Finite basis representations with nondirect product basis functions having structure similar to that of spherical harmonics

Gábor Czakó
Institute of Chemistry, Eötvös University, P.O. Box 32, H-1518 Budapest 112, Hungary

Viktor Szalay[a)]
Crystal Physics Laboratory, Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary

Attila G. Császár[b)]
Institute of Chemistry, Eötvös University, P.O. Box 32, H-1518 Budapest 112, Hungary

(Received 17 February 2005; accepted 4 November 2005; published online 6 January 2006)

The currently most efficient finite basis representation (FBR) method [Corey *et al.*, in *Numerical Grid Methods and Their Applications to Schrödinger Equation*, NATO ASI Series C, edited by C. Cerjan (Kluwer Academic, New York, 1993), Vol. 412, p. 1; Bramley *et al.*, J. Chem. Phys. **100**, 6175 (1994)] designed specifically to deal with nondirect product bases of structures $\phi_n^l(s)f_l(u)$, $\chi_m^l(t)\phi_n^l(s)f_l(u)$, etc., employs very special l-independent grids and results in a symmetric FBR. While highly efficient, this method is not general enough. For instance, it cannot deal with nondirect product bases of the above structure efficiently if the functions $\phi_n^l(s)$ [and/or $\chi_m^l(t)$] are discrete variable representation (DVR) functions of the infinite type. The optimal-generalized FBR(DVR) method [V. Szalay, J. Chem. Phys. **105**, 6940 (1996)] is designed to deal with general, i.e., direct and/or nondirect product, bases and grids. This robust method, however, is too general, and its direct application can result in inefficient computer codes [Czakó *et al.*, J. Chem. Phys. **122**, 024101 (2005)]. It is shown here how the optimal-generalized FBR method can be simplified in the case of nondirect product bases of structures $\phi_n^l(s)f_l(u)$, $\chi_m^l(t)\phi_n^l(s)f_l(u)$, etc. As a result the commonly used symmetric FBR is recovered and simplified nonsymmetric FBRs utilizing very special l-dependent grids are obtained. The nonsymmetric FBRs are more general than the symmetric FBR in that they can be employed efficiently even when the functions $\phi_n^l(s)$ [and/or $\chi_m^l(t)$] are DVR functions of the infinite type. Arithmetic operation counts and a simple numerical example presented show unambiguously that setting up the Hamiltonian matrix requires significantly less computer time when using one of the proposed nonsymmetric FBRs than that in the symmetric FBR. Therefore, application of this nonsymmetric FBR is more efficient than that of the symmetric FBR when one wants to diagonalize the Hamiltonian matrix either by a direct or via a basis-set contraction method. Enormous decrease of computer time can be achieved, with respect to a direct application of the optimal-generalized FBR, by employing one of the simplified nonsymmetric FBRs as is demonstrated in noniterative calculations of the low-lying vibrational energy levels of the H_3^+ molecular ion. The arithmetic operation counts of the Hamiltonian matrix vector products and the properties of a recently developed diagonalization method [Andreozzi *et al.*, J. Phys. A Math. Gen. **35**, L61 (2002)] suggest that the nonsymmetric FBR applied along with this particular diagonalization method is suitable to large scale iterative calculations. Whether or not the nonsymmetric FBR is competitive with the symmetric FBR in large-scale iterative calculations still has to be investigated numerically. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2141947]

I. INTRODUCTION

Solution of the molecular rovibrational Schrödinger equation and the calculation of reaction dynamics may be carried out efficiently by employing the method of discrete variable representation (DVR).[1] The utility and basic aspects of DVR were realized by different authors independently and somewhat different methods were developed: discrete variable representation,[2,3] Lagrange-mesh method,[4] and quadrature discretization method.[5,6] The Fourier grid method[7–9] should also be mentioned.

In the DVR method one employs both a set of basis functions and a set of grid points. Within this method the operators of physical quantities may be represented by matrices whose indices refer either to the grid points or to the spectral basis functions. The former is the DVR, the latter is the finite basis representation (FBR) of the operator. The DVR of the potential-energy operator is a diagonal matrix with the (ii)th diagonal element equal to the value of the

[a)]Author to whom correspondence should be addressed. Electronic mail: viktor@mail.szfki.hu
[b)]Electronic mail: csaszar@chem.elte.hu

potential-energy function taken at the *i*th grid point. The FBR of the potential-energy operator corresponds to evaluating the defining integrals of the potential matrix elements in the spectral basis by numerical quadrature, where the quadrature grid is identical to the one defining the DVR. The DVR and FBR of an operator may be transformed into each other.

Initially, the DVR was developed with standard orthogonal polynomial bases and the associated Gaussian quadratures. The same number of basis functions and quadrature points was employed. DVRs based on such basis sets, quadrature points, and weights possess a number of remarkable properties. The most important is the diagonality of the potential-energy matrix. Another important property is related to the eigenvectors obtained by solving the matrix representation of the time-independent Schrödinger equation set up in a DVR. At convergence the *i*th element of the *n*th eigenvector is proportional to the value of the *n*th eigenfunction taken at the *i*th quadrature point. The proportionality factor is just the square root of the *i*th quadrature weight. A more complete list of the various interesting and useful properties of the DVR is given, for example, in Ref. 10.

Generalizations of the DVR method to general basis functions depending on a single variable and to multidimensional nondirect product basis sets have been developed.[3,10–16] These generalizations could be achieved only by sacrificing some of the important properties which the original DVR features.

For example, for general one-dimensional bases one may construct a DVR (Refs. 11, 12, 17, and 18) by utilizing the transformation method.[19,20] While the representation so derived can still give highly accurate results, and, in fact, it can be related to Gaussian quadrature,[12] the elements of the eigenvectors one obtains are no longer proportional to the values of the eigenfunctions taken at the grid points.

The multidimensional generalization of the DVR by Corey and co-workers[13,21] sacrifices the diagonality of the potential-energy matrix and employs more grid points than basis functions. The simple relation between eigenvectors and eigenfunctions of the standard DVR is also broken down in this representation. Since the number of grid points is higher than the number of basis functions it is not the Corey-Tromp DVR,[13] but the related symmetric FBR developed by various authors[21–23] which has been employed in practice[22–27] and became the common method for dealing with nondirect product bases such as the spherical harmonics basis set.

With the application of joint approximate diagonalization methods[28–33] one may generalize the transformation method to multidimensional nondirect product bases and one can construct nondirect product DVRs.[14] However, like in the case of the generalization to one-dimensional (1D) general basis functions, the simple relation of eigenvectors and eigenfunctions is no longer valid. Although this method has been employed successfully in a number of problems,[14,34] its efficiency still has to be demonstrated with as standard nondirect product bases as the spherical harmonics basis set.

The coherent DVR has been introduced recently.[15] It is restricted to two-dimensional (2D) nondirect product bases. It preserves neither the diagonality of the potential-energy matrix nor the simple relation of the eigenvectors and eigenfunctions. Similar to the DVRs based on joint approximate diagonalization, the method's capabilities have been demonstrated neither with spherical harmonics nor with nondirect product basis functions with structure similar to that of spherical harmonics.

The standard DVR and its generalizations mentioned so far are special in that they require very special quadrature points. The question whether a truly generalized DVR, a DVR based on both a general set of quadrature points and a set of general one- or multidimensional basis functions, can be derived was raised two decades ago by Light *et al.*,[3] who described a method for constructing such a DVR.[3] A successful numerical application of this method involved the associated Legendre polynomials, $P_n^L(\cos\vartheta)$, with $L=0, 1,\ldots, L_{\max}$; $n=L, L+1,\ldots, N_{\max}$.[35]

The optimal-generalized DVR was introduced in Ref. 10. It is optimal in the sense that, as shown both analytically and numerically, it gives the best possible results with a given set of grid points and basis functions within a family of generalized discrete variable representation (GDVR) methods including the method of Light *et al.*[3] Of the various generalizations it is the optimal-generalized DVR method which preserves most of the characteristic properties of the standard DVR, including the diagonality of the potential-energy matrix and the simple relation of eigenvectors and eigenfunctions. In addition, as shown in Ref. 16, it has also exponential convergence. However, it has disadvantages, as well: (a) the optimal GDVR leads to a nonsymmetric matrix representation, and (b) in the particular case of spherical harmonics and basis functions of structure similar to that of spherical harmonics a randomly selected grid generally leads to linear dependencies which degrade the accuracy of the results. Nevertheless, the method has shown a certain degree of success even with the spherical harmonics basis.[10]

One way of overcoming the difficulty mentioned above in selecting grid points in the optimal GDVR is to employ a corresponding finite basis representation,[10] to be called optimal-generalized finite basis representation (GFBR). Another might be the construction of a nondirect product grid by joint approximate diagonalization. In a GFBR one can use more grid points than basis functions, thereby improving the accuracy of the results. Recently, we have tested the GFBR by solving the vibrational Schrödinger equation for the molecular ion H_3^+ by treating the singular terms of the triatomic Sutcliffe-Tennyson vibrational Hamiltonian[36] exactly by a judicious choice of basis functions.[37] Basis sets which can handle the singularities in the Sutcliffe-Tennyson vibrational Hamiltonian properly contain nondirect product basis functions of the general form $\chi_m^l(t)\phi_n^l(s)f_l(u)$ or $\phi_n^l(s)f_l(u)$, with $f_l(u)=P_l(\cos\vartheta)$, where $P_l(\cos\vartheta)$ are Legendre polynomials, ϑ is the Jacobi angle, and s and t stand for the radial variables r and R of the Jacobi(Radau) internal coordinate system, or for some function, depending on the particular choice of the functions ϕ_n^l and χ_m^l, of them. The functions ϕ_n^l and χ_m^l may be chosen at least in four different ways: (a) associated-Laguerre polynomials, (b) associated-Laguerre DVR functions (i.e., different DVR functions for different values of l),

