

Using reduced-rank iterative methods to calculate vibrational spectra

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The memory cost of calculating vibrational spectra of polyatomic molecules can be dramatically reduced by using low-rank tensor formats. The n^D coefficients which represent a wavefunction in a direct product basis (n being the number of 1-D basis functions for each of the D coordinates) can often be deduced from a much smaller set of numbers by using approximate, low-rank tensor decompositions. One possible choice is the CP (Canonical Polyadic) format [1], i.e. a sum of outer products of vectors. Its memory cost scales as $O(nD)$. The CP format is a cousin of the MCTDH format, with the important difference that there is no need for a multidimensional core tensor.

Intermediate basis functions can be constructed in the CP format by using adapted versions of well-known iterative algorithms, followed by direct diagonalisations to obtain the vibrational wavefunctions and frequencies. A compromise should be found between the rank limitation (the rank being the number of terms in the sum-of-products representations) and the desire to have sufficient flexibility to correctly describe the wavefunctions. We have developed reduced-rank iterative methods based on the power method [2,3], Chebyshev iterations and Davidson-like iterations [4] in this framework, with applications to realistic molecules.

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