Supplementary Materials to

Code Generation in ORCA: Progress, Efficiency and Tight Integration

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Input Related to CCSDT

Listing A1 Input required to generate the UHF CCSD equations.

```
$order_E 2
$order_residuals 4
$class IA Tia(i,a) 1.0 E(a,i)
$class IJAB Tijab(ab,ij) 0.25 E(a,i)E(b,j); 1.0 E(a,i)E(b,j))";

Parser p(uhf_ccsd_input);
make_uhf_cc_sigma_ec(p.Parse());
uhf_ccsd_sigma = read_file("uhf_cc_sigma.eq");
```

Listing A2 Input required to generate the UHF CCSDT equations.

```
$order_E 2
$order_residuals 4
$class IA Tia(i,a) 1.0 E(a,i)
$class IJAB Tijab(ab,ij) 0.25 E(a,i)E(b,j); 1.0 E(a,i)E(b,j)
$class IJKABC Tijkabc(abc,ijk) 0.02777777777778 E(a,i)E(b,j)E(c,k); 1.0 E(a,i)E(b,j)E(c,k))";

Parser p(uhf_ccsdt_input);
make_uhf_cc_sigma_ec(p.Parse());
uhf_ccsdt_sigma = read_file("uhf_cc_sigma.eq");
```

Listing A3 Input required to generate the UHF CCSDT-1 equations, $T_3 \rightarrow T_1$ contribution.

```
$UHF
$USE_FOCK
$H_BO
$PRINT_OPTION .eq
$TARGET Sia(i,a)
$BRA E(a,i)
$DAGGER_BRA
$KET E(A1,I1)E(A2,I2)E(A3,I3)
$KET_AMP Tijkabc(A1A2A3,I1I2I3)
$FACTOR 0.02777777777778
$<COMMUTE_H_KET>
$PRINT_H
```

Listing A4 Input required to generate the UHF CCSDT-1 equations, $T_3 \rightarrow T_2$ contribution.

```
$UHF
$USE_FOCK
$H_BO
$PRINT_OPTION .eq
$TARGET Sijab(ab,ij)
$BRA E(a,i)E(b,j)
$DAGGER_BRA
$KET E(A1,I1)E(A2,I2)E(A3,I3)
$KET_AMP Tijkabc(A1A2A3,I1I2I3)
$FACTOR 0.02777777777778
$<COMMUTE_H_KET>
$PRINT_H
```

Listing A5 Input required to generate the UHF CCSDT-1 equations, $T_2 \rightarrow T_3$ contribution.

```
$UHF
$USE_FOCK
$H_BO
$PRINT_OPTION .eq
$TARGET Sijkabc(abc,ijk)
$BRA E(a,i)E(b,j)E(c,k)
$DAGGER_BRA
$KET E(A1,I1)E(A2,I2)
$KET_AMP Tijab(A1A2,I1I2)
$FACTOR 0.25
$<COMMUTE_H_KET>
$PRINT_H
```

Listing A6 Input required to generate the UHF CCSDT-1 equations, $T_3 \rightarrow T_3$ contribution.

```
$UHF
$USE_FOCK
$H_FC
$TARGET Sijkabc(abc,ijk)
$PRINT_OPTION .eq
$FACTOR 0.027777777777777776
$BRA E(a,i)E(b,j)E(c,k)
$DAGGER_BRA
$KET E(A1,I1)E(A2,I2)E(A3,I3)
$KET_AMP Tijkabc(A1A2A3,I1I2I3)
$<COMMUTE_H_KET>
$SIMPLIFY_H
$PRINT_H
```

Fully-internally-contracted Multireference Coupled Cluster (fic-MRCC)

Denoting the reference wave function as $|0\rangle$, the fic-MRCC ansatz, $|\Psi\rangle = e^{\hat{T}} | 0 \rangle$, uses the same excitation operators $\hat{T}$ and separation into excitation classes (taken from Eq. (23) of the main text),

$$\begin{aligned}\hat{T} = &\frac{1}{2} t^{ij}_{ab} \hat{E}^a_i \hat{E}^b_j + t^{ij}_{at} \hat{E}^a_i \hat{E}^t_j + \frac{1}{2} t^{ij}_{tu} \hat{E}^t_i \hat{E}^u_j \\ &+ t^{it}_{ab} \hat{E}^a_i \hat{E}^b_t + t^{it}_{au} \hat{E}^a_i \hat{E}^u_t + t^{it}_{ua} \hat{E}^u_i \hat{E}^a_t \\ &+ t^{it}_{uv} \hat{E}^u_i \hat{E}^v_t + \frac{1}{2} t^{tu}_{ab} \hat{E}^a_t \hat{E}^b_u + t^{tu}_{av} \hat{E}^a_t \hat{E}^v_u ,\end{aligned} \tag{1}$$

in our implementation that are also employed in the fic-NEVPT2, fic-CASPT2 and the fic-MRCI ansatz.[1-3] The coupled cluster energy and residual equation

$$E = \langle 0 | \bar{H} | 0 \rangle, \tag{2}$$

$$r_K = \langle \tilde{\Phi}_K | \bar{H} | 0 \rangle, \tag{3}$$

follow from the Baker-Campbell-Hausdorff expansion of the similarity transformed Hamiltonian

$$\bar{H} = \hat{H} + [\hat{H}, \hat{T}] + \tfrac{1}{2} [[\hat{H}, \hat{T}], \hat{T}], \tag{4}$$

where the commutator is truncated at second order. Here, $\widehat{H}$ denotes the Born-Oppenheimer Hamiltonian and the subscript K, a compound index for the internally contracted configuration state functions (CSFs), $|\Phi_K\rangle$, e.g. $|\Phi_{ij}^{ab}\rangle = \widehat{E}_i^a \widehat{E}_j^b |0\rangle$. As discussed elsewhere,[4] we use contra-variant CSFs ($\widetilde{\Phi}_K$) for the projection in three of the excitation classes:

$$\left|\widetilde{\Phi}_{ij}^{ab}\right\rangle = \frac{1}{6}(2\left|\Phi_{ij}^{ab}\right\rangle + \left|\Phi_{ij}^{ba}\right\rangle), \quad (5)$$

$$\left|\widetilde{\Phi}_{it}^{ab}\right\rangle = \frac{1}{3}(2\left|\Phi_{it}^{ab}\right\rangle + \left|\Phi_{it}^{ba}\right\rangle), \quad (6)$$

$$\left|\widetilde{\Phi}_{ij}^{at}\right\rangle = \frac{1}{3}(2\left|\Phi_{ij}^{at}\right\rangle + \left|\Phi_{ij}^{ta}\right\rangle). \quad (7)$$

1. K. Andersson, P. A. Malmqvist, B. O. Roos, A. J. Sadlej and K. Wolinski, *J. Phys. Chem.*, 2002, **94**, 5483-5488.
2. C. Angeli, R. Cimiraglia and J.-P. Malrieu, *J. Chem. Phys.*, 2002, **117**, 9138-9153.
3. M. Saitow, Y. Kurashige and T. Yanai, *J. Chem. Phys.*, 2013, **139**, 044118.
4. K. Sivalingam, M. Krupička, A. A. Auer and F. Neese, *J. Chem. Phys.*, 2016, **145**, 054104.