A tensor decomposition method for calculating vibrational spectra of molecules

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Abstract

Computation of vibrational spectra of molecules is useful for predicting and interpreting experimentally observed spectra. It is also used to analyse and generate potential energy surfaces. Standard techniques for calculating vibrational spectra of polyatomic molecules suffer from the so-called curse of dimensionality: the exponential increase of the cost of the calculation with the size of the molecule. We developed a method that avoids the need to store large vectors and matrices. We use a tensor format called Canonical Polyadic (CP) format to represent vectors. As a result, the memory cost scales linearly with the dimensionality of the molecule. Our method of solving the Schrödinger equation is called the Multiple Shift Block Inverse Iteration(MSBII) eigensolver. In CP format a vector is represented as a sum of terms. An Alternating Least Squares (ALS) approach is used so that the number of terms in the CP vectors are constant. We improved the MSBII method by using a tree-like structure, thereby solving Schrödinger equation sequentially in reduced dimensions. This improvement results in a significant reduction in the CPU time of the calculation. These ideas are tested by computing vibrational spectra of a 64-D bilinearly coupled model Hamiltonian and acetonitrile(12-D) molecule.