j \left[\hat{H}_n, \hat{T}_1 \right] + E_a^i E_b^j \left[\hat{H}_n, \hat{T}_2 \right] | 0 \rangle \tag{167}$$

where

$$\begin{aligned}
\langle 0 | E_a^i E_b^j \left[\hat{H}_n, \hat{T}_1 \right] | 0 \rangle &= \langle 0 | E_a^i E_b^j \sum_{ck} t_c^k \left(\sum_{fen} \langle fe | nc \rangle E_n^f E_k^e - \sum_{eon} f_{kj} \langle ek | on \rangle E_o^e E_n^c \right) | 0 \rangle \\
&= \sum_{ck} t_c^k \left(\sum_{fen} \langle fe | nc \rangle \langle 0 | E_a^i E_b^j E_n^f E_k^e | 0 \rangle - \sum_{eon} f_{kj} \langle ek | on \rangle \langle 0 | E_a^i E_b^j E_o^e E_n^c | 0 \rangle \right) \\
&= \sum_{ck} t_c^k \left(\sum_{fen} \langle fe | nc \rangle \left\langle \phi_{ab}^{ij} \middle| \phi_{nk}^{fe} \right\rangle - \sum_{eon} \langle ek | on \rangle \left\langle \phi_{ab}^{ij} \middle| \phi_{on}^{ec} \right\rangle \right) \\
&= \sum_{ck} t_c^k \left(\sum_{fen} \langle fe | nc \rangle P_{ij}^{ab} \delta_{aibj,fnek} - \sum_{eon} \langle ek | on \rangle P_{ij}^{ab} \delta_{aibj,eocn} \right) \\
&= \sum_{c} P_{ij}^{ab} t_c^j \langle ab | ic \rangle - \sum_{k} P_{ij}^{ab} t_b^k \langle ak | ij \rangle
\end{aligned} \tag{168}$$

$$
\begin{aligned}
R^{ij}_{ab} =& \frac{1}{2} K^{ij}_{ab} + \sum_{e} t^{ij}_{ae} f_{be} - \frac{1}{2} \sum_{em} t^{ij}_{ae} f^{m}_{e} t^{m}_{b} \\
&+ \sum_{emf} t^{ij}_{ae} t^{m}_{f} L_{mbfe} - \sum_{emnf} t^{ij}_{ae} t^{mn}_{bf} - \frac{1}{2} \sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
&- \frac{1}{2} \sum_{em} t^{ij}_{ae} t^{m}_{b} f_{me} - \frac{1}{2} \sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
&- \sum_{m} t^{im}_{ab} f_{mj} - \frac{1}{2} \sum_{me} t^{im}_{ab} t^{j}_{e} f^{m}_{e} - \sum_{mne} t^{im}_{ab} t^{n}_{e} L_{mnje} - \sum_{mnef} t^{im}_{ab} t^{jn}_{ef} L_{mnje} \\
&- \frac{1}{2} \sum_{mnef} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} - \frac{1}{2} \sum_{me} t^{im}_{ab} t^{j}_{e} f_{me} - \frac{1}{2} \sum_{menf} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} \\
&+ \frac{1}{2} \sum_{mn} t^{mn}_{ab} K_{mnij} + \frac{1}{2} \sum_{mne} t^{mn}_{ab} t^{j}_{e} K_{mnie} + \frac{1}{2} \sum_{mne} t^{mn}_{ab} t^{i}_{e} K_{mnej} \\
&+ \frac{1}{2} \sum_{mnef} t^{mn}_{ab} t^{ij}_{ef} K^{mn}_{ef} + \frac{1}{2} \sum_{mnef} t^{mn}_{ab} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2} \sum_{mn} t^{m}_{a} t^{n}_{b} K_{mnij} \\
&+ \frac{1}{2} \sum_{mne} t^{m}_{a} t^{n}_{b} t^{j}_{e} K_{mnie} + \frac{1}{2} \sum_{mne} t^{m}_{a} t^{n}_{b} t^{i}_{e} K_{mnej} + \frac{1}{2} \sum_{mnef} t^{m}_{a} t^{n}_{b} t^{ij}_{ef} K^{mn}_{ef} \\
&+ \frac{1}{2} \sum_{mnef} t^{m}_{a} t^{n}_{b} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2} \sum_{ef} t^{ij}_{ef} K_{abef} + \frac{1}{2} \sum_{ef} t^{i}_{e} t^{j}_{f} K_{abef} \\
&- \sum_{mef} t^{m}_{a} K_{mbef} t^{ij}_{ef} - \sum_{mef} t^{m}_{a} K_{mbef} t^{i}_{e} t^{j}_{f} \\
&+ \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
&- \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2} \sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ea} K_{mbej} - \sum_{mef} t^{im}_{ea} t^{j}_{f} K_{mbef} \\
&+ \sum_{men} t^{im}_{ea} t^{n}_{b} K_{mnej} + \sum_{menf} \frac{1}{2} t^{im}_{ea} t^{jn}_{fb} K^{mn}_{ef} + \sum_{menf} t^{im}_{ea} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} - \frac{1}{2} \sum_{menf} t^{im}_{ea} t^{nj}_{fb} L^{mn}_{ef} \\
&+ \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
&- \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2} \sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ae} K_{mbje} - \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbfe} \\
&+ \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnje} + \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{fe} + \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{fe} \\
&- \sum_{me} t^{mj}_{ae} K_{mbie} - \sum_{mef} t^{mj}_{ae} t^{i}_{f} K_{mbfe} + \sum_{men} t^{mj}_{ae} t^{n}_{b} K_{mnie} + \sum_{menf} \frac{1}{2} t^{mj}_{ae} t^{in}_{fb} K^{mn}_{fe} + \sum_{menf} t^{mj}_{ae} t^{i}_{f} t^{n}_{b} K^{mn}_{fe} \\
&- \sum_{me} t^{i}_{e} t^{m}_{a} K_{mbej} + \sum_{me} t^{i}_{e} t^{m}_{b} K_{maje} + \sum_{e} t^{i}_{e} K_{abej} - \sum_{m} t^{m}_{a} K_{mbij}
\end{aligned}
\tag{169}
$$

and

$$\langle 0| E^i_a E^j_b \big[\hat{H}_n, \hat{T}_2\big] |0\rangle = \frac{1}{2}\sum_{cdkl} t^{kl}_{cd}\Big(\langle 0| E^i_a E^j_b \big[\big[\hat{H}_n, E_{ck}\big], E_{dl}\big] |0\rangle + \langle 0| E^i_a E^j_b E^d_l \big[\hat{H}_n, E_{ck}\big] |0\rangle + \langle 0| E^i_a E^j_b E^c_k \big[\hat{H}_n, E_{dl}\big] |0\rangle \Big) \tag{170}$$

such that the first term is

$$\begin{aligned}
&\frac{1}{2}\sum_{cdkl} t^{kl}_{cd} \langle 0| E^i_a E^j_b \big[\big[\hat{H}_n, E_{ck}\big], E_{dl}\big] |0\rangle \\
&= \frac{1}{2}\sum_{cdkl} t^{kl}_{cd} \langle 0| E^i_a E^j_b P^{cd}_{kl}\Big(-\sum_{em}(\langle le|mc\rangle E_{dm}E_{ek} + \langle el|mc\rangle E_{em}E_{dk}) \\
&\quad + \frac{1}{2}\sum_{ef}\langle ef|cd\rangle E_{ek}E_{fl} + \frac{1}{2}\sum_{mn}\langle kl|mn\rangle E_{cm}E_{dn}\Big) |0\rangle \\
&= \frac{1}{2}\sum_{cdkl} t^{kl}_{cd} \langle 0| E^i_a E^j_b \Big(-\sum_{em}(\langle le|mc\rangle E_{dm}E_{ek} + \langle el|mc\rangle E_{em}E_{dk}) \\
&\quad + \frac{1}{2}\sum_{ef}\langle ef|cd\rangle E_{ek}E_{fl} + \frac{1}{2}\sum_{mn}\langle kl|mn\rangle E_{cm}E_{dn}\Big) |0\rangle \\
&\quad - \sum_{em}(\langle ke|md\rangle E_{cm}E_{el} + \langle ek|md\rangle E_{em}E_{cl}) \\
&\quad + \frac{1}{2}\sum_{ef}\langle ef|dc\rangle E_{el}E_{fk} + \frac{1}{2}\sum_{mn}\langle lk|mn\rangle E_{dm}E_{cn}\Big) |0\rangle \\
&= \frac{1}{2}\Big(-\sum_{em}\sum_{cdkl} t^{kl}_{cd}\langle le|mc\rangle \langle 0| E^i_a E^j_b E_{dm}E_{ek} |0\rangle - \sum_{em}\sum_{cdkl} t^{kl}_{cd}\langle el|mc\rangle \langle 0| E^i_a E^j_b E_{em}E_{dk} |0\rangle \\
&\quad + \frac{1}{2}\sum_{ef}\sum_{cdkl} t^{kl}_{cd}\langle ef|cd\rangle \langle 0| E^i_a E^j_b E_{ek}E_{fl} |0\rangle + \frac{1}{2}\sum_{mn}\sum_{cdkl} t^{kl}_{cd}\langle kl|mn\rangle \langle 0| E^i_a E^j_b E_{cm}E_{dn} |0\rangle \\
&\quad - \sum_{em}\sum_{cdkl} t^{kl}_{cd}\langle ke|md\rangle \langle 0| E^i_a E^j_b E_{cm}E_{el} |0\rangle - \sum_{em}\sum_{cdkl} t^{kl}_{cd}\langle ek|md\rangle \langle 0| E^i_a E^j_b E_{em}E_{cl} |0\rangle \\
&\quad + \frac{1}{2}\sum_{ef}\sum_{cdkl} t^{kl}_{cd}\langle ef|dc\rangle \langle 0| E^i_a E^j_b E_{el}E_{fk} |0\rangle + \frac{1}{2}\sum_{mn}\sum_{cdkl} t^{kl}_{cd}\langle lk|mn\rangle \langle 0| E^i_a E^j_b E_{dm}E_{cn} |0\rangle \Big)
\end{aligned} \tag{171}$$

$$
\begin{aligned}
&= \frac{1}{2}P^{ij}_{ab}\bigg(-\sum_{em}\sum_{cdkl} t^{kl}_{cd} \langle le|mc\rangle \, \delta_{abij,demk} - \sum_{em}\sum_{cdkl} t^{kl}_{cd} \langle el|mc\rangle \, \delta_{abij,edmk} \\
&\quad + \frac{1}{2}\sum_{ef}\sum_{cdkl} t^{kl}_{cd} \langle ef|cd\rangle \, \delta_{abij,efkl} + \frac{1}{2}\sum_{mn}\sum_{cdkl} t^{kl}_{cd} \langle kl|mn\rangle \, \delta_{abij,cdmn} \\
&\quad - \sum_{em}\sum_{cdkl} t^{kl}_{cd} \langle ke|md\rangle \, \delta_{abij,ceml} - \sum_{em}\sum_{cdkl} t^{kl}_{cd} \langle ek|md\rangle \, \delta_{abij,ecml} \\
&\quad + \frac{1}{2}\sum_{ef}\sum_{cdkl} t^{kl}_{cd} \langle ef|dc\rangle \, \delta_{abij,eflk} + \frac{1}{2}\sum_{mn}\sum_{cdkl} t^{kl}_{cd} \langle lk|mn\rangle \, \delta_{abij,dcmn} \bigg) \\
&= \frac{1}{2}P^{ij}_{ab}\bigg(-\sum_{cl} t^{jl}_{ca} \langle lb|ic\rangle - \sum_{cl} t^{jl}_{cb} \langle al|ic\rangle \\
&\quad + \frac{1}{2}\sum_{cd} t^{ij}_{cd} \langle ab|cd\rangle + \frac{1}{2}\sum_{kl} t^{kl}_{ab} \langle kl|ij\rangle \\
&\quad - \sum_{dk} t^{kj}_{ad} \langle kb|id\rangle - \sum_{dk} t^{kj}_{bd} \langle ak|id\rangle \\
&\quad + \frac{1}{2}\sum_{cd} t^{ji}_{cd} \langle ab|dc\rangle + \frac{1}{2}\sum_{cdkl} t^{kl}_{ba} \langle lk|ij\rangle \bigg)
\end{aligned}
$$