(c) spherical Bessel functions, and (d) Bessel-DVR functions.[38–40] At this point a number of comments are in order. In cases (a) and (b) s and t denote the square of the respective radial variables. The basis set corresponding to selection (a) has been employed for solving the vibrational Schrödinger equation of triatomic molecules, see, e.g., Refs. 23, 41, and 42. To the best of our knowledge the basis sets corresponding to choices (b) and (c) have not been tried. Choice (d) was investigated in Ref. 37. Choices (b) and (d) correspond to choosing localized radial functions which is advantageous when calculating the matrix elements of the potential-energy operator by numerical quadrature. Finding the appropriate quadrature for choices (a) and (b) is simple, but it is less obvious for the case when Bessel-DVR functions of the infinite type[38] are used. Clearly, the basis functions corresponding to selection (d) with Bessel-DVR functions of the infinite type are ideal for testing the usefulness of the GFBR scheme. The results obtained in Ref. 37 demonstrated the high accuracy that can be achieved by the optimal GFBR. The calculations of the matrix elements of the potential-energy operator, however, required extremely long computer time, on the order of days.

The main purpose of this communication is to show how the optimal GFBR scheme with nondirect product basis functions of the structures $\phi_n^l(s)f_l(u)$ and $\chi_m^l(t)\phi_n^l(s)f_l(u)$ can be modified to make the computer time required for calculating the matrix elements of the potential-energy operator negligibly small, on the order of seconds instead of days, without compromising the accuracy of the final results (Sec. II). Our results are of special interest, since many analytically known nondirect product bases consist of functions of this particular or of similar structure. The new scheme is tested first by calculating the eigenvalues of a simple model Hamiltonian with the nondirect product basis of spherical harmonics and then by calculating the vibrational energy levels of the H_3^+ molecular ion with nondirect product basis functions formed by coupling Legendre polynomials with Bessel-DVR functions of the infinite type[38] (Sec. III). The results are summarized in Sec. IV.

II. OPTIMAL-GENERALIZED FINITE BASIS REPRESENTATIONS

To begin with it is appropriate to recall some of the relevant ideas and relations of the optimal-generalized discrete variable representation and the related optimal-generalized finite basis representation. Then it will be shown how the optimal GFBR method can be modified by taking advantage of the special structure of the nondirect product basis functions employed. It is assumed that the matrix elements of the kinetic-energy operator can be calculated analytically. Thus the discussion is focused on the problem of evaluating the matrix elements of the potential-energy operator.

A. Generalized finite basis representations

Let $|\phi_n\rangle$, $n=0, 1,\ldots$ be a complete set of orthonormal states in a Hilbert space. The matrix elements of the self-adjoint operator $\hat{V}$ representing the potential energy are defined by

$$\mathcal{V}_{mn} = \langle \phi_m | \hat{V} | \phi_n \rangle \tag{1}$$

in this basis. In practical numerical calculations one works with a truncated basis $|\phi_n\rangle$, $n=0,1,\ldots, N-1$. Then the potential energy may be represented by an N by N real symmetric matrix $\boldsymbol{\mathcal{V}}$. The effect of the potential-energy operator on a basis state may be expressed as

$$\hat{V}|\phi_n\rangle = \sum_{m=0}^{N-1} \mathcal{V}_{mn}|\phi_m\rangle + \sum_{p=N}^{\infty} \mathcal{V}_{pn}|\phi_p\rangle. \tag{2}$$

With $|\mathbf{q}\rangle$ denoting an eigenstate of the coordinate operator $\hat{\mathbf{q}}$ acting in a D-dimensional coordinate space, that is, $\hat{\mathbf{q}}|\mathbf{q}\rangle = \mathbf{q}|\mathbf{q}\rangle$, where $\mathbf{q}=(q_1, q_2, \ldots, q_D)$ is a D tuple of coordinates q_1, q_2,..., q_D, the coordinate representation of Eqs. (2) and (4) can be derived. The coordinate representation of Eq. (2) reads as

$$V(\mathbf{q})\phi_n(\mathbf{q}) = \sum_{m=0}^{N-1} \mathcal{V}_{mn}\phi_m(\mathbf{q}) + \sum_{p=N}^{\infty} \mathcal{V}_{pn}\phi_p(\mathbf{q}), \tag{3}$$

and the coordinate representation of Eq. (1) is

$$\mathcal{V}_{mn} = \int_a^b \phi_m(\mathbf{q}) V(\mathbf{q}) \phi_n(\mathbf{q}) d\tau, \tag{4}$$

where real basis functions are assumed, $d\tau$ is the volume element of integration, and a and b are the lower and upper integration limits, respectively, characteristic of the coordinate space and basis functions considered.

In most cases of practical interest the complexity of the potential-energy function $V(\mathbf{q})$ prevents analytical evaluation of the potential matrix elements; therefore, one has to resort to approximate numerical quadratures. Ideally, the construction of DVRs requires the application of the same number of quadrature points, $\{\mathbf{q}_i\}_{i=0}^{N-1} = \{(q_{1i}, q_{2i}, \ldots, q_{Di})\}_{i=0}^{N-1}$, and weights, $\{w_i\}_{i=0}^{N-1}$, as the number of basis functions employed. This set of N quadrature points and weights is supposed to give an approximation of reasonable accuracy for $N(N+1)/2$ different integrals (note that $\boldsymbol{\mathcal{V}}$ is symmetric) simultaneously. If, in addition, one places no restriction on the points, except that they should be distinct, one faces the challenge of developing, as required for construction of a truly generalized DVR, a quadrature formula which is of reasonable accuracy for all the $N(N+1)/2$ different integrals irrespective of the choice of the N distinct grid points.

In Ref. 10 quadrature formulas were derived allowing the evaluation of the potential matrix elements by employing a general grid and a general basis set. These can be summarized in the expression

$$\mathcal{V}_{mn} \approx \sum_{i=0}^{N-1} \sum_{j=0}^{N-1} \sum_{k=0}^{N-1} F_{mi}(\boldsymbol{\Delta}^{-d})_{ij} V(\mathbf{q}_j)(\boldsymbol{\Delta}^{d-1})_{jk} F_{nk}, \tag{5}$$

where

$$F_{mi} = (\mathbf{F})_{mi} = w_i^{1/2} \phi_m(\mathbf{q}_i), \tag{6}$$

$$\mathbf{\Delta} = \mathbf{F}^T \mathbf{F}, \tag{7}$$

real basis functions are assumed, superscript T denotes transposition, and d can take any real value. That is, the matrix of the potential-energy operator is approximated as

$$\boldsymbol{\mathcal{V}} \approx \mathbf{F} \mathbf{\Delta}^{-d} \mathbf{V} \mathbf{\Delta}^{d-1} \mathbf{F}^T, \tag{8}$$

where $\mathbf{V}$ denotes a diagonal potential-energy matrix whose elements are defined as

$$V_{ij} = \delta_{ij} V(\mathbf{q}_i), \tag{9}$$

where

$$\delta_{ij} = \begin{cases} 1 \text{ if } & i = j \\ 0 \text{ if } & i \neq j. \end{cases} \tag{10}$$

d parametrizes an infinite number of quadrature formulas and approximations to $\boldsymbol{\mathcal{V}}$. Of these, the quadrature with $d=1$ gives the most accurate results and leads to the representations called optimal-generalized finite basis representation and optimal-generalized discrete variable representation. For $d=1$

$$\boldsymbol{\mathcal{V}} \approx \mathbf{F} \mathbf{\Delta}^{-1} \mathbf{V} \mathbf{F}^T. \tag{11}$$

The superiority of the quadrature given in Eq. (11) with respect to those corresponding to $d \neq 1$, and thus the optimal nature of the related generalized FBR and DVR, can be shown as follows.

