DFOCC: DF-CCSD(T) equations

Reference: DFOCC in Psi4 by Uğur Bozkaya (performs density-fitted orbital-optimized CC calculations)

1 Notations

Four-index integral (in chemists' notation):

$$(pq|rs) = \sum_Q B_{pq}^Q B_{rs}^Q, \tag{1}$$

Four-index integral (in physicists' notation):

$$\langle pr|qs\rangle = \sum_Q B_{pq}^Q B_{rs}^Q, \tag{2}$$

where B_{pq}^Q is the three-index density fitting integral.

Orbital and Basis Information:

- Number of doubly occupied orbitals $(i, j, \ldots)$: N_O
- Number of virtual orbitals $(a, b, \ldots)$: N_V
- Number of molecular orbitals: $N_O + N_V$
- Number of auxiliary basis functions (Q): N_{aux}
- Orbital energy of orbital p: ϵ_p

2 3-index intermediates

First, we construct three-index intermediates that are used in $\hat{T}_1$ and $\hat{T}_2$ equations. The intermediates in Table 1. will be used in the following sections.

Table 1: Explicit expression of three-index intermediates.

$\mathbf{T^Q_{ia}} = \sum_{jb} B^Q_{jb} u^{ab}_{ij}$, where $u^{ab}_{ij} = 2t^{ab}_{ij} - t^{ba}_{ij}$
$\mathbf{t^Q} = 2\sum_{mf} t^f_m B^Q_{mf}$
$\mathbf{t^Q_{ij}} = \sum_e t^e_i t^Q_{je}$, $\mathbf{t^Q_{ia}} = \sum_e t^f_i t^Q_{fa}$, $\mathbf{t^Q_{ai}} = \sum_e t^a_m t^Q_{mi}$, $\mathbf{t^Q_{ab}} = \sum_e t^a_m t^Q_{mb}$
$\mathbf{\tilde{T}^Q_{ia}} = \sum_m t^a_m t^Q_{im}$
$\mathbf{t'^Q_{ia}} = t^Q_{ia} - t^Q_{ai} - \tilde{T}^Q_{ia}$
$\mathbf{Tau^Q_{ia}} = \sum_{mf} (2\tau^{af}_{im} - \tau^{af}_{mi}) B^Q_{mf}$, where $\tau^{ab}_{ij} = \frac{1}{2} t^a_i t^b_j$
$\mathbf{Tau'^Q_{ia}} = t^Q_{ia} + Tau^Q_{ia}$
$\mathbf{Tau''^Q_{ia}} = -t^Q_{ia} + Tau^Q_{ia}$

Table 2: t_1-transformed Fock matrix blocks

$\mathbf{F_{ov}} \Rightarrow \mathbf{F_{me}} = \sum_Q B^Q_{me} t^Q - \sum_{Qn} t^Q_{nm} B^Q_{ne}$
$\mathbf{F_{oo}} \Rightarrow \mathbf{F_{mi}} = \sum_Q B^Q_{mi} t^Q + \sum_{Qe} Tau''^Q_{ie} B^Q_{me} + \frac{1}{2}\sum_e t^e_i F_{me}$
$\mathbf{F_{vv}} \Rightarrow \mathbf{F_{ae}} = \sum_Q B^Q_{me} t^Q - \sum_{Qm} Tau'^Q_{ma} B^Q_{me} - \frac{1}{2}\sum_m t^a_m F_{me}$

3 $\hat{T}_1$ equation

3.1 F intermediates

3.2 $\hat{T}_1$ residual

The terms are arranged to match Equation (19)-(22)

$$
\begin{aligned}
R^a_i = &\sum_e F_{ae} t^e_i - \sum_m t^a_m F_{mi} && \Rightarrow F_{ai} \\
&+ \sum_Q t^Q B^Q_{ia} + \sum_{Qe} T^Q_{ie} B^Q_{ea} && \Rightarrow A^a_i \\
&- \sum_{Qm} (T^Q_{ma} + t^Q_{ma}) B^Q_{mi} && \Rightarrow B^a_i \\
&+ \sum_{me} u^{ae}_{im} F_{me} && \Rightarrow C^a_i
\end{aligned}
\tag{3}
$$

Update the $\hat{T}_1$ amplitude,

$$t^a_i = t^a_i + R^a_i / D^a_i. \tag{4}$$

The denominator is defined as

$$D^a_i = \epsilon_a - \epsilon_i, \tag{5}$$

where ϵ_p is the orbital energy of the orbital p.

