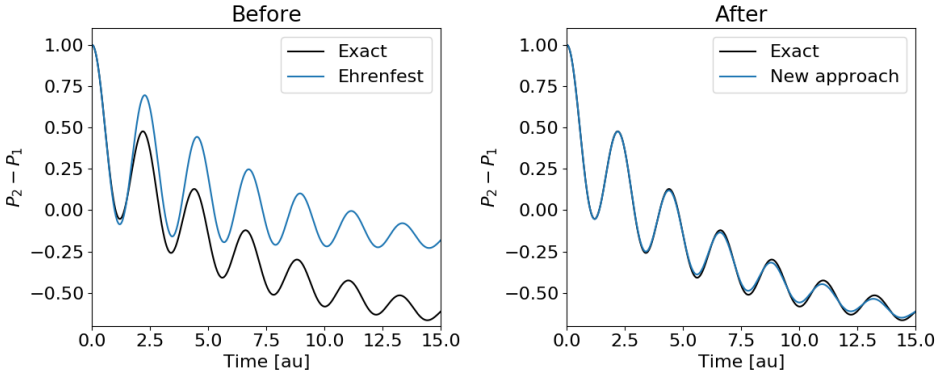
Spin-mapping approach to nonadiabatic dynamics

Johan E. Runeson and Jeremy O. Richardson

Department of Chemistry and Applied Biosciences, ETH Zürich
johan.runeson@phys.chem.ethz.ch

One way to simulate nonadiabatic processes is in terms of classical trajectories on multiple electronic surfaces. A commonly used approach is the Meyer-Miller-Stock-Thoss mapping [1,2] that replaces the electronic levels with a singly excited harmonic oscillator. The mapping is exact on the quantum level, but has some well-known deficiencies when used to generate classical trajectories. Most important is the unphysical flow of electronic zero-point energy between the oscillators. As a consequence, the mapped operators have to be projected back onto the physical subspace of singly-excited oscillators.
We have recently proposed [3] an alternative mapping for two-level systems that requires no such projections. It is based on a coherent-state representation of spin-1/2 systems, which just like the MMST mapping is exact on a quantum level, and gives rise to the same equations of motion. Nonetheless, there are a couple of differences which can be summarized in two main points. First we restrict the distribution of the mapping variables to a sphere of all directions of a fictitious spin vector. Second we construct correlation functions of electronic operators in terms of their Stratonovich-Weyl transforms, which can be interpreted as using the quantum-mechanical magnitude of the spin in place of the classical magnitude.
Our mapping does not add any computational complexity and is as easy to implement as standard MMST-approaches. When comparing to benchmark results for population transfer in various spin-boson systems, we find that our approach is consistently more accurate than both MMST and Ehrenfest dynamics, in particular for asymmetric systems.



Population difference between two electronic states for a spin-boson system that is initially in its excited state. Ehrenfest dynamics predicts completely wrong final state populations, whereas our method is in almost perfect agreement with the exact result.

References

1. H.-D. Meyer and W. H. Miller. *J. Chem. Phys.* **70**, 3214 (1979).
2. G. Stock and M. Thoss. *Phys. Rev. Lett.* **78**, 578 (1997).
3. J. E. Runeson and J. O. Richardson. arXiv:1904.08293 [physics.chem-ph] (2019).