First, note that by introducing $d = 1 + p$

$$\boldsymbol{\mathcal{V}} \approx \mathbf{F} \mathbf{\Delta}^{-d} \mathbf{V} \mathbf{\Delta}^{d-1} \mathbf{F}^T = \mathbf{F} \mathbf{\Delta}^{-1} \mathbf{\Delta}^{-p} \mathbf{V} \mathbf{\Delta}^{p} \mathbf{F}^T \tag{12}$$

$$= \mathbf{F} \mathbf{\Delta}^{-1} \mathbf{V} \mathbf{F}^T + \mathbf{F} \mathbf{\Delta}^{-1} \mathbf{\Delta}^{-p} [\mathbf{V}, \mathbf{\Delta}^p] \mathbf{F}^T \tag{13}$$

with $[\mathbf{V}, \mathbf{\Delta}^p]$ denoting the commutator of $\mathbf{V}$ and $\mathbf{\Delta}^p$. Second, note that

$$(\mathbf{V}\mathbf{F}^T)_{in} = w_i^{1/2} V(\mathbf{q}_i) \phi_n(\mathbf{q}_i), \tag{14}$$

and from Eqs. (3) and (6)

$$w_i^{1/2} V(\mathbf{q}_i) \phi_n(\mathbf{q}_i) = \sum_{m=0}^{N-1} \mathcal{V}_{mn} F_{mi} + \sum_{p=N}^{\infty} \mathcal{V}_{pn} F_{pi}. \tag{15}$$

Therefore, one can find, by combining Eqs. (13)–(15), that

$$\begin{aligned} \mathcal{V}_{mn} &\approx (\mathbf{F} \mathbf{\Delta}^{-d} \mathbf{V} \mathbf{\Delta}^{d-1} \mathbf{F}^T)_{mn} \\ &= \mathcal{V}_{mn} + \sum_{p=N}^{\infty} \sum_{i=0}^{N-1} \sum_{j=0}^{N-1} F_{mi} (\mathbf{\Delta}^{-1})_{ij} F_{pj} \mathcal{V}_{pn} \\ &\quad + \sum_{i=0}^{N-1} \sum_{j=0}^{N-1} \sum_{k=0}^{N-1} F_{mi} (\mathbf{\Delta}^{-1})_{ij} \{\mathbf{\Delta}^{-p} [\mathbf{V}, \mathbf{\Delta}^p]\}_{jk} F_{nk}, \end{aligned} \tag{16}$$

where use has been made of the relation

$$\mathbf{F} \mathbf{\Delta}^{-1} \mathbf{F}^T = \mathbf{I}_{N \times N}, \tag{17}$$

where $\mathbf{I}_{N \times N}$ denotes the N by N unit matrix. The second and third terms in the right-hand side of Eq. (16) are the error terms arising due to the quadrature approximation. The second term is called aliasing error. It may appear whenever the space spanned by the truncated basis is not closed with respect to the operation by the potential-energy operator, i.e., when $\mathcal{V}_{pn} \neq 0$. The expression for the aliasing error is the same for all GFBRs. The third term depends on p. Thus, it distinguishes various GFBR (and GDVR) methods. Since the commutator $[\mathbf{V}, \mathbf{\Delta}^p]$ does not in general vanish, unless $p = 0$, i.e., $d=1$, the GFBR approximation with $d=1$ is the best. In the $d=1$ case the approximation even changes to equality for all matrix elements if $\hat{V}|\phi_n\rangle$, $n=0, 1, \ldots, N-1$ remain in the space spanned by the truncated basis.

It must be noted that in the derivations starting from Eq. (12) no use has been made of the definition of the $\mathbf{\Delta}$ matrix up until Eq. (16). The first term in the right-hand side in Eq. (16) is equal to $\mathcal{V}_{mn}$, that is, a reasonable approximation can be obtained if and only if $\mathbf{\Delta}$ is defined such that it satisfies Eq. (17) [or Eq. (7)]. Equation (17) can also be viewed as the defining equation of $\mathbf{\Delta}$. The fulfillment of Eq. (17) is a necessary condition of obtaining a reasonable approximation to the potential-matrix elements. As long as the $\mathbf{\Delta}$ matrix so defined is not singular one may expect results of reasonable accuracy, but if $\mathbf{\Delta}$ is singular the accuracy may be lower due to large aliasing error.

The application of the optimal GFBR and the equivalent optimal GDVR revealed unanticipated difficulties when spherical harmonics[10] and basis functions suitable for treating the singularities in the Sutcliffe-Tennyson vibrational Hamiltonian[37] were used. Randomly selected distinct grid points led to singular $\mathbf{\Delta}$ matrices, that is, to linear dependencies, which severely degraded the accuracy of the results. Finding grid points causing no linear dependencies turned out to be difficult. In fact, a search algorithm, the genetic algorithm, was called for selecting a suitable grid in the case of spherical harmonics. As to the other set of basis functions we considered a different strategy. We gave up efforts of searching for suitable grid points of the same number as the number of basis functions. We decided to use more grid points than the number of basis functions employed.

The GFBR allows one to use more grid points than basis functions. Let us introduce a matrix, $\mathbf{S}$, defined as

$$\mathbf{S} = \mathbf{F}\mathbf{F}^T. \tag{18}$$

One can show that

$$\mathbf{\Delta}^{-d} = \mathbf{F}^T \mathbf{S}^{-d-1} \mathbf{F}. \tag{19}$$

By using Eq. (19) one may replace $\mathbf{\Delta}$ with $\mathbf{S}$ in the quadrature formulas. In particular, the optimal GFBR of the potential-energy operator and the necessary condition for obtaining a quadrature of reasonable accuracy read as

$$\boldsymbol{\mathcal{V}} \approx \mathbf{S}^{-1} \mathbf{F} \mathbf{V} \mathbf{F}^T \tag{20}$$

and

$$\mathbf{S}^{-1} \mathbf{F} \mathbf{F}^T = \mathbf{I}_{N \times N}, \tag{21}$$

respectively. Once the replacement has been made it is irrelevant how the resulting equations were derived and more grid points than basis functions can be employed. What one hopes for is that by employing more grid points than basis functions $\mathbf{S}$ becomes nonsingular and accurate results are obtained.

This strategy has been quite successful in all but one respect.[37] The evaluation of the potential-energy matrix by the optimal GFBR expression, Eq. (20), required too much computer time to be practical when basis functions of structure $\chi_m^l(t)\phi_n^l(s)f_l(u)$ were employed. In the next subsection we show how this expression can be simplified, without losing accuracy, thereby making the calculations efficient.

In passing we note that one may improve the accuracy of Eq. (20) by dealiasing. The fulfillment of the equation

$$\mathbf{S}^{-1}\mathbf{F}(\mathbf{F}^T\mathbf{F}_{\text{alias}}^T) = (\mathbf{I}_{N\times N}\mathbf{0}_{N\times M}), \tag{22}$$

where $\mathbf{F}_{\text{alias}}$ is an M by N matrix whose elements are defined in Eq. (1) with $m=N, N+1,\ldots, N+M$ and $\mathbf{0}_{N\times M}$ denotes a matrix of the size $N\times M$ having all elements equal to zero, ensures the removal of M aliasing terms, as can be seen from Eq. (16) once it has been expressed in terms of the $\mathbf{S}$ matrix. This and a Monte Carlo-based dealiasing method have been pointed out along with the fact that the optimal-generalized FBR formula, Eq. (20), corresponds to that one obtains when calculating the potential-energy matrix by the least-squares pseudospectral method of Friesner,[43] in Ref. 10.

B. Modified optimal GFBR for nondirect product bases of special structure

By considering the optimal GFBR formula, Eq. (20) and Eqs. (14) and (15), one can see that $\mathbf{S}^{-1}\mathbf{F}$ projects out the desired potential matrix elements from $\mathbf{V}\mathbf{F}^T$. One is allowed to modify $\mathbf{S}^{-1}\mathbf{F}$. As long as Eq. (21) is satisfied by the modified matrix, this modification will essentially preserve the accuracy of the original GFBR. We say *essentially* as a modification may either decrease or increase the quadrature error due to aliasing.

Since Eq. (21) defines $\mathbf{S}$, one can modify only the matrix $\mathbf{F}$. Let $\tilde{\mathbf{F}}$ denote such a modified $\mathbf{F}$ matrix. The most significant simplification in Eq. (20) may be achieved by choosing an $\tilde{\mathbf{F}}$ such that it satisfies

$$\tilde{\mathbf{F}}\mathbf{F}^T = \mathbf{I}_{N\times N}, \tag{23}$$

or

$$\tilde{\mathbf{F}}(\mathbf{F}^T\mathbf{F}_{\text{alias}}^T) = (\mathbf{I}_{N\times N}\mathbf{0}_{N\times M}), \tag{24}$$

when dealiasing is required.

Then,

$$\mathcal{V} \approx \tilde{\mathbf{F}}\mathbf{V}\mathbf{F}^T. \tag{25}$$

Note that the approximation in Eq. (25) is expected to have similar accuracy as in Eq. (20), since, due to the fulfillment of Eq. (23), the (mn)th element of the approximating matrix, $(\tilde{\mathbf{F}}\mathbf{V}\mathbf{F}^T)_{mn}$, is equal to the sum of the exact matrix element, $\mathcal{V}_{mn}$, of the potential-energy operator and an aliasing term, exactly as in the case of the quadrature approximation of Eq. (20) under the condition Eq. (21).

As shown below, the simplified GFBR expression, Eq. (25), can be implemented in practice for nondirect product basis functions having structure similar to that of spherical harmonics, e.g., $\chi_m^l(t)\phi_n^l(s)f_l(u)$, $\phi_n^l(s)f_l(u)$, etc.

