COLLOCATION METHODS FOR COMPUTING VIBRATIONAL SPECTRA

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When the potential energy surface (PES) does not have a special form (e.g. a sum of products), it is common to use quadrature to compute a vibrational spectrum. Direct-product quadrature grids are most popular. The size of a direct-product grid scales exponentially with the number of atoms and it is not not possible to store values of the PES for molecules with more than 5 atoms. One option is to use a Smolyak quadrature grid. In this talk, I shall present collocation methods with Smolyak-type grids. Collocation has advantages: 1) point selection is less important; 2) no integrals, no quadratures, no weights; 3) easy to use with complicated kinetic energy operators; 4) it can be used with any (the best possible) coordinates and basis functions; 5) in many cases fewer collocation than quadrature points are required; 6) the length of the vectors one must store is reduced. Collocation can be used with the Multiconfiguration Time-Dependent Hartree (MCTDH) approach. The collocation-based MCTDH method I shall present can be used with general potential energy surfaces. This is imperative if one wishes to compute very accurate spectra. When the basis is good, the accuracy of collocation solutions to the Schroedinger equation is not sensitive to the choice of the collocation points. The original collocation-MCTDH (C-MCTDH) method [J. Chem. Phys. 148, 044115 (2018)] uses, as is also true in standard MCTDH, a direct product basis. Because we do not rely on having a sum-of-products potential energy surface, we also have a direct product grid. By using generalized hierarchical basis functions, that span the same space as the single particle functions we introduced in the first C-MCTDH paper, and a Smolyak grid, we have developed C-MCTDH approach that makes it possible to prune both the basis and the grid.