ANALYSIS OF THE TAILORED COUPLED-CLUSTER METHOD IN QUANTUM CHEMISTRY

FABIAN M. FAULSTICH*, ANDRE LAESTADIUS*, SIMEN KVAAL*, ÖRS LEGEZA†, AND REINHOLD SCHNEIDER‡

We analyze mathematical properties of tailored coupled-cluster (TCC) methods as finite dimensional non-linear Galerkin schemes. This multi-reference formalism combines the single-reference coupled-cluster (CC) approach with a full configuration interaction solution covering the static correlation [1]. This keeps the computational costs low as the full configuration interaction solution is calculated for a subsystem and guarantees the high accuracy of the CC method for the dynamical correlation.

Based on Zarantonello's Theorem, we prove that TCC schemes attain locally unique solutions fulfilling a quasi-optimal error bound. To meet that end, we formally characterize the TCC function and show local strongly monotonicity and Lipschitz continuity. We introduce a CAS-EXT-gap assumption for multi-reference problems replacing the HOMO-LUMO gap which is unreasonable for statically correlated systems. From this new assumption, results from previous analyses [4, 2, 3] are adaptable to the TCC formalism presented here.

Further we perform a first error analysis revealing the mathematical complexity of the TCC-methods. Due to the basis-splitting nature of the TCC formalism, the error decomposes into several parts. Using the Aubin-Nitsche-duality method we derive a quadratic (Newton type) error bound. However, as TCC-methods do not converge to the Full-CI solution a methodological error enters this bound. This can be qualitatively explained by the basis-splitting, although the quantitative connection corresponds to a long known and unsolved problem in quantum information theory.

The motivation and importance of our work is i.a. based on the recent approach in which the Full-CI solution was approximated by the density matrix renormalization group (DMRG) method [5]. The computational results presented in [5] for the chromium dimer Cr_2 show that the precession of the DMRG-TCC method outruns traditional high accuracy CC methods like CCSD(T) and even CCSDTQ. The outstanding performance of the young DMRG-TCC method makes it an extremely promising candidate for the computation of strongly correlated systems.

REFERENCES

[1] T. KINOSHITA, O. HINO, AND R. J. BARTLETT, *Coupled-cluster method tailored by configuration interaction*, The Journal of chemical physics, 123 (2005), p. 074106, https://doi.org/10.1063/1.2000251.

[2] T. ROHWEDDER, *The continuous coupled cluster formulation for the electronic schrödinger equation*, ESAIM: Mathematical Modelling and Numerical Analysis, 47 (2013), pp. 421–447, https://doi.org/10.1051/m2an/2012035.

[3] T. ROHWEDDER AND R. SCHNEIDER, *Error estimates for the coupled cluster method*, ESAIM: Mathematical Modelling and Numerical Analysis, https://doi.org/10.1051/m2an/2013075.

[4] R. SCHNEIDER, *Analysis of the projected coupled cluster method in electronic structure calculation*, Numerische Mathematik, 113 (2009), pp. 433–471, https://doi.org/10.1007/s00211-009-0237-3.

[5] L. VEIS, A. ANTALÍK, J. BRABEC, F. NEESE, O. LEGEZA, AND J. PITTNER, *Correction to coupled cluster method with single and double excitations tailored by matrix product state wave functions*, The Journal of Physical Chemistry Letters, 8 (2016), pp. 291–291, https://doi.org/10.1021/acs.jpclett.6b01908.

*Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway (f.m.faulstich@kjemi.uio.no).

†Strongly Correlated Systems "Lendület" Research Group, Wigner Research Center for Physics, H-1525, Budapest, Hungary.

‡Modeling, Simulation and Optimization in Science, Department of Mathematics, Technische Universität Berlin, Sekretariat MA 5-3, Straße des 17. Juni 136, 10623 Berlin,Germany