Let the discussion be confined to basis functions of structure $\phi_n^l(s)f_l(u)$. Assume that the basis functions are real valued. (This is not a severe restriction, since one can easily obtain the appropriate expressions by replacing transposition with Hermitian conjugation and by invoking complex conjugation when required.) Furthermore, assume that the basis functions are orthonormal, that is,

$$\langle \phi_m^k f_k | \phi_n^l f_l\rangle = \langle f_k|f_l\rangle\langle \phi_m^k|\phi_n^l\rangle = \delta_{kl}\langle \phi_m^l|\phi_n^l\rangle = \delta_{kl}\delta_{m_l n_l}, \tag{26}$$

where subscript l is attached to the indices m and n to indicate that they number the functions $\phi_{(*)}^l$. For ϕ_n^l, from now on we shall also use the notation $\phi_{n_l}^l$.

Consider the truncated basis defined by letting the indices l and n_l take the following values:

$$l = 0,1,\ldots,L-1, \quad n_l = 0,1,\ldots,N_l - 1.$$

This truncated basis consists of $\Sigma_{l=0}^{L-1}N_l$ basis functions.

To achieve our goal we must give up using arbitrary grid points. Only particular grid points will do.

1. The choice of grid points: Grid I

Choose an $\mathcal{L}$-point grid, $\{u_i\}_{i=0}^{\mathcal{L}-1}$ for the variable u such that with appropriate weights $w_{u,i}$

$$\sum_{i=0}^{\mathcal{L}-1} w_{u,i} f_k(u_i) f_l(u_i) = \delta_{kl}, \tag{27}$$

where subscript u reminds us that the weights belong to a quadrature approximation of integrals with respect to the coordinate u. Discretize the variable s on the grid

$$s_{i_l}, i_l = 0,1,\ldots,\mathcal{N}_l - 1, \quad l = 0,1,\ldots,\mathcal{L}-1$$

defined such that with appropriate weights

$$\sum_{i_l=0}^{\mathcal{N}_l-1} w_{s,i_l}\phi_m^l(s_{i_l})\phi_n^l(s_{i_l}) = \delta_{n_l m_l}. \tag{28}$$

Then, a 2D grid is obtained by taking direct product of the u grid and the s_l grids (with subscript l indicating that for each value of l there is a different s grid). Altogether we have $\mathcal{L}\Sigma_{l=0}^{\mathcal{L}-1}\mathcal{N}_l$ grid points. In the discussion to come we shall assume the smallest grid which may satisfy Eqs. (27) and (28), that is, the grid corresponding to $\mathcal{L}=L$ and $\mathcal{N}_l=N_l$.

2. A suitable $\tilde{\mathbf{F}}$ matrix defined with grid I

Form the matrix $\mathbf{F}$ according to the standard GFBR prescription, Eq. (6),

$$F_{ln_l,ii_k} = w_{s,i_k}^{1/2} w_{u,i}^{1/2}\phi_{n_l}^l(s_{i_k})f_l(u_i). \tag{29}$$

This is a matrix of size $(\Sigma_{l=0}^{L-1}N_l)\times L\Sigma_{l=0}^{L-1}N_l$.

A matrix $\tilde{\mathbf{F}}$ obeying Eq. (23) can be obtained from $\mathbf{F}$ as

$$\tilde{F}_{ln_l,ii_k} = \begin{cases} 0 & \text{if } l \neq k \\ F_{ln_l,ii_l} & \text{if } l = k. \end{cases} \tag{30}$$

Direct substitution shows that Eq. (23) is satisfied:

$$(\tilde{\mathbf{F}}\mathbf{F}^T)_{km_k,ln_l} = \sum_{i=0}^{L-1}\sum_{l'=0}^{L-1}\sum_{i_{l'}=0}^{N_{l'}-1} \tilde{F}_{km_k,ii_{l'}} F_{ln_l,ii_{l'}}$$
$$= \sum_{i=0}^{L-1}\sum_{i_k=0}^{N_k-1} F_{km_k,ii_k} F_{ln_l,ii_k}$$
$$= \sum_{i=0}^{L-1}\sum_{i_k=0}^{N_k-1} w_{s,i_k}^{1/2} w_{u,i}^{1/2} \phi_{m_k}^k(s_{i_k}) f_k(u_i)$$
$$\times w_{s,i_k}^{1/2} w_{u,i}^{1/2} \phi_{n_l}^l(s_{i_k}) f_l(u_i)$$
$$= \sum_{i_k=0}^{N_k-1} w_{s,i_k} \phi_{m_k}^k(s_{i_k}) \phi_{n_l}^l(s_{i_k})$$
$$\times \sum_{i=0}^{L-1} w_{u,i} f_k(u_i) f_l(u_i)$$
$$= \sum_{i_k=0}^{N_k-1} w_{s,i_k} \phi_{m_k}^k(s_{i_k}) \phi_{n_k}^k(s_{i_k}) \delta_{kl} = \delta_{kl}\delta_{m_k n_k}, \quad (31)$$

where use has been made of Eqs. (27) and (28).

The quadrature approximation to an element of the potential-energy matrix is then

$$\mathcal{V}_{km_k,ln_l} \approx (\tilde{\mathbf{F}}\mathbf{V}\mathbf{F}^T)_{km_k,ln_l}$$
$$= \sum_{i=0}^{L-1}\sum_{l'=0}^{L-1}\sum_{i_{l'}=0}^{N_{l'}-1} \tilde{F}_{km_k,ii_{l'}} V(s_{i_{l'}},u_i) F_{ln_l,ii_{l'}}$$
$$= \sum_{i=0}^{L-1}\sum_{i_k=0}^{N_k-1} \tilde{F}_{km_k,ii_k} V(s_{i_k},u_i) F_{ln_l,ii_k}$$
$$= \sum_{i=0}^{L-1}\sum_{i_k=0}^{N_k-1} w_{s,i_k} w_{u,i} \phi_{m_k}^k(s_{i_k}) f_k(u_i) V(s_{i_k},u_i) \phi_{n_l}^l(s_{i_k}) f_l(u_i). \quad (32)$$

If one can choose the basis functions $\phi_m^k(s)$ such that they have the property

$$w_{s,i_k}^{1/2} \phi_m^k(s_{i_k}) = \delta_{m_k i_k}, \quad (33)$$

then

$$\tilde{F}_{km_k,ii_l} = \begin{cases} 0 & \text{if } l \neq k \\ \delta_{m_k i_l} w_{u,i}^{1/2} f_k(u_i) & \text{if } l = k, \end{cases} \quad (34)$$

and the quadrature formula simplifies further:

$$\mathcal{V}_{km_k,ln_l} \approx \sum_{i=0}^{L-1}\sum_{i_k=0}^{N_k-1} \tilde{F}_{km_k,ii_k} V(s_{i_k},u_i) F_{ln_l,ii_k}$$
$$= \sum_{i=0}^{L-1} w_{u,i}^{1/2} f_k(u_i) V(s_{m_k},u_i) F_{ln_l,im_k}$$
$$= \sum_{i=0}^{L-1} w_{s,m_k}^{1/2} w_{u,i} f_k(u_i) V(s_{m_k},u_i) \phi_{n_l}^l(s_{m_k}) f_l(u_i). \quad (35)$$

Similar discussion applies to the case of basis functions of structure $\chi_m^l(t)\phi_n^l(s)f_l(u)$. Therefore, it suffices to present the final quadrature formulas. By using the truncated basis $\{\chi_{m_l}^l(t)\phi_{n_l}^l(s)f_l(u)\}_{l=0,n_l=0,m_l=0}^{L-1,N_l-1,M_l-1}$ they read as

$$\mathcal{V}_{km_k o_k,ln_l p_l} \approx \sum_{i=0}^{L-1}\sum_{j_k=0}^{M_k-1}\sum_{i_k=0}^{N_k-1} w_{t,j_k} w_{s,i_k} w_{u,i}$$
$$\times \chi_{o_k}^k(t_{j_k}) \phi_{m_k}^k(s_{i_k}) f_k(u_i) V(t_{j_k},s_{i_k},u_i)$$
$$\times \chi_{p_l}^l(t_{j_k}) \phi_{n_l}^l(s_{i_k}) f_l(u_i) \quad (36)$$

and

$$\mathcal{V}_{km_k o_k,ln_l p_l} \approx \sum_{i=0}^{L-1} w_{t,o_k}^{1/2} w_{s,m_k}^{1/2} w_{u,i} f_k(u_i) V(t_{o_k},s_{m_k},u_i)$$
$$\times \chi_{p_l}^l(t_{o_k}) \phi_{n_l}^l(s_{m_k}) f_l(u_i), \quad (37)$$

where in deriving the latter approximation the functions $\phi_m^k(s)$ are assumed to satisfy Eq. (33), and the functions $\chi_o^k(t)$ are assumed to satisfy similar equations.

When compared to the detailed expression of the potential matrix elements arising from Eq. (20), the simplicity, and thus the efficiency, of the quadrature formulas given in Eqs. (32) and (35)–(37) are obvious. The effectiveness of this approach also becomes obvious from counting the number of multiplications and additions required to evaluate these expressions, as given in Tables I and II.

The accuracy of the quadrature formulas given in Eqs. (32) and (35)–(37) is to be similar to that of Eq. (20) due to the fulfillment of the condition Eq. (21).

While it is possible, it is not worth transforming Eqs. (32) and (35)–(37) to the DVR, since the potential-energy matrix will not be diagonal, and the size of the DVR will be larger than that of the FBR.

