

Supplementary Materials to

Code Generation in ORCA: Progress, Efficiency and Tight Integration

Marvin H. Lechner,^{*a} Anastasios Papadopoulos,^{*a} Kantharuban Sivalingam,^a Alexander A. Auer,^a Axel Koslowski,^a Ute Becker,^a Frank Wennmohs^a and Frank Neese^{*a}

^a Department of Molecular Theory and Spectroscopy, Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany.

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) 0.027777777777778 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 0.027777777777778
$<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 0.0277777777777778
$<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 0.02777777777777776
$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),

$$\begin{aligned} \hat{T} = & \frac{1}{2}t_{ab}^{ij}\hat{E}_i^a\hat{E}_j^b + t_{at}^{ij}\hat{E}_i^a\hat{E}_t^t + \frac{1}{2}t_{tu}^{ij}\hat{E}_i^t\hat{E}_j^u \\ & + t_{ab}^{iu}\hat{E}_i^a\hat{E}_t^b + t_{au}^{it}\hat{E}_i^a\hat{E}_t^u + t_{ua}^{it}\hat{E}_i^u\hat{E}_t^a \\ & + t_{uv}^{iu}\hat{E}_i^u\hat{E}_t^v + \frac{1}{2}t_{ab}^{tu}\hat{E}_i^t\hat{E}_u^b + t_{av}^{tu}\hat{E}_i^t\hat{E}_u^v, \end{aligned} \quad (1)$$

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

$$E = \langle 0|\bar{H}|0\rangle, \quad (2)$$

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

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

$$\bar{H} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2}[[\hat{H}, \hat{T}], \hat{T}], \quad (4)$$

where the commutator is truncated at second order. Here, \hat{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. $|\Phi_{ij}^{ab}\rangle = \hat{E}_i^a \hat{E}_j^b |0\rangle$. As discussed elsewhere,⁴ we use contra-variant CSFs ($\tilde{\Phi}_K$) for the projection in three of the excitation classes:

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

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

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

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.