Note that t_1-dressed B^Q_{pq} integrals are not explicitly computed as described in the reference, but arranged into the equations with t_1 and bare B^Q_{pq}.

4 $\hat{T}_2$ equation

4.1 Four-index intermediates

Table 3: Two-particle excitation terms

$\mathbf{u_{ij}^{ab}} = 2t_{ij}^{ab} - t_{ji}^{ab}$
$\mathbf{Tau_{ij}^{ab}} = t_{ij}^{ab} + t_i^a t_j^b$
$\mathbf{\tilde{Tau}_{ij}^{ab}} = t_{ij}^{ab} + \frac{1}{2} t_i^a t_j^b$

4.2 $\mathbf{W_{mnij}T_2 \rightarrow R_{ij}^{ab}}$

$$W_{mnij} = \langle mn|ij\rangle + \sum_Q (t_{im}^Q B_{jn}^Q + t_{jn}^Q B_{im}^Q) + \sum_{ef} Tau_{ij}^{ef} \langle mn|ef\rangle \tag{6}$$

- For the first term, the two-electron integral(TEI) is calculated as

$$W_{mnij} = \langle mn|ij\rangle = \sum_Q B_{im}^Q B_{jn}^Q. \tag{7}$$

- For the second term, we have

$$X_{ij}^{mn} = \sum_Q t_{im}^Q B_{jn}^Q \tag{8}$$

and then

$$W_{mnij} + = P_{ij}^{mn} X_{ij}^{mn}, \tag{9}$$

where P_{ij}^{ab} is the permutation operator defined as $P_{ij}^{ab} X_{ij}^{ab} = X_{ij}^{ab} + X_{ji}^{ba}$.

- For the third term, the packed symmetric(+) and antisymmetric(-) four-index tensor is utilized for both Tau_{ij}^{ef} and $\langle mn|ef\rangle$ for an efficient algorithm. Define the symmetric and antisymmetric operators as

$$\hat{S} \equiv \frac{1}{2}(\hat{I} + \hat{P}) \tag{10}$$

and

$$\hat{A} \equiv \frac{1}{2}(\hat{I} - \hat{P}) \tag{11}$$

respectively, where $\hat{I}$ is the identity operator and $\hat{P} X_{ij}^{ab} = X_{ji}^{ab}$ or X_{ij}^{ba} so that $\hat{P}^2 = \hat{I}$. To achieve more savings, the summation can be limited to $i \geq j$ and $a \geq b$ for a tensor X_{ij}^{ab}.
Tau_{ij}^{ef} :

$$(+)Tau_{i \geq j}^{a \geq b} = \frac{1}{2}(Tau_{ij}^{ef} + Tau_{ji}^{ef})(2 - \delta_{ef}) \tag{12}$$

$$(-)Tau_{i \geq j}^{a \geq b} = \frac{1}{2}(Tau_{ij}^{ef} - Tau_{ji}^{ef})(2 - \delta_{ef}) \tag{13}$$

$\langle mn|ef\rangle \Rightarrow V_{mn}^{ef}$:

$$V_{mn}^{e \geq f} = \sum_Q B_{me}^Q B_{nf}^Q \tag{14}$$

$$(+)V_{m \geq n}^{e \geq f} = \frac{1}{2}(V_{mn}^{ef} + V_{nm}^{ef}) \tag{15}$$

$$(-)V_{m\geq n}^{e\geq f} = \frac{1}{2}(V_{mn}^{ef} - V_{nm}^{ef}) \tag{16}$$

W_{mnij}:

$$(+)W_{mnij}\ (m \geq n, i \geq j) = \sum_{e\geq f} (+)Tau_{i\geq j}^{e\geq f} (+)V_{m\geq n}^{e\geq f} \tag{17}$$

$$(-)W_{mnij}\ (m \geq n, i \geq j) = \sum_{e\geq f} (-)Tau_{i\geq j}^{e\geq f} (-)V_{m\geq n}^{e\geq f} \tag{18}$$

$$W_{mnij} += (+)W_{mnij} + \epsilon_{mn}\epsilon_{ij}(-)W_{mnij}, \tag{19}$$

where

$$\epsilon_{pq} = \begin{cases} 1 & \text{if } p \geq q \\ -1 & \text{if } p < q \end{cases} \tag{20}$$

The same technique can be applied to the contraction between W_{mnij} and the $\hat{T}_2$ amplitude in the next step.

