Vibrational Spectra Computing Iterative Method

Joel Bowman*

Department of Mathematics and Physics, The University of Edinburgh, USA

Introduction

In the past thirty years, efficient computational techniques have been developed to compute the vibrational spectra of polyatomic molecules by solving the time-independent Schroedinger equation. They are crucial when perturbation theory-based approximations, which are frequently used, are not precise enough. Almost all approaches start with selecting a basis for the Hamiltonian and wavefunction representation, followed by the solution of a linear algebraic equation. These two fundamental responsibilities are not independent of one another; an organized basis favors iterative linear algebra techniques. It is helpful for experimentalists to assign and understand observed spectra by computing vibrational spectra [1].

Description

There are numerous ways to calculate vibrational spectra by solving the time-independent Schroedinger equation. The techniques I outline can be made more inclusive so they can also be used to calculate ro-vibrational spectra. Iterative methods are all of the techniques described here that find solutions to the Schroedinger problem from a space created by analyzing matrix-vector products (MVPs). I won't discuss multimode-type approaches (MM), which are effective for semi-rigid molecules since normal coordinates are appropriate when the potential energy surface (PES) is a sum of terms that depend on a subset of the coordinates (referred to as an MM representation). I will also exclude multiconfiguration time-dependent Hartree (MCTDH) approaches, despite their widespread use. To calculate precise vibrational energy levels, they can be combined with a block power approach, a "enhanced relaxation" method, or a block Lanczos method. However, the most prevalent MCTDH method for calculating spectra, enhanced relaxation, converges poorly in cases where the density of states is high, making it impossible to compute a significant number of levels for a big molecule [2].

It is preferable to avoid computing a Hamiltonian matrix when utilizing iterative approaches. The Hamiltonian matrix cannot be stored in memory because the foundation of many calculations is too massive. The assessment of MVPs is necessary for iterative techniques. How may MVPs be calculated without creating a Hamiltonian representational matrix? I'll start by outlining concepts that enable using a product foundation to assess MVPs without a Hamiltonian matrix. They take advantage of the kinetic energy operator, the quadrature grid, and the basic structure. Vectors representing wavefunctions and the vector representing the PES on the quadrature grid are so big for molecules with more than five atoms that they take up too much memory. A contracted basis is used in the first technique. It must be feasible to evaluate MVPs in the contracted basis without switching to a large product grid for the contracted basis technique to be useful. The second approach makes use of a trimmed basis and grid. The largest vectors that must be stored are much smaller after pruning [3].

***Address for Correspondence**: Joel Bowman, Department of Mathematics and Physics, The University of Edinburgh, USA, Email: joelbowman85@gmail.com*

Direct output Popular DVR and VBR bases are. Despite their size, direct product bases can be utilized to effectively evaluate the MVPs needed for iterative approaches by taking advantage of the basis' structure. The time-independent Schroedinger equation is frequently solved iteratively using the Lanczos and filter diagonalization methods. They enable the vibrational Schroedinger equation to be solved with a general PES for molecules with up to five atoms, even on a direct product basis. The main concepts have been gone over multiple times. They are all founded on performing sums in order. A VBR basis is preferable to a DVR basis if the KEO has significant singularities. The KEO is singular and vibrational wavefunctions have significant amplitude at an important singularity. Singularities typically happen when one coordinate takes a limiting value while the other is indefinite. By performing sums consecutively in a VBR basis, the potential MVP may be determined [4].

Good basis functions are always nondirect product functions, which are products of functions of the coordinate that is undefined and the coordinate that takes a limiting value, with a shared index, if there is an important singularity. It is feasible to calculate vibrational spectra using the concepts presented in this section without creating and storing a Hamiltonian matrix. However, the memory cost of storing vectors in a direct product basis is unaffordable for molecules with more than five atoms. To lower the memory cost of calculations for molecules with more than five atoms, new concepts must be added [5].

DVR to Make a Contracted Basis

It is usual to utilize basis functions that are the products of factors that depend on more than one coordinate in order to include information about coupling in the basic functions. The multi-dimensional factors will be referred to as contracted basis functions. Designing sound algorithms for contract-based MVP evaluation is crucial. Contract bases must must be more complex, which means that they have less structure. Structure is used to analyze MVPS effectively. The narrower spectral range of the contracted-basis Hamiltonian matrix is a significant benefit of contracted bases. The quantity of MVPs needed to compute the eigenvalues is reduced as the spectral range is narrowed.

Conclusion

It is desirable to employ diagonalizing matrices with contracted functions that represent the Hamiltonian with one or more fixed coordinates for molecules with more than three atoms. The basis functions are direct products of coordinate functions or coordinate group functions.

References

1. Kosloff, Ronnie. "Time-dependent quantum-mechanical methods for molecular dynamics." *J Phys Chem* 92 (1988): 2087-2100.

2. Bowman, Joel M., Tucker Carrington, and Hans-Dieter Meyer. "Variational quantum approaches for computing vibrational energies of polyatomic molecules." *Mol Phys* 106 (2008): 2145-2182.

3. Avila, Gustavo, and Tucker Carrington Jr. "Nonproduct quadrature grids for solving the vibrational Schrödinger equation." *J Phys Chem* 131 (2009): 174103.

4. Dawes, Richard, Xiao-Gang Wang, Ahren W. Jasper, and Tucker Carrington Jr. "Nitrous oxide dimer: A new potential energy surface and rovibrational spectrum of the nonpolar isomer." *J Phys Chem* 133, (2010): 134304.

5. Szidarovszky, Tamás, Csaba Fábri, and Attila G. Császár. "The role of axis embedding on rigid rotor decomposition analysis of variational rovibrational wave functions." *J Phys Chem* 136 (2012): 174112.