$$
\begin{aligned}
R^{ij}_{ab} =& \frac{1}{2}K^{ij}_{ab} + \sum_{e} t^{ij}_{ae} f_{be} - \frac{1}{2}\sum_{em} t^{ij}_{ae} f^{m}_{e} t^{m}_{b} \\
& + \sum_{emf} t^{ij}_{ae} t^{m}_{f} L_{mbfe} - \sum_{emnf} t^{ij}_{ae} t^{mn}_{bf} - \frac{1}{2}\sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
& - \frac{1}{2}\sum_{em} t^{ij}_{ae} t^{m}_{b} f_{me} - \frac{1}{2}\sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
& - \sum_{m} t^{im}_{ab} f_{mj} - \frac{1}{2}\sum_{me} t^{im}_{ab} t^{j}_{e} f^{m}_{e} - \sum_{mne} t^{im}_{ab} t^{n}_{e} L_{mnje} - \sum_{mnef} t^{im}_{ab} t^{jn}_{ef} L_{mnje} \\
& - \frac{1}{2}\sum_{mnef} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} - \frac{1}{2}\sum_{me} t^{im}_{ab} t^{j}_{e} f_{me} - \frac{1}{2}\sum_{menf} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} \\
& + \frac{1}{2}\sum_{mn} t^{mn}_{ab} K_{mnij} + \frac{1}{2}\sum_{mne} t^{mn}_{ab} t^{j}_{e} K_{mnie} + \frac{1}{2}\sum_{mne} t^{mn}_{ab} t^{i}_{e} K_{mnej} \\
& + \frac{1}{2}\sum_{mnef} t^{mn}_{ab} t^{ij}_{ef} K^{mn}_{ef} + \frac{1}{2}\sum_{mnef} t^{mn}_{ab} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2}\sum_{mn} t^{m}_{a} t^{n}_{b} K_{mnij} \\
& + \frac{1}{2}\sum_{mne} t^{m}_{a} t^{n}_{b} t^{j}_{e} K_{mnie} + \frac{1}{2}\sum_{mne} t^{m}_{a} t^{n}_{b} t^{i}_{e} K_{mnej} + \frac{1}{2}\sum_{mnef} t^{m}_{a} t^{n}_{b} t^{ij}_{ef} K^{mn}_{ef} \\
& + \frac{1}{2}\sum_{mnef} t^{m}_{a} t^{n}_{b} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2}\sum_{ef} t^{ij}_{ef} K_{abef} + \frac{1}{2}\sum_{ef} t^{i}_{e} t^{j}_{f} K_{abef} \\
& - \sum_{mef} t^{m}_{a} K_{mbef} t^{ij}_{ef} - \sum_{mef} t^{m}_{a} K_{mbef} t^{i}_{e} t^{j}_{f} \\
& + \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
& - \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2}\sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ea} K_{mbej} - \sum_{mef} t^{im}_{ea} t^{j}_{f} K_{mbef} \\
& + \sum_{men} t^{im}_{ea} t^{n}_{b} K_{mnej} + \sum_{menf} \frac{1}{2} t^{im}_{ea} t^{jn}_{fb} K^{mn}_{ef} + \sum_{menf} t^{im}_{ea} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} - \frac{1}{2}\sum_{menf} t^{im}_{ea} t^{nj}_{fb} L^{mn}_{ef} \\
& + \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
& - \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2}\sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ae} K_{mbje} - \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbfe} \\
& + \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnje} + \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{fe} + \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{fe} \\
& - \sum_{me} t^{mj}_{ae} K_{mbie} - \sum_{mef} t^{mj}_{ae} t^{i}_{f} K_{mbfe} + \sum_{men} t^{mj}_{ae} t^{n}_{b} K_{mnie} + \sum_{menf} \frac{1}{2} t^{mj}_{ae} t^{in}_{fb} K^{mn}_{fe} + \sum_{menf} t^{mj}_{ae} t^{i}_{f} t^{n}_{b} K^{mn}_{fe} \\
& - \sum_{me} t^{i}_{e} t^{m}_{a} K_{mbej} + \sum_{me} t^{i}_{e} t^{m}_{b} K_{maje} + \sum_{e} t^{i}_{e} K_{abej} - \sum_{m} t^{m}_{a} K_{mbij}
\end{aligned}
\tag{172}
$$

while the second term is

$$
\begin{aligned}
\frac{1}{2}\sum_{cdkl} t_{cd}^{kl} \langle 0| E_a^i E_b^j E_l^d \big[\hat{H}_n, E_{ck}\big] |0\rangle &= \frac{1}{2}\sum_{cdkl} t_{cd}^{kl} \langle 0| E_a^i E_b^j E_l^d \left(\sum_g f_{gc} E_k^g - \sum_o f_{ko} E_o^c + \sum_{go} L_{gkoc} E_o^g \right) |0\rangle \\
&= \frac{1}{2}\sum_{cdklg} t_{cd}^{kl} f_{gc} \langle 0| E_a^i E_b^j E_l^d E_k^g |0\rangle - \frac{1}{2}\sum_{cdklo} t_{cd}^{kl} f_{ko} \langle 0| E_a^i E_b^j E_l^d E_o^c |0\rangle \\
&+ \sum_{cdklgo} t_{cd}^{kl} L_{gkoc} \langle 0| E_a^i E_b^j E_l^d E_o^g |0\rangle \\
&= P_{ij}^{ab}\Bigg(\frac{1}{2}\sum_{cdklg} t_{cd}^{kl} f_{gc} \delta_{abij,dglk} - \frac{1}{2}\sum_{cdklo} t_{cd}^{kl} f_{ko} \delta_{abij,dclo} \\
&+ \sum_{cdklgo} t_{cd}^{kl} L_{gkoc} \delta abij, dglo \Bigg) \\
&= P_{ij}^{ab}\Bigg(\frac{1}{2}\sum_{c} t_{ca}^{ji} f_{gc} - \frac{1}{2}\sum_{k} t_{ba}^{ki} f_{kj} \\
&+ \sum_{ck} t_{ca}^{ki} L_{bkjc} \Bigg)
\end{aligned}
\tag{173}
$$

such that the third term is the same leading to a prefactor of 2.

$$
\begin{aligned}
R^{ij}_{ab} =& \frac{1}{2} K^{ij}_{ab} + \sum_{e} t^{ij}_{ae} f_{be} - \frac{1}{2} \sum_{em} t^{ij}_{ae} f^{m}_{e} t^{m}_{b} \\
& + \sum_{emf} t^{ij}_{ae} t^{m}_{f} L_{mbfe} - \sum_{emnf} t^{ij}_{ae} t^{mn}_{bf} - \frac{1}{2} \sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
& - \frac{1}{2} \sum_{em} t^{ij}_{ae} t^{m}_{b} f_{me} - \frac{1}{2} \sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
& - \sum_{m} t^{im}_{ab} f_{mj} - \frac{1}{2} \sum_{me} t^{im}_{ab} t^{j}_{e} f^{m}_{e} - \sum_{mne} t^{im}_{ab} t^{n}_{e} L_{mnje} - \sum_{mnef} t^{im}_{ab} t^{jn}_{ef} L_{mnje} \\
& - \frac{1}{2} \sum_{mnef} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} - \frac{1}{2} \sum_{me} t^{im}_{ab} t^{j}_{e} f_{me} - \frac{1}{2} \sum_{menf} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} \\
& + \frac{1}{2} \sum_{mn} t^{mn}_{ab} K_{mnij} + \frac{1}{2} \sum_{mne} t^{mn}_{ab} t^{j}_{e} K_{mnie} + \frac{1}{2} \sum_{mne} t^{mn}_{ab} t^{i}_{e} K_{mnej} \\
& + \frac{1}{2} \sum_{mnef} t^{mn}_{ab} t^{ij}_{ef} K^{mn}_{ef} + \frac{1}{2} \sum_{mnef} t^{mn}_{ab} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2} \sum_{mn} t^{m}_{a} t^{n}_{b} K_{mnij} \\
& + \frac{1}{2} \sum_{mne} t^{m}_{a} t^{n}_{b} t^{j}_{e} K_{mnie} + \frac{1}{2} \sum_{mne} t^{m}_{a} t^{n}_{b} t^{i}_{e} K_{mnej} + \frac{1}{2} \sum_{mnef} t^{m}_{a} t^{n}_{b} t^{ij}_{ef} K^{mn}_{ef} \\
& + \frac{1}{2} \sum_{mnef} t^{m}_{a} t^{n}_{b} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2} \sum_{ef} t^{ij}_{ef} K_{abef} + \frac{1}{2} \sum_{ef} t^{i}_{e} t^{j}_{f} K_{abef} \\
& - \sum_{mef} t^{m}_{a} K_{mbef} t^{ij}_{ef} - \sum_{mef} t^{m}_{a} K_{mbef} t^{i}_{e} t^{j}_{f} \\
& + \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
& - \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2} \sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ea} K_{mbej} - \sum_{mef} t^{im}_{ea} t^{j}_{f} K_{mbef} \\
& + \sum_{men} t^{im}_{ea} t^{n}_{b} K_{mnej} + \sum_{menf} \frac{1}{2} t^{im}_{ea} t^{jn}_{fb} K^{mn}_{ef} + \sum_{menf} t^{im}_{ea} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} - \frac{1}{2} \sum_{menf} t^{im}_{ea} t^{nj}_{fb} L^{mn}_{ef} \\
& + \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
& - \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2} \sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ae} K_{mbje} - \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbfe} \\
& + \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnje} + \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{fe} + \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{fe} \\
& - \sum_{me} t^{mj}_{ae} K_{mbie} - \sum_{mef} t^{mj}_{ae} t^{i}_{f} K_{mbfe} + \sum_{men} t^{mj}_{ae} t^{n}_{b} K_{mnie} + \sum_{menf} \frac{1}{2} t^{mj}_{ae} t^{in}_{fb} K^{mn}_{fe} + \sum_{menf} t^{mj}_{ae} t^{i}_{f} t^{n}_{b} K^{mn}_{fe} \\
& - \sum_{me} t^{i}_{e} t^{m}_{a} K_{mbej} + \sum_{me} t^{i}_{e} t^{m}_{b} K_{maje} + \sum_{e} t^{i}_{e} K_{abej} - \sum_{m} t^{m}_{a} K_{mbij}
\end{aligned}
\tag{174}
$$

