Efficient quantum dynamics with the time-dependent density matrix renormalization group.

Alberto Baiardi and Markus Reiher

ETH Zürich, Laboratorium für Physikalische Chemie, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland
alberto.baiardi@phys.chem.ethz.ch

Thanks to the design of increasingly more accurate ultrafast spectroscopic techniques, it is nowadays possible to resolve the dynamics of a molecule on the natural time scales of both its electronic and nuclear motions. The most accurate algorithms available in the literature to simulate molecular dynamics at the quantum level [1-2] rely on full configuration interaction (CI) expansions of the wave function. The exponential increase of the computational cost with the system size hinders, however, straightforward extensions to large molecular systems. This unfavorable scaling can be limited by expressing the wavefunction as a matrix product state, a parametrization employed in the well-known density matrix renormalization group algorithm (DMRG). The different strategies that have been designed to integrate the resulting equation of motion are broadly defined as time-dependent DMRG (TD-DMRG).

In the present contribution, we generalize a recently developed TD-DMRG algorithm [3] to electronic- [4] and vibrational-structure [5-6] quantum chemical Hamiltonians. We apply the resulting theory to simulate both the nuclear and electronic dynamics, possibly coupled together, of molecules with several dozens of degrees of freedom [7]. We assess the accuracy of the simulations by comparison with state-of-the-art experimental measurements obtained from time-resolved techniques. Moreover, we show that TD-DMRG outperforms its time-independent parallel in the calculation of high-order molecular properties and in the simulation of spectra in regions with a high density of excited states.

References

1. H.D. Meyer, *WIRES Comp. Mol. Sci.*, **2** (2011), 351.
2. T. Sato, K.L. Ishikawa, *Phys. Rev. A*, **88**, (2013), 023402.
3. J. Haegeman, C. Lubich, I. Oseledets, B. Vandereycken, F. Verstraete, *Phys. Rev. B* **94** (2016), 1.
4. S. Keller, M. Dolfi, M. Troyer, M. Reiher, *J. Chem. Phys.* **143** (2015) 244118.
5. A. Baiardi, C.J. Stein, V. Barone, M. Reiher, *J. Chem. Theo. Comput.* **13** (2017) 3764.
6. A. Baiardi, C.J. Stein, V. Barone, M. Reiher, *J. Chem. Phys* **150** (2019), 094113.
7. A. Baiardi, M. Reiher *J. Chem. Theo. Comput.* DOI: 10.1021/acs.jctc.9b00301 (2019)