Variational discrete variable representation

Gregory C. Corey and John W. Tromp

Citation: The Journal of Chemical Physics **103**, 1812 (1995); doi: 10.1063/1.469755
View online: http://dx.doi.org/10.1063/1.469755
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/103/5?ver=pdfcov
Published by the AIP Publishing

Variational discrete variable representation

Gregory C. Corey
Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada and Département de chimie, Université de Montréal, C.P. 6128, succursale A, Montréal, PQ H3C 3J7, Canada

John W. Tromp
Département de chimie, Université de Montréal, C. P. 6128, succursale A, Montréal, PQ H3C 3J7, Canada

(Received 30 November 1994; accepted 28 April 1995)

In developing a pseudospectral transform between a nondirect product basis of spherical harmonics and a direct product grid, Corey and Lemoine [J. Chem. Phys. **97**, 4115 (1992)] generalized the Fourier method of Kosloff and the discrete variable representation (DVR) of Light by introducing more grid points than spectral basis functions. Assuming that the potential energy matrix is diagonal on the grid destroys the variational principle in the Fourier and DVR methods. In the present article we (1) demonstrate that the extra grid points in the generalized discrete variable representation (GDVR) act as dealiasing functions that restore the variational principle and make a pseudospectral calculation equivalent to a purely spectral one, (2) describe the general principles for extending the GDVR to other nondirect product spectral bases of orthogonal polynomials, and (3) establish the relation between the GDVR and the least squares method exploited in the pseudospectral electronic structure and adiabatic pseudospectral bound state calculations of Friesner and collaborators.

I. INTRODUCTION

During the past decade there has been an extraordinary interest in the use of grid techniques, both in chemical dynamics and in electronic structure calculations. This interest has arisen primarily due to the work of Kosloff, Light and Friesner. Unfortunately, the relationships among the Fourier method of Kosloff,[1,2] the discrete variable representation (DVR) of Light[3,4] and the pseudospectral method of Friesner[5,6] have remained obscure for three reasons.

(1) Friesner's method and the Fourier method are explicitly pseudospectral. A pseudospectral algorithm[7–9] exploits two representations of the Hamiltonian. One, is a spectral representation in which the wave function is expanded in a finite number of square-integrable functions chosen to simplify the kinetic energy matrix. The other is a grid representation in which the wave function is expanded in a set of continuous functions, localized at discrete values of the coordinate operator. In the propagation of wave packets and in a pseudospectral implementation of the Lanczos algorithm in calculations of the ro-vibrational spectra of polyatomic molecules, the *explicit construction* of the Hamiltonian matrix can be avoided. The computational implementation of those algorithms consists of repetitive evaluations of the Hamiltonian matrix times a vector of wave function expansion coefficients. The matrix-vector products are evaluated through a transformation between the spectral and grid representations, with differential operators evaluated in the spectral representation and coordinate operators evaluated in the grid representation.

In contrast the DVR has been used predominately in the context of successive diagonalization truncation schemes,[4,10,11] in which the sparseness of the DVR Hamiltonian matrix, and the diagonality of the potential energy matrix have been exploited to construct a contracted basis tailored to the shape of the potential energy surface. The ro-vibrational energy levels of polyatomic molecules were then calculated by using conventional algorithms (e.g. Householder/QL) to diagonalize the Hamiltonian matrix in the reduced-dimensional contracted basis. In this approach the transformation between the spectral and grid representations has been used only in the *explicit* construction of the DVR Hamiltonian matrix.

(2) The coordinate systems and basis functions used in chemical dynamics and in electronic structure calculations are very different. The Fourier and DVR methods have been used most often in calculations on small polyatomic molecules, with three or four nuclei, in which the wave functions for nuclear motion were expanded in a basis of (single center) orthogonal polynomials. (It is now well understood that the Fourier basis is equivalent to a basis of Chebychev polynomials.[7–9,12]) Consequently, in applications of the Fourier and DVR methods in chemical dynamics, one has not been forced to confront the challenges of calculating multicentered integrals or devising an efficient and accurate algorithm for representing the contracted Gaussian or Slater functions of electronic structure calculations, on a grid.

(3) The three methods treat aliasing terms, that is components outside the spectral basis $\{\phi_i(x); i=1,\ldots,N\}$ produced by the operation $\hat{H}\phi_i$, quite differently. Purely spectral methods project out the alias exactly. One solution to the presence of aliasing terms in grid-based methods, and in fact the strategy adopted in all applications of the Fourier and DVR methods, is simply to ignore them. Numerical tests indicate that, when converged, the eigenvalues obtained through this simple solution are numerically equivalent to the eigenvalues obtained from a converged calculation in the spectral basis. Even though the calculated eigenvalues in the Fourier and DVR methods are not in error, there is a hidden computational cost in ignoring the aliasing terms. As discussed in Sec. IV, this computational cost arises from the

 0021-9606/95/103(5)/1812/9/$6.00

need to augment the basis set beyond the size that would be necessary to converge a purely spectral calculation.

The simple strategy of ignoring the aliasing terms is not valid in pseudospectral electronic structure calculations. Due to the aliasing terms produced in the application of the Coulomb and exchange operators to the contracted Gaussian and Slater basis functions used in quantum chemistry, small perturbations of the grid lead to large fluctuations in the calculated eigenvalues. Friesner[5] has dealt with the aliasing terms in pseudospectral electronic structure calculations by introducing more grid points $\{x_\alpha;\alpha=1,\ldots,M>N\}$ than spectral basis functions. In his approach, the transformation of the vector of wave function expansion coefficients from the spectral to the grid representation is defined by the $M\times N$ rectangular collocation matrix $R_{\alpha i}=\phi_i(x_\alpha)$. The $N\times M$ back transformation from the grid to the spectral representation is defined by the *pseudoinverse*[13] $\mathscr{R}^{-1}=[\mathbf{R}^\dagger\mathbf{w}\mathbf{R}]^{-1}\mathbf{R}^\dagger$ obtained from a least squares fit of the spectral expansion coefficients, where $\mathbf{w}$ is a matrix of grid weights. In chemical dynamics, little attention has been paid to Friesner's more general least squares method because neglecting the aliasing terms does not introduce numerical instabilities or errors into the Fourier and DVR methods.

In curvilinear coordinates, the singularities in the kinetic energy operator $\hat{T}$ impose constraints on the wave function. Those constraints imply that the eigenfunctions of $\hat{T}$ are nondirect products of functions of the coordinates ''coupled'' by the singularities. Our interest in devising a transformation between a *nondirect* product spectral representation defined by the eigenfunctions of $\hat{T}$ and a *direct* product grid, led us to generalize the Fourier and DVR methods by introducing more grid points than spectral basis functions.[14–16] The transform that we have developed has been exploited in the propagation of wave packets[14,16] in inelastic scattering, and in pseudospectral Lanczos calculations[17–19] of the vibrational spectra of polyatomic molecules. Recently, Lemoine[20,21] has extended this approach to a nondirect product basis of radial Bessel functions and spherical harmonics.