- Term 3

$$\frac{1}{2!}\langle\phi_{ij}^{ab}|\left[\left[\hat{H},\hat{T}\right],\hat{T}\right]|\Phi_0\rangle = \frac{1}{2}\langle 0|E_a^iE_b^j\left[\left[\hat{H},\hat{T}_1\right],\hat{T}_1\right]|0\rangle$$
$$+\frac{1}{2}\langle 0|E_a^iE_b^j\left[\left[\hat{H},\hat{T}_1\right],\hat{T}_2\right]|0\rangle+\frac{1}{2}\langle 0|E_a^iE_b^j\left[\left[\hat{H},\hat{T}_2\right],\hat{T}_1\right]|0\rangle \quad (175)$$
$$+\frac{1}{2}\langle 0|E_a^iE_b^j\left[\left[\hat{H},\hat{T}_2\right],\hat{T}_2\right]|0\rangle$$

such that the first term is

$$\frac{1}{2}\langle 0|E_a^iE_b^j\left[\left[\hat{H},\hat{T}_1\right],\hat{T}_1\right]|0\rangle$$
$$=\frac{1}{2}\sum_{cdkl}t_c^kt_d^l\langle 0|E_a^iE_b^j\left[\left[\hat{H}_n,E_{ck}\right],E_{dl}\right]|0\rangle$$
$$=\frac{1}{2}\sum_{cdkl}t_c^kt_d^l\langle 0|E_a^iE_b^jP_{kl}^{cd}\Bigg(-\sum_{em}(\langle le|mc\rangle E_{dm}E_{ek}+\langle el|mc\rangle E_{em}E_{dk})$$
$$+\frac{1}{2}\sum_{ef}\langle ef|cd\rangle E_{ek}E_{fl}+\frac{1}{2}\sum_{mn}\langle kl|mn\rangle E_{cm}E_{dn}\Bigg)|0\rangle$$
$$=\frac{1}{2}\sum_{cdkl}t_c^kt_d^l\langle 0|E_a^iE_b^j\Bigg(-\sum_{em}(\langle le|mc\rangle E_{dm}E_{ek}+\langle el|mc\rangle E_{em}E_{dk})$$
$$+\frac{1}{2}\sum_{ef}\langle ef|cd\rangle E_{ek}E_{fl}+\frac{1}{2}\sum_{mn}\langle kl|mn\rangle E_{cm}E_{dn}\Bigg)|0\rangle$$
$$-\sum_{em}(\langle ke|md\rangle E_{cm}E_{el}+\langle ek|md\rangle E_{em}E_{cl})$$
$$+\frac{1}{2}\sum_{ef}\langle ef|dc\rangle E_{el}E_{fk}+\frac{1}{2}\sum_{mn}\langle lk|mn\rangle E_{dm}E_{cn}\Bigg)|0\rangle$$
$$=\frac{1}{2}\Bigg(-\sum_{em}\sum_{cdkl}t_c^kt_d^l\langle le|mc\rangle\langle 0|E_a^iE_b^jE_{dm}E_{ek}|0\rangle-\sum_{em}\sum_{cdkl}t_c^kt_d^l\langle el|mc\rangle\langle 0|E_a^iE_b^jE_{em}E_{dk}|0\rangle$$
$$+\frac{1}{2}\sum_{ef}\sum_{cdkl}t_c^kt_d^l\langle ef|cd\rangle\langle 0|E_a^iE_b^jE_{ek}E_{fl}|0\rangle+\frac{1}{2}\sum_{mn}\sum_{cdkl}t_c^kt_d^l\langle kl|mn\rangle\langle 0|E_a^iE_b^jE_{cm}E_{dn}|0\rangle$$
$$-\sum_{em}\sum_{cdkl}t_c^kt_d^l\langle ke|md\rangle\langle 0|E_a^iE_b^jE_{cm}E_{el}|0\rangle-\sum_{em}\sum_{cdkl}t_c^kt_d^l\langle ek|md\rangle\langle 0|E_a^iE_b^jE_{em}E_{cl}|0\rangle$$
$$+\frac{1}{2}\sum_{ef}\sum_{cdkl}t_c^kt_d^l\langle ef|dc\rangle\langle 0|E_a^iE_b^jE_{el}E_{fk}|0\rangle+\frac{1}{2}\sum_{mn}\sum_{cdkl}t_c^kt_d^l\langle lk|mn\rangle\langle 0|E_a^iE_b^jE_{dm}E_{cn}|0\rangle\Bigg)$$
$$(176)$$

$$
\begin{aligned}
= \frac{1}{2} P_{ab}^{ij} \Bigg(&- \sum_{em} \sum_{cdkl} t_c^k t_d^l \langle le|mc \rangle \delta_{abij,demk} - \sum_{em} \sum_{cdkl} t t_c^k t_d^l \langle el|mc \rangle \delta_{abij,edmk} \\
&+ \frac{1}{2} \sum_{ef} \sum_{cdkl} t t_c^k t_d^l \langle ef|cd \rangle \delta_{abij,efkl} + \frac{1}{2} \sum_{mn} \sum_{cdkl} t_c^k t_d^l \langle kl|mn \rangle \delta_{abij,cdmn} \\
&- \sum_{em} \sum_{cdkl} t_c^k t_d^l \langle ke|md \rangle \delta_{abij,ceml} - \sum_{em} \sum_{cdkl} t_c^k t_d^l \langle ek|md \rangle \delta_{abij,ecml} \\
&+ \frac{1}{2} \sum_{ef} \sum_{cdkl} t_c^k t_d^l \langle ef|dc \rangle \delta_{abij,eflk} + \frac{1}{2} \sum_{mn} \sum_{cdkl} t_c^k t_d^l \langle lk|mn \rangle \delta_{abij,dcmn} \Bigg) \\
= \frac{1}{2} P_{ab}^{ij} \Bigg(&- \sum_{cl} t_c^j t_a^l \langle lb|ic \rangle - \sum_{cl} t_c^j t_b^l \langle al|ic \rangle \\
&+ \frac{1}{2} \sum_{cd} t_c^i t_d^j \langle ab|cd \rangle + \frac{1}{2} \sum_{kl} t_a^k t_b^l \langle kl|ij \rangle \\
&- \sum_{dk} t_a^k t_d^j \langle kb|id \rangle - \sum_{dk} t_b^k t_d^j \langle ak|id \rangle \\
&+ \frac{1}{2} \sum_{cd} t_c^j t_d^i \langle ab|dc \rangle + \frac{1}{2} \sum_{cdkl} t_b^k t_a^l \langle lk|ij \rangle \Bigg)
\end{aligned}
$$

$$
\begin{aligned}
R^{ij}_{ab} =& \frac{1}{2} K^{ij}_{ab} + \sum_{e} t^{ij}_{ae} f_{be} - \frac{1}{2} \sum_{em} t^{ij}_{ae} f^{m}_{e} t^{m}_{b} \\
& + \sum_{emf} t^{ij}_{ae} t^{m}_{f} L_{mbfe} - \sum_{emnf} t^{ij}_{ae} t^{mn}_{bf} - \frac{1}{2} \sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
& - \frac{1}{2} \sum_{em} t^{ij}_{ae} t^{m}_{b} f_{me} - \frac{1}{2} \sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
& - \sum_{m} t^{im}_{ab} f_{mj} - \frac{1}{2} \sum_{me} t^{im}_{ab} t^{j}_{e} f^{m}_{e} - \sum_{mne} t^{im}_{ab} t^{n}_{e} L_{mnje} - \sum_{mnef} t^{im}_{ab} t^{jn}_{ef} L_{mnje} \\
& - \frac{1}{2} \sum_{mnef} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} - \frac{1}{2} \sum_{me} t^{im}_{ab} t^{j}_{e} f_{me} - \frac{1}{2} \sum_{menf} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} \\
& + \frac{1}{2} \sum_{mn} t^{mn}_{ab} K_{mnij} + \frac{1}{2} \sum_{mne} t^{mn}_{ab} t^{j}_{e} K_{mnie} + \frac{1}{2} \sum_{mne} t^{mn}_{ab} t^{i}_{e} K_{mnej} \\
& + \frac{1}{2} \sum_{mnef} t^{mn}_{ab} t^{ij}_{ef} K^{mn}_{ef} + \frac{1}{2} \sum_{mnef} t^{mn}_{ab} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2} \sum_{mn} t^{m}_{a} t^{n}_{b} K_{mnij} \\
& + \frac{1}{2} \sum_{mne} t^{m}_{a} t^{n}_{b} t^{j}_{e} K_{mnie} + \frac{1}{2} \sum_{mne} t^{m}_{a} t^{n}_{b} t^{i}_{e} K_{mnej} + \frac{1}{2} \sum_{mnef} t^{m}_{a} t^{n}_{b} t^{ij}_{ef} K^{mn}_{ef} \\
& + \frac{1}{2} \sum_{mnef} t^{m}_{a} t^{n}_{b} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2} \sum_{ef} t^{ij}_{ef} K_{abef} + \frac{1}{2} \sum_{ef} t^{i}_{e} t^{j}_{f} K_{abef} \\
& - \sum_{mef} t^{m}_{a} K_{mbef} t^{ij}_{ef} - \sum_{mef} t^{m}_{a} K_{mbef} t^{i}_{e} t^{j}_{f} \\
& + \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
& - \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2} \sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ea} K_{mbej} - \sum_{mef} t^{im}_{ea} t^{j}_{f} K_{mbef} \\
& + \sum_{men} t^{im}_{ea} t^{n}_{b} K_{mnej} + \sum_{menf} \frac{1}{2} t^{im}_{ea} t^{jn}_{fb} K^{mn}_{ef} + \sum_{menf} t^{im}_{ea} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} - \frac{1}{2} \sum_{menf} t^{im}_{ea} t^{nj}_{fb} L^{mn}_{ef} \\
& + \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
& - \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2} \sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ae} K_{mbje} - \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbfe} \\
& + \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnje} + \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{fe} + \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{fe} \\
& - \sum_{me} t^{mj}_{ae} K_{mbie} - \sum_{mef} t^{mj}_{ae} t^{i}_{f} K_{mbfe} + \sum_{men} t^{mj}_{ae} t^{n}_{b} K_{mnie} + \sum_{menf} \frac{1}{2} t^{mj}_{ae} t^{in}_{fb} K^{mn}_{fe} + \sum_{menf} t^{mj}_{ae} t^{i}_{f} t^{n}_{b} K^{mn}_{fe} \\
& - \sum_{me} t^{i}_{e} t^{m}_{a} K_{mbej} + \sum_{me} t^{i}_{e} t^{m}_{b} K_{maje} + \sum_{e} t^{i}_{e} K_{abej} - \sum_{m} t^{m}_{a} K_{mbij}
\end{aligned}
\tag{177}
$$

Term 3.2

$$\frac{1}{2}\langle 0|\, E^i_a E^j_b \Big[\Big[\hat{H},\hat{T}_1\Big],\hat{T}_2\Big]|0\rangle = \frac{1}{4}\sum_{cdelkm} t^k_c t^{lm}_{de}\Bigg(\langle 0|\, E^i_a E^j_b \Big[\Big[\Big[\hat{H},E^c_k\Big],E^d_l\Big],E^e_m\Big] + \langle 0|\, E^i_a E^j_b E^e_m \Big[\Big[\hat{H},E^c_k\Big],E^d_l\Big] + \langle o|\, E^i_a E^j_b E^d_l \Big[\Big[\hat{H},E^c_k\Big],E^e_m\Big]\Bigg)|0\rangle \tag{178}$$

