PROGRESS TOWARDS THE ACCURATE CALCULATION OF ANHARMONIC VIBRATIONAL STATES OF FLUXIONAL MOLECULES AND CLUSTERS WITHOUT A POTENTIAL ENERGY SURFACE

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The accurate calculation of anharmonic vibrational states of highly fluxional systems is complicated by the need to first obtain the full-dimensional potential energy surface(PES). Although commonly exploited as a way around this problem, grid-based methodologies scale exponentially with system size while reduced dimensional approaches are highly system dependent, both in terms of the details of their application and in terms of their suitability. Moreover, the achievement of converged variational calculations of highly anharmonic systems is complicated by the necessity of using a very large basis and hence the construction and diagonalization of enormous Hamiltonian matrices.

We report here our recent efforts to develop an algorithm capable of accurately calculating anharmonic vibrational energies, even for very floppy systems, without first obtaining a PES and using only a handful of basis functions per degree of freedom. More specifically, the potential energy and G-matrix elements are calculated on a set of points obtained from a Monte Carlo sampling of the most important regions of configuration space, allowing for a significant reduction in the number of required sampling points. The Hamiltonian matrix is then constructed using an evolving basis which, with each iteration, captures the effect of building $\mathbf{H}$ from an ever-expanding basis despite the fact that the actual dimensionality of $\mathbf{H}$ is fixed throughout the calculation. This latter property of the algorithm also greatly reduces the size of basis needed for the calculation relative to more traditional variational approaches. The results obtained from the application of our method to several test systems, including ion water complexes, will be reported along with its observed convergence properties.