Friesner has speculated that algorithmic developments in the pseudospectral method for electronic structure calculations and in the DVR should be transferable between the two formalism.[5] The goal of the present article is to explore the formal properties of our generalization of the Fourier and DVR methods, and to establish the relation between a pseudospectral implementation of the algorithm and Friesner's least squares method. The article is organized as follows. Sec. 2 of Ref. 15 reviews the conventional one-dimensional DVR and summarizes a novel and simple demonstration of the well known equivalence between a finite basis representation[3] (FBR) of orthogonal polynomials and the corresponding DVR, first derived by Dickinson and Certain,[22] which has provided the formal basis for the DVR method. Using the notation introduced in Ref. 15, Sec. II of the present article summarizes the one-dimensional generalized discrete variable representation (GDVR). Sec. III discusses the general principles for developing a multidimensional transform between a nondirect product spectral basis of orthogonal polynomials and the corresponding direct product grid. Ignoring the aliasing terms produced by the operation $\hat{H}\phi_i$ destroys the variational principle when the Hamiltonian matrix is diagonalized in the DVR or in the FBR.[3] In Sec. IV we discuss the role played by the extra grid points, in the GDVR, as dealiasing functions that restore the variational principle and make a pseudospectral calculation equivalent to a purely spectral one. Our conclusions are presented in Sec. V.

II. GENERALIZED DISCRETE VARIABLE REPRESENTATION

A. Overview

Conventionally, the DVR is defined in terms of a set of N orthogonal basis functions localized on a grid in the coordinate representation. There are two approaches for choosing the grid points which label the DVR basis functions. One approach starts by diagonalizing a function of the coordinate operator in a set of N delocalized spectral basis functions chosen to simplify the kinetic energy matrix.[23,24] The eigenvalues define a set of grid points in the coordinate representation, and the matrix of eigenvectors defines an $N\times N$ unitary transformation between the discrete variable and spectral bases. The other approach identifies the unitary transformation matrix by introducing a quadrature approximation for the evaluation of the spectral overlap and potential matrix elements.[3] The grid is defined by the quadrature points. If the spectral basis functions are orthogonal polynomials with an argument equal to the function of the coordinate operator, and the matrix elements are evaluated by Gaussian quadrature then these two approaches are equivalent.[22] Both approaches can be generalized easily to a multidimensional *direct* product representation, but only the latter can be generalized to a *nondirect* product representation. In the discussion below, we follow the second approach.

Consider a Hamiltonian that can be written as a sum of a kinetic and a potential energy term,

$$\hat{H}=\hat{h}+\hat{V}. \tag{1}$$

Often $\hat{h}$ is equivalent to the kinetic energy operator $\hat{T}$, but in general this is not necessary. For example, $\hat{h}$ could be defined by adding $\hat{T}$ to a model potential.[17] Then $\hat{V}$ would be defined as the difference between the intermolecular potential and the model potential. In a variational or purely spectral calculation the Hamiltonian matrix elements

$$\langle i|H|j\rangle=\langle i|h|j\rangle+\langle i|V|j\rangle, \tag{2}$$

are evaluated exactly in a truncated orthonormal basis $\{\phi_i(x),i=1,\ldots,N\}$.

We will assume (1) that the one-dimensional spectral basis functions are a set of normalized classical polynomials $\{p_i(x)\}$ (i.e., Chebychev, Hermite, Jacobi, Laguerre or Legendre) orthogonal with respect to a weight function $\Omega(x)$, and (2) that the basis functions include a dependence on the square root of $\Omega(x)$. Explicitly, we assume that $\int\Omega(x)p_i^*(x)p_j(x)dx=\delta_{ij}$, where $\phi_i(x)=\Omega^{1/2}(x)p_i(x)$. (The plane wave basis commonly used in the Fourier method[1,2] is equivalent to a basis of Chebychev polynomials.)

In a conventional finite basis representation (FBR) the exact integrals of the potential

$$\langle i|V|j\rangle = \int \phi_i^*(x)V(x)\phi_j(x)dx \tag{3}$$

are approximated by an N-point Gaussian quadrature

$$\langle i|V^{\mathrm{FBR}}|j\rangle = \sum_{\alpha=1}^{N} \phi_i^*(x_\alpha)V(x_\alpha)\phi_j(x_\alpha)w_\alpha, \tag{4}$$

where $\{x_\alpha\}$ and $\{w_\alpha\}$ are a set of Gaussian quadrature points and weights associated with the spectral basis functions $\{\phi_i(x)\}$.[3] The transformation matrix between the FBR and the DVR defined by

$$L_{i\alpha}^{\dagger} = \phi_i^*(x_\alpha)w_\alpha^{1/2}, \tag{5}$$

is unitary and the DVR basis function defined by

$$\delta_\alpha(x) = \sum_{i=1}^{N} \phi_i(x)L_{i\alpha}^{\dagger} = \sum_{i=1}^{N} w_\alpha^{1/2}\phi_i^*(x_\alpha)\phi_i(x) \tag{6}$$

is an analogue of the Dirac delta function $\delta(x-x_\alpha)$ localized at the discrete grid point x_α.[15]

In this Section we develop the formal properties of an M-point DVR when a set of quadrature points $\{x_\alpha\}$ and weights $\{w_\alpha\}$ ($\alpha=1,...,M$, where $M>N$) can be chosen such that the spectral basis functions remain orthonormal when elements of the overlap matrix are evaluated by an M-point quadrature. That is,

$$S_{ij} = \sum_{\alpha=1}^{M} w_\alpha \phi_i^*(x_\alpha)\phi_j(x_\alpha) = \delta_{ij}. \tag{7}$$

While choosing more grid points than spectral basis functions may appear counter intuitive, its advantages are that it gives sufficient flexibility to the generalized discrete variable representation (GDVR): (1) to restore the variational principle and make a pseudospectral calculation equivalent to a purely spectral one, and (2) to develop a numerically exact, fast transform between a multidimensional nondirect product spectral basis and a direct product grid. There is not a suitable function of the coordinate operator in a multidimensional nondirect product representation that can be diagonalized to define a unitary transformation between the spectral and the discrete variable representations. Thus, it is not known how to use an alternative strategy based on diagonalizing the coordinate operator.

Now consider the evaluation of elements of the potential matrix in the FBR using the M-point quadrature scheme:

$$\langle \phi_i|V^{\mathrm{FBR}}|\phi_j\rangle = \sum_{\alpha=1}^{M} w_\alpha \phi_i^*(x_\alpha)V(x_\alpha)\phi_j(x_\alpha). \tag{8}$$

As in a conventional N-point DVR, we can define a transformation matrix $\mathbf{L}$ between the generalized discrete variable and finite basis representations by

$$L_{i\alpha}^{\dagger} = w_\alpha^{1/2}\phi_i^*(x_\alpha). \tag{9}$$

This allows us to write $\mathbf{H}^{\mathrm{FBR}}$ in terms of the M-point quadrature scheme as

$$H_{ij}^{\mathrm{FBR}} = \langle i|h|j\rangle + \sum_{\alpha=1}^{M} L_{i\alpha}^{\dagger}V(x_\alpha)L_{\alpha j}, \tag{10}$$

or in matrix notation

$$\mathbf{H}^{\mathrm{FBR}} = \mathbf{h}^{\mathrm{FBR}} + \mathbf{L}^{\dagger}\mathbf{V}^{\mathrm{CR}}\mathbf{L}, \tag{11}$$

where CR denotes the diagonal coordinate representation.

In contrast to a conventional N-point DVR, the transformation matrix $\mathbf{L}$ is now rectangular, since the number of grid points M is greater than the number of spectral basis functions N. Since $\mathbf{L}$ is rectangular, the overlap matrix in the spectral representation $\mathbf{S}=\mathbf{L}^{\dagger}\mathbf{L}$ is an $N\times N$ matrix, while the GDVR overlap matrix $\mathbf{\Delta}=\mathbf{L}\mathbf{L}^{\dagger}$ is an $M\times M$ matrix. Eq. (7), showing the orthonormality of the spectral basis functions under the discrete quadrature, clearly implies that $\mathbf{S}=\mathbf{1}$. However, $\mathbf{\Delta}\neq\mathbf{1}$.