Term 3.2.1

$$\begin{aligned}
&\frac{1}{4}\sum_{cdelkm} t^k_c t^{lm}_{de}\,\langle 0|\, E^i_a E^j_b \Big[\Big[\Big[\hat{H},E^c_k\Big],E^d_l\Big],E^e_m\Big]|0\rangle \\
&= \frac{1}{4}\sum_{cdelkm} t^k_c t^{lm}_{de}\,\langle 0|\, E^i_a E^j_b P^{cde}_{klm}\Bigg(-\sum_g \langle mg|cd\rangle\, E^g_l E^e_k + \sum_n \langle mg|co\rangle\, E^d_n E^e_k\Bigg)|0\rangle \\
&= \frac{1}{4}\sum_{cdelkm} t^k_c t^{lm}_{de}\,\langle 0|\, E^i_a E^j_b \Bigg(-\sum_g \langle mg|cd\rangle\, E^g_l E^e_k|0\rangle - \sum_g \langle lg|ce\rangle\, E^g_m E^d_k|0\rangle - \sum_g \langle mg|dc\rangle\, E^g_k E^e_l|0\rangle \\
&\quad - \sum_g \langle kg|de\rangle\, E^g_m E^c_l|0\rangle - \sum_g \langle lg|ec\rangle\, E^g_k E^d_m|0\rangle - \sum_g \langle kg|ed\rangle\, E^g_l E^c_m|0\rangle \\
&\quad + \sum_n \langle mg|cn\rangle\, E^d_n E^e_k|0\rangle + \sum_n \langle lg|cn\rangle\, E^e_n E^d_k|0\rangle + \sum_n \langle mg|dn\rangle\, E^c_n E^e_l|0\rangle \\
&\quad + \sum_n \langle kg|dn\rangle\, E^e_n E^c_l|0\rangle + \sum_n \langle lg|en\rangle\, E^c_n E^d_m|0\rangle + \sum_n \langle kg|en\rangle\, E^d_n E^c_m|0\rangle \\
&= \frac{1}{4}\Bigg(-\sum_g\sum_{cdelkm} t^k_c t^{lm}_{de}\langle mg|cd\rangle\langle 0|\, E^i_a E^j_b E^g_l E^e_k|0\rangle - \sum_g\sum_{cdelkm} t^k_c t^{lm}_{de}\langle lg|ce\rangle\langle 0|\, E^i_a E^j_b E^g_m E^d_k|0\rangle \\
&\quad - \sum_g\sum_{cdelkm} t^k_c t^{lm}_{de}\langle mg|dc\rangle\langle 0|\, E^i_a E^j_b E^g_k E^e_l|0\rangle - \sum_g\sum_{cdelkm} t^k_c t^{lm}_{de}\langle kg|de\rangle\langle 0|\, E^i_a E^j_b E^g_m E^c_l|0\rangle \\
&\quad - \sum_g\sum_{cdelkm} t^k_c t^{lm}_{de}\langle lg|ec\rangle\langle 0|\, E^i_a E^j_b E^g_k E^d_m|0\rangle - \sum_g\sum_{cdelkm} t^k_c t^{lm}_{de}\langle kg|ed\rangle\langle 0|\, E^i_a E^j_b E^g_l E^c_m|0\rangle \\
&\quad + \sum_n\sum_{cdelkm} t^k_c t^{lm}_{de}\langle mg|cn\rangle\langle 0|\, E^i_a E^j_b E^d_n E^e_k|0\rangle + \sum_n\sum_{cdelkm} t^k_c t^{lm}_{de}\langle lg|cn\rangle\langle 0|\, E^i_a E^j_b E^e_n E^d_k|0\rangle \\
&\quad + \sum_n\sum_{cdelkm} t^k_c t^{lm}_{de}\langle mg|dn\rangle\langle 0|\, E^i_a E^j_b E^c_n E^e_l|0\rangle + \sum_n\sum_{cdelkm} t^k_c t^{lm}_{de}\langle kg|dn\rangle\langle 0|\, E^i_a E^j_b E^e_n E^c_l|0\rangle \\
&\quad + \sum_n\sum_{cdelkm} t^k_c t^{lm}_{de}\langle lg|en\rangle\langle 0|\, E^i_a E^j_b E^c_n E^d_m|0\rangle + \sum_n\sum_{cdelkm} t^k_c t^{lm}_{de}\langle kg|en\rangle\langle 0|\, E^i_a E^j_b E^d_n E^c_m|0\rangle
\end{aligned} \tag{179}$$

$$
\begin{aligned}
= \frac{1}{4} P_{ab}^{ij} \Bigg(& - \sum_{g} \sum_{cdelkm} t_c^k t_{de}^{lm} \langle mg|cd \rangle \, \delta_{abij,gelk} - \sum_{g} \sum_{cdelkm} t_c^k t_{de}^{lm} \langle lg|ce \rangle \, \delta_{abij,gdmk} \\
& - \sum_{g} \sum_{cdelkm} t_c^k t_{de}^{lm} \langle mg|dc \rangle \, \delta_{abij,gekl} - \sum_{g} \sum_{cdelkm} t_c^k t_{de}^{lm} \langle kg|de \rangle \, \delta_{abij,gcml} \\
& - \sum_{g} \sum_{cdelkm} t_c^k t_{de}^{lm} \langle lg|ec \rangle \, \delta_{abij,gdkm} - \sum_{g} \sum_{cdelkm} t_c^k t_{de}^{lm} \langle kg|ed \rangle \, \delta_{abij,gclm} \\
& + \sum_{n} \sum_{cdelkm} t_c^k t_{de}^{lm} \langle mg|cn \rangle \, \delta_{abij,denk} + \sum_{n} \sum_{cdelkm} t_c^k t_{de}^{lm} \langle lg|cn \rangle \, \delta_{abij,ednk} \\
& + \sum_{n} \sum_{cdelkm} t_c^k t_{de}^{lm} \langle mg|dn \rangle \, \delta_{abij,cenl} + \sum_{n} \sum_{cdelkm} t_c^k t_{de}^{lm} \langle kg|dn \rangle \, \delta_{abij,ecnl} \\
& + \sum_{n} \sum_{cdelkm} t_c^k t_{de}^{lm} \langle lg|en \rangle \, \delta_{abij,cdnm} + \sum_{n} \sum_{cdelkm} t_c^k t_{de}^{lm} \langle kg|en \rangle \, \delta_{abij,dcnm}
\end{aligned}
$$

$$
\begin{aligned}
= \frac{1}{4} P_{ab}^{ij} \Bigg(& - \sum_{cdm} t_c^j t_{db}^{im} \langle ma|cd \rangle - \sum_{cel} t_c^j t_{be}^{li} \langle la|ce \rangle \\
& - \sum_{cdm} t_c^i t_{db}^{jm} \langle ma|dc \rangle - \sum_{dek} t_b^k t_{de}^{ji} \langle ka|de \rangle \\
& - \sum_{cel} t_c^i t_{be}^{lj} \langle la|ec \rangle - \sum_{dek} t_b^k t_{de}^{ij} \langle ka|ed \rangle \\
& + \sum_{clm} t_c^j t_{ab}^{lm} \langle mg|ci \rangle + \sum_{clm} t_c^j t_{ba}^{lm} \langle lg|ci \rangle \\
& + \sum_{dkm} t_a^k t_{db}^{jm} \langle mg|di \rangle + \sum_{dkm} t_b^k t_{da}^{jm} \langle kg|di \rangle \\
& + \sum_{elk} t_a^k t_{be}^{lj} \langle lg|ei \rangle + \sum_{elk} t_b^k t_{ae}^{lj} \langle kg|ei \rangle
\end{aligned}
$$

$$
\begin{aligned}
R^{ij}_{ab} = & -\frac{1}{2}\sum_{me} t^{im}_{ab} t^{j}_{e} f^{m}_{e} - \sum_{mne} t^{im}_{ab} t^{n}_{e} L_{mnje} - \frac{1}{2}\sum_{me} t^{im}_{ab} t^{j}_{e} f_{me} + \frac{1}{2}\sum_{mne} t^{mn}_{ab} t^{j}_{e} K_{mnie} + \frac{1}{2}\sum_{mne} t^{mn}_{ab} t^{i}_{e} K_{mnej} \\
& - \sum_{mef} t^{m}_{a} K_{mbef} t^{ij}_{ef} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} \\
& - \sum_{mef} t^{im}_{ea} t^{j}_{f} K_{mbef} + \sum_{men} t^{im}_{ea} t^{n}_{b} K_{mnej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} \\
& - \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbfe} + \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnje} - \sum_{mef} t^{mj}_{ae} t^{i}_{f} K_{mbfe} + \sum_{men} t^{mj}_{ae} t^{n}_{b} K_{mnie}
\end{aligned}
\tag{180}
$$

Term 3.2.2

$$
\begin{aligned}
&\frac{1}{4}\sum_{cdelkm} t_c^k t_{de}^{lm} \langle 0| E_a^i E_b^j E_{em}\big[\big[\hat{H}_n,\{E_{ck}\}\big],\{E_{dl}\}\big]|0\rangle \\
&= \frac{1}{4}\sum_{cdelkm} t_c^k t_{de}^{lm} \langle 0| E_a^i E_b^j E_{em} P_{kl}^{cd}\bigg(-f_{lc}E_k^d - \sum_n L_{klcn}E_n^d + \sum_f L_{flcd}E_k^f\bigg)|0\rangle \\
&= \frac{1}{4}\sum_{cdelkm} t_c^k t_{de}^{lm} \langle 0| E_a^i E_b^j E_{em}\bigg(-f_{lc}E_k^d|0\rangle - f_{kd}E_l^c|0\rangle - \sum_n L_{klcn}E_n^d|0\rangle \\
&\quad - \sum_n L_{lkdn}E_n^c|0\rangle + \sum_f L_{flcd}E_k^f|0\rangle + \sum_f L_{fkdc}E_l^f|0\rangle\bigg) \\
&= \frac{1}{4}\bigg(\sum_{cdelkm} t_c^k t_{de}^{lm} - f_{lc}\langle 0| E_a^i E_b^j E_{em}E_k^d|0\rangle - \sum_{cdelkm} t_c^k t_{de}^{lm} f_{kd}\langle 0| E_a^i E_b^j E_{em}E_l^c|0\rangle \\
&\quad - \sum_n\sum_{cdelkm} t_c^k t_{de}^{lm} L_{klcn}\langle 0| E_a^i E_b^j E_{em}E_n^d|0\rangle - \sum_n\sum_{cdelkm} t_c^k t_{de}^{lm} L_{lkdn}\langle 0| E_a^i E_b^j E_{em}E_n^c|0\rangle \\
&\quad + \sum_f\sum_{cdelkm} t_c^k t_{de}^{lm} L_{flcd}\langle 0| E_a^i E_b^j E_{em}E_k^f|0\rangle + \sum_f\sum_{cdelkm} t_c^k t_{de}^{lm} L_{fkdc}\langle 0| E_a^i E_b^j E_{em}E_l^f|0\rangle\bigg) \\
&= \frac{1}{4}P_{ab}^{ij}\bigg(-\sum_{cdelkm} t_c^k t_{de}^{lm} f_{lc}\delta_{abij,edmk} - \sum_{cdelkm} t_c^k t_{de}^{lm} f_{kd}\delta_{abij,ecml} \\
&\quad - \sum_n\sum_{cdelkm} t_c^k t_{de}^{lm} L_{klcn}\delta_{abij,edmn} - \sum_n\sum_{cdelkm} t_c^k t_{de}^{lm} L_{lkdn}\delta_{abij,ecmn} \\
&\quad + \sum_f\sum_{cdelkm} t_c^k t_{de}^{lm} L_{flcd}\delta_{abij,efmk} + \sum_f\sum_{cdelkm} t_c^k t_{de}^{lm} L_{fkdc}\delta_{abij,efml}\bigg) \\
&= \frac{1}{4}P_{ab}^{ij}\bigg(-\sum_{cl} t_c^j t_{ba}^{li} f_{lc} - \sum_{dk} t_b^k t_{da}^{ji} f_{kd} - \sum_{clk} t_c^k t_{ba}^{li} L_{klcj} \\
&\quad - \sum_{dlk} t_b^k t_{da}^{li} L_{lkdj} + \sum_{cdl} t_c^j t_{da}^{li} L_{blcd} + \sum_{cdk} t_c^k t_{da}^{ji} L_{bkdc}\bigg)
\end{aligned} \tag{181}
$$

Term 3.4

$$\frac{1}{2}\langle 0|\, E_a^i E_b^j \Big[\Big[\hat{H}, \hat{T}_2\Big], \hat{T}_2\Big] |0\rangle = \frac{1}{8}\langle 0|\, E_a^i E_b^j \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \Big[\Big[\Big[\Big[\hat{H}_n, E_k^c\Big], E_l^d\Big], E_m^e\Big], E_n^f\Big] |0\rangle$$
$$+ \frac{1}{2}\langle 0|\, E_a^i E_b^j E_k^c \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \Big[\Big[\Big[\hat{H}_n, E_l^d\Big], E_m^e\Big], E_n^f\Big] |0\rangle$$
$$+ \frac{1}{2}\langle 0|\, E_a^i E_b^j E_k^c E_m^e \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \Big[\Big[\hat{H}_n, E_l^d\Big], E_n^f\Big] |0\rangle \tag{182}$$