$$S(W_{mnij}) = \frac{1}{2}(W_{mnij} + W_{nmij}) \tag{21}$$

$$A(W_{mnij}) = \frac{1}{2}(W_{mnij} - W_{nmij}) \tag{22}$$

$$S_{i\geq j}^{a\geq b} = \sum_{m\geq n} (+)Tau_{m\geq n}^{a\geq b} S(W_{mnij})_{m\geq n, i\geq j} \tag{23}$$

$$A_{i\geq j}^{a\geq b} = \sum_{m\geq n} (-)Tau_{m\geq n}^{a\geq b} A(W_{mnij})_{m\geq n, i\geq j} \tag{24}$$

Finally, we have the contribution to the $\hat{T}_2$ residual as

$$\sum_{mn} Tau_{mn}^{ab} W_{mnij} \Rightarrow S_{ij}^{ab} + \epsilon_{ij}\epsilon_{ab} A_{ij}^{ab} \to R_{ij}^{ab}. \tag{25}$$

Note that limiting the summation to $e \geq f$ in Eq. 12 reduces the cost of the construction of the four-index tensor by a factor 2. The cost of the contraction with the CC amplitudes is reduced by a factor 4 as shown in Eq. 15, 16 and Eq. 21, 22.

4.3 $\mathbf{W_{mbej} T_2 \to R_{ij}^{ab}}$

We first calculate

$$W_{mbej} = \langle mb|ej\rangle + \sum_{Q} ({t'}_{jb}^{Q} + \frac{1}{2}T_{jb}^{Q}) B_{me}^{Q} - \frac{1}{2}\sum_{nf} t_{jn}^{bf} \langle mn|ef\rangle, \tag{26}$$

where the TEIs are calculated as

$$\langle mb|ej\rangle = \sum_{Q} B_{me}^{Q} B_{jb}^{Q} \tag{27}$$

and

$$\langle mn|ef\rangle = \sum_{Q} B_{me}^{Q} B_{nf}^{Q}. \tag{28}$$

And then we calculate

$$W'_{mbej} = \langle me|jb\rangle + X_{jm}^{be} - \frac{1}{2}\sum_{nf} \langle mn|ef\rangle t_{nj}^{bf}, \tag{29}$$

where

$$\langle me|jb\rangle = \sum_{Q} B_{mj}^{Q} B_{eb}^{Q}, \tag{30}$$

$$\langle mn|ef\rangle = \sum_{Q} B_{me}^{Q} B_{nf}^{Q}, \tag{31}$$

and

$$X_{jm}^{be} = -\sum_{Q} t_{be}^{Q}(t_{jm}^{Q} + B_{jm}^{Q}) + \sum_{Q} t_{jm}^{Q} B_{be}^{Q} \tag{32}$$

With W_{mbej} and W'_{mbej}, we construct

$$C_{ij}^{ab} = -\sum_{me} t_{mi}^{ae} W'_{mbej}, \tag{33}$$

$$\tilde{C}_{ij}^{ab} = \frac{1}{2}(C_{ij}^{ab} + C_{ji}^{ba}), \tag{34}$$

and

$$D_{ij}^{ab} = \frac{1}{2}\sum_{me} u_{im}^{ae}(2W_{mbej} - W'_{mbej}). \tag{35}$$

The contribution to the $\hat{T}_2$ residual is obtained from

$$(\tilde{C}_{ij}^{ab} + 2\tilde{C}_{ij}^{ba}) + (D_{ij}^{ab} + D_{ji}^{ba}) \to R_{ij}^{ab}. \tag{36}$$

4.4 $\mathbf{W_{ijam} T_2 \to R_{ij}^{ab}}$

$$W_{ijam} = \sum_{ef} Tau_{ij}^{ef} \langle am|ef\rangle \tag{37}$$

Both Tau_{ij}^{ef} and $\langle am|ef\rangle$ are constructed using packed symmetric and antisymmetric four-index tensors as described in section 4.1. For $\langle am|ef\rangle$ specifically, since it contains three virtual indices, the three-index intermediate for a fixed m is calculated to avoid storing the whole set of $N_O N_V^3$ tensors. Its contribution to W_{mnij} for a fixed m is then calculated in each loop.