3. The choice of grid points: Grid II

Discretize the coordinate u as in grid I. Then, if the coordinate s can be discretized, say, on a P-point, l-independent grid such that the equations

$$\sum_{i=0}^{P-1} w_{s,i} \phi_m^l(s_i) \phi_n^l(s_i) = \delta_{n_l m_l}, \quad l = 0,1,\ldots,L-1 \quad (38)$$

hold, $\tilde{\mathbf{F}} = \mathbf{F}$ is an appropriate choice. Then, $\mathbf{S} = \mathbf{F}\mathbf{F}^T$ is identical to a unit matrix, and the optimal GFBR simplifies to the symmetric form

$$\boldsymbol{\mathcal{V}} \approx \mathbf{F}\mathbf{V}\mathbf{F}^T. \quad (39)$$

This symmetric FBR has been introduced in Refs. 21 and 23 and became a commonly employed method.[24–26,44] It is also the FBR corresponding to the Corey-Tromp GDVR.[13,21] Note that in the case of the truncated three-dimensional (3D) nondirect product basis an equation similar to Eq. (38) applies to the function of variable t with an upper summation limit, M, say.

The simplified nonsymmetric FBRs compare favorably with the symmetric FBR if we consider the evaluation of the potential-energy matrix. Indeed, its evaluation with the sym-

TABLE I. The number of arithmetic operations required to evaluate the potential matrix element $\mathcal{V}_{km_k,ln_l}$ and the potential matrix in the truncated nondirect product basis $\{\phi^l_{n_l}(s)f_l(u)\}^{L-1,N_l-1}_{l=0,n_l=0}$ by different quadrature grids and formulas. In calculating the number of operations it was assumed that the quadrature weights had been built into the basis functions. In addition to the exact number of operations, an estimated number of operations relative to the quadrature of least operation count is also given. It is equal to or smaller than the ratio of the exact operation count in a given quadrature formula and that in the reference quadrature formula. Thus, it is equal to 1 for the reference quadrature.

Basis	$\{\phi^l_{n_l}(s)f_l(u)\}^{L-1,N_l-1}_{l=0,n_l=0}$			
Number of basis functions	$N=\Sigma_{l=0}^{L-1}N_l$			
Number of points	LN[a]	LN	LN	PL
Number of matrix elements to be calculated	N^2	N^2	N^2	$N(N+1)/2$[b]
Quadrature formula	Eq. (20)[c]	Eq. (32)	Eq. (35)	Eq. (39)
Matrix element: $\mathcal{V}_{km_k,ln_l}$				
Number of multiplications	$2N(L+1)$	$2N_k(L+1)$	$2L+1$	$2P(L+1)$
Number of additions	$NL-1$	N_kL-1	$L-1$	$PL-1$
Potential matrix evaluation				
Number of multiplications	$2N^3(L+1)$	$2N(L+1)\Sigma_{l=0}^{L-1}N_l^2$	$N^2(2L+1)$	$PN(N+1)(L+1)$
Number of additions	N^3L-N^2	$N(\Sigma_{l=0}^{L-1}N_l^2)L-N^2$	$N^2(L-1)$	$N(N+1)(PL-1)/2$
Matrix element: $\mathcal{V}_{km_k,ln_l}$				
Relative number of multiplications	$\geqq N$	$\geqq N_k$	1	$\geqq P$
Relative number of additions	$\geqq N$	$\geqq N_k$	1	$\geqq P$
Potential matrix evaluation				
Relative number of multiplications	$\geqq N$	$\geqq N^{-1}\Sigma_{l=0}^{L-1}N_l^2$	1	$\geqq P/2$
Relative number of additions	$\geqq N$	$\geqq N^{-1}\Sigma_{l=0}^{L-1}N_l^2$	1	$\geqq P/2$

[a]This is the minimum number of points which may satisfy Eqs. (27) and (28).
[b]It suffices to calculate fewer matrix elements, since this quadrature leads to a symmetric potential matrix.
[c]In this case $\boldsymbol{V}^{\mathrm{FBR}}=\mathbf{S}^{-1}(\mathbf{F}\mathbf{V}\mathbf{F}^T)$ and the operation counts refer to that of the expression in the parentheses.

TABLE II. The exact and estimated relative number of arithmetic operations in evaluating the potential matrix element $\mathcal{V}_{km_ko_k,ln_lp_l}$ and the estimated relative number of operations in calculating the potential matrix with the truncated nondirect product basis $\{\chi^l_{m_l}(t)\phi^l_{n_l}(s)f_l(u)\}^{L-1,N_l-1,M_l-1}_{l=0,n_l=0,m_l=0}$ by different quadrature grids and formulas. When calculating the number of operations it was assumed that the quadrature weights had been built into the basis functions. The estimated relative number of arithmetic operations is equal to or smaller than the ratio of the exact operation count in a given quadrature formula and that in the reference quadrature formula. Thus, it is equal to 1 for the reference quadrature.

Basis	$\{\chi^l_{m_l}(t)\phi^l_{n_l}(s)f_l(u)\}^{L-1,N_l-1,M_l-1}_{l=0,n_l=0,m_l=0}$			
Number of basis functions	$N=\Sigma_{l=0}^{L-1}M_lN_l$			
Number of points	$NP=L(\Sigma_{l=0}^{L-1}N_l)(\Sigma_{l=0}^{L-1}M_l)$[a]	NP	NP	MPL
Number of matrix elements to be calculated	N^2	N^2	N^2	$N(N+1)/2$[b]
Quadrature formula	Eq. (20)[c]	Eq. (36)	Eq. (37)	Eq. (39)
Matrix element: $\mathcal{V}_{km_ko_k,ln_lp_l}$				
Number of multiplications	$2L(\Sigma_{l=0}^{L-1}M_l)(\Sigma_{l=0}^{L-1}N_l)+2(\Sigma_{l=0}^{L-1}M_l)(\Sigma_{l=0}^{L-1}N_l)+2\Sigma_{l=0}^{L-1}N_l$	$2LM_kN_k+2M_kN_k+2N_k$	$2L+2$	$2LMP+2MP+2P$
Number of additions	$L(\Sigma_{l=0}^{L-1}M_l)(\Sigma_{l=0}^{L-1}N_l)-1$	LM_kN_k-1	$L-1$	$LMP-1$
Relative number of multiplications	$\geqq(\Sigma_{l=0}^{L-1}M_l)(\Sigma_{l=0}^{L-1}N_l)$	$\geqq M_kN_k$	1	$\geqq MP$
of additions	$\geqq(\Sigma_{l=0}^{L-1}M_l)(\Sigma_{l=0}^{L-1}N_l)$	$\geqq M_kN_k$	1	$\geqq MP$
Potential matrix evaluation				
Relative number of multiplications	$\geqq(\Sigma_{l=0}^{L-1}M_l)(\Sigma_{l=0}^{L-1}N_l)$	$\geqq N^{-1}\Sigma_{l=0}^{L-1}M_l^2N_l^2$	1	$\geqq MP/2$
of additions	$\geqq(\Sigma_{l=0}^{L-1}M_l)(\Sigma_{l=0}^{L-1}N_l)$	$\geqq N^{-1}\Sigma_{l=0}^{L-1}M_l^2N_l^2$	1	$\geqq MP/2$

[a]This is the minimum number of points which may satisfy Eqs. (27) and (28).
[b]It suffices to calculate fewer matrix elements, since this quadrature leads to a symmetric potential matrix.
[c]In this case $\boldsymbol{V}^{\mathrm{FBR}}=\mathbf{S}^{-1}(\mathbf{F}\mathbf{V}\mathbf{F}^T)$ and the operation counts refer to that of the expression in the parentheses.

metric FBR requires at least $P/2$ and $PM/2$ times more arithmetic operations than the application of the simplified nonsymmetric FBR given in Eqs. (35) and (37), respectively (see Tables I and II). Thus, even with assuming a small value, say, $P=10$ and $M=10$, the simplified nonsymmetric FBRs will be at least 5 and 50 times faster. As to the simplified nonsymmetric FBRs given in Eqs. (32) and (36) we note that with typical choices of the functions ϕ_n^l and χ_m^l, e.g., associated Legendre polynomials, the smallest P-point quadrature satisfying Eq. (38) may have $P=\max\{N_l;l=0,1,\ldots,L-1\}$. In this case the nonsymmetric FBRs, Eqs. (32) and (36), are only slightly more efficient than the symmetric FBR. With $P>\max\{N_l,l=0,1,\ldots,L-1\}$, and this may be the general situation, the nonsymmetric FBRs of Eqs. (32) and (36) clearly outperform the symmetric FBR.

The operation counts given in Tables I and II are obtained by sequential summation.[21,45] Since the order of summations with respect to some of the indices can still be interchanged, different operation counts can be obtained. However, the relative operation counts remain the same irrespective of these changes.

The symmetric and nonsymmetric FBRs are expected to have similar accuracy, since Eq. (21) is obeyed in both cases.

