DMRG-based Approaches to Molecular Quantum Many-Body Problems

N. Glaser,[1] **M. Reiher**[1]

[1] *Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich, Switzerland*

Quantum chemical algorithms based on tensor factorizations are continuously expanding the scope of wave function-based molecular simulation methods. By leveraging very compact many-body wave function parametrizations, tensor network-based methods such as the density matrix renormalization group (DMRG) algorithm [1] can tame the computational cost of full configuration interaction (CI)-type calculations for strongly correlated molecular systems. While the DMRG algorithm is routinely applied to ground-state electronic structure problems, we present a versatile framework enabling its application to a broader range of many-body quantum problems [2,3]. We demonstrate the versatility of our DMRG-based framework by introducing the n-mode vibrational DMRG method [4], which by expressing the vibrational CI wave function as a compact matrix product state can target systems with up to 30 coupled vibrational modes described by complex potential energy surfaces. We extend our framework to excited-states algorithms, enabling the large-scale calculation of both low- and high-energy excitations. To gain further insights into the correlated wave functions and to optimize the construction of efficient tensor factorizations, we generalize quantum information measures originally introduced for electronic systems also to vibrational degrees of freedom [5]. In addition to static molecular structure calculations, we also develop time-dependent DMRG-based approaches to enable large-scale quantum dynamics simulations of molecular processes such as photoinduced exciton migration. The combination of powerful tensor-based wave function representations and efficient numerical algorithms paves the way towards the accurate characterization of a large variety of high-dimensional quantum systems.

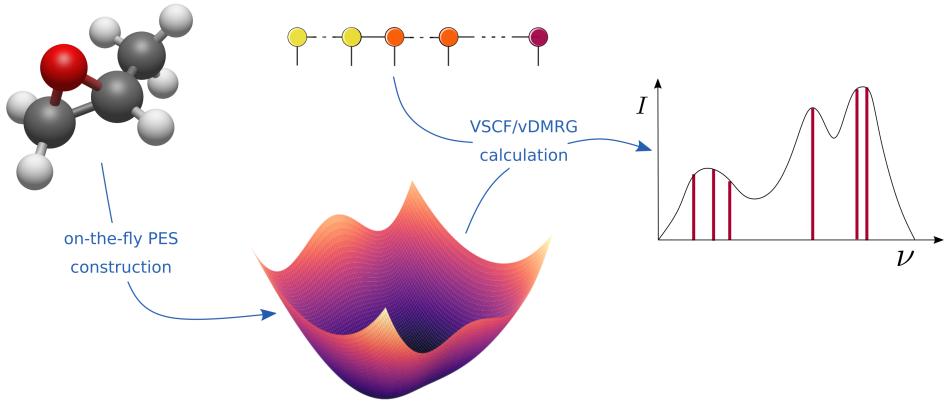

Figure 1: Illustration of the computational workflow of a n-mode vDMRG calculation

[1] S. R. White, *Phys. Rev. Lett.* **69**, 2863–2866 (1992).
[2] A. Baiardi, C. J. Stein, V. Barone, M. Reiher, *J. Chem. Theory Comput.* **13**, 3764–3777 (2017).
[3] N. Glaser, A. Baiardi, M. Reiher. In *Vibrational Dynamics of Molecules* J. M. Bowman, Ed. World Scientific, 80-144 (2022).
[4] N. Glaser, A. Baiardi, M. Reiher, *J. Chem. Theory Comput.*, preprint at arXiv:2308.08703 (2023)
[5] N. Glaser, A. Lieberherr, A. Baiardi, M. Reiher, manuscript in preparation