Term 3.4.1

$$\frac{1}{8}\langle 0|\, E_a^i E_b^j \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \Big[\Big[\Big[\Big[\hat{H}_n, E_k^c\Big], E_l^d\Big], E_m^e\Big], E_n^f\Big] |0\rangle$$
$$= \frac{1}{16}\langle 0|\, E_a^i E_b^j \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} P_{klmn}^{cdef}\Big(\langle mn|cd\rangle\, E_l^f E_k^e |0\rangle \Big)$$
$$= \frac{1}{16}\langle 0|\, E_a^i E_b^j \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn}\Big(\langle mn|cd\rangle\, E_l^f E_k^e |0\rangle + \langle nm|cd\rangle\, E_l^e E_k^f |0\rangle$$
$$+ \langle ln|ce\rangle\, E_m^f E_k^d |0\rangle + \langle nl|ce\rangle\, E_m^d E_k^f |0\rangle + \langle lm|cf\rangle\, E_n^e E_k^d |0\rangle + \langle ml|cf\rangle\, E_n^d E_k^e |0\rangle$$
$$+ \langle mn|dc\rangle\, E_k^f E_l^e |0\rangle + \langle nm|dc\rangle\, E_k^e E_l^f |0\rangle + \langle kn|de\rangle\, E_m^f E_l^c |0\rangle + \langle nk|de\rangle\, E_m^c E_l^f |0\rangle$$
$$+ \langle km|df\rangle\, E_n^e E_l^c |0\rangle + \langle mk|df\rangle\, E_n^c E_l^e |0\rangle + \langle ln|ec\rangle\, E_k^f E_m^d |0\rangle + \langle nl|ec\rangle\, E_k^d E_m^f |0\rangle$$
$$+ \langle ln|ed\rangle\, E_m^f E_k^c |0\rangle + \langle lk|ed\rangle\, E_m^c E_n^f |0\rangle + \langle kl|ef\rangle\, E_n^d E_m^c |0\rangle + \langle lk|ef\rangle\, E_n^c E_m^d |0\rangle$$
$$+ \langle lm|fc\rangle\, E_k^e E_n^d |0\rangle + \langle ml|fc\rangle\, E_k^d E_n^e |0\rangle + \langle km|fd\rangle\, E_l^e E_n^c |0\rangle + \langle mk|fd\rangle\, E_l^c E_n^e |0\rangle$$
$$+ \langle kl|fe\rangle\, E_m^d E_n^c |0\rangle + \langle lk|fe\rangle\, E_m^c E_n^d |0\rangle \tag{183}$$

$$
\begin{aligned}
= \frac{1}{16}\Bigg(& \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle mn|cd\rangle \langle 0| E^i_a E^j_b E^f_l E^e_k |0\rangle + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle nm|cd\rangle \langle 0| E^i_a E^j_b E^e_l E^f_k |0\rangle \\
& + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle ln|ce\rangle \langle 0| E^i_a E^j_b E^f_m E^d_k |0\rangle + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle nl|ce\rangle \langle 0| E^i_a E^j_b E^d_m E^f_k |0\rangle \\
& + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle lm|cf\rangle \langle 0| E^i_a E^j_b E^e_n E^d_k |0\rangle + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle ml|cf\rangle \langle 0| E^i_a E^j_b E^d_n E^e_k |0\rangle \\
& + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle mn|dc\rangle \langle 0| E^i_a E^j_b E^f_k E^e_l |0\rangle + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle nm|dc\rangle \langle 0| E^i_a E^j_b E^e_k E^f_l |0\rangle \\
& + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle kn|de\rangle \langle 0| E^i_a E^j_b E^f_m E^c_l |0\rangle + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle nk|de\rangle \langle 0| E^i_a E^j_b E^c_m E^f_l |0\rangle \\
& + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle km|df\rangle \langle 0| E^i_a E^j_b E^e_n E^c_l |0\rangle + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle mk|df\rangle \langle 0| E^i_a E^j_b E^c_n E^e_l |0\rangle \\
& + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle ln|ec\rangle \langle 0| E^i_a E^j_b E^f_k E^d_m |0\rangle + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle nl|ec\rangle \langle 0| E^i_a E^j_b E^d_k E^f_m |0\rangle \\
& + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle ln|ed\rangle \langle 0| E^i_a E^j_b E^f_m E^c_k |0\rangle + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle lk|ed\rangle \langle 0| E^i_a E^j_b E^c_m E^f_n |0\rangle \\
& + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle kl|ef\rangle \langle 0| E^i_a E^j_b E^d_n E^c_m |0\rangle + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle lk|ef\rangle \langle 0| E^i_a E^j_b E^c_n E^d_m |0\rangle \\
& + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle lm|fc\rangle \langle 0| E^i_a E^j_b E^e_k E^d_n |0\rangle + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle ml|fc\rangle \langle 0| E^i_a E^j_b E^d_k E^e_n |0\rangle \\
& + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle km|fd\rangle \langle 0| E^i_a E^j_b E^e_l E^c_n |0\rangle + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle mk|fd\rangle \langle 0| E^i_a E^j_b E^c_l E^e_n |0\rangle \\
& + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle kl|fe\rangle \langle 0| E^i_a E^j_b E^d_m E^c_n |0\rangle + \sum_{cdefklmn} t^{kl}_{cd} t^{mn}_{ef} \langle lk|fe\rangle \langle 0| E^i_a E^j_b E^c_m E^d_n |0\rangle
\end{aligned}
$$

$$
\begin{aligned}
= \frac{1}{16} P_{ab}^{ij} \Bigg(& \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle mn|cd \rangle \, \delta_{abij,felk} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle nm|cd \rangle \, \delta_{abij,eflk} \\
& + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle ln|ce \rangle \, \delta_{abij,fdmk} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle nl|ce \rangle \, \delta_{abij,dfmk} \\
& + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle lm|cf \rangle \, \delta_{abij,ednk} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle ml|cf \rangle \, \delta_{abij,denk} \\
& + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle mn|dc \rangle \, \delta_{abij,fekl} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle nm|dc \rangle \, \delta_{abij,efkl} \\
& + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle kn|de \rangle \, \delta_{abij,fcml} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle nk|de \rangle \, \delta_{abij,cfml} \\
& + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle km|df \rangle \, \delta_{abij,ecnl} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle mk|df \rangle \, \delta_{abij,cenl} \\
& + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle ln|ec \rangle \, \delta_{abij,fdkm} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle nl|ec \rangle \, \delta_{abij,dfkm} \\
& + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle ln|ed \rangle \, \delta_{abij,fcmk} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle lk|ed \rangle \, \delta_{abij,cfmn} \\
& + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle kl|ef \rangle \, \delta_{abij,dcnm} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle lk|ef \rangle \, \delta_{abij,cdnm} \\
& + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle lm|fc \rangle \, \delta_{abij,edkn} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle ml|fc \rangle \, \delta_{abij,dekn} \\
& + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle km|fd \rangle \, \delta_{abij,ecln} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle mk|fd \rangle \, \delta_{abij,celn} \\
& + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle kl|fe \rangle \, \delta_{abij,dcmn} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \langle lk|fe \rangle \, \delta_{abij,cdmn}
\end{aligned}
$$

$$
\begin{aligned}
= \frac{1}{16} P_{ab}^{ij} \Bigg(& \sum_{cdmn} t_{cd}^{ji} t_{ba}^{mn} \langle mn|cd \rangle + \sum_{cdmn} t_{cd}^{ji} t_{ab}^{mn} \langle nm|cd \rangle \\
& + \sum_{celn} t_{cb}^{jl} t_{ea}^{in} \langle ln|ce \rangle + \sum_{celn} t_{ca}^{jl} t_{eb}^{in} \langle nl|ce \rangle \\
& + \sum_{cflm} t_{cb}^{jl} t_{af}^{mi} \langle lm|cf \rangle + \sum_{cflm} t_{ca}^{jl} t_{bf}^{mi} \langle ml|cf \rangle \\
& + \sum_{cdmn} t_{cd}^{ij} t_{ba}^{mn} \langle mn|dc \rangle + \sum_{cdmn} t_{cd}^{ij} t_{ab}^{mn} \langle nm|dc \rangle \\
& + \sum_{dekn} t_{bd}^{kj} t_{ea}^{in} \langle kn|de \rangle + \sum_{dekn} t_{ad}^{kj} t_{eb}^{in} \langle nk|de \rangle \\
& + \sum_{dfkm} t_{bd}^{kj} t_{af}^{mi} \langle km|df \rangle + \sum_{dfkm} t_{ad}^{kj} t_{bf}^{mi} \langle mk|df \rangle \\
& + \sum_{celn} t_{cb}^{il} t_{ea}^{jn} \langle ln|ec \rangle + \sum_{celn} t_{ca}^{il} t_{eb}^{jn} \langle nl|ec \rangle \\
& + \sum_{deln} t_{bd}^{jl} t_{ea}^{in} \langle ln|ed \rangle + \sum_{dekl} t_{ad}^{kl} t_{eb}^{ij} \langle lk|ed \rangle \\
& + \sum_{efkl} t_{ba}^{kl} t_{ef}^{ji} \langle kl|ef \rangle + \sum_{efkl} t_{ab}^{kl} t_{ef}^{ji} \langle lk|ef \rangle \\
& + \sum_{cflm} t_{cb}^{il} t_{af}^{mj} \langle lm|fc \rangle + \sum_{cflm} t_{ca}^{il} t_{bf}^{mj} \langle ml|fc \rangle \\
& + \sum_{dfkm} t_{bd}^{ki} t_{af}^{mj} \langle km|fd \rangle + \sum_{dfkm} t_{ad}^{ki} t_{bf}^{mj} \langle mk|fd \rangle \\
& + \sum_{efkl} t_{ba}^{kl} t_{ef}^{ij} \langle kl|fe \rangle + \sum_{efkl} t_{ab}^{kl} t_{ef}^{ij} \langle lk|fe \rangle
\end{aligned}
$$

$$
\begin{aligned}
R^{ij}_{ab} =& \frac{1}{2}K^{ij}_{ab} + \sum_{e} t^{ij}_{ae} f_{be} - \frac{1}{2}\sum_{em} t^{ij}_{ae} f^{m}_{e} t^{m}_{b} \\
&+ \sum_{emf} t^{ij}_{ae} t^{m}_{f} L_{mbfe} - \sum_{emnf} t^{ij}_{ae} t^{mn}_{bf} - \frac{1}{2}\sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
&- \frac{1}{2}\sum_{em} t^{ij}_{ae} t^{m}_{b} f_{me} - \frac{1}{2}\sum_{emnf} t^{ij}_{ae} t^{m}_{b} t^{n}_{f} L^{mn}_{ef} \\
&- \sum_{m} t^{im}_{ab} f_{mj} - \frac{1}{2}\sum_{me} t^{im}_{ab} t^{j}_{e} f^{m}_{e} - \sum_{mne} t^{im}_{ab} t^{n}_{e} L_{mnje} - \sum_{mnef} t^{im}_{ab} t^{jn}_{ef} L_{mnje} \\
&- \frac{1}{2}\sum_{mnef} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} - \frac{1}{2}\sum_{me} t^{im}_{ab} t^{j}_{e} f_{me} - \frac{1}{2}\sum_{menf} t^{im}_{ab} t^{j}_{e} t^{n}_{f} L^{mn}_{ef} \\
&+ \frac{1}{2}\sum_{mn} t^{mn}_{ab} K_{mnij} + \frac{1}{2}\sum_{mne} t^{mn}_{ab} t^{j}_{e} K_{mnie} + \frac{1}{2}\sum_{mne} t^{mn}_{ab} t^{i}_{e} K_{mnej} \\
&+ \frac{1}{2}\sum_{mnef} t^{mn}_{ab} t^{ij}_{ef} K^{mn}_{ef} + \frac{1}{2}\sum_{mnef} t^{mn}_{ab} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2}\sum_{mn} t^{m}_{a} t^{n}_{b} K_{mnij} \\
&+ \frac{1}{2}\sum_{mne} t^{m}_{a} t^{n}_{b} t^{j}_{e} K_{mnie} + \frac{1}{2}\sum_{mne} t^{m}_{a} t^{n}_{b} t^{i}_{e} K_{mnej} + \frac{1}{2}\sum_{mnef} t^{m}_{a} t^{n}_{b} t^{ij}_{ef} K^{mn}_{ef} \\
&+ \frac{1}{2}\sum_{mnef} t^{m}_{a} t^{n}_{b} t^{i}_{e} t^{j}_{f} K^{mn}_{ef} + \frac{1}{2}\sum_{ef} t^{ij}_{ef} K_{abef} + \frac{1}{2}\sum_{ef} t^{i}_{e} t^{j}_{f} K_{abef} \\
&- \sum_{mef} t^{m}_{a} K_{mbef} t^{ij}_{ef} - \sum_{mef} t^{m}_{a} K_{mbef} t^{i}_{e} t^{j}_{f} \\
&+ \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
&- \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2}\sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ea} K_{mbej} - \sum_{mef} t^{im}_{ea} t^{j}_{f} K_{mbef} \\
&+ \sum_{men} t^{im}_{ea} t^{n}_{b} K_{mnej} + \sum_{menf} \frac{1}{2} t^{im}_{ea} t^{jn}_{fb} K^{mn}_{ef} + \sum_{menf} t^{im}_{ea} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} - \frac{1}{2}\sum_{menf} t^{im}_{ea} t^{nj}_{fb} L^{mn}_{ef} \\
&+ \sum_{me} t^{im}_{ae} K_{mbej} + \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbef} - \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnej} - \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{ef} \\
&- \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{ef} + \frac{1}{2}\sum_{menf} t^{im}_{ae} t^{nj}_{fb} L^{mn}_{ef} - \sum_{me} t^{im}_{ae} K_{mbje} - \sum_{mef} t^{im}_{ae} t^{j}_{f} K_{mbfe} \\
&+ \sum_{men} t^{im}_{ae} t^{n}_{b} K_{mnje} + \sum_{menf} \frac{1}{2} t^{im}_{ae} t^{jn}_{fb} K^{mn}_{fe} + \sum_{menf} t^{im}_{ae} t^{j}_{f} t^{n}_{b} K^{mn}_{fe} \\
&- \sum_{me} t^{mj}_{ae} K_{mbie} - \sum_{mef} t^{mj}_{ae} t^{i}_{f} K_{mbfe} + \sum_{men} t^{mj}_{ae} t^{n}_{b} K_{mnie} + \sum_{menf} \frac{1}{2} t^{mj}_{ae} t^{in}_{fb} K^{mn}_{fe} + \sum_{menf} t^{mj}_{ae} t^{i}_{f} t^{n}_{b} K^{mn}_{fe} \\
&- \sum_{me} t^{i}_{e} t^{m}_{a} K_{mbej} + \sum_{me} t^{i}_{e} t^{m}_{b} K_{maje} + \sum_{e} t^{i}_{e} K_{abej} - \sum_{m} t^{m}_{a} K_{mbij}
\end{aligned}
\tag{184}
$$

