Hilbert space multireference coupled clusters tailored by matrix product states: study of tetramethyleneethane

Ondřej Demel[1], **Jan Brandejs**[1], **Jakub Lang**[1], **Jiří Brabec**[1], **Libor Veis**[1], **Örs Legeza**[2], **Jiří Pittner**[1]

[1] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 18223 Prague 8, Czech Republic
[2] Strongly Correlated Systems "Lendület" Research group, Wigner Research Centre for Physics, H-1525, Budapest, Hungary

In the last decade, the quantum chemical version of the density matrix renormalization group (DMRG) method[1] has established itself as the method of choice for calculations of strongly correlated molecular systems. However, despite its favorable scaling, it is in practice not suitable for computations of dynamic correlation. Several approaches to include that in post-DMRG methods exist; in our group we focused on the tailored-CC (TCC) approach [2, 3], which employs T_1 and T_2 amplitudes from the DMRG active space to externally correct the single-reference CC method. This method works well in many situations, however, in exactly degenerate cases (with two or more determinants of equal weight), it exhibits a bias towards the reference determinant representing the Fermi vacuum. Although in some cases it is possible to use a compensation scheme to avoid this bias for energy differences, as we did in a previous work on the singlet-triplet gap in the tetramethylenethane (TME) molecule, it is certainly a drawback.

In order to overcome the single-reference bias of the TCC method, we have developed a Hilbert-space multireference version of tailored CC, which can treat several determinants on an equal footing. We have employed a multireference analysis of the DMRG wave function in the matrix product state form to get the active amplitudes for each reference determinant and their constant contribution to the effective Hamiltonian. We have implemented and compared the performance of three Hilbert-space MRCC variants - the state universal one, and the Brillouin-Wigner and Mukherjee's state specific ones.

We assess these approaches on the tetramethylenethane (TME) molecules, which is a diradical with exactly degenerate determinants at a certain geometry. Two DMRG active spaces have been selected based on orbital entropies, while the MRCC active space comprised the HOMO and LUMO orbitals needed for description of the diradical. We have also investigated the sensitivity of the results on orbital rotation of the HOMO-LUMO pair, as it is well known that Hilbert-space MRCC methods are not invariant to such transformations.

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