On one-dimensional discrete variable representations with general basis functions

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The method of discrete variable representation (DVR) is based on standard orthogonal polynomial bases and the associated Gaussian quadratures. General basis functions correspond either to nonpolynomial expressions or to nonstandard orthogonal polynomials. Although one cannot directly relate any Gaussian quadrature to general basis functions, the DVR-like representation derivable with such basis sets via the transformation (diagonalization) method is, as proved here, of Gaussian quadrature accuracy. The optimal generalized DVR (GDVR) is an alternative to and entirely different from this DVR-like representation. Yet, when built from the same general basis functions and the corresponding quadrature points obtained by the diagonalization method, the two representations are found to give almost identical numerical results. The intricate relationship between the optimal GDVR and the transformation method is discussed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1621619]

I. INTRODUCTION

There are several ways of setting up a matrix representation for solving the Schrödinger equation, say, of the vibrational Hamiltonian of a molecule. One of these methods is the method of discrete variable representation (DVR).[1–4] The DVR is based on truncated standard orthonormal polynomial bases, $\{\phi_n(q)\}_{n=0}^{N-1}$, and the corresponding Gaussian quadratures. Orthonormality means that the integrals $\int_a^b \phi_m^*(q)\phi_n(q)\rho(q)\mathrm{d}q$, where the actual functional form of the positive weight function $\rho(q)$ and the actual values of the limits of integration depend on the basis considered, are equal to 1 for $m=n$ and 0 for $m\neq n$.

In the DVR the matrix elements of differential operators are calculated exactly, whereas those of the operators which are local in the coordinate representation, e.g., the potential energy operator, are calculated approximately, with Gaussian quadrature accuracy. For a given number of points and weights the Gaussian quadrature gives the most accurate approximation to an integral. This contributes to the accuracy and efficiency of the DVR method.

One may calculate the quadrature points, $q_i, i=1,2,\ldots,N$, the quadrature weights, $w_i, i=1,2,\ldots,N$, and the matrix $\mathbf{T}$ transforming to the DVR by diagonalizing the matrix of the coordinate operator, i.e., the matrix $\mathbf{Q}$ with elements $Q_{m,n}=\int_a^b \phi_m^*(q)q\phi_n(q)\rho(q)\mathrm{d}q$.[1,3,4] The eigenvalues of $\mathbf{Q}$ give the quadrature points. The eigenvector matrix of $\mathbf{Q}$ is identical with the transformation matrix $\mathbf{T}$. Specifically, the equation

$$\mathbf{T}=\boldsymbol{\mathcal{F}}, \tag{1}$$

where

$$\mathcal{F}_{n,i}=w_i^{1/2}\phi_n^*(q_i) \tag{2}$$

also holds. Often this method is called the transformation or diagonalization method. Its close relation to Gaussian quadrature has been shown by Dickinson and Certain[4] and it explains its high accuracy.

If $\{\phi_n(q)\}_{n=0}^{N-1}$ is a truncated general, i.e., nonpolynomial or nonstandard orthogonal polynomial, orthonormal basis one can still use the transformation method. One can set up $\mathbf{Q}$ and calculate quadrature points q_i and a transformation matrix $\mathbf{T}$ leading to a DVR-like representation. However, $\mathbf{T}$ can no longer be expressed as in Eq. (1) and the q_i's can no longer be considered as Gaussian quadrature points associated with the $\{\phi_n(q)\}_{n=0}^{N-1}$ basis. Yet, even in this case, the transformation method is of Gaussian quadrature accuracy, as shown in Sec. II, where the proof of equivalence of the transformation method and the Gaussian quadrature approximation, as given by Dickinson and Certain[4] for the case of standard orthogonal polynomial bases, is extended to general bases.

