A MULTILAYER SUM-OF-PRODUCTS METHOD FOR COMPUTING VIBRATIONAL SPECTRA WITHOUT STORING FULL-DIMENSIONAL VECTORS OR MATRICES

PHILLIP THOMAS, TUCKER CARRINGTON, Department of Chemistry, Queen’s University, Kingston, ON, Canada.

By optimizing sum-of-products (SOP) basis functions, it is possible to compute vibrational spectra, using a direct product basis, without storing vectors with as many components as there are product basis functions. These ideas are presented in a recent paper: Leclerc and Carrington, J. Chem. Phys 140 174111 (2014). In that paper, the SOP basis functions are products of factors that depend on a single coordinate. When using factors that depend on one coordinate the number of terms (rank) in the SOP basis functions increases with the size of the molecule and the coupling strength. Using multi-dimensional factors makes it possible to incorporate some of the coupling into the factors and to calculate spectra of molecules with more than a dozen atoms. We use multi-dimensional factors that are eigenfunctions of reduced-dimension Hamiltonians. These can be constructed, in different ways, by organizing the factors into a multiple layer tree. Each node in a layer of a tree represents eigenfunctions of a reduced-dimension Hamiltonian for a group of coordinates. We have done calculations with tensor-train and binary tree structures. Efficiency is significantly enhanced by representing the potential with the same tree structure. The ideas are tested by computing energy levels of a 64-D model coupled oscillator Hamiltonian and of CH3CN (12 dimensions) with a realistic potential.