# CALCULATING ANHARMONIC VIBRATIONAL STATES WITHOUT A PRE-EXISTING POTENTIAL ENERGY SURFACE

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The calculation of anharmonic vibrational states, especially of highly fluxional systems, is complicated by the need to first obtain the full-dimensional potential energy surface (PES). Reduced dimensional approaches, where appropriate, can greatly help to ease the computational cost of these calculations but their application is highly system dependent, preventing the development of a general methodology. 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. More specifically, the potential energy and G-matrix elements are calculated on a grid of points obtained from a Monte Carlo sampling of the most important regions of configuration space. The Hamiltonian matrix is then constructed using an evolving basis which, with each iteration, captures the effect of building $\mathbf{H}$ from an ever-increasing harmonic oscillator 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 will also be reported along with its observed convergence properties.