The product of the potential-energy matrix, $\mathbf{V}^{\mathrm{FBR}}$, with a vector of expansion coefficients, $\mathbf{c}$, i.e. $\mathbf{c}'=\mathbf{V}^{\mathrm{FBR}}\mathbf{c}$, must be calculated repeatedly, when diagonalizing the Hamiltonian matrix by an iterative method, such as the Lanczos algorithm.[46] If the potential matrix is not symmetric, one must also calculate $\mathbf{v}'=(\mathbf{V}^{\mathrm{FBR}})^T\mathbf{c}$. To compare the efficiency of the symmetric FBR and the simplified nonsymmetric FBRs in evaluating the potential matrix vector product, let us consider the case of the 2D truncated basis.

Assuming that the quadrature weights have been built into the basis functions, introducing

$$d_{lk^*}=\sum_{i=0}^{L-1} f_k(u_i)V(u_i,s_*)f_l(u_i), \tag{40}$$

and employing sequential summation, $\mathbf{c}'$ can be evaluated according to the expressions

$$c'_{km_k}=\sum_{t=0}^{P-1}\phi_{m_k}^k(s_t)\sum_{l=0}^{L-1}d_{lkt}\sum_{n_l=0}^{N_l-1}\phi_{n_l}^l(s_t)c_{ln_l}, \tag{41}$$

$$c'_{km_k}=\sum_{i_k=0}^{N_k-1}\phi_{m_k}^k(s_{i_k})\sum_{l=0}^{L-1}d_{lki_k}\sum_{n_l=0}^{N_l-1}\phi_{n_l}^l(s_{i_k})c_{ln_l}, \tag{42}$$

and

$$c'_{km_k}=\sum_{l=0}^{L-1}d_{lkm_k}\sum_{n_l=0}^{N_l-1}\phi_{n_l}^l(s_{m_k})c_{ln_l}, \tag{43}$$

corresponding to the symmetric FBR, the simplified nonsymmetric FBR of Eq. (32), and the simplified nonsymmetric FBR of Eq. (35), respectively. $\mathbf{v}'$ can be evaluated according to the expressions

$$v'_{ln_l}=\sum_{k=0}^{L-1}\sum_{i_k=0}^{N_k-1}d_{lki_k}\phi_{n_l}^l(s_{i_k})\sum_{m_k=0}^{N_k-1}\phi_{m_k}^k(s_{i_k})c_{km_k}, \tag{44}$$

and

$$v'_{ln_l}=\sum_{k=0}^{L-1}\sum_{m_k=0}^{N_k-1}d_{lkm_k}\phi_{n_l}^l(s_{m_k})c_{km_k}, \tag{45}$$

corresponding to the nonsymmetric FBRs of Eqs. (32) and (35), respectively.

The number of multiplications and additions performed in evaluating these expressions is summarized in Table III.

One can see from Table III that the relative performance of the symmetric and nonsymmetric FBRs in evaluating the product of the potential-energy matrix with a vector may depend on the particular basis and truncation scheme employed and neither representation can claim superiority, in general. Indeed, if $P<N$ the symmetric FBR may be the fastest, but if $N<P$ the simplified nonsymmetric FBR of Eq. (35) is the fastest. With reasonable truncation schemes and the most well-known 2D nondirect product bases of structure similar to that of spherical harmonics $P<N$. Nevertheless, even when $P<N$ the simplified nonsymmetric FBR may be employed in solving large scale eigenvalue problems efficiently.

As displayed in Table III, the simplified nonsymmetric FBR of Eq. (35) is significantly, about P times, faster in evaluating an individual element of the potential-energy matrix vector product than the symmetric FBR. One may take advantage of this fact in calculating selected eigenpairs of the Hamiltonian matrix with a recent generalization of the variational optimal relaxation method.[47,48] This method requires only as many elements of the Hamiltonian matrix vector product as the number of eigenvalues sought, it extends easily to nonsymmetric matrix eigenvalue problems, and it has been shown to be competitive with the Lanczos algorithm.[47,48] We shall explore this type of computation in future works.

Besides the promise of being suitable for large scale computations there is another reason why l-dependent grid simplified nonsymmetric FBR calculations can be useful.

In general, no l-independent grid can satisfy Eq. (38) and no grid can satisfy Eq. (27) exactly. For the special case of spherical Bessel functions Lemoine[49,50] has found quadrature points and weights satisfying Eq. (38) with sufficient accuracy to allow one to do calculations efficiently (i.e., $P<N$) and accurately. In general, a direct product grid of equidistant grids can satisfy these equations approximately and they can do so to any desired accuracy at the price of increasing grid size. Then, if one is willing to accept the loss of some accuracy and a substantial increase of computational time, one can use the symmetric FBR.

This might be the way of dealing with nondirect product basis functions wherein the Bessel-DVR functions of the infinite type,[38] $\mathcal{J}_n^{l+1/2}(r)$, are coupled to Legendre polynomials, i.e., $\phi_n^l(s)f_l(u)\propto\mathcal{J}_n^{l+1/2}(r)P_l(\cos\vartheta)$, had it not been trivial to find an l-dependent grid satisfying Eq. (28) and a u grid satisfying Eq. (27). Indeed, for this case of basis functions, no l-independent grid, which would allow one to employ the

TABLE III. The number of arithmetic operations required to evaluate the potential matrix vector product and a single element of this product in the truncated nondirect product basis $\{\phi_{n_l}^l(s)f_l(u)\}_{l=0,n_l=0}^{L-1,N_l-1}$ by different quadrature grids and formulas. In calculating the number of operations it was assumed that the quadrature weights had been built into the basis functions. An estimated relative number of arithmetic operations is also given. It is equal to or smaller than the ratio of the exact operation count in a given quadrature formula and that in the reference quadrature formula. Thus, it is equal to 1 for the reference quadrature.

Basis	$\{\phi_{n_l}^l(s)f_l(u)\}_{l=0,n_l=0}^{L-1,N_l-1}$		
Number of basis functions		$N=\sum_{l=0}^{L-1}N_l$	
Number of points	LN[a]	LN	PL
Quadrature formula	Eq. (32)	Eq. (35)	Eq. (39)
Potential matrix vector product $\mathbf{V}^{\mathrm{FBR}}\mathbf{c}$			
Number of multiplications	$N^2+LN+\sum_{k=0}^{L-1}N_k^2$	N^2+LN	$2PN+PL^2$
Number of additions	$N^2+LN+\sum_{k=0}^{L-1}N_k^2-2N$	N^2-N	$2PN+PL^2-2PL-N$
Relative number			
of multiplications	>1	1	$>P/N$
of additions	$>1-1/(N-1)$	1	$>2P/N-1/N$
$\mathbf{c}^T\mathbf{V}^{\mathrm{FBR}}$			
Number of multiplications	$2N^2+\sum_{k=0}^{L-1}N_k^2$	$2N^2$	$2PN+PL^2$
Number of additions	$N^2+LN+\sum_{k=0}^{L-1}N_k^2-2N$	N^2-N	$2PN+PL^2-2PL-N$
Relative number			
of multiplications	>1	1	$>P/N$
of additions	$>1-1/(N-1)$	1	$>2P/N-1/N$
A single element of the potential matrix vector product $(\mathbf{V}^{\mathrm{FBR}}\mathbf{c})_{km_k}$			
Number of multiplications	$N_kN+N_kL+N_k$	$N+L$	$PN+PL+P$
Number of additions	N_kN-1	$N-1$	$PN-1$
Relative number			
of multiplications	$>N_k$	1	$>P$
of additions	$>N_k$	1	$>P$
$(\mathbf{c}^T\mathbf{V}^{\mathrm{FBR}})_{ln_l}$			
Number of multiplications	$2N+\sum_{k=0}^{L-1}N_k^2$	$2N$	$PN+PL+P$
Number of additions	$\sum_{k=0}^{L-1}N_k^2-1$	$N-1$	$PN-1$
Relative number			
of multiplications	>1	1	$>P/2$
of additions	>1	1	$>P$

[a]This is the minimum number of points which may satisfy Eqs. (27) and (28).

simplest FBR formula efficiently, has been derived. However, efficient use can be made of the simplified nonsymmetric FBR expression, Eq. (25), with l-dependent grid points, as is demonstrated by the numerical results presented in the next Section.

4. The choice of grid points: Grid III

In principle, one might look for a nondirect product grid of, say, P points such that

$$\sum_{i=0}^{P-1} w_i\phi_m^k(s_i)f_k(u_i)\phi_n^l(s_i)f_l(u_i) = \delta_{km_k,ln_l}. \tag{46}$$

The corresponding FBR would be that of the simplest symmetric form. Practically, however, little is known about how such grid points and weights could be determined. The Lebedev grid developed for spherical harmonics[51] is a notable exception. An example of its application to nuclear motions in a molecule is given in Ref. 52.

III. APPLICATIONS

In this section we demonstrate numerically that (a) the optimal GFBR formulas, Eqs. (32) and (35)–(37), have similar accuracy, and (b) they have superiority, in terms of computational time, when compared with the more robust optimal GFBR expression, Eq. (20), and the symmetric FBR, Eq. (39).

Two examples will be considered. One involves the same simple model Hamiltonian as employed by Sharafeddin and Light[53] in their study of "pointwise" versus basis representations for two-dimensional spherical dynamics. The other example deals with a more complicated problem, the

TABLE IV. Selected eigenvalues of $\hat{H}$ given in Eq. (47) as calculated with various quadratures and quadrature formulas in two different basis sets.