B. GDVR overlap matrix

The structure of the *diagonal* representation of the GDVR overlap matrix can be deduced from arguments similar to those employed in Sec. 2 of Ref. 15 to demonstrate that the transformation matrix between a conventional N-point DVR and the FBR is unitary. Since $\mathbf{L}$ is column orthogonal, $\mathbf{\Delta}$ is idempotent, i.e.

$$\mathbf{\Delta}^2 = \mathbf{L}(\mathbf{L}^{\dagger}\mathbf{L})\mathbf{L}^{\dagger} = \mathbf{L}\mathbf{L}^{\dagger} = \Delta. \tag{12}$$

The invariance of the trace of a product of matrices under cyclic permutation implies that

$$\mathrm{tr}(\mathbf{L}\mathbf{L}^{\dagger}) = \mathrm{tr}(\mathbf{L}^{\dagger}\mathbf{L}) = N. \tag{13}$$

Since the eigenvalues of an idempotent matrix are either zero or one, $\mathbf{\Delta}$ must have N eigenvalues equal to one, and $M-N$ eigenvalues equal to zero. The matrix representation of a projection operator is idempotent, and below we will establish that, provided aliasing terms can be neglected, $\mathbf{\Delta}$ projects a vector evaluated on the GDVR grid onto the space spanned by the N-dimensional spectral basis.

As in a conventional N-point DVR, we construct the generalized discrete variable representation of the Hamiltonian by multiplying $\mathbf{H}^{\mathrm{FBR}}$ on the left with $\mathbf{L}$ and on the right with $\mathbf{L}^{\dagger}$:

$$\begin{aligned}\mathbf{H}^{\mathrm{GDVR}} &= \mathbf{L}\mathbf{H}^{\mathrm{FBR}}\mathbf{L}^{\dagger} = \mathbf{L}\mathbf{h}^{\mathrm{FBR}}\mathbf{L}^{\dagger} + \mathbf{L}\mathbf{L}^{\dagger}\mathbf{V}^{\mathrm{CR}}\mathbf{L}\mathbf{L}^{\dagger} \\ &= \mathbf{L}\mathbf{h}^{\mathrm{FBR}}\mathbf{L}^{\dagger} + \mathbf{\Delta}\mathbf{V}^{\mathrm{CR}}\mathbf{\Delta}.\end{aligned} \tag{14}$$

Note that the potential energy operator *is not* diagonal in this M-point GDVR, because $\mathbf{L}\mathbf{L}^{\dagger}\neq\mathbf{1}$.

Since $\mathbf{\Delta}$, the overlap matrix in the GDVR, does not equal the identity matrix and the rectangular matrix $\mathbf{L}$ is not unitary, the eigensolutions of the Hamiltonian are not invariant with respect to the transformation in Eq. (14). However, it is easy to show that $\mathbf{H}^{\mathrm{GDVR}}$ has N eigenvalues equal to the eigenvalues of the $N\times N$ matrix $\mathbf{H}^{\mathrm{FBR}}$ and an additional $M-N$ eigenvalues equal to zero. Thus, even though the eigensolutions of $\mathbf{H}$ are not invariant with respect to the transformation in Eq. (14), the spectral range (the difference between the largest and smallest eigenvalues) of $\mathbf{H}$ is invariant with respect to this transformation.

The demonstration is straightforward. Consider the N eigenvalue equations in the FBR,

$$\mathbf{H}^{\mathrm{FBR}}\psi_n^{\mathrm{FBR}}=\epsilon_n\psi_n^{\mathrm{FBR}}, \tag{15}$$

where ψ_n^{FBR} is an eigenvector (of length N) of $\mathbf{H}^{\mathrm{FBR}}$ with eigenvalue ϵ_n. Now insert $\mathbf{L}^\dagger\mathbf{L}=\mathbf{1}$ between $\mathbf{H}^{\mathrm{FBR}}$ and ψ_n^{FBR}, and multiply on the left with $\mathbf{L}$ to obtain

$$(\mathbf{L}\mathbf{H}^{\mathrm{FBR}}\mathbf{L}^\dagger)(\mathbf{L}\psi_n^{\mathrm{FBR}})=\epsilon_n(\mathbf{L}\psi_n^{\mathrm{FBR}}). \tag{16}$$

Making the identifications $\mathbf{H}^{\mathrm{GDVR}}=\mathbf{L}\mathbf{H}^{\mathrm{FBR}}\mathbf{L}^\dagger$ and $\psi_n^{\mathrm{GDVR}}=\mathbf{L}\psi_n^{\mathrm{FBR}}$, Eq. (16) can be rewritten as

$$\mathbf{H}^{\mathrm{GDVR}}\psi_n^{\mathrm{GDVR}}=\epsilon_n\psi_n^{\mathrm{GDVR}}. \tag{17}$$

This shows that the N eigenvalues of $\mathbf{H}^{\mathrm{FBR}}$ are also eigenvalues of $\mathbf{H}^{\mathrm{GDVR}}$, and the corresponding eigenvectors (of length M) are simply the eigenvectors of $\mathbf{H}^{\mathrm{FBR}}$ transformed into the GDVR with the matrix $\mathbf{L}$.

The $M\times M$ matrix $\mathbf{H}^{\mathrm{GDVR}}$ has an additional $M-N$ eigenvalues. These can be obtained by considering the trace of the square of the Hamiltonian matrix. It is easy to see that the trace of $(\mathbf{H}^{\mathrm{GDVR}})^2$ equals the trace of $(\mathbf{H}^{\mathrm{FBR}})^2$ by using the invariance of the trace of a product of matrices under cyclic permutation and the identity $\mathbf{L}^\dagger\mathbf{L}=\mathbf{1}$:

$$\begin{aligned}\mathrm{tr}((\mathbf{H}^{\mathrm{GDVR}})^2)&=\mathrm{tr}(\mathbf{L}\mathbf{H}^{\mathrm{FBR}}(\mathbf{L}^\dagger\mathbf{L})\mathbf{H}^{\mathrm{FBR}}\mathbf{L}^\dagger)\\&=\mathrm{tr}((\mathbf{H}^{\mathrm{FBR}})^2\mathbf{L}^\dagger\mathbf{L})=\mathrm{tr}((\mathbf{H}^{\mathrm{FBR}})^2).\end{aligned} \tag{18}$$

Since the trace of a matrix is equal to the sum of its eigenvalues and N eigenvalues of $\mathbf{H}^{\mathrm{GDVR}}$ are identical to the N eigenvalues of $\mathbf{H}^{\mathrm{FBR}}$, Eq. (18) shows that the sum of the squares of the $M-N$ remaining eigenvalues is zero. Since the matrix is Hermitian, each of these eigenvalues must equal zero.

Now, we will clarify the role of $\mathbf{\Delta}$ in the GDVR Hamiltonian. In a conventional representation with N grid points and N basis functions, the DVR and FBR are isomorphic. Thus, the amplitude of a function at a grid point always can be represented as a linear combination of the N FBR basis functions. However, in an M-point GDVR there are only N FBR basis functions, so it is clear that all values at the M grid points cannot be chosen freely and also be guaranteed to be consistent with the underlying FBR basis. It is easy to see that the role of the matrix $\mathbf{\Delta}$ is to confine a function evaluated on the M-dimensional grid to the space spanned by the FBR basis functions.