$\langle am|ef\rangle$ with fixed m is calculated as

$$V_{ae,f}^{[m]} = \sum_{Q} B_{ae}^{Q} B_{[m]f}^{Q} \tag{38}$$

The symmetric and antisymmetric tensors are constructed as

$$(+)V_{ae,f}^{[m]} = \frac{1}{2}(V_{ae,f}^{[m]} + V_{af,e}^{[m]}) \tag{39}$$

and

$$(-)V_{ae,f}^{[m]} = \frac{1}{2}(V_{ae,f}^{[m]} - V_{af,e}^{[m]}) \tag{40}$$

respectively. For the contraction with the $\hat{T}_2$ amplitude, we have

$$S_{i\geq j,a}^{[m]} = \sum_{e\geq f} (+)Tau_{i\geq j}^{e\geq f}(+)V_{a,e\geq f}^{[m]} \tag{41}$$

$$A_{i\geq j,a}^{[m]} = \sum_{e\geq f} (-)Tau_{i\geq j}^{e\geq f}(-)V_{a,e\geq f}^{[m]} \tag{42}$$

After looping over m, we obtain $S_{i\geq j,am}$ and $A_{i\geq j,am}$ as symmetric and antisymmetric tensors for W_{ijam} when $i \geq j$.

$$W_{ijam} = S_{i\geq j,am} + \epsilon_{ij} A_{i\geq j,am} \tag{43}$$

Its contribution to the residual is calculated as

$$X_{ij}^{ab} = -\sum_{m} t_{m}^{b} W_{ijam} \tag{44}$$

$$X_{ij}^{ab} + X_{ji}^{ba} \to R_{ij}^{ab} \tag{45}$$

4.5 $\mathbf{W_{abef} T_2 \rightarrow R_{ij}^{ab}}$

In this part, the four-virtual-index tensor $\langle ab|ef\rangle$ is needed. To avoid constructing and storing the whole set of N_V^4 tensor, three-index tensors with fixed a are calculated in each loop.

$\langle ab|ef\rangle$ with fixed a is calculated as

$$V_{bf,e}^{[a]} = \sum_Q B_{[a]e}^Q B_{bf}^Q \tag{46}$$

$$(+)V_{b,e\geq f}^{[a]} = \frac{1}{2}(V_{bf,e}^{[a]} + V_{be,f}^{[a]}) \tag{47}$$

$$(-)V_{b,e\geq f}^{[a]} = \frac{1}{2}(V_{bf,e}^{[a]} - V_{be,f}^{[a]}) \tag{48}$$

For the contraction with the $\hat{T}_2$ amplitude, the symmetric/antisymmetric tensors are obtained as

$$S_{i\geq j,b}^{[a]} = \sum_{e\geq f}(+)Tau_{i\geq j}^{e\geq f}(+)V_{b,e\geq f}^{[a]} \tag{49}$$

$$A_{i\geq j,b}^{[a]} = \sum_{e\geq f}(-)Tau_{i\geq j}^{e\geq f}(-)V_{b,e\geq f}^{[a]} \tag{50}$$

After looping over a when limiting the summation to $a \geq b$, the contribution to the residual is calculated as

$$S_{i\geq j}^{a\geq b} + \epsilon_{ij}\epsilon_{ab}A_{i\geq j}^{a\geq b} \rightarrow R_{ij}^{ab} \tag{51}$$

4.6 $\hat{T}_2$ residual

With $W_{mnij}T_2$, $W_{mbej}T_2$, $W_{ijam}T_2$, and $W_{abef}T_2$ as parts of the $\hat{T}_2$ residual, we can write the whole residual as

$$R_{ij}^{ab} = P_{ij}^{ab}X_{ij}^{ab} + \langle ij|ab\rangle + W_{mnij}T_2 + W_{mbej}T_2 + W_{ijam}T_2 + W_{abef}T_2, \tag{52}$$

where

$$X_{ij}^{ab} = \sum_e t_{ij}^{ae}F_{be} - \sum_m t_{mj}^{ab}F_{mi} + \sum_Q {t'}_{ia}^{Q}B_{jb}^Q - \sum_Q t_{ai}^Q t_{jb}^Q \tag{53}$$

and

$$\langle ij|ab\rangle = \sum_Q B_{ia}^Q B_{jb}^Q. \tag{54}$$

Update the $\hat{T}_2$ amplitude,

$$t_{ij}^{ab} = t_{ij}^{ab} + R_{ij}^{ab}/D_{ij}^{ab}. \tag{55}$$

The denominator is defined as

$$D_{ij}^{ab} = \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j. \tag{56}$$