Term 3.4.2

$$
\begin{aligned}
&\frac{1}{2}\langle 0|\, E_a^i E_b^j E_k^c \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \left[\left[\left[\hat{H}_n, E_l^d\right], E_m^e\right], E_n^f\right] |0\rangle \\
&= \frac{1}{2}\langle 0|\, E_a^i E_b^j E_k^c \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} P_{lmn}^{cde}\Big(- L_{lmdf} E_n^l\, |0\rangle \Big) \\
&= \frac{1}{2}\langle 0|\, E_a^i E_b^j E_k^c \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn}\Big(- L_{lmdf} E_n^l\, |0\rangle - L_{lnde} E_m^f\, |0\rangle \\
&\quad - L_{mlef} E_n^d\, |0\rangle - L_{mned} E_l^f\, |0\rangle - L_{nlfe} E_m^d\, |0\rangle - L_{nmfd} E_l^e\, |0\rangle \Big) \\
&= -\frac{1}{2}\Big(\sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{lmdf}\, \langle 0|\, E_a^i E_b^j E_k^c E_n^e\, |0\rangle + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{lnde}\, \langle 0|\, E_a^i E_b^j E_k^c E_m^f\, |0\rangle \\
&\quad + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{mlef}\, \langle 0|\, E_a^i E_b^j E_k^c E_n^d\, |0\rangle + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{mned}\, \langle 0|\, E_a^i E_b^j E_k^c E_l^f\, |0\rangle \\
&\quad + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{nlfe}\, \langle 0|\, E_a^i E_b^j E_k^c E_m^d\, |0\rangle + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{nmfd}\, \langle 0|\, E_a^i E_b^j E_k^c E_l^e\, |0\rangle \Big) \\
&= -\frac{1}{2} P_{ij}^{ab}\Big(\sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{lmdf} \delta_{abij,cekn} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{lnde} \delta_{abij,cfkm} \\
&\quad + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{mlef} \delta_{abij,cdkn} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{mned} \delta_{abij,cfkl} \\
&\quad + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{nlfe} \delta_{abij,cdkm} + \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{nmfd} \delta_{abij,cekl} \Big) \\
&= -\frac{1}{2} P_{ij}^{ab}\Big(\sum_{dflm} t_{ad}^{il} t_{bf}^{mj} L_{lmdf} + \sum_{deln} t_{ad}^{il} t_{eb}^{jn} L_{lnde} + \sum_{eflm} t_{ab}^{il} t_{ef}^{mj} L_{mlef} \\
&\quad + \sum_{demn} t_{ad}^{ij} t_{eb}^{mn} L_{mned} + \sum_{efln} t_{ab}^{il} t_{ef}^{jn} L_{nlfe} + \sum_{dfmn} t_{ad}^{ij} t_{bf}^{mn} L_{nmfd} \Big)
\end{aligned}
\tag{185}
$$

Term 3.4.3

$$\begin{aligned}
\frac{1}{2}\langle 0| E_a^i E_b^j E_k^c E_m^e \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \left[\left[\hat{H}_n, E_l^d\right], E_n^f\right] |0\rangle \\
= \frac{1}{2} P_{ln}^{df} \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{lndf} \left\langle \phi_{ij}^{ab} \middle| \phi_{km}^{ce} \right\rangle \\
= \frac{1}{2} \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{lndf} \left\langle \phi_{ij}^{ab} \middle| \phi_{km}^{ce} \right\rangle + \frac{1}{2} \sum_{cdefklmn} t_{cf}^{kn} t_{ed}^{ml} L_{nlfd} \left\langle \phi_{ij}^{ab} \middle| \phi_{km}^{ce} \right\rangle \\
= \frac{1}{2} \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} L_{lndf} \delta_{abij,cekm} + \frac{1}{2} \sum_{cdefklmn} t_{cf}^{kn} t_{ed}^{ml} L_{nlfd} \delta_{abij,cekm} \\
= \frac{1}{2} \sum_{dfln} t_{ad}^{il} t_{bf}^{jn} L_{lndf} + \frac{1}{2} \sum_{dfln} t_{af}^{in} t_{bd}^{jl} L_{nlfd}
\end{aligned} \tag{186}$$

Term 4

$$\begin{aligned}
\frac{1}{3!}\left\langle \phi_{ij}^{ab}\right| \left[\left[\left[\hat{H}, \hat{T}\right], \hat{T}\right], \hat{T}\right] |\Phi_0\rangle = \frac{1}{6}\left\langle \phi_{ij}^{ab}\right| \left[\left[\left[\hat{H}, \hat{T}_1\right], \hat{T}_1\right], \hat{T}_1\right] |\Phi_0\rangle + \frac{1}{6}\left\langle \phi_{ij}^{ab}\right| \left[\left[\left[\hat{H}, \hat{T}_2\right], \hat{T}_1\right], \hat{T}_1\right] |\Phi_0\rangle \\
+ \frac{1}{6}\left\langle \phi_{ij}^{ab}\right| \left[\left[\left[\hat{H}, \hat{T}_1\right], \hat{T}_2\right], \hat{T}_1\right] |\Phi_0\rangle + \frac{1}{6}\left\langle \phi_{ij}^{ab}\right| \left[\left[\left[\hat{H}, \hat{T}_1\right], \hat{T}_1\right], \hat{T}_2\right] |\Phi_0\rangle
\end{aligned} \tag{187}$$

Term 4.1 is exactly like term 3.2.1 but the t-amplitudes is composed of three t1-amplitudes instead of one t1-amplitude and one t2-amplitude and instead of $\frac{1}{4}$ it is $\frac{1}{6}$ coming from double counting of the unrestricted sum of a cubic term.

$$\begin{aligned}
\frac{1}{6}\left\langle \phi_{ij}^{ab}\right| \left[\left[\left[\hat{H}, \hat{T}_1\right], \hat{T}_1\right], \hat{T}_1\right] |\Phi_0\rangle = \frac{1}{6}\left\langle \phi_{ij}^{ab}\right| t_k^c t_l^d t_m^e \left[\left[\left[\hat{H}, E_k^c\right], E_l^d\right], E_m^e\right] |\Phi_0\rangle \\
= \frac{1}{6} P_{klm}^{cde} \left\langle \phi_{ij}^{ab}\right| t_k^c t_l^d t_m^e \left(\sum_g \langle mg|cd\rangle E_l^g E_k^e + \sum_o \langle ml|co\rangle E_o^d E_k^e \right) |\Phi_0\rangle
\end{aligned} \tag{188}$$

where the term 4.1.1 is

$$
\begin{aligned}
= \frac{1}{6} P_{ab}^{ij} \Big(& -\sum_{cdm} t_c^j t_d^i t_d^i \langle ma|cd\rangle - \sum_{cel} t_c^j t_b^l t_e^i \langle la|ce\rangle \\
& -\sum_{cdm} t_c^i t_d^j t_b^m \langle ma|dc\rangle - \sum_{dek} t_b^k t_d^j t_e^i \langle ka|de\rangle \\
& -\sum_{cel} t_c^i t_b^l t_e^l \langle la|ec\rangle - \sum_{dek} t_b^k t_d^i t_e^j \langle ka|ed\rangle \\
& +\sum_{clm} t_c^j t_a^l t_a^l t_b^m \langle mg|ci\rangle + \sum_{clm} t_c^j t_b^l t_a^m \langle lg|ci\rangle \\
& +\sum_{dkm} t_a^k t_d^j t_b^m \langle mg|di\rangle + \sum_{dkm} t_b^k t_d^j t_a^m \langle kg|di\rangle \\
& +\sum_{elk} t_a^k t_b^l t_e^j \langle lg|ei\rangle + \sum_{elk} t_b^k t_a^l t_e^j \langle kg|ei\rangle \Big)
\end{aligned}
\tag{189}
$$

