CONTRACTED BASIS LANCZOS METHODS FOR COMPUTING NUMERICALLY EXACT ROVIBRATIONAL LEVELS OF METHANE

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We present the first numerically exact calculation of rovibrational levels of a five-atom molecule, extending the method we used for calculating vibrational levels of the same molecule[a]. Two contracted basis Lanczos strategies are proposed. The first and preferred strategy is a two-stage contraction. Products of eigenfunctions of a 4D stretch problem and eigenfunctions of 5D bend-rotation problems, one for each K, are used as basis functions for computing eigenfunctions and eigenvalues (for each K) of the Hamiltonian without the Coriolis coupling term. Finally, energy levels of the full Hamiltonian are calculated in a basis of the eigenfunctions of the Hamiltonian without the Coriolis coupling term. The second strategy is a one-stage contraction in which energy levels of the full Hamiltonian are computed in the product contracted basis (without first computing eigenfunctions of the Hamiltonian without the Coriolis coupling term). The two-stage contraction strategy, albeit more complicated, has the crucial advantage that it is trivial to parallelize the calculation so that the CPU and memory costs are independent of J. We use the polar coordinates associated with orthogonal Radau vectors and spherical harmonic type rovibrational basis functions. A new parity-adapted rovibrational basis suitable for a five-atom molecule is proposed and employed to obtain bend-rotation eigenfunctions in the first step of both contraction methods. The effectiveness of the two methods is demonstrated by calculating a large number of converged $J = 1$ rovibrational levels of methane (up to 8000 cm^{-1}) using a global potential energy surface.
We also present the use of C_{3v} invariant quadrature grid to implement the C_{3v} symmetry in computing rovibrational levels of methane.

[a] X. G. Wang, T. Carrington, Jr, J. Chem. Phys. **118**, 6946 (2003) and **119**, 101 (2003).