Note that the equations above can also match with Equation (10) to (16) in the reference as

$$\begin{aligned} R_{ij}^{ab} = {} & P_{ij}^{ab}X_{ij}^{ab} \\ & + \langle ij|ab\rangle && \Rightarrow \text{first term from non-}t_1\text{-transformed } B_{ia}^Q \\ & + W_{mnij}T_2 && \Rightarrow B_{ij}^{ab} \\ & + W_{mbej}T_2 && \Rightarrow C_{ij}^{ab} + D_{ij}^{ab} \\ & + W_{ijam}T_2 && \Rightarrow G_{ij}^{ab} \text{ except for the first term} \\ & + W_{abef}T_2 && \Rightarrow A_{ij}^{ab} + E_{ij}^{ab} \text{ except for the first term} \end{aligned} \tag{57}$$

and

$$
\begin{aligned}
X_{ij}^{ab} = &\sum_e t_{ij}^{ae} F_{be} && \Rightarrow \text{first term in } E_{ij}^{ab} \\
&- \sum_m t_{mj}^{ab} F_{mi} && \Rightarrow \text{first term in } G_{ij}^{ab} \\
&+ \sum_Q {t'}_{ia}^{Q} B_{jb}^{Q} - \sum_Q t_{ai}^{Q} t_{jb}^{Q} && \Rightarrow \text{first term from } t_1\text{-transformed } B_{ia}^{Q} \text{ that involves } t_1.
\end{aligned} \tag{58}
$$

5 (T) correction

$$E_{(T)} = \frac{1}{3} \sum_{ijk} \sum_{abc} [(4W_{ijk}^{abc} + W_{ijk}^{bca}) + W_{ijk}^{cba})(V_{ijk}^{abc} - V_{ijk}^{cba})]/D_{ijk}^{abc}, \tag{59}$$

where

$$W_{ijk}^{abc} = P_{ijk}^{abc} (\sum_e \langle ib|ae\rangle t_{jk}^{ec} - \sum_m \langle jm|kc\rangle t_{im}^{ab}), \tag{60}$$

$$V_{ijk}^{abc} = W_{ijk}^{abc} + t_i^a \langle jk|bc\rangle + t_j^b \langle ik|ac\rangle + t_k^c \langle ij|ab\rangle + f_{ia} t_{jk}^{bc} + f_{jb} t_{ik}^{ac} + f_{kc} t_{ij}^{ab}, \tag{61}$$

and

$$D_{ijk}^{abc} = \epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k. \tag{62}$$

P_{ijk}^{abc} is the permutation operator defined as $P_{ijk}^{abc} X_{ijk}^{abc} = X_{ijk}^{abc} + X_{ikj}^{acb} + X_{jik}^{bac} + X_{jki}^{bca} + X_{kij}^{cab} + X_{kji}^{cba}$.

A few points in the implementation are worth mentioning:

- W and V intermediates are calculated for a fixed set of i, j, k and only $i \geq j \geq k$ for an efficient algorithm.
- four-index integrals that contain one or two virtual indices are calculated on-the-fly and stored in core.
- four-index integrals that contain three virtual indices are read in as N_V^3 tensors for a fixed i if they are stored out of core.
- $E_{(T)}$ is calculated for only $i \geq j \geq k$ and $a \geq b \geq c$.

  Define

$$X_{ijk}^{abc} = P_{ijk}^{abc} (W_{abc}^{[ijk]} V_{abc}^{[ijk]}) \tag{63}$$

$$Y_{ijk}^{abc} = \tilde{V}_{abc}^{[ijk]} + \tilde{V}_{bca}^{[ijk]} + \tilde{V}_{cab}^{[ijk]} \tag{64}$$

$$Z_{ijk}^{abc} = \tilde{V}_{bac}^{[ijk]} + \tilde{V}_{cba}^{[ijk]} + \tilde{V}_{acb}^{[ijk]} \tag{65}$$

$$W^{(Y)} = W_{abc}^{[ijk]} + W_{bca}^{[ijk]} + W_{cab}^{[ijk]} \tag{66}$$

$$W^{(Z)} = W_{bac}^{[ijk]} + W_{cba}^{[ijk]} + W_{acb}^{[ijk]} \tag{67}$$

$$E_{(T)} = \sum_{i \geq j \geq k} \sum_{a \geq b \geq c} \frac{2 - (\delta_{ij} + \delta_{jk} + \delta_{ik})}{D_{ijk}^{abc}} [(Y - 2Z) W^{(Y)} + (Z - 2Y) W^{(Z)} + 3X] \tag{68}$$