Term 4.2

$$
\begin{aligned}
\frac{1}{6} \langle \phi_{ij}^{ab} | \Big[\Big[\Big[\hat{H}, \hat{T}_2\Big], \hat{T}_1\Big], \hat{T}_1\Big] |\Phi_0\rangle = & \frac{1}{12} \langle 0| E_a^i E_b^j \sum_{cdefklmn} t_{cd}^{kl} t_e^m t_f^n \Big[\Big[\Big[\Big[\hat{H}_n, E_k^c\Big], E_l^d\Big], E_m^e\Big], E_n^f\Big] |0\rangle \\
& + \frac{1}{6} \langle 0| E_a^i E_b^j E_k^c \sum_{cdefklmn} t_{cd}^{kl} t_e^m t_f^n \Big[\Big[\Big[\hat{H}_n, E_l^d\Big], E_m^e\Big], E_n^f\Big] |0\rangle
\end{aligned}
\tag{190}
$$

where term 4.2.1 is exactly the same as term 3.4.1 but the t-amplitudes is composed of two t1-amplitude and one t2-amplitude instead of two t2-amplitudes and instead of $\frac{1}{16}$ it is $\frac{1}{24}$ coming from the double counting of the unrestricted sum ($\frac{1}{6}$), the t2-amplitude ($\frac{1}{2}$), and the evaluation of the quartric term ($\frac{1}{2}$):

$$
\begin{aligned}
&\langle 0| E_a^i E_b^j \sum_{cdefklmn} t_{cd}^{kl} t_{ef}^{mn} \left[\left[\left[\left[\hat{H}_n, E_k^c\right], E_l^d\right], E_m^e\right], E_n^f\right] |0\rangle \\
&= \frac{1}{24} \langle 0| E_a^i E_b^j \sum_{cdefklmn} t_{cd}^{kl} t_e^m t_f^n P_{klmn}^{cdef} \Big(\langle mn|cd\rangle E_l^f E_k^e |0\rangle \Big) \\
&= \frac{1}{24} P_{ab}^{ij} \Big(\sum_{cdmn} t_{cd}^{ji} t_b^m t_a^n \langle mn|cd\rangle + \sum_{cdmn} t_{cd}^{ji} t_a^m t_b^n \langle nm|cd\rangle \\
&+ \sum_{celn} t_{cb}^{jl} t_e^i t_a^n \langle ln|ce\rangle + \sum_{celn} t_{ca}^{jl} t_e^i t_b^n \langle nl|ce\rangle \\
&+ \sum_{cflm} t_{cb}^{jl} t_a^m t_f^i \langle lm|cf\rangle + \sum_{cflm} t_{ca}^{jl} t_b^m t_f^i \langle ml|cf\rangle \\
&+ \sum_{cdmn} t_{cd}^{ij} t_b^m t_a^n \langle mn|dc\rangle + \sum_{cdmn} t_{cd}^{ij} t_a^m t_b^n \langle nm|dc\rangle \\
&+ \sum_{dekn} t_{bd}^{kj} t_e^i t_a^n \langle kn|de\rangle + \sum_{dekn} t_{ad}^{kj} t_{eb}^{in} \langle nk|de\rangle \\
&+ \sum_{dfkm} t_{bd}^{kj} t_a^m t_f^i \langle km|df\rangle + \sum_{dfkm} t_{ad}^{kj} t_b^m t_f^i \langle mk|df\rangle \\
&+ \sum_{celn} t_{cb}^{il} t_e^j t_a^n \langle ln|ec\rangle + \sum_{celn} t_{ca}^{il} t_e^j t_b^n \langle nl|ec\rangle \\
&+ \sum_{deln} t_{bd}^{jl} t_e^i t_a^i \langle ln|ed\rangle + \sum_{dekl} t_{ad}^{kl} t_e^i t_b^j \langle lk|ed\rangle \\
&+ \sum_{efkl} t_{ba}^{kl} t_e^j t_f^i \langle kl|ef\rangle + \sum_{efkl} t_{ab}^{kl} t_e^j t_f^j \langle lk|ef\rangle \\
&+ \sum_{cflm} t_{cb}^{il} t_a^m t_f^j \langle lm|fc\rangle + \sum_{cflm} t_{ca}^{il} t_b^m t_f^j \langle ml|fc\rangle \\
&+ \sum_{dfkm} t_{bd}^{ki} t_a^m t_f^j \langle km|fd\rangle + \sum_{dfkm} t_{ad}^{ki} t_b^m t_f^j \langle mk|fd\rangle \\
&+ \sum_{efkl} t_{ba}^{kl} t_e^i t_f^j \langle kl|fe\rangle + \sum_{efkl} t_{ab}^{kl} t_e^i t_f^j \langle lk|fe\rangle \Big)
\end{aligned}
\tag{191}
$$

Term 4.2.2 This term is exactly the same as term 3.4.2 but the t-amplitudes is composed of two t1-amplitude and one t2-amplitude instead of two t2-amplitudes and instead of -$\frac{1}{2}$ it is -$\frac{1}{6}$ coming from the double counting of the unrestricted sum ($\frac{1}{6}$), the t2-amplitude ($\frac{1}{2}$), the equivalent expression where the singly excited unitary group generator, E_k^c, is swapped with E_l^d (2), and the negative sign is from evaluating the commutator expansion :

$$\frac{1}{6}\langle 0|\, E_a^i E_b^j E_k^c \sum_{cdefklmn} t_{cd}^{kl} t_e^m t_f^n \left[\left[\left[\hat{H}_n, E_l^d\right], E_m^e\right], E_n^f\right] |0\rangle$$
$$= -\frac{1}{6} P_{ij}^{ab} \Bigg(\sum_{dflm} t_{ad}^{il} t_b^m t_f^j L_{lmdf} + \sum_{deln} t_{ad}^{il} t_e^j t_b^n L_{lnde} + \sum_{eflm} t_{ab}^{il} t_e^m t_f^j L_{mlef}$$
$$+ \sum_{demn} t_{ad}^{ij} t_e^m t_b^n L_{mned} + \sum_{efln} t_{ab}^{il} t_e^j t_f^n L_{nlfe} + \sum_{dfmn} t_{ad}^{ij} t_b^m t_f^n L_{nmfd} \Bigg) \tag{192}$$

Term 4.3 and Term 4.4 is exactly the same as term 4.2 since the $\hat{T}$ are commutes therefore they are equivalent and we can assign a factor of 3 in front of term 4.2 instead.

Term 5

$$\frac{1}{24}\langle \phi_{ij}^{ab}| \left[\left[\left[\left[\hat{H}, \hat{T}_1\right], \hat{T}_1\right], \hat{T}_1\right], \hat{T}_1\right] |\Phi_0\rangle = \frac{1}{24}\langle 0|\, E_a^i E_b^j \sum_{cdefklmn} t_c^k t_d^l t_e^m t_f^n \left[\left[\left[\left[\hat{H}_n, E_k^c\right], E_l^d\right], E_m^e\right], E_n^f\right] |0\rangle \tag{193}$$

Term 5 is exactly the same as term 4.2 but the t-amplitude is composed of four t1-amplitude instead of one t2-amplitude and two t1-amplitudes and instead of $\frac{1}{24}$ it is $\frac{1}{48}$ coming from the double counting of the unrestricted sum ($\frac{1}{24}$) and evaluating the quintic term ($\frac{1}{2}$):

$$
\begin{aligned}
\frac{1}{\ } \langle 0| E^i_a E^j_b \sum_{cdefklmn} t^k_c t^l_d t^m_e t^n_f \Big[\Big[\Big[\Big[\hat{H}_n, E^c_k\Big], E^d_l\Big], E^e_m\Big], E^f_n\Big] |0\rangle \\
= \frac{1}{48} P^{ij}_{ab} \Bigg(\sum_{cdmn} t^j_c t^i_d t^m_b t^n_a \langle mn|cd\rangle + \sum_{cdmn} t^j_c t^j_d t^m_a t^n_b \langle nm|cd\rangle \\
+ \sum_{celn} t^j_c t^l_b t^i_e t^n_a \langle ln|ce\rangle + \sum_{celn} t^j_c t^l_a t^i_e t^n_b \langle nl|ce\rangle \\
+ \sum_{cflm} t^j_c t^l_b t^m_a t^i_f \langle lm|cf\rangle + \sum_{cflm} t^j_c t^l_a t^m_b t^i_f \langle ml|cf\rangle \\
+ \sum_{cdmn} t^i_c t^j_d t^m_b t^n_a \langle mn|dc\rangle + \sum_{cdmn} t^i_c t^j_d t^m_a t^n_b \langle nm|dc\rangle \\
+ \sum_{dekn} t^k_b t^j_d t^i_e t^n_a \langle kn|de\rangle + \sum_{dekn} t^k_a t^j_d t^i_e t^n_b \langle nk|de\rangle \\
+ \sum_{dfkm} t^k_b t^j_d t^m_a t^i_f \langle km|df\rangle + \sum_{dfkm} t^k_a t^j_d t^m_b t^i_f \langle mk|df\rangle \\
+ \sum_{celn} t^l_b t^i_c t^j_e t^n_a \langle ln|ec\rangle + \sum_{celn} t^{il}_{ca} t^j_e t^n_b \langle nl|ec\rangle \\
+ \sum_{deln} t^j_b t^l_d t^i_e t^i_a \langle ln|ed\rangle + \sum_{dekl} t^k_a t^l_d t^i_e t^j_b \langle lk|ed\rangle \\
+ \sum_{efkl} t^k_b t^l_a t^j_e t^i_f \langle kl|ef\rangle + \sum_{efkl} t^k_a t^l_b t^j_e t^j_f \langle lk|ef\rangle \\
+ \sum_{cflm} t^i_c t^l_b t^m_a t^j_f \langle lm|fc\rangle + \sum_{cflm} t^i_c t^l_a t^m_b t^j_f \langle ml|fc\rangle \\
+ \sum_{dfkm} t^k_b t^i_d t^m_a t^j_f \langle km|fd\rangle + \sum_{dfkm} t^k_a t^i_d t^m_b t^j_f \langle mk|fd\rangle \\
+ \sum_{efkl} t^k_b t^l_a t^i_e t^j_f \langle kl|fe\rangle + \sum_{efkl} t^k_a t^l_b t^i_e t^j_f \langle lk|fe\rangle \Bigg)
\end{aligned}
\tag{194}
$$

2. PNO spin-adapted CCSD

In order to account for the nonorthogonality of different pair external correlation spaces is to generalized the form of the expression via Wick's theorem to include nonorthogonal basis. When evaluating particle contractions, the virtual contraction results to an overlap term due to the nonorthogonal nature of the virtual space of the PNO basis:

$$\langle \phi_i^{\bar{a}} | \phi_k^c \rangle = S_{ac}\delta_{i,k} \tag{195}$$

and

$$\left\langle \phi_{ij}^{\bar{a}\bar{b}} \middle| \phi_{kl}^{cd} \right\rangle = P_{ij}^{ab} S_{ac} S^{bd} \delta_{ij,kl} = P_{kl}^{cd} S_{ac} S_{bd} \delta_{ij,kl}. \tag{196}$$

There are assumptions made throughout the scheme such that for any amplitudes the excitation is associated to a specific pair occupied. For single amplitudes, t_a^i, we assume the excitation to be from the diagonal pairs, ii , while for the doubles amplitudes, t_{ab}^{ij} , we assume the excitation from a specific pair ij. This also goes for the residuals, R_a^I and R_{ab}^{ij}. Another assumption we make is for any integrals that is associated to those amplitudes would contain the same pair excitation. For instance, taking a look at the energy equation, 2.1 Energy Term 1.1

$$\langle 0| \left[\hat{H}_n, \hat{T}_1\right] |0\rangle = 2f_{a_{ii}}^i t_{a_{ii}}^i, \tag{197}$$

Term 1.2

$$\frac{1}{2}\left[\hat{H}_n, \hat{T}_1, \hat{T}_1\right] = \frac{1}{2} P_{ab}^{ij} t_{a_{ii}}^i t_{b_{jj}}^j L_{ija_{ii}b_{jj}} = t_{a_{ii}}^i t_{b_{jj}}^j L_{ija_{ii}b_{jj}}, \tag{198}$$

and Term 1.3

$$\langle 0| \left[\hat{H}_n, \hat{T}_2\right] |0\rangle = \frac{1}{2} P_{ab}^{ij} t_{a_{ij}b_{ij}}^{ij} L_{ija_{ij}b_{ij}} = t_{a_{ij}b_{ij}}^{ij} L_{ija_{ij}b_{ij}}. \tag{199}$$

The evaluation of the energy expression results to

$$E = 2f_{a_{ii}}^i + t_{a_{ii}}^i t_{b_{jj}}^j L_{ija_{ii}b_{jj}} + t_{a_{ij}b_{ij}}^{ij} L_{ija_{ij}b_{ij}} = 2f_{a_{ii}}^i + \tau_{a_{ij}b_{ij}}^{ij} L_{ija_{ij}b_{ij}} \tag{200}$$

2.2 Singles residual

- Term 1

$$
\begin{aligned}
\langle\phi_i^a|\,\hat{H}\,|\Phi_0\rangle &= \sum_{pq} f_{pq}\,\langle\Phi_0|\,E_a^i E_p^q\,|\Phi_0\rangle + \frac{1}{2}\sum_{pqrs} g_{rs}^{pq}\,\langle\Phi_0|\,E_a^i E_{rs}^{pq}\,|\Phi_0\rangle \\
&= \sum_{pq} f_q^p \delta_p^i \delta_q^a \\
&= f_{a_{ii}}^i
\end{aligned}
\tag{201}
$$