This can be seen by considering the multiplication of a GDVR vector (of length M) by $\mathbf{\Delta}=\mathbf{L}\mathbf{L}^\dagger$. First, multiplication by $\mathbf{L}^\dagger$ yields a vector (of length N) of FBR coefficients, extracted by a Gaussian quadrature overlap with the wave function. That is,

$$(L^\dagger\psi^{\mathrm{GDVR}})_i=\sum_{\alpha=1}^{M} w_\alpha\phi_i^*(x_\alpha)\psi(x_\alpha) \tag{19}$$

since $\psi_\alpha^{\mathrm{GDVR}}=\sqrt{w_\alpha}\psi(x_\alpha)$. Then, multiplication by $\mathbf{L}$ reconstructs a GDVR vector from the FBR coefficients. If the initial GDVR wave function could be expressed exactly as a linear combination of the FBR basis functions, it is clear that this procedure leaves the GDVR vector unchanged. If not, it projects the GDVR vector onto the space spanned by the FBR basis.

Thus, it is seen that, within the FBR approximation, the role of the matrix $\mathbf{\Delta}$ in the GDVR Hamiltonian of Eq. (14) is to project a function evaluated on the grid onto the space spanned by the spectral basis. Aliasing terms are components outside of the spectral basis $\{\phi_i(x)\}$ produced by the operation $\hat{H}\phi_i(x)$. In the conventional FBR-DVR method the aliasing terms are ignored. Ignoring the aliasing terms is equivalent to the FBR approximation. If the number of grid points M is chosen as discussed in Eq. (7), so that elements of the spectral overlap matrix are evaluated exactly by quadrature, the projection operator does not remove the aliasing terms. In Sec. IV we show how introducing more grid points than specified by the criteria in Eq. (7) can remove the aliasing terms in a pseudospectral algorithm, in both direct product and nondirect product representations. These additional grid points act as dealiasing functions that make a pseudospectral calculation equivalent to a purely spectral calculation.

C. GDVR basis functions

Let us now consider the basis functions in this representation. Since the GDVR is labeled by the grid points $\{x_\alpha\}$, there are M GDVR basis functions defined in terms of the N spectral basis functions by

$$\delta_\alpha(x)=\sum_{i=1}^{N}\phi_i(x)L_{i\alpha}^\dagger. \tag{20}$$

Unlike a conventional N-point DVR the M GDVR basis functions are *not* eigenfunctions of the coordinate operator. This is easy to see, since the number of spectral basis functions is less than the number of GDVR basis functions. Clearly, diagonalizing the $N\times N$ matrix of a function of the coordinate operator $\hat{x}$ in the spectral basis cannot yield M eigenvalues and eigenfunctions, if $M>N$. Furthermore, the conventional N-point DVR basis functions are zero at all grid points other than the one by which they are labeled. This Dirac delta function property is characteristic of *orthogonal* DVR basis functions.[15] This is not true in the GDVR, as can be seen by setting $x=x_\beta$ in Eq. (20),

$$\delta_\alpha(x_\beta)=\sum_{i=1}^{N}\phi_i(x_\beta)L_{i\alpha}^\dagger. \tag{21}$$

Now, using the relation $\phi_i(x_\beta)=L_{\beta i}/w_\beta^{1/2}$, we have

$$\delta_\alpha(x_\beta)=w_\beta^{-1/2}\sum_{i=1}^{N}L_{\beta i}L_{i\alpha}^\dagger \tag{22}$$

$$=w_\beta^{-1/2}\Delta_{\beta\alpha}. \tag{23}$$

Thus, unlike a conventional N-point DVR, the functions $\{\delta_\alpha(x)\}$ do not form an orthogonal basis set. This can be seen easily by considering elements of the GDVR overlap matrix. However, even though the GDVR basis functions are not orthogonal, they are localized on the grid.

D. Generalized eigenvalue problem

Normally, when calculating the eigenvalues of a Hamiltonian in a nonorthogonal basis, one must take account of the nonorthogonality of the basis by solving the generalized eigenvalue problem

$$\det(\mathbf{H}-\mathbf{B}\epsilon)=0, \tag{24}$$

for the eigenvalues ϵ, where $\mathbf{B}$ is the overlap matrix of the basis functions. We now show that this is done implicitly in the M-point GDVR through the inclusion of the projection operator $\mathbf{\Delta}$ in the definition of $\mathbf{H}^{\mathrm{GDVR}}$.

If the overlap matrix $\mathbf{B}$ is not singular, solving Eq. (24) is equivalent to solving

$$\det(\mathbf{B}^{-1/2}\mathbf{H}\mathbf{B}^{-1/2}-\epsilon)=0, \tag{25}$$

where the symmetric placement of the matrix $\mathbf{B}^{-1/2}$ ensures that $\mathbf{B}^{-1/2}\mathbf{H}\mathbf{B}^{-1/2}$ is Hermitian. Of course, for the M-point GDVR basis the overlap matrix $\mathbf{B}$, which is equivalent to $\mathbf{\Delta}$, is singular since it has $M-N$ zero eigenvalues. Singularities (or very small eigenvalues) in the overlap matrix are signatures of linear dependence in the basis set, and the linearly dependent part of the basis must be removed. If $\mathbf{B}$ were not singular, $\mathbf{B}^{-1/2}$ would be calculated by diagonalizing $\mathbf{B}$, taking the inverse square root of the diagonal representation, and then using the unitary transformation that diagonalized $\mathbf{B}$ to construct $\mathbf{B}^{-1/2}$. That is, if we can write

$$\mathbf{B}=\mathbf{U}\mathbf{b}\mathbf{U}^{\dagger}, \tag{26}$$

where $\mathbf{U}$ is the unitary matrix that diagonalizes $\mathbf{B}$, and $\mathbf{b}$ is the diagonal matrix of the eigenvalues of $\mathbf{B}$, then $\mathbf{B}^{-1/2}$ is given by

$$\mathbf{B}^{-1/2}=\mathbf{U}\mathbf{b}^{-1/2}\mathbf{U}^{\dagger}. \tag{27}$$

If the eigenvalues are singular, then either $b_i^{-1/2}$ is undefined or the transformation in Eq. (27) is numerically unstable.

One can circumvent this problem with canonical orthogonalization.[25] In performing the projection (within the diagonal representation of $\mathbf{B}$) onto the space of linearly independent basis functions, $b_i^{-1/2}$ is replaced by zero if the eigenvalue b_i is singular. Denoting the projected matrices by $\tilde{\mathbf{b}}$ and $\tilde{\mathbf{B}}$, then $\tilde{\mathbf{B}}^{-1/2}\mathbf{H}\tilde{\mathbf{B}}^{-1/2}$ will have as many zero eigenvalues as were projected out. In the M-point GDVR, all of the eigenvalues of the overlap matrix are either identically zero or one. Therefore, $\mathbf{\Delta}=\mathbf{U}\mathbf{P}\mathbf{U}^{\dagger}$ where $\mathbf{P}$ is a diagonal matrix with N ones and $M-N$ zeros along the diagonal.

Thus,

$$\tilde{\mathbf{\Delta}}^{-1/2}=\mathbf{\Delta} \tag{28}$$

and

$$\tilde{\mathbf{\Delta}}^{-1/2}\mathbf{H}^{\mathrm{GDVR}}\tilde{\mathbf{\Delta}}^{-1/2}=\mathbf{\Delta}\mathbf{H}^{\mathrm{GDVR}}\mathbf{\Delta}=\mathbf{H}^{\mathrm{GDVR}}. \tag{29}$$

Consequently, diagonalizing $\mathbf{H}^{\mathrm{GDVR}}$ is equivalent to solving the generalized eigenvalue problem of Eq. (24).

