From Canonical CCSD to Local CCSD

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1. Spin-adapted CCSD

The derivation of the spin-adapted CCSD is currently in progress using Wick's theorem with the addition of the biorthogonal basis for the doubles residual. The expression given so far has been translated from the implementation of this method within PyCC.

Notation

For Fock matrices that contains occupied and virtual indices such as f_{ia} will be written as f_a^i for clarity when comparing canonical and PNO forms of the CCSD. With the same reasoning, the single and double amplitudes are written as t_a^i and t_{ab}^{ij}. 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

$$\begin{aligned} R_a^i =& f_a^i + \sum_e t_e^i F_{ae} - \sum_m t_a^m F_{mi} + \sum_{me} \left(2t_{ae}^{im} - t_{ea}^{im}\right) F_{me} \\ &+ \sum_{nf} t_f^n L_{nafi} + \sum_{mef} \left(2t_{ef}^{mi} - t_{fe}^{mi}\right) K_{maef} - \sum_{mne} t_{ae}^{mn} L_{nmei} \end{aligned} \tag{1}$$

where K is the two-electron integral and L is $2K_{ab}^{ij} - K_{ba}^{ij}$.

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

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

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

and

$$\left|\bar{a}^{ij}\right\rangle = \sum_a d^{ij}_{a\bar{a}} \left|a\right\rangle . \tag{15}$$

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

$$\left\langle \bar{a}^{ij} \middle| \bar{b}^{kl} \right\rangle \equiv S^{ij,kl}_{\bar{a}_{ij}\bar{b}_{kl}}. \tag{16}$$

Though, the overlap terms appears 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 single amplitudes is only 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

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

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 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 residuals 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 double amplitudes expanded with the PNOs of pair mn. Looking at the double residuals now, we notice that F_{be} intermediate is coupled to the double 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 the double 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

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

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

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

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

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

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

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