Calculation of two-dimensional spectra using the stochastic hierarchy of pure states (HOPS)

Z. Li, P.-P. Zhang and A. Eisfeld

Max Planck Institute for the Physics of Complex Systems,
Nöthnitzer Straße 38, D-01187 Dresden, Germany

Reliable theoretical calculations necessary for the correct interpretation of two-dimensional spectra are impeded by large system sizes and vibrational degrees of freedom Here we demonstrate that a numerical approach based on a stochastic hierarchy of pure states (HOPS) does allow to calculate two-dimensional spectra, notwithstanding the stochasticity of our method.

In recent years we have developed numerically efficient approaches to calculate the reduced density matrix using stochastic wave-functions within the non-Markovian Quantum State Diffusion (NMQSD) frame-work. In particular the stochastic hierarchy of pure states (HOPS) can recover the reduced density matrix exactly (for infinite number of trajectories and infinite depth). For the case of the excitation transfer in light harvesting systems we have demonstrated that for typical parameters one has fast convergence with respect to the number of trajectories and the depth of the hierarchy. Our studies indicate that compared to the density matrix based HEOM approach one not only has a reduced size (wavefunction versus density matrix), but HOPS also converges faster with the depth of the hierarchy.

In the present work we demonstrate that HOPS is also suitable to calculate 2D spectra. To this end we will use a non-perturbative approach in the electric field strength. This approach depends sensitively on the phases of the Laser-pulses. Nevertheless, we will show that one gets reasonably fast convergence with respect to the number of trajectories.

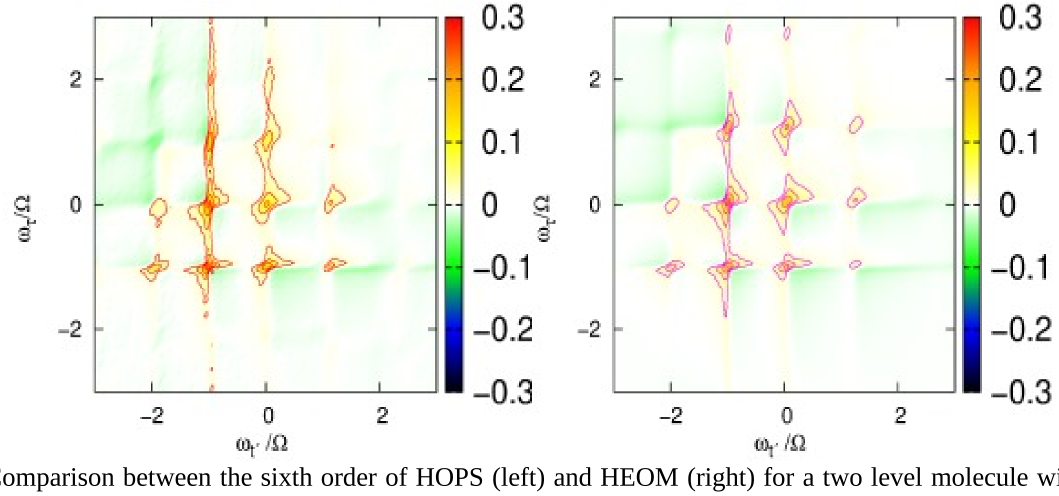

Fig.1 Comparison between the sixth order of HOPS (left) and HEOM (right) for a two level molecule with one nuclear coordinate and harmonic Born-Oppenheimer surfaces. Note that in the HEOM case the equidistant spacing of the peaks is not conserved.

[1] D. Suess, A. Eisfeld and W. T. Strunz; Phys. Rev. Lett. 113 150403 (2014).
[2] D. Suess, W. Strunz and A. Eisfeld; Journal of Statistical Physics 159 1408 (2015).