E. Summary

To summarize, the rectangular transformation $\mathbf{L}$ maps the N eigenvectors of $\mathbf{H}^{\mathrm{FBR}}$ with eigenvalues $\{\epsilon_1,...,\epsilon_N\}$ onto a set of M eigenvectors, of which N have eigenvalues $\{\epsilon_1,...,\epsilon_N\}$ and $M-N$ have eigenvalues equal to zero. $\mathbf{L}$ is not invertible. However, the above arguments demonstrate that $\tilde{\mathbf{L}}^{-1}=\mathbf{L}^{\dagger}$, where $\tilde{\mathbf{L}}^{-1}$ denotes the *pseudoinverse*[13] of $\mathbf{L}$. Here, the pseudoinverse is defined as the inverse transformation between the subspace spanned by the N (M-component) eigenvectors of $\mathbf{H}^{\mathrm{GDVR}}$ with eigenvalues $\{\epsilon_1,\ldots,\epsilon_N\}$ and the space spanned by the N (N-component) eigenvectors of $\mathbf{H}^{\mathrm{FBR}}$. Thus, the transformation of the vector of wave function expansion coefficients from the FBR to the grid representation is defined by the $M\times N$ matrix $\mathbf{L}$, and the back transformation from the grid to the FBR is given by its adjoint $\mathbf{L}^{\dagger}$. The spectral range (the difference between the largest and smallest eigenvalues) of $\mathbf{H}$ is invariant with respect to these transformations.

III. MULTIDIMENSIONAL TRANSFORM BETWEEN THE NONDIRECT PRODUCT SPECTRAL AND THE GENERALIZED DISCRETE VARIABLE REPRESENTATIONS

The curvilinear coordinates which are most useful in describing nuclear motion in molecules are: (1) stretches (bond lengths) r, (2) in-plane bends (bond angles) θ, and (3) out-of-plane bends, that is, azimuthal angles (rotation about a space-fixed z-axis) ϕ and torsional or dihedral angles (rotation about the body-fixed z-axis) χ. The multidimensional eigenfunctions of the kinetic energy operator $\hat{T}$ in curvilinear coordinates have a common structure. They are defined in terms of a Fourier function $e^{im\phi}$ or $e^{i\Omega\chi}$ for the out-of-plane bend, times a Jacobi polynomial $P_{j-m}^{(m-\Omega,m+\Omega)}(\cos\theta)$ for the in-plane bend, times (usually) a generalized Laguerre polynomial $L_n^j(r)$ or spherical Bessel function $J_{j+1/2}(k_n r)$ for the stretch. (Legendre polynomials $P_j(\cos\theta)$, associated Legendre functions $P_j^m(\cos\theta)$, and the θ-dependent part of Wigner or symmetric top functions $d_{m\Omega}^j(\theta)$ and hyperspherical harmonics are special cases of Jacobi polynomials.[26]) The eigenfunctions of $\hat{T}$ are *nondirect* products of one-dimensional functions, since the in-plane and out-of-plane bends are coupled by the projection quantum numbers m and Ω, and the in-plane bend and stretch are coupled by the angular momentum quantum number j. Because these functions are orthogonal polynomials, there is a simple prescription for devising a multidimensional transform between a nondirect product spectral basis and the corresponding GDVR basis functions, which are labeled by direct product grid points.[14,17]

In defining the one-dimensional transform in Sec. II, we assumed that a set of M grid points and weights could be chosen so that all elements of the $N\times N$ spectral overlap matrix in Eq. (7) are exact when evaluated by quadrature. The Fourier functions are equivalent to Chebychev polynomials, and a trapezoid rule quadrature (with the same number of grid points as Fourier basis functions) on a grid of evenly spaced points in ϕ and χ is of Gaussian quadrature accuracy. The functions of the other coordinates are classical polynomials orthogonal with respect to appropriate weight functions $\Omega(x)$. The quadrature points and weights in the GDVR do not depend on the weight functions. Consequently, the grid is not optimal in the sense that the quadrature scheme

would be of Gaussian accuracy only if $\Omega(x)=1$. Therefore, to maintain the orthonormality of the spectral basis functions one must introduce extra grid points to account for the presence of the weight function in the integrand. Since the polynomial part of the weight function is of degree $2k$, Eq. (7) will be satisfied if $M=N+k$.

Consequently, labeling the three-dimensional spectral basis functions by n,j,Ω and the r,θ,χ grid points by α,β,γ, respectively, the multidimensional transform between a nondirect product spectral basis in curvilinear coordinates and a direct product grid can be defined by

$$L^{\dagger}_{nj\Omega,\alpha\beta\gamma}=R^{j\dagger}_{n\alpha}\Theta^{\Omega\dagger}_{j\beta}\chi^{\dagger}_{\Omega\gamma}. \tag{30}$$

In Eq. (30), $R^{j\dagger}_{n\alpha}$, $\Theta^{\Omega\dagger}_{j\beta}$, and $\chi^{\dagger}_{\Omega\gamma}$ denote the matrix elements of one-dimensional transforms for the r,θ and χ degrees of freedom. $\chi^{\dagger}$ denotes a conventional unitary FBR-DVR transform, whereas $\mathbf{R}^{j\dagger}$ and $\Theta^{\Omega\dagger}$ denote rectangular FBR-GDVR transforms defined as in Eq. (9). The multidimensional transform in Eq. (30) can be factored into a product of one-dimensional matrices (one for each degree of freedom), each of which can be evaluated sequentially. The evaluation of Hamiltonian matrix-vector products is the rate-determining step in the propagation of wave packets and in the Lanczos algorithm. The factorizable structure of the transform in Eq. (30) implies that in a pseudospectral algorithm the Hamiltonian matrix-vector products can be evaluated in $\mathcal{O}(N\log N)$ scalar operations.[9,15,17]

IV. DEALIASING

Aliasing terms are components outside of the spectral basis $\{\phi_i(x)\}$ produced by the operation $\hat{H}\phi_i(x)$. In the Fourier and DVR methods, the spectral basis is chosen to simplify the kinetic energy matrix. In fact, the spectral basis functions often are chosen to be the eigenfunctions of the kinetic energy operator $\hat{T}$. In that case $\hat{T}\phi_i(x)$ does not produce any aliasing terms and the kinetic energy is described exactly. However, the operation of the potential $\hat{V}\phi_i(x)$ does produce aliasing terms.

