Overcoming *the curse of dimensionality*: a hierarchical collocation method for solving the rotational-vibrational Schrödinger equation for polyatomic molecules

Emil J. Zak and Tucker Carrington
Department of Chemistry, Queen's University, Kingston, ON, Canada

In variational calculations of rotational-vibrational energy levels of polyatomic molecules the total wavefunction is typically represented as a linear combination of basis functions. The size of the multidimensional direct-product basis grows exponentially with the number of atoms. As a result, the memory requirements for variational calculations become prohibitive for molecules with more than 4-5 atoms - this is often referred to as *the curse of dimensionality* [1].

Here we propose a method which circumvents the problem of the exponential scaling of the basis set size. This is achieved through the *collocation approach* [2], in which the Schrödinger equation is solved at a set of points, avoiding the need for an accurate multidimensional quadrature.

The new collocation method has the following advantages: 1) the size of the matrix eigenvalue problem is the size of the required pruned (non-direct product) polynomial-type basis; 2) it requires solving a regular, and not a generalized matrix eigenvalue problem; 3) accurate results are obtained even if quadrature points and weights are not good enough to yield a nearly exact overlap matrix; 4) the potential matrix is diagonal; 5) the matrix-vector products required to compute eigenvalues and eigenvectors can be evaluated by doing sums sequentially, despite the fact that the basis is pruned; 6) unlike in popular MCTDH and tensor rank-reduction methods, here no sum-of-product form of the potential energy surface (PES) is required.

To achieve these advantages we use sets of nested Leja grid points and special hierarchical basis functions. Matrix-vector products needed for iterative eigensolvers are inexpensive because transformation matrices between the basis and the grid, and their inverses, are lower triangular. Vibrational energy levels of CH_2NH are calculated with the new method.

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[1] T. Carrington, J. Chem. Phys; 146, 12, 120902 (2017).
[2] G. Avila and T. Carrington, J. Chem. Phys; 147, 6, 064103 (2017).