Basis[a]	Basis I: $\{\propto P_n^{\lvert l\rvert}(\cos\vartheta)\exp(il\varphi)\}_{n=0,l=-n}^{L_{\max},n}$			Basis II: $\{\propto \mathcal{P}_\alpha^{\lvert l\rvert}(\cos\vartheta)\exp(il\varphi)\}_{\alpha=1,l=0}^{L_{\max}-\lvert l\rvert,L_{\max}}$			
Grid	Grid I L dependent		Grid II L independent	Grid I L dependent		Grid II L independent	
Number of points	765	765	153	765	765	153	
Method	Eq. (20)	Eq. (32)	Eq. (39)	Eq. (20)	Eq. (35)	Eq. (39)	VBR
State							
1	−6.045 08	−6.045 08	−6.045 08	−6.045 08	−6.045 08	−6.045 08	−6.045 08
5	3.911 46	3.911 46	3.911 46	3.911 46	3.911 46	3.911 46	3.911 46
10	10.685 16	10.685 18	10.685 18	10.685 16	10.685 18	10.685 18	10.685 18
15	12.681 09	12.681 10	12.681 10	12.681 09	12.681 10	12.681 10	12.681 10
20	19.721 56	19.721 32	12.721 32	19.721 56	19.721 32	12.721 32	12.721 32
25	20.671 08	20.670 81	20.670 81	20.671 08	20.670 81	20.670 81	20.670 80
30	30.027 38	30.026 65	30.026 66	30.027 38	30.026 65	30.026 66	30.026 72
35	30.388 94	30.385 61	30.385 61	30.388 94	30.385 61	30.385 61	30.385 61
40	41.752 18	41.758 20	41.758 20	41.752 18	41.758 20	41.758 20	41.758 20
45	42.191 16	42.216 13	42.216 13	42.191 16	42.216 13	42.216 13	42.216 13
50	55.522 10	55.639 29	55.639 56	55.522 10	55.639 29	55.639 56	55.640 43
55	55.742 63	55.948 69	55.948 69	55.742 63	55.948 69	55.948 69	55.948 69
60	56.014 13	56.198 82	56.199 03	56.014 13	56.198 82	56.199 03	56.234 60
65	69.054 55	68.943 40	69.060 77	69.054 55	68.943 40	69.060 77	72.000 00
70	72.737 77	72.667 50	72.667 50	72.737 77	72.667 50	72.667 50	72.667 50
75	73.358 89	73.168 42	73.168 37	73.358 89	73.168 42	73.168 37	73.296 81
80	73.931 90	73.480 77	73.480 77	73.931 90	73.480 77	73.480 77	73.480 77
81	77.991 05	78.099 28	77.969 30	77.991 05	78.099 28	77.969 30	73.503 69
Relative CPU time of evaluating $\mathbf{V}^{\mathrm{FBR}}$	91	12	10	90	1	10	
Predicted relative CPU time of evaluating $\mathbf{V}^{\mathrm{FBR}}$	81(83)[b]	3.5(3.6)	4.5(4.7)	81(83)	1	4.5(4.7)	

[a]In each calculation a truncated basis corresponding to $L_{\max}=8$ was employed.
[b]The numbers in parentheses were calculated using the exact number of operation counts, those not in parentheses are obtained by the approximate expressions (see Table I).

calculation of some of the vibrational energy levels of the H_3^+ molecular ion. The numerical GFBR results presented were obtained by direct diagonalization.

A. Simple model calculations

Consider the Hamiltonian

$$\hat{H} = -\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta} - \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2} + 10\sin\vartheta\cos\varphi, \quad (47)$$

where ϑ and φ are spherical polar coordinates. Find approximate solutions of the corresponding eigenvalue equation by employing two basis sets. Basis I is a truncated spherical harmonics basis defined as $\phi_n^l(s)f_l(u)\propto P_n^{|l|}(\cos\vartheta)\exp(il\varphi)$ with $n=0,\ 1,\ldots,\ N-1$ and $l=-n,\ -n+1,\ldots,\ n$. Basis II is obtained from basis I by replacing the associated Legendre polynomials with the corresponding associated Legendre-DVR functions,[54] i.e., $\phi_\alpha^l(s)f_l(u)\propto\mathcal{P}_\alpha^{|l|}(\cos\vartheta)\exp(il\varphi)$, with $\alpha=0,\ldots,\ N-|l|-1$ and $l=0,\ \pm1,\ldots,\ \pm(N-1)$. While the two basis sets are different, they span the same space and contain the same number of basis functions, $(L_{\max}+1)^2$, where $L_{\max}=|l_{\max}|=N-1$.

The matrix elements of the Hamiltonian can be calculated analytically in these basis sets. Thus variational basis representations (VBRs) of the eigenvalue equation can be set up. The results of the variational calculations provide the reference to which the results of different FBR calculations will be compared.

We employed in our calculations $L_{\max}=8$, that is, 81 basis functions. In the FBR calculations we used different grids and different quadrature formulas for evaluating the matrix elements of the potential-energy operator approximately, but the matrix elements of the kinetic-energy operator were calculated exactly by employing analytical expressions.

Two different sets of quadrature points and weights were employed. In both sets the grid for the azimuthal angle was a Fourier grid defined as $\varphi_j=2\pi j/(2L_{\max}+1);\ j=0,\ \pm1,\ldots,\ \pm L_{\max}$, and the corresponding quadrature weights were $w_{\varphi,j}=1/(2L_{\max}+1)$. In grid I we employed l-dependent Gauss-associated Legendre quadrature points and weights, i.e., different sets of points and weights for different values of $L=|l|$, for the variable $s=\cos\vartheta$. In grid II an L-independent quadrature consisting of Gauss-Legendre quadrature points and the associated weights was employed. The number of quadrature points and weights employed was as small as minimally required to ensure the fulfillment of Eqs. (27) and (28) in the case of grid I and the fulfillment of Eqs. (27) and

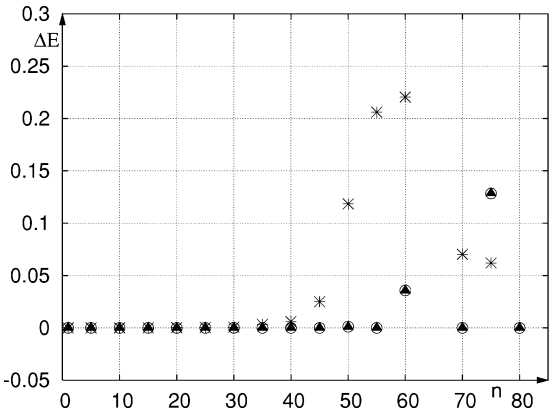

FIG. 1. Absolute deviation of the approximate eigenvalues of the Hamiltonian given in Eq. (47) calculated by different FBR methods from those of the VBR calculations (see Table IV). Filled triangles, empty circles, and asterisks denote the deviations of the results obtained by using Eq. (32) [and Eq. (35)], Eq. (39), and Eq. (20), respectively. The deviations corresponding to levels $n=65$ and $n=81$ are relatively large and not shown in the figure.

(38) in the case of grid II with the given truncated bases. That is, the calculations with grids I and II involved $(2L_{\max}+1)(L_{\max}+1)(L_{\max}+2)/2$ and $(2L_{\max}+1)(L_{\max}+1)$ quadrature points (and weights), respectively. The quadrature formulas employed are given in Table IV.

The results of our numerical calculations with different combinations of the basis sets, quadratures, and quadrature formulas are presented in Table IV and Fig. 1. The most important conclusions one can draw from the numerical results are as follows.

(1) Calculations using an L-dependent quadrature of the minimum number of points required to satisfy Eqs. (27) and (28) along with the simplified nonsymmetric FBR formulas, Eqs. (32) and (35), are as accurate as calculations using an L-independent quadrature of the minimum number of points required to satisfy Eqs. (27) and (38) along with the symmetric FBR expression, Eq. (39).
(2) The L-dependent grid calculations with Eq. (32) are as efficient as, whereas the calculations with Eq. (35) are more efficient than, the L-independent grid calculations with the symmetric FBR, even though the former employ more grid points.
(3) The simplified nonsymmetric FBR calculations are significantly faster than, yet as accurate as, the calculations with the more general and robust FBR formula, Eq. (20).

These are remarkable results, since L-dependent grids have generally been considered not worth applying and thus they are avoided in favor of L-independent grids.[13,23,25,53] Furthermore, there are basis sets where an efficient L-independent grid, i.e., an L-independent grid satisfying Eq. (38) with $P<N$, is yet to be determined, whereas the construction of an appropriate L-dependent grid is almost trivial. For such basis sets the approach adapted, for instance, in Refs. 13, 23, 25, and 53, cannot be employed, but application of the simplified nonsymmetric FBR is straightforward. In the next subsection we describe such an example.

