Calculating the CH_5^+ IR Spectrum with the Phase Integration Method

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The Phase Integration Method (PIM)[1,2] is a novel approximate quantum dynamical technique developed for computing system's time dependent observables when exact methods become limited due to their exponential scaling on the number of system's degrees of freedom and to simulation times of the order of picoseconds. This method belongs to a class of so-called linearization techniques and it exploits the presence of two propagators in the correlation function to introduce an approximation accurate to second order in an $\hbar$ expansion of the potential. PIM employs an algorithm in which the exact sampling of the quantum thermal density is combined with a linearized approximation of the quantum time propagators represented in the path integral formalism that reduces the evolution to classical dynamics. The quantities of interest can then be computed by combining classical molecular dynamics algorithms with an original generalized Monte Carlo scheme to sample initial conditions. We have applied the PIM for computation of the CH_5^+ cation infrared spectrum in gas phase, which is a well now system for its highly anharmonic potential due to the correlated scrambling of its hydrogen atoms around the central carbon atom,[3] in order to further improve the method and its current implementation. Here I represent some of the recent results of our progress.

References

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