INTERFERENCE AND QUANTIZATION IN SEMICLASSICAL VIBRATIONAL RESPONSE FUNCTIONS

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The calculation of an optical response function is a direct way to predict the results of a wide range of linear and nonlinear spectroscopic measurements. As quantum response theory is impratical for large systems and as classical response functions can be qualitativly incorrect, there is a need for a method to calculate spectroscopic response functions semiclassically. The semiclassical Herman-Kluk propagator has previously been applied to both linear and third–order vibrational response functions. In this approach, spectroscopic response functions are expressed as multiple phase-space integrals over pairs of classical trajectories and their associated stability matrices. For anharmonic oscillators this procedure has demonstrated quantitative agreement with quantum response functions; however, the calculations were computationally challenging even for small systems[a]. Here we determine how the Herman-Kluk linear response function reproduces the quantum result using only classical dynamical information. This analysis identifies the pairs of trajectories that are most important on different time scales as well as suggests a simplifying procedure wherein the interference between pairs of classical trajectories is treated approximately, resulting in an integral over a single average trajectory, as in a purely classical calculation[b]. The extension of this procedure to nonlinear response functions is also considered.

[a] W. Noid, G. Ezra, and R. Loring, J. Chem. Phys. 119, 1003 (2003).
[b] S. Gruenbaum and R. Loring, J. Chem. Phys. 128, in press (2008).