In the Fourier and DVR methods, the matrix representation of the coordinate operator $\hat{x}$ is diagonal on the grid. The fundamental approximation in those methods is to assume that matrices of all functions of the coordinate operator, including the potential, are also diagonal on the grid. This approximation destroys the variational principle. Often the approximation is described by introducing a finite basis representation[3] (FBR) (defined by evaluating potential matrix elements in the spectral representation by numerical quadrature) which is isomorphic to the DVR. By construction the quadrature is exact for those components of $\hat{V}\phi_i(x)$ which remain within the spectral basis. The error in the quadrature approximation is due to aliasing terms. Purely spectral methods project out the alias exactly. However, aliasing terms which are orthogonal to the spectral basis when the potential matrix elements are evaluated exactly are not orthogonal when the integrals are evaluated approximately.[3,5,23]

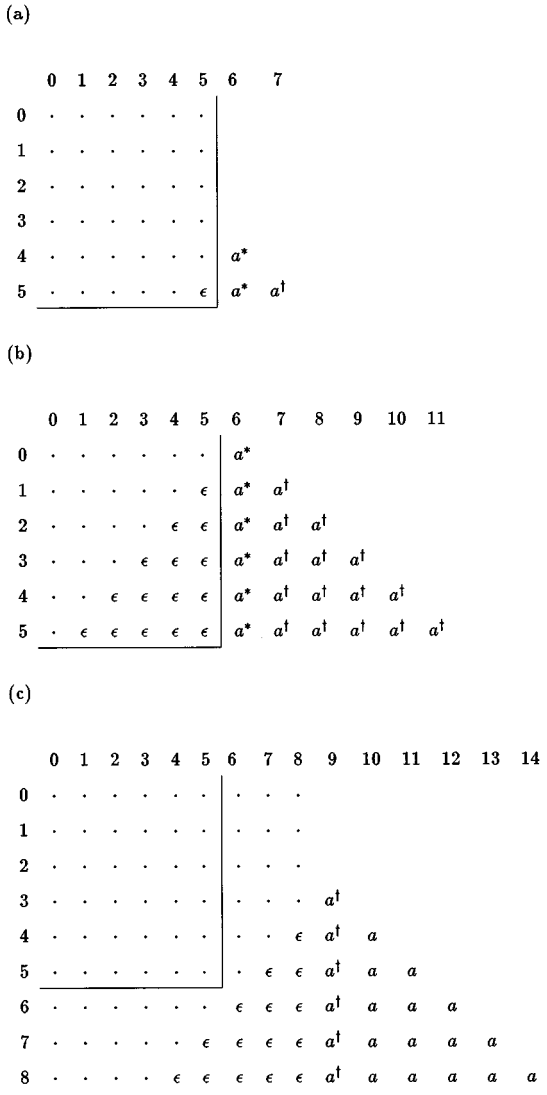

FIG. 1. The FBR potential matrix elements, and the aliasing terms in the Fourier and DVR methods produced by $\hat{V}\phi_i(x)$. $N=6$. (The spectral basis functions are orthogonal polynomials of degree 0,...,5.) The numerals denote the degree of the spectral basis functions and aliasing terms; a denotes the aliasing terms, and ϵ denotes the FBR potential matrix elements that are in error due to the aliases. (a) Limit of no anharmonicity in the potential, or nearly free internal rotational motion in the molecule. (b) Limit of high-order anharmonicity, hindered internal rotation, or large-amplitude vibration. (c) The potential matrix elements and aliasing terms in the augmented FBR basis. *These terms are dealiased exactly with an N-point Gaussian quadrature. †These terms are dealiased exactly with an $(N+m)$-point Gaussian quadrature that restores the variational principle.

In principle the potential, like the wave function, can be expanded as a linear combination of the eigenfunctions of $\hat{T}$,

$$V(x)=\sum_{i=0}^{\lambda} V_i\phi_i(x). \tag{31}$$

This may not be a rapidly converging expansion, but it serves to illustrate the origin of the aliasing terms. This is depicted in Fig. 1 for two limiting cases within the Fourier and DVR methods. By using the GDVR to add m extra grid

points, both the spectral overlap matrix elements and the potential matrix elements can be evaluated exactly by quadrature. Introducing these extra grid points results in an exact dealiasing. Thus, the GDVR method can be used to restore the variational principle and make a pseudospectral calculation equivalent to a purely spectral one.

If λ (the highest-order term in the potential expansion) is even, then $m=\lambda/2$; if λ is odd, then $m=(\lambda-1)/2$. The simplicity of this prescription is due to choosing orthogonal polynomials as spectral basis functions. This is analogous to the exact dealiasing achieved in hydrodynamic pseudospectral codes. The degree of the aliasing terms in the Navier-Stokes equations, which are quadratically nonlinear, is at most $2N$, where N denotes the highest wave vector in a spectral basis of Fourier functions or Chebychev polynomials. An exact dealiasing is achieved with a grid of $3N/2$ points.[7,9]

A. Implications

If x denotes a stretching or bending coordinate, then Fig. 1(a) corresponds to the limit of no anharmonicity in the potential, or of nearly free internal rotational motion in the molecule. As illustrated for a small spectral basis, in this limit ($\lambda=2$) the potential produces only three aliasing terms from the two spectral basis functions $\phi_{N-1}(x)$ and $\phi_N(x)$. Two of those terms are dealiased exactly due to the accuracy of Gaussian quadrature. The other introduces an error into only one element of the potential matrix, $\langle N|V|N\rangle$. Fig. 1(b) illustrates the physically more interesting limit of high-order anharmonicity, hindered internal rotation or wide-amplitude vibration, where the highest-order term in the potential expansion can be of the same degree as the highest-order member of the spectral basis, i.e $\lambda=\mathcal{O}(N)$. In this case $\hat{V}\phi_i(x)$ produces aliasing terms from every member of the spectral basis. Only N of those terms are dealiased exactly by an N-point Gaussian quadrature. Consequently, all $N(N-1)/2$ upper triangular potential matrix elements are in error. The structure in Fig. 1 is independent of N in the sense that if $\lambda=2$, then only one element of the potential matrix will be in error. Similarly, if $\lambda=N$, then all upper triangular elements of the potential matrix will be in error.

In the conventional FBR-DVR method the errors in the potential matrix elements are removed *implicitly* by augmenting the basis. Suppose that a purely spectral calculation could be converged with N basis functions. Then, as illustrated in Fig. 1(c), all matrix elements in the $N\times N$ block in the upper left hand corner of the augmented potential matrix will be evaluated exactly by Gaussian quadrature if m functions are added to the basis. In the limit $N=\lambda$, there would be $3N/2$ functions in this augmented basis.

Obviously, augmenting the FBR-DVR basis increases both the cost of a conventional Householder/QL diagonalization, as well as the cost of each **H**-vector multiplication in an iterative algorithm. It also increases the spectral range (the difference between the largest and smallest eigenvalues) of **H**. In the propagation of wave packets, the numerical efficiency of algorithms for evaluating the quantum mechanical propagator is inversely proportional to the spectral range of **H**.[14] Similarly, in variational calculations of the rovibrational spectra of polyatomic molecules, the numerical efficiency of the Lanczos algorithm depends on the local gap structure of the eigenvalues relative to the most widely separated eigenvalues of **H**, with a large spectral range reducing the algorithm's efficiency.[17,27] We have demonstrated in Sec. II that the spectral range of **H** is invariant when the number of grid points is increased in the GDVR method. Thus, as in pseudospectral electronic structure and fluid dynamics calculations, it is numerically more efficient to augment the grid by adding m points than to augment the spectral basis by adding m eigenfunctions of $\hat{T}$.

B. Spectral basis as the primary representation

The presence of aliasing terms in discrete Fourier transforms[28] and hydrodynamic pseudospectral codes[7,9] is well known. The errors in the potential matrix elements due to aliasing terms also have been discussed in two seminal papers on the DVR.[3,23] Furthermore, it is well known that the aliasing terms are not removed in a conventional implementation of the DVR, in which the $N\times N$ transformation matrix between the FBR and grid representations is used only in the explicit construction of the DVR Hamiltonian matrix.

To see how the aliasing terms can be removed in a pseudospectral algorithm it is important to distinguish clearly between the FBR, the GDVR and the spectral representation. The FBR and the spectral representation are defined in terms of N basis functions which are chosen to simplify the kinetic energy matrix. The FBR differs from the spectral representation in that FBR matrix elements of functions of the coordinate operator are evaluated approximately by quadrature on a grid. In the spectral representation the matrix elements are evaluated exactly. In a direct product representation if the quadrature is defined in terms of N Gaussian points and the corresponding weights, then the elements of the spectral overlap matrix and matrix elements of the coordinate operator are exact. Matrix elements of all other functions of the coordinate operator, e.g. moments of inertia or the intermolecular potential, are in error.

