

Tensor network states for computing vibrational and electronic states

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Mostly independently from each other, the fields of electronic structure and vibrational quantum dynamics developed powerful methods in order to accurately solve the Schrödinger equation. In particular, methods that decompose the high-dimensional wavefunction as a complicated contraction over smaller dimensional functions have attracted much attention. They have led to impressive applications for challenging quantum systems in both fields. While the underlying wavefunction representations, tensor network states, are very similar, the algorithms used to solve the Schrödinger equation for electronic and vibrational motions are very different. A systematic comparison of the strengths and weaknesses of the different approaches is missing but would allow for a better understanding and useful cross-fertilization of ideas. Here, first attempts in this direction are made.

In the first part of my talk, I will show how to use a method from electronic structure theory, the density matrix renormalization group (DMRG), for vibrational simulations.¹ I will compare the DMRG to an algorithm used for vibrational dynamics, the multi-layer multi-configuration time-dependent Hartree (ML-MCTDH) method. I will apply these algorithms to the vibrational spectra simulation the Zundel ion, H_5O_2^+ , where a proton is sandwiched between two water units, a challenging system exhibiting large amplitude motion and Fermi resonances. For this system, I will show how the DMRG method can compute eigenstates at least an order of magnitude faster than the ML-MCTDH method. By computing 1000 eigenstates to high accuracy, I will show how subtle energetic effects will lead to a vastly different infrared spectrum of the Zundel ion.²

In the second part of my talk, I will show how a technique widely used for MCTDH can allow for faster electronic structure DMRG calculations whenever many virtual orbitals with few electronic excitations are involved.³ With a combination of this and existing methods, I will then show how to compute a very accurate potential energy curve (PEC) of the chromium dimer, a grand challenge problem of small molecule spectroscopy, where theory and experiment have been at odds for decades. The computed PEC allows for a new analysis of the existing experimental data and hints at a new assignment of the vibrational levels of the chromium dimer.⁴

¹: H.R. Larsson, Computing vibrational eigenstates with tree tensor network states. *J. Chem. Phys.* 151, 204102 (2019).

²: H.R. Larsson et al., State-resolved infrared spectrum of the protonated water dimer. *Chem. Sci.* 13, 11119-11125 (2022)

³: H.R. Larsson, H. Zhai, K. Gunst, G.K. Chan, Matrix Product States with Large Sites. *J. Chem. Theory Comput.* 2022, 18, 2, 749-762

⁴: H.R. Larsson, H. Zhai, C.J. Umrigar, G.K. Chan, The chromium dimer: closing a chapter of quantum chemistry. *J. Am. Chem. Soc.*, 144, 15932-15937 (2022)