

A path-integral sampling (trajectory-free) approach to the calculation of quantum time correlation functions

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One of the major outstanding challenges in computational chemistry is the calculation of thermal quantum time correlation functions in condensed phases. Of the methods most commonly employed, semi-classical approaches generally require the generation of a very large number of trajectories with a high associated computational overhead. Alternatively, the accuracy of popular centroid[1] and ring-polymer[2] MD algorithms often satisfactory for linear operators under the appropriate conditions but degrades for non-linear operators, and routes to systematic improvement of these methods are not obvious. In this talk, I will introduce a scheme for approximating quantum time correlation functions numerically within the Feynman path integral formulation[3]. Starting with the symmetrized version of the correlation function expressed as a discretized path integral, a change of integration variables, often used in the derivation of trajectory-based semiclassical methods, is introduced. In particular, a transformation to sum and difference variables between forward and backward complex-time propagation paths. It can be shown that a formal integration over the path-difference variables yields a function of the path-sum variables that can be shown to be positive definite, thereby allowing the problem to be formulated as a sampling problem in the path-sum variables. The manner in which this procedure is carried out results in an open-chain path integral (in the remaining sum variables) with a modified potential that is evaluated using imaginary-time path-integral sampling rather than requiring the generation of a large ensemble of trajectories. Consequently, any number of path integral sampling schemes can be employed to compute the remaining path integral, including Monte Carlo, path-integral molecular dynamics, or enhanced path-integral molecular dynamics. This approach constitutes a different perspective in semiclassical-type approximations to quantum time correlation functions. As a practical approximation to the path-difference variable integrals, the potential is expanded in powers of these variables and the integral is performed analytically. The scheme is compared to the ring-polymer MD[2] and thermal-Gaussian LSC-IVR[4] approaches for a handful of example problems. Other formal considerations for rate theory and electronic excitation spectroscopy will also be discussed.

References

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