As in a conventional DVR, in the GDVR the wave function expansion coefficients are proportional to the amplitude of the wave function evaluated at a grid point. It is possible to construct a GDVR that is equivalent to either the FBR or the spectral representation. If in a nondirect product representation $M=N+k$ is chosen as discussed in Secs. II and III, the matrix elements of functions of the coordinate operator will have the same structure as in a conventional direct product FBR when they are evaluated by quadrature on a grid. That is, elements of the spectral overlap matrix and matrix elements of the coordinate operator will be evaluated exactly. Matrix elements of all other functions of the coordinate operator will be in error. However, if, as discussed above, an additional m points are added the aliasing terms can be removed and all matrix elements can be evaluated exactly.

However, the utility of an M-point grid does not lie in the explicit construction of matrix elements of functions of the coordinate operator. In fact an iterative algorithm in which the matrix elements in either the FBR or the spectral representation were constructed explicitly prior to the evalu-

ation of Hamiltonian matrix-vector products would not be numerically competitive with the DVR. A pseudospectral evaluation of the Hamiltonian matrix-vector products is essential to obtain a numerically efficient algorithm. As illustrated below, the M-point grid is used to construct a transform between the spectral and GDVR representations, rather than to explicitly construct the Hamiltonian matrix elements in the spectral representation. To simplify notation, the implementation of the algorithm is illustrated for a one-dimensional Hamiltonian. The factorizable structure of a multidimensional transform is illustrated in Eq. (30). This factorizable structure can be exploited to evaluate a multidimensional transform in $\mathcal{O}(N\log N)$ scalar multiplications.[15,17]

In a pseudospectral algorithm the wave function is expanded in the spectral representation (SR) as

$$\psi(x)=\sum_i \psi_i^{\mathrm{SR}}\phi_i(x), \tag{32}$$

and the Hamiltonian is partitioned into two terms $\hat{H}=\hat{h}+\hat{V}$. As discussed in the Introduction, in an **H**-vector multiplication $\hat{h}$ is evaluated in the spectral representation, and $\hat{V}$ is evaluated in the grid representation. Consider,

$$(H^{\mathrm{SR}}\psi^{\mathrm{SR}})_i=k_i\psi_i^{\mathrm{SR}}+\sum_{\alpha j} L_{i\alpha}^{\dagger}V_{\alpha}^{\mathrm{CR}}L_{\alpha j}\psi_j^{\mathrm{SR}}, \tag{33}$$

where $\{k_i\}$ denotes the eigenvalues of $\hat{h}$ in the spectral representation and **L** denotes the rectangular SR-GDVR transform discussed in Secs. II and III. The potential term is evaluated in three steps:

(1) ψ^{SR}, the vector of wave function expansion coefficients in the spectral basis, is transformed from the spectral to the grid representation by evaluating

$$\psi_{\alpha}^{\mathrm{GDVR}}=\sum_j L_{\alpha j}\psi_j^{\mathrm{SR}}. \tag{34}$$

(2) ψ^{GDVR}, the vector of wave function expansion coefficients in the GDVR basis, is multiplied by $\mathbf{V}^{\mathrm{CR}}$, the potential matrix in the coordinate representation, which is *rigorously diagonal*:

$$\chi_{\alpha}^{\mathrm{GDVR}}=V_{\alpha}^{\mathrm{CR}}\psi_{\alpha}^{\mathrm{GDVR}}. \tag{35}$$

(3) Finally, this product is back transformed from the grid to the spectral representation with $\mathbf{L}^{\dagger}$ (the pseudoinverse of **L**):

$$\chi_i^{\mathrm{SR}}=(V^{\mathrm{SR}}\psi^{\mathrm{SR}})_i=\sum_{\alpha} L_{i\alpha}^{\dagger}\chi_{\alpha}^{\mathrm{GDVR}}. \tag{36}$$

Then, the potential energy term in Eq. (36) is added to the *diagonal* kinetic energy term in Eq. (33), yielding

$$(H^{\mathrm{SR}}\psi^{\mathrm{SR}})_i=k_i\psi_i^{\mathrm{SR}}+\chi_i^{\mathrm{SR}}. \tag{37}$$

The transforms in Eqs. (34) and (36) are illustrated in Fig. 2 for the one-dimensional spectral basis of $N=6$ orthogonal polynomials depicted in Fig. 1(b), and $M=9$ GDVR grid points.

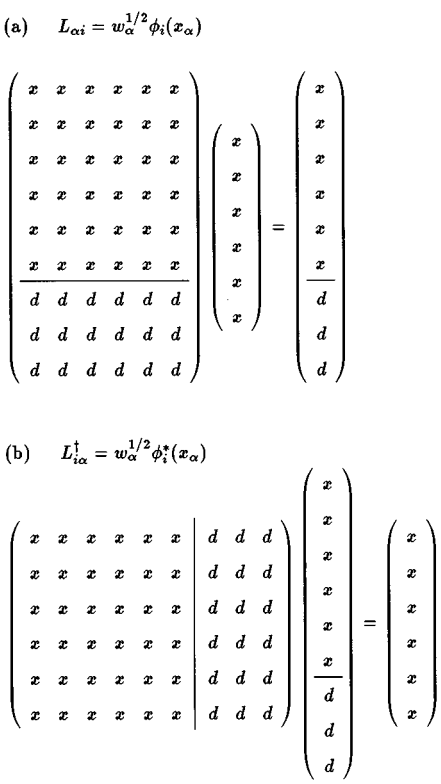

FIG. 2. (a) The $M\times N$ rectangular transformation of a vector from the spectral to the grid representation. (b) The $N\times M$ back transformation from the grid to the spectral representation. The transforms **L** and $\mathbf{L}^{\dagger}$ are illustrated for a spectral basis of $N=6$ orthogonal polynomials and $M=9$ grid points; d denotes the $N/2$ extra grid points introduced in the GDVR to exactly dealiase the aliasing terms depicted in Fig. 1(b) and restore the variational principle.

C. Least squares method

As discussed in the Introduction, in Friesner's[5,29,30] adaptation of the collocation method the $N\times M$ back transformation from the grid to the spectral representation is defined by the pseudoinverse $\mathscr{R}^{-1}=[\mathbf{R}^{\dagger}\mathbf{w}\mathbf{R}]^{-1}\mathbf{R}^{\dagger}$ obtained from a least squares fit of the spectral expansion coefficients ψ^{SR}. $R_{\alpha i}=\phi_i(x_{\alpha})$ is an element of the collocation matrix, and **w** is a matrix of grid weights. We have incorporated the grid weights into our definition of the SR-GDVR transform $L_{\alpha i}=w_{\alpha}^{1/2}R_{\alpha i}$, so that when $M=N$ the grid basis functions are orthonormal. In our approach, $\mathbf{R}^{\dagger}\mathbf{w}\mathbf{R}=\mathbf{1}$ by construction, so that $\mathscr{R}^{-1}=\mathbf{R}^{\dagger}$. Our choice of an orthogonal grid avoids a need to invert the square matrix $\mathbf{R}^{\dagger}\mathbf{w}\mathbf{R}$ and guarantees that the back transformation from the grid to the spectral representation is factorizable.

