

Adaptive eigenvalue solver for efficient calculation of anharmonic IR spectra in high-dimensional spaces.

Vincent LEBRIS

IPREM, e2s UPPA.

The Adaptive Vibrational Configuration Interaction (A-VCI) algorithm is an iterative process that computes the anharmonic spectrum of a molecule using nested bases to discretize the Hamiltonian operator. For large molecular systems, the size of the discretization space and the computation time quickly become prohibitive. It is therefore necessary to develop new methods to further limit the number of basis functions. Most of the time, the interpretation of an experimental infrared spectrum does not require the calculation of all eigenvalues but only those corresponding to vibrational states with significant infrared intensity. In this presentation, a technique that uses these intensities is introduced to select a subset of eigenvalues to be precisely calculated by the algorithm. Thus, we build smaller nested bases and reduce both the memory footprint and the computational time. We validate the advantages of this new approach on a few examples, in particular through comparison with experimental infrared data.