B. The vibrational energy levels of H_3^+

The singularities present in the Sutcliffe-Tennyson vibrational Hamiltonian of a triatomic molecule may be treated by employing a nondirect product basis set. In one suitable basis set Legendre polynomials, $P_l(\cos\vartheta)$, are coupled to Bessel-DVR functions of the infinite type, $\mathcal{J}_m^{l+1/2}(R)$ and $\mathcal{J}_n^{l+1/2}(r)$, that is, $\chi_{m_l}^l(t)\phi_{n_l}^l(s)f_l(u)\propto\mathcal{J}_{m_l}^{l+1/2}(R)\mathcal{J}_{n_l}^{l+1/2}(r)P_l(\cos\vartheta)$. Recently, we have employed this basis set with $l=0,1,\ldots,L-1=15$ and 9; $m_l=0,1,\ldots,M-1=15$ and 9; and $n_l=0,1,\ldots,N-1=15$ and 9 in calculating the vibrational energy levels of H_3^+.[37] Unlike for other basis sets, such as those employed in Ref. 23, for this basis set no efficient l-independent grid has been derived. The l-independent grids tried by us proved to be unacceptable. Therefore, we employed a grid formed by taking the direct product of $L=16(10)$ Gauss-Legendre quadrature points with a grid of the variable R consisting of $M=16(10)$ points for each value of l, i.e., for $l=0,1,\ldots,15(9)$, and with a grid of the variable r consisting of $N=16(10)$ points for each value of l. This grid proved to be successful and it was used along with the optimal GFBR, Eq. (20), in evaluating the potential matrix and in eventually solving the vibrational eigenvalue problem of H_3^+. Not surprisingly, the calculations turned out to be very time consuming, but we were not aware of any other method of employing such an l-dependent grid more efficiently.

But now, by observing that the radial grid and basis functions employed in Ref. 37 satisfy Eq. (33), the simplified nonsymmetric FBR evaluating the potential matrix elements according to Eq. (37) can be used instead of the more robust and general GFBR expression, Eq. (20). The application of this simplified nonsymmetric FBR leads to an enormous decrease of computer time, but no loss of accuracy, in comparison with calculations carried out by the direct use of the optimal GFBR formula, as is demonstrated by the numerical results given in Table V. The relative CPU times obtained are in accord with the operation counts predicting at least 10 000 and at least 65 000 times faster computation with the smaller and larger basis sets, respectively, when employing Eq. (37).

IV. SUMMARY

In quantum-mechanical calculations of nuclear motion dynamics in molecules the form of the Hamiltonian chosen is indicative of the kind of basis functions to be employed. Often it suggests the use of nondirect product basis sets. Many analytically known nondirect product basis sets consist of basis functions having structure identical or similar to that of the functions $\chi_m^l(t)\phi_n^l(s)f_l(u)$, $\phi_n^l(s)f_l(u)$, etc. Since with realistic potential-energy surfaces the potential matrix elements cannot be obtained analytically, one should employ some approximate numerical quadrature for their evaluation. Finding a numerical quadrature for nondirect product bases that is both efficient and accurate is not always simple. Nevertheless, nondirect product basis sets of the above type have been applied successfully to a number of complicated systems. For instance, Leforestier and Rasmussen *et al.* used Wigner functions in calculating nuclear motion dynamics of $Ar\cdot H_2O$,[25] $(H_2O)_2$,[26] and ketene,[24] Bramley *et al.* employed spherical oscillator functions in their benchmark quality cal-

TABLE V. Selected vibrational energy levels of H_3^+ obtained by different methods. For the sake of comparison, converged, accurate eigenvalues calculated by the DOPI algorithm (Ref. 55) are also given.

Basis	$\{\mathcal{J}_{m_l}^{l+1/2}(R)\mathcal{J}_{n_l}^{l+1/2}(r)P_l(\cos\vartheta)\}_{l=0,m_l=0,n_l=0}^{9,9,9}$		$\{\mathcal{J}_{m_l}^{l+1/2}(R)\mathcal{J}_{n_l}^{l+1/2}(r)P_l(\cos\vartheta)\}_{l=0,m_l=0,n_l=0}^{15,15,15}$		
Number of basis functions	1000		4096		
Number of points	100 000		1 048 576		
Method	Eq. (20)	Eq. (37)	Eq. (20)	Eq. (37)	DOPI
State [a]					
1	4375.95	4366.78	4362.30	4362.30	4362.30
2	2449.29	2452.88	2521.19	2521.17	2521.19
3	2569.12	2560.97	2521.20	2521.19	2521.19
4	3232.63	3222.24	3179.21	3179.19	3179.20
5	4854.15	4831.45	4777.66	4777.65	4777.63
6	4893.82	4836.20	4997.61	4997.61	4997.60
7	5135.71	5114.48	4997.64	4997.63	4997.60
8	5492.34	5485.60	5554.82	5554.78	5554.82
9	5723.98	5551.59	5554.93	5554.82	5554.82
10	6432.95	6361.02	6263.94	6263.77	6263.85
Approximate CPU time	h	s	day	s	
Relative number of arithmetic operations in evaluating $\mathbf{V}^{\mathrm{FBR}}$ [b]	>10 000	1	>65 536	1	

[a]The energies of states 2,3,… are referred to the ground state. They are given in units of cm^{-1}.
[b]Calculated by using formulas presented in Table II.

culation of the vibrational energy levels of H_3^+ (Ref. 23) and HF_2^-,[41] Corey and Lemoine, and Somers *et al.* used spherical harmonics in calculations of scattering of molecules on surfaces,[22,44] and Sharafeddin and Light employed spherical harmonics in their exploratory study on the use of DVR versus FBR methods with nondirect product bases.[53] With no exception these calculations employed l-independent quadratures and more quadrature points than basis functions (cf. Sec. III). The use of l-dependent quadratures has been considered impractical.[22,23]

The optimal GDVR (Ref. 10) provides a DVR with general, direct and/or nondirect product bases. The optimal GDVR possesses more characteristic properties of the standard DVR than any other generalized DVR method developed so far. Applications of the method have revealed that finding appropriate grid points is difficult in the case of nondirect product basis functions of structure identical or similar to that of spherical harmonics.[10,37] The FBR related to the optimal GDVR has turned out to be easier to employ, even though it requires the use of more grid points than basis functions.[37] Our calculations of the vibrational energy levels of H_3^+ by this optimal-generalized FBR method employed a nondirect product basis of structure similar to that of spherical harmonics for which no l-independent grid has been derived. While being highly accurate, the calculations were slow, due to the slowness of the evaluation of the potential-energy matrix with the l-dependent grid which we were forced to employ. Thus, we had to ask the question if l-dependent grids could be used efficiently inspite of their bad reputation.

In this communication we have described a method for the efficient use of l-dependent grids with nondirect product basis functions of structures $\chi_m^l(t)\phi_n^l(s)f_l(u)$, $\phi_n^l(s)f_l(u)$, etc. In particular, we have shown how and under what condition the robust generalized FBR formula, Eq. (20), can be simplified to a form, Eq. (25), essentially retaining the accuracy of Eq. (20), whose evaluation does not require the inversion of a matrix. Fulfillment of the condition, Eq. (24), derived requires the use of special grid points whereby the generality of Eq. (20) is lost. We have pointed out that the complexity of the simplified nonsymmetric FBR formula, Eq. (25), can be decreased further, resulting in extremely simple expressions, such as given in Eqs. (35) and (37). This only requires the modification of the basis functions, i.e., the replacement of the functions ϕ_n^l (and possibly χ_m^l), present in the nondirect product basis functions, with their DVR-function counterparts satisfying Eq. (33). The simplified nonsymmetric FBR formulas exhibit low arithmetic operation counts in evaluating the potential-energy matrix elements and the individual elements of the product of the potential matrix with a vector (see Tables I–III). This ensures the efficiency of l-dependent grid-simplified nonsymmetric FBR calculations with direct (i.e., noniterative) diagonalization methods and with the iterative diagonalization method of the generalized variational optimal relaxation.[47,48] As far as large scale iterative calculations are concerned, it still remains to be investigated numerically whether or not the l-dependent grid-nonsymmetric FBR calculations are competitive with calculations employing the l-independent grid-symmetric FBR,[21,23] i.e., the FBR corresponding to the generalized

DVR method of Corey and co-workers.[13,21] This symmetric FBR has been rederived as a special case of the GDVR(FBR) method of Ref. 10.

The efficiency and high accuracy of the new simplified FBR expressions have been demonstrated by calculating the eigenvalues of a simple model Hamiltonian with employing basis sets admitting both *l*-independent and *l*-dependent grids and by calculating the vibrational energy levels of H_3^+ with employing a nondirect product basis which is not as yet amenable to *l*-independent grid calculations. The matrix eigenvalue equations were solved by noniterative, direct diagonalization. The first example has demonstrated that even in the case of a simple Hamiltonian and a small basis set, an *l*-dependent grid-nonsymmetric-simplified GFBR calculation can be more efficient than an *l*-independent grid-symmetric FBR calculation. The second example has demonstrated the enormous decrease of CPU time which can be achieved, with respect to that of a direct application of the GFBR formula, Eq. (20), by employing the nonsymmetric-simplified GFBR.

A couple of related problems remain. The efficiency of the simplified nonsymmetric FBR in large scale iterative calculation of selected eigenpairs still has to be demonstrated numerically, and there is the question how *l*-dependent grids can be used efficiently in wave-packet propagation.

ACKNOWLEDGMENT

The work described received a small amount of support from the Hungarian Scientific Research Fund, OTKA, through Grant Nos. T047185 and T045955.

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