V. DISCUSSION

In one dimension, the numerical cost of **H**-vector multiplications in the GDVR pseudospectral algorithm will scale semi-linearly with respect to basis set size if there is a fast transform, such as the FFT, for the evaluation of the SR-GDVR transformations. Choosing orthogonal polynomials as spectral basis functions and defining the grid in terms of Gaussian quadrature points yields an exponential conver-

gence of both the spectral and the GDVR bases. As we have discussed in more detail elsewhere,[15,17] this choice also confers a factorizable structure on the multidimensional analogues of the SR-GDVR transform **L**, and its adjoint. For molecules with two or more coupled modes, this factorizable structure can be exploited to evaluate the multidimensional transforms in $\mathcal{O}(N\log N)$ scalar multiplications.

For many molecules, nuclear configurations for which the kinetic energy operator is singular are energetically accessible. In a series of papers[15–17,19] we have proposed using the FBR as the *primary* representation (i.e, the representation in which **H**-vector multiplications are performed) in pseudospectral calculations on such molecules. More recently, Lemoine[31] has proposed using the FBR as the primary representation even when there is not significant amplitude in the wave function near singular nuclear configurations. Our analysis in Sec. IV showing that it is possible to restore the variational principle in a pseudospectral algorithm by introducing extra grid points led to the conclusion that in fact the spectral basis and not the FBR should be chosen as the primary representation. In a recent paper reporting a transform between a spectral basis of Wigner functions and a grid for the Euler angles, Leforestier[18] independently developed a variational pseudospectral algorithm in which potential matrix elements are evaluated exactly by introducing more grid points than spectral basis functions. Leforestier applied the algorithm to the calculation of the bound states of the $Ar–H_2O$ van der Waals complex.

On the other hand, when there is a good adiabatic separation between one or more strong bonds and floppy modes, such as in HCN/HNC or in van der Waals molecules, it will be more appropriate initially to use the DVR as a primitive representation in which to construct a contracted basis.[4,10,11] Contraction schemes replace the spatially localized DVR basis functions with a compact set of delocalized functions. Then this contracted basis is used as the primary representation in which to evaluate **H**-vector multiplications.[29,30,32] Since the contracted basis is a linear combination of orthogonal polynomials, an optimal grid will be defined by a direct product of Gaussian quadrature points.

In summary, in a pseudospectral algorithm the GDVR has all the advantages of the conventional DVR and Fourier methods without being restricted to a direct product representation. It is especially suitable for (1) linear or quasilinear semirigid molecules, (2) floppy molecules for which kinetic energy singularities require special consideration because singular nuclear configurations are energetically accessible, (3) molecules in which intermode coupling is so strong that it is not possible to devise effective contraction schemes, and (4) van der Waals complexes consisting of a nonlinear monomer or two polyatomic monomers. (The orientation of a monomer in a van der Waals complex is defined by a set of Euler angles, and nondirect product Wigner or symmetric top functions are the most suitable basis functions for representing the angular degrees of freedom.[33,34]) Moreover, even when singular nuclear configurations are not energetically accessible, the restriction of a multidimensional DVR to a direct product basis and the quadrature approximation in evaluating potential matrix elements has meant that the DVR basis is often less compact than a spectral basis. This limitation is removed in the GDVR, by no longer seeking a one-to-one correspondence between the number of spectral basis functions and the number of grid points. Even in a direct product representation it is numerically more efficient to augment the grid than to augment the spectral basis. Thus, in conclusion, the utility of the GDVR should be explored further in pseudospectral calculations of the ro-vibrational spectra of polyatomic molecules, as well as in the context of time-dependent and time-independent inelastic or reactive scattering, and photodissociation processes.

ACKNOWLEDGMENTS

Funding for this research has been provided in part by the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Network of Centres of Excellence in Molecular and Interfacial Dynamics (CEMAID).

[1] D. Kosloff and R. Kosloff, J. Comput. Phys. **52**, 35 (1983).
[2] R. Kosloff, J. Phys. Chem. **92**, 2087 (1988).
[3] J. C. Light, I. P. Hamilton, and J. V. Lill, J. Chem. Phys. **82**, 1400 (1985).
[4] Z. Bačić and J. C. Light, Annu. Rev. Phys. Chem. **40**, 469 (1989).
[5] R. A. Friesner, J. Chem. Phys. **85**, 1462 (1986).
[6] R. A. Friesner, Annu. Rev. Phys. Chem. **42**, 341 (1991).
[7] D. Gotlieb and S. Orszag, *Numerical Analysis of Spectral Methods: Theory and Applications* (SIAM, Philadelphia, 1977).
[8] D. Gottlieb, M. Y Hussaini, and S. A. Orszag, in *Spectral Methods for Partial Differential Equations*, edited by R. G. Voigt, D. Gottlieb, and Y. Hussaini (SIAM, Philadelphia, 1984).
[9] J. P. Boyd, *Chebyshev and Fourier Spectral Methods* (Springer, New York, 1989).
[10] Z. Bačić and J. C. Light, J. Chem. Phys. **85**, 4594 (1986).
[11] J. C. Light and Z. Bačić, J. Chem. Phys. **87**, 4008 (1987).
[12] J. T. Muckerman, Chem. Phys. Lett. **175**, 200 (1990).
[13] G. Strang, *Linear Algebra and Its Applications* (Harcourt, Brace, Janovich, San Diego, 1988).
[14] G. C. Corey and D. Lemoine, J. Chem. Phys. **97**, 4115 (1992).
[15] G. C. Corey, J. W. Tromp, and D. Lemoine, in *Numerical Grid Methods and Their Application to Schrodinger's Equation*, edited by C. Cerjan (Kluwer Academic, Boston, 1993).
[16] D. Lemoine and G. C. Corey, J. Chem. Phys. (unpublished).
[17] M. Bramley, J. W. Tromp, T. Carrington, Jr., and G. C. Corey, J. Chem. Phys. **100**, 6175 (1994).
[18] C. Leforestier, J. Chem. Phys. **101**, 7357 (1994).
[19] M. J. Bramley, G. C. Corey, and I. P. Hamilton, J. Chem. Phys. (submitted).
[20] D. Lemoine, Chem. Phys. Lett. **224**, 483 (1994).
[21] D. Lemoine, J. Chem. Phys. **101**, 3936 (1994).
[22] A. S. Dickinson and P. R. Certain, J. Chem. Phys. **49**, 4209 (1968).
[23] D. O. Harris, G. G. Engerholm, and W. D. Gwinn, J. Chem. Phys. **43**, 1515 (1965).
[24] S. Kanfer and M. Shapiro, J. Phys. Chem. **88**, 3964 (1984).
[25] A. Szabo and N. S. Oslund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (McGraw-Hill, New York, 1989).
[26] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, 1974).
[27] J. Cullum and R. A. Willoughby, J. Comput. Phys. **44**, 329 (1981).
[28] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in C The Art of Scientific Computing* (Cambridge University, Cambridge, 1992).
[29] R. A. Friesner, J. A. Bentley, M. Menou, and C. Leforestier, J. Chem. Phys. **99**, 324 (1993).
[30] J. Antikainen, R. Friesner, and C. Leforestier, J. Chem. Phys **102**, 1270 (1995).
[31] D. Lemoine, J. Chem. Phys. **101**, 10526 (1994).
[32] M. J. Bramley and T. Carrington, Jr., J. Chem. Phys. **101**, 8494 (1994).
[33] R. C. Cohen and R. J. Saykally, Annu. Rev. Phys. Chem. **42**, 369 (1991).
[34] A. van der Avoird, P. E. S. Wormer, and R. Moszynski, Chem. Rev. **94**, 1931 (1994).