- Term 2

$$
\langle\phi_i^a|\left[\hat{H},\hat{T}\right]|\Phi_0\rangle = \langle 0|\,E_a^i\big[\hat{H}_n,\hat{T}_1\big] + E_a^i\big[\hat{H}_n,\hat{T}_2\big]\,|0\rangle \tag{202}
$$

where

$$
\begin{aligned}
\langle 0|\,E_a^i\big[\hat{H}_n,\hat{T}_1\big]\,|0\rangle &= \langle 0|\,E_a^i \sum_{ck} t_c^k \big(\sum_b f_{bc}E_k^b - \sum_j f_{kj}E_j^c + \sum_{bj} L_{bkjc}E_j^b\big)\,|0\rangle \\
&= \sum_{ck} t_c^k \big(\sum_b f_{bc}\,\langle\phi_i^a|\phi_k^b\rangle - \sum_j f_{kj}\,\langle\phi_i^a|\phi_j^c\rangle + \sum_{bj} L_{bkjc}\,\langle\phi_i^a|\phi_j^b\rangle\big) \\
&= \sum_{ck} t_c^k \Big(\sum_b f_{bc}S_{ab}(\delta_{i,k}) - \sum_j f_{kj}S_{ac}(\delta_{i,j}) + \sum_{bj} L_{bkjc}S_{ab}(\delta_{i,j})\Big) \\
&= \sum_{cb} f_{bc_{ii}}S_{ab}t_{c_{ii}}^i - \sum_{ck} f_{ki}t_c^k S_{ac} + \sum_{ckb} L_{bkic}S_{ab}t_c^k = 0
\end{aligned}
\tag{203}
$$

and

$$
\begin{aligned}
\langle 0|\,E_a^i\big[\hat{H}_n,\hat{T}_2\big]\,|0\rangle =& \frac{1}{2}\sum_{cdkl} t_{cd}^{kl}\Big(\langle 0|\,E_a^i\big[\big[\hat{H}_n,E_{ck}\big],E_{dl}\big]\,|0\rangle \\
&+ \langle 0|\,E_a^i E_l^d\big[\hat{H}_n,E_{ck}\big]\,|0\rangle + \langle 0|\,E_a^i E_k^c\big[\hat{H}_n,E_{dl}\big]\,|0\rangle\Big)
\end{aligned}
\tag{204}
$$

such that the first term is

$$
\begin{aligned}
\frac{1}{2}\sum_{cdkl} t^{kl}_{cd} \langle 0| E^i_a \big[\big[\hat{H}_n, E_{ck}\big], E_{dl}\big] |0\rangle &= \frac{1}{2}\sum_{cdkl} t^{kl}_{cd} \langle 0| E^i_a \Big(- f_{lc} E_{dk} - \sum_m L_{klcm} E_{dm} + \sum_e L_{elcd} E_{ek} \Big) |0\rangle \\
&= \frac{1}{2}\sum_{cdkl} t^{kl}_{cd} \Big(- f_{lc} \langle 0| E^i_a E_{dk} |0\rangle - \sum_m L_{klcm} \langle 0| E^i_a E_{dm} |0\rangle \\
&+ \sum_e L_{elcd} \langle 0| E^i_a E_{ek} |0\rangle \Big) \\
&= \frac{1}{2}\sum_{cdkl} t^{kl}_{cd} \Big(- f_{lc} \left\langle \phi^a_i \middle| \phi^d_k \right\rangle - \sum_m L_{klcm} \left\langle \phi^a_i \middle| \phi^d_m \right\rangle + \sum_e L_{elcd} \left\langle \phi^a_i \middle| \phi^e_k \right\rangle \Big) \\
&= \frac{1}{2}\sum_{cdkl} t^{kl}_{cd} \Big(- f_{lc}(2\delta_{ai,dk}) - \sum_m L_{klcm}(2\delta_{ai,dm}) + \sum_e L_{elcd}(2\delta_{ai,ek}) \Big) \\
&= -\sum_{cl} t^{il}_{ca} f_{lc} - \sum_{ckl} t^{kl}_{ca} L_{klci} + \sum_{cdl} t^{il}_{cd} L_{alcd} = 0
\end{aligned}
\tag{205}
$$

The other two terms are

$$
\begin{aligned}
\frac{1}{2}\sum_{cdkl} t^{kl}_{cd} \langle 0| E^i_a E^d_l \big[\hat{H}_n, E_{ck}\big] |0\rangle &= \langle 0| E^i_a \frac{1}{2}\sum_{cdkl} t^{kl}_{cd} 2 f_{kc} |0\rangle \\
&= \frac{1}{2}\sum_{cdkl} t^{kl}_{cd} 2 f_{kc} \langle 0| E^i_a E_{dl} |0\rangle \\
&= \frac{1}{2}\sum_{cdkl} t^{kl}_{cd} 2 f_{kc} \left\langle \phi^a_i \middle| \phi^d_l \right\rangle \\
&= \frac{1}{2}\sum_{cdkl} t^{kl}_{cd} 2 f_{kc} (2\delta_{ai,dl}) \\
&= \sum_{ck} 2 t^{ki}_{ca} f_{kc} = 0
\end{aligned}
\tag{206}
$$

and

$$\begin{aligned}
\langle 0| E^i_a E^c_k \big[\hat{H}_n, E_{dl}\big] |0\rangle &= \langle 0| E^i_a \sum_{cdkl} t^{kl}_{cd} 2 f_{ld} |0\rangle \\
&= \sum_{cdkl} t^{kl}_{cd} 2 f_{ld} \langle 0| E^i_a E_{ck} |0\rangle \\
&= \sum_{cdkl} t^{kl}_{cd} 2 f_{ld} \langle \phi^a_i | \phi^c_k \rangle \\
&= \sum_{cdkl} t^{kl}_{cd} 2 f_{ld} (2\delta_{ai,ck}) \\
&= \sum_{dl} 2 t^{il}_{ad} f_{ld} = 0
\end{aligned} \tag{207}$$

2. History of Local Correlation

Article Title: Author: Year: Summary: Implementation:

Article Title: Efficient and accurate local approximations to coupled-electron pair approaches: An attempt to revive the pair natural orbital method **Author:** Frank Neese, Frank Wennmohs, and Andreas Hansen **Year:** 2009

Summary: Efficient production level implementation of the closed shell CEPA and CPF methods is reported that can be applied to medium sized molecules in the range of 50-100 atoms and up to about 2000 basis functions. The internal space is localized while the external space is compressed through the method pair natural orbitals (PNOs). The DF or RI approximation is used to speed up the integral transformation. Cutoff parameters are used to control the size of the significant pair list, the average number of PNOs per electron pair, and the number of contributing basis functions per PNO.

Important details: Improvement of PNOs through the use of symmetric and antisymmetric combinations of the amplitudes and integrals.

Truncation parameters: (1) Truncation of the PNO expansion of each pair is parameterized by the cutoff, T_{cutPNO}, which is compared to the occupation number $\bar{n}^{ij}_{\tilde{a}}$ obtained through the diagonalization of the pair density. The default is $3.33 * 10^{-7}$. (2) Locality is exploited for occupied pairs but still keep the virtual space of those pairs (3) Mulliken population

Implementation: (1) With RI approximation, the three sets of three index integrals are generated, $(ij|K)$, $(ia|K)$, $(ab|K)$. (2) four index integral classes are produced and stored, $(ik|jl)$,$(ik|ja)$, $(ij|ab)$, and $(ia|jb)$. Note this is the worst scaling step of the entire procedure N^5 (3) Generate the PNO, obtaining the transformation matrix, from the pair density (N^4) (4) For a given pair, transform them into a quasicanonical form that diagonalizes the Fock operator ... advantageeous for the amplitude update procedure and also saves some computer time in the intrapair contributions to the residual vector that involve the virtual part of the Fock operator. (5) (Skipping the transformation of the RI approximated integrals) A loop over pairs is used to generate the integrals over PNOs Looks like the transformation scales to N^4 if we assume that the dimensionality of the transformation matrix becomes constant for larger molecules (6) Calculate of the pair-pair interaction of the Coulomb and Exchange operators of pair ij to various pairs (7) the most expensive contribution involves the four internal exchange integrals $(ik|jl)$ with the doubles amplitudes ($N^8 -> o^4 v_{ij}^4$). For speed-up, check the absolute value of the integral and cut it off with a conservative threshold of 10^{-14}.

Previous work done for the development of low-order scaling correlation methods: (1) Werner and co-workers M. Schütz, G. Hetzer, and H. J. Werner, J. Chem. Phys. 111, 5691 (1999)

Article Title: Efficient and accurate approximations to the local coupled cluster singles doubles method using a truncated pair natural basis **Author:** Frank Neese, Andres Hansen, and Dimitrios G. Liakos **Year:** 2009 **Summary:** A production level implementation of LPNO-QCISD and LPNO-CCSD is reported with two variants: (1) $LPNO_2 - CCSD$ recovering $98.7\% - 99.3\%$ with modest disk space requirements and (2) $LPNO_1$ - CCSD recovers $99.75\% - 99.95\%$ with the requirement of storing the Coulomb and exchange operator with up to two-external indcies to be stored on disk. The total wall clock time required for medium sized molecules is only two to four times that of the preceding SCF. **Important details:** The most expensive term are the evaluation of the external exchange operator, eq. 15, which contains $\tau_a^{ij} = \sum_{cd}(ac|bd)\tau_{cd}^{ij}(N^6 - > o^2v^4)$ In practice, only need 10-30 PNOs on average to recover more than $99.8\% - >$ this average changes roughly as the square root of the number of basis function for fixed system size. Implementation: $LPNO_2 - CCSD$ (1) Initial integral transformation, the Coulomb and Exchange operators are generated and are then projected on the fly to the PNO basis of the "target" pair in question using overlap terms (these overlap terms are precomputed and stored -¿ only increases linearly with system size) (2) only integrals over canonical orbitals that are stored are the integrals with no and at most one-external label. All the others are generated and converted to PNOS then stored. (3) singles Fock Matrix G(t1) is calculated in an AO direct fashion $- >$ can get expensive but there is an approximation that can be used (RIJCOSX) which is for $LPNO_1$ CCSD (4) Problematic issue within the PNO form of the doubles residuals, for example, is equation 15 in the PNO form where there is an unrestricted sum over k that involves integrals that have not been generated since this cannot be done without significant increased effort which is ignored as an approximation. (5) Singles amplitudes are projected onto the PNO basis of appropriate pair whenever necessary.

Difference with $LPNO_1 - CCSD$

(6) The projection from one pair to the other introduces a significant error (due to it not being exact?) therefore instead $- >$ the pair-pair interaction are precomputed as in the LPNO-CEPA method and doing the (7) of the LPNO-CEPA 2009 implementation for the linear terms but for nonlinear terms is kept like (1)

Article Title: An efficient and near linear scaling pair natural orbital based local coupled cluster method **Author:** Christoph Riplinger and Frank Neese **Year:** 2013 **Summary:** Redesign of LPNO-CCSD $- >$ DLPNO-CCSD with the construction of the PNOs which are expanded in a set of PAOs and transformation and truncation of singles amplitude leading to nearly linear scaling wrt to system size. No other approximation is made with the largest calculation reported > 8800 basis functions > 450 atoms, taking less time than the preceding SCF calculation. **Important details:** The construction of the PNOs using PAOs requires the extended domain for each pair ij such that using the T_{cutMKN} leads to union of ij, ik, kj. Electron pair prescreening (read more if needed) Implementation: (1) Singles are hence expanded in a set of PNOs that conice with the PNOs of the diagonal pairs. (2) The most complicated integral transformation generates a linear scaling set of integrals $(\tilde{u}'\tilde{v}'|K)$. (3) The second integral transformation generates all required integrals over PNOs, relevant subset of integrals: $(\tilde{u}'\tilde{v}'|K)$, $(k\tilde{v}'|K)$, and $(kl|K)$. Also, Three index integrals and four index integrals are generated and stored. (5) The third integral transformation: the pair-pair interaction is now generated to the appropriate pair instead of a projection of one pair to the other. Therefore each pair ij that interacts with J^{ik} and K^{ik} are generated and stored in a "pair interaction file".