The representation obtained by the diagonalization method is not the only DVR-like representation that can be derived by employing the same quadrature points and general basis functions. The optimal generalized DVR method[5] gives another, completely different DVR-like representation. The question arises whether the accuracy of these different representations are comparable when, for instance, applied to solving the eigenvalue equation of a Hamiltonian operator. The answer is given in Sec. III by considering simple numerical examples. In Sec. IV we summarize the results.

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II. THE TRANSFORMATION METHOD USING GENERAL BASES

A. Setting the problem up

Consider a simple one-dimensional Hamiltonian,

$$\hat{H}=\hat{K}+\hat{V}=-\frac{\mathrm{d}^2}{\mathrm{d}q^2}+V(q), \tag{3}$$

with a kinetic energy operator $\hat{K}$ and a potential energy function $V(q)$. Let $\{\phi_n(q)\}_{n=0}^{N-1}$ be a truncated general basis, orthonormal with respect to a positive weighting function $\rho(q)$. Derive the quadrature points q_i and the transformation matrix $\mathbf{T}$ by diagonalizing the matrix of the coordinate operator given in the ϕ_n basis. Then, a matrix representation for the Schrödinger equation of $\hat{H}$ can be written as

$$(\mathbf{K}+\mathbf{TVT}^{\dagger})\mathbf{C}=\mathbf{CE}, \tag{4}$$

where $\mathbf{K}$ is the kinetic energy matrix with elements

$$K_{m,n}=\int_a^b \rho^{1/2}(q)\phi_m^*(q)\hat{K}\rho^{1/2}(q)\phi_n(q)\mathrm{d}q, \tag{5}$$

$\mathbf{V}$ is a diagonal matrix,

$$V_{j,i}=\delta_{j,i}V(q_i), \tag{6}$$

with $\delta_{j,i}$ the Kronecker-delta symbol, the superscript † stands for Hermitian conjugation, and the pth eigenfunction $\Psi_p(q)$ is approximated as

$$\Psi_p(q)\simeq\sum_{n=0}^{N-1} C_{n,p}\phi_n(q). \tag{7}$$

Note that the $\Psi_p(q)$'s so defined are orthonormal with respect to the weight function $\rho(q)$. In this representation, called a finite basis representation (FBR), the potential matrix elements are approximated by

$$V_{m,n}^{\mathrm{VBR}}=\int_a^b \phi_m^*(q)V(q)\phi_n(q)\rho(q)\mathrm{d}q$$
$$\simeq V_{m,n}^{\mathrm{FBR}}=(\mathbf{TVT}^{\dagger})_{m,n}, \tag{8}$$

where VBR is the acronym for variational basis representation.

The FBR of Eq. (4) can be transformed into a DVR-like representation:

$$(\mathbf{T}^{\dagger}\mathbf{KT}+\mathbf{V})(\mathbf{T}^{\dagger}\mathbf{C})=(\mathbf{T}^{\dagger}\mathbf{C})\mathbf{E}. \tag{9}$$

The transformation leaves the eigenvalues intact; the two representations are equivalent in this sense.

Therefore, to judge the accuracy of the DVR-like representation in solving the Schrödinger equation it suffices to investigate the accuracy of the approximation to the potential matrix elements in the FBR given in Eq. (4), or that in any FBR,

$$(\mathbf{MKM}^{\dagger}+\mathbf{MTVT}^{\dagger}\mathbf{M}^{\dagger})(\mathbf{MC})=(\mathbf{MC})\mathbf{E}, \tag{10}$$

obtained by a unitary transformation $\mathbf{M}$ from Eq. (4). Equation (4) and Eq. (10) are equivalent FBRs. The transformation by $\mathbf{M}$ amounts to introducing a new basis set, $\{\psi_n(q)\}_{n=0}^{N-1}$, related to the original set by the unitary transformation $\mathbf{M}$:

$$\psi_n(q)=\sum_{m=0}^{N-1} M_{n,m}^*\phi_m(q). \tag{11}$$

In what follows it is shown that with a suitable choice of M the approximation

$$V_{m,n}^{\mathrm{VBR}}=\int_a^b \psi_m^*(q)V(q)\psi_n(q)\rho(q)\mathrm{d}q$$
$$\simeq V_{m,n}^{\mathrm{FBR}}=(\mathbf{MTVT}^{\dagger}\mathbf{M}^{\dagger})_{m,n} \tag{12}$$

corresponds to Gaussian quadrature approximation with the q_i's as quadrature points.

