Novel methods in quantum dynamics and spectroscopy: (i) Hierarchical equations of motion for momentum system-bath couplings and (ii) thermo-field dynamics tensor-train approach

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I will give a brief introduction to two novel methods developed by us recently, (i) Hierarchical equations of motion (HEOM) for momentum system-bath couplings and (ii) thermo-field dynamics (TFD) tensor-train (TT) approach.

(i) For a broad class of quantum models of practical interest, we demonstrate that the Hamiltonian of the system nonlinearly coupled to a harmonic bath through the system and bath coordinates can be equivalently mapped into the Hamiltonian of the system bilinearly coupled to the bath through the system and bath momenta. We show that the Hamiltonian with bilinear system − bath momentum coupling can be treated by the HEOM method and present the corresponding proof-of-principle simulations. The developed methodology creates the opportunity to scrutinize a new family of nonlinear quantum systems by the numerically accurate HEOM method.

(ii) We have developed a fully quantum, numerically accurate wave function-based approach for the calculation of third-order spectroscopic signals of polyatomic molecules and molecular aggregates at finite temperature [2,3]. The systems are described by multimode nonadiabatic vibronic-coupling Hamiltonians, in which diagonal terms are treated in harmonic approximation, while off-diagonal interstate couplings are assumed to be coordinate independent. The approach is based on the TFD representation of quantum mechanics and TT machinery for efficient numerical simulation of quantum evolution of systems with many degrees of freedom. Application of the developed TFD-TT approach is illustrated by the calculation of time- and frequency-resolved fluorescence spectra of the Fenna–Matthews–Olson (FMO) antenna complex at room temperature taking into account finite time-frequency resolution in fluorescence detection, orientational averaging, and static disorder.

[1] Maxim F. Gelin, Raffaele Borrelli, and Lipeng Chen. Hierarchical Equations-of-Motion Method for Momentum System − Bath Coupling. *J. Phys. Chem. B* **2021**, https://doi.org/10.1021/acs.jpcb.1c02431.

[2] Raffaele Borrelli and Maxim F. Gelin. Finite temperature quantum dynamics of complex systems: Integrating thermo-field theories and tensor-train methods. *WIREs Comput Mol Sci*. **2021**, https://doi.org/10.1002/wcms.1539

[3] Maxim F. Gelin and Raffaele Borrelli. Simulation of Nonlinear Femtosecond Signals at Finite Temperature via a Thermo Field Dynamics-Tensor Train Method: General Theory and Application to Time- and Frequency-Resolved Fluorescence of the Fenna–Matthews–Olson Complex. *J. Chem. Theory Comput.* **2021**, https://doi.org/10.1021/acs.jctc.1c00158