

Tensor train algorithms for quantum dynamics simulations

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We introduce the “tensor-train split-operator Fourier transform” (TT-SOFT) algorithm for simulations of multidimensional nonadiabatic quantum dynamics [[J. Chem. Theory Comput. 13: 4034-4042 \(2017\)](#)]. TT-SOFT is essentially the grid-based SOFT method implemented in dynamically adaptive tensor-train representations. In the same spirit of all matrix product states, the tensor-train format enables the representation, propagation, and computation of observables of multidimensional wave functions in terms of the grid-based wavepacket tensor components, bypassing the need of actually computing the wave function in its full-rank tensor product grid space. We demonstrate the accuracy and efficiency of the TT-SOFT method as applied to propagation of 24-dimensional wave packets, describing the S_1/S_2 interconversion dynamics of pyrazine after UV photoexcitation to the S_2 state. Our results show that the TT-SOFT method is a powerful computational approach for simulations of quantum dynamics of polyatomic systems since it avoids the exponential scaling problem of full-rank grid-based representations. The development of ultrafast laser technology has also opened the possibility to control ultrafast reaction dynamics in excited electronic states. Thus, we report a Floquet theoretical study of quantum control of the ultrafast cis-trans photoisomerization dynamics of rhodopsin [[J. Chem. Theory Comput. 14\(3\): 1198-1205 \(2018\)](#)]. The predicted light-induced potentials, including light-induced conical intersections, can open new reaction channels or modify the product yields of existing pathways. The nonadiabatic dynamics is described by a 3-state 2-dimensional wave-packet, coupled to a bath of 23 vibrational modes, evolving according to an empirical model Hamiltonian with frequencies and excited-state gradients parameterized to reproduce the observed resonance Raman excitations of rhodopsin. We analyze the effect of different control pulses on the photoisomerization dynamics, including changes in pulse duration and intensity. We interpret the results in terms of 'dressed states' and we exploit the Floquet description where the effect of control pulses is naturally decoupled along the different channels. Results obtained with 300 fs-long pulses suggest that it should be possible to delay the excited-state isomerization for hundreds of femtoseconds. Our findings are thus particularly relevant to the development of ultrafast optical switches based on visual pigments.