Combining DMRG and coupled cluster approaches for static and dynamic correlation

Jiří Pittner[1], Andrej Antalík[1], Jiří Brabec[1], Jan Brandejs[1], Ondřej Demel[1], Libor Veis[1], Örs Legeza[2], Karol Kowalski[3]

[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*
[3] *William R. Wiley Environmental Molecular Sciences Laboratory, Battelle, Pacific Northwest National Laboratory, K8-91, P.O.Box 999, Richland, WA 99352, USA*

In the last decade, the quantum chemical version of the density matrix renormalization group (DMRG) method has established itself as the method of choice for calculations of strongly correlated molecular systems. Despite its favorable scaling, it is in practice not suitable for computations of dynamic correlation. Recently we presented a method for accurate "post-DMRG" treatment of dynamic correlation based on the tailored coupled cluster (TCC) approach [2] in which the DMRG method is responsible for the proper description of non-dynamic correlation, whereas dynamic correlation is incorporated through the framework of the CC theory [3, 4]. In order to overcome the computational scaling bottleneck of traditional CC methods, we have developed an implementation of the DMRG-tailored coupled cluster method [6] based on the local pair natural orbital formalism (LPNO) [7] and domain LPNO (DLPNO) [8] approaches.

However, the tailored CC approach is based on a single reference determinant and (for a truncated T operator) thus exhibits a certain bias, particularly if several determinants have equal or comparable weight. We have thus extended the tailored-CC idea to the Hilbert-space multireference CC, where a small CAS1 space contains these most strongly contributing determinants, while a relatively large CAS2 space is treated at the DMRG level. The amplitudes in the Jeziorski-Monkhorst ansatz over CAS1 are then tailored within the CAS2 space employing a multireference generalization of the CC amplitude analysis.

Motivated by the excitation subalgebra CC approach recently introduced by Kowalski [9], we suggest an intertwined iterative combination of DMRG and CC, where DMRG represents the first iteration, tailored CC the second one, and DMRG with a Hamiltonian similarity-transformed by the T_{ext} operator obtained from previous step the third one etc. Due to the subalgebra CC properties [9], for untruncated T operator and full DMRG bond dimension this procedure converges to full CI. We developed a pilot implementation of this approach for unlimited rank of the T operator and present first numerical results.

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