B. Expressing the FBR matrix elements of Eq. (12) in terms of polynomials

The coordinate operator is Hermitian and its matrix $\mathbf{Q}$ given in the general basis $\{\phi_n(q)\}_{n=0}^{N-1}$ is a Hermitian matrix. Therefore, one can choose the unitary matrix $\mathbf{M}$ such that the matrix of the coordinate operator given in the $\{\psi_n(q)\}_{n=0}^{N-1}$ basis, $\mathbf{Q}_T$, is real, symmetric, and tridiagonal, that is

$$\mathbf{Q}_T=\begin{pmatrix} \alpha_0 & \beta_0 & . & . & . & 0 \\ \beta_0 & \alpha_1 & \beta_1 & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ . & . & . & \beta_{N-3} & \alpha_{N-2} & \beta_{N-2} \\ 0 & . & . & . & \beta_{N-2} & \alpha_{N-1} \end{pmatrix}, \tag{13}$$

with real entries. Naturally, $\mathbf{Q}$ and $\mathbf{Q}_T$ have the same set, $\{q_i\}_{i=1}^{N}$, of eigenvalues.

Let the polynomials $\{\sigma_n(q)\}_{n=0}^{N-1}$ and $\tilde{\sigma}_N(q)=\beta_{N-1}\sigma_N(q)$ be defined by the equations

$$\begin{aligned} &\beta_{n-1}\sigma_n(q)=[q-\alpha_{n-1}]\sigma_{n-1}(q)-\beta_{n-2}\sigma_{n-2}(q), \\ &n=1,2,\ldots,N \\ &\sigma_{-1}(q)=0, \\ &\sigma_0(q)=1. \end{aligned} \tag{14}$$

Save the case of standard orthogonal polynomial bases the entries in $\mathbf{Q}_T$ depend on N (i.e., the values of α_0, β_0, etc. depend on N), therefore the polynomials σ_n obtained with different N's are different.

Denote the zeros of the polynomial $\tilde{\sigma}_N(q)$ by $\{x_i\}_{i=1}^{N}$.

By relying on the recurrence relation one can derive, as described in the Appendix as well as in Refs. 6 and 7, the Christoffel–Darboux identity and establish the equations

$$\sum_{n=0}^{N-1} w_i^{1/2}\sigma_n(x_i)w_j^{1/2}\sigma_n(x_j)=\delta_{i,j}, \tag{15}$$

with w_i denoting the weights

$$w_i=\left[\left(\frac{\mathrm{d}\tilde{\sigma}_N(q)}{\mathrm{d}q}\right)_{q=x_i}\sigma_{N-1}(x_i)\right]^{-1}, \tag{16}$$

and $i,j=1,2,\ldots,N$. By making use of Eqs. (14) and Eq. (15) one can also show, similarly to the treatment in Ref. 4, that the matrix $\mathbf{F}$,

$$F_{n,i}=w_i^{1/2}\sigma_n(x_i), \qquad (17)$$
$$n=0,1,\ldots,N-1; \quad i=1,2,\ldots,N,$$

diagonalizes $\mathbf{Q}_T$ with the ith column in $\mathbf{F}$ corresponding to the ith eigenvector and x_i corresponding to the ith eigenvalue of $\mathbf{Q}_T$. Thus the zeros of $\tilde{\sigma}_N(q)$ are also the eigenvalues of $\mathbf{Q}_T$, i.e., $x_i=q_i, i=1,2,\ldots,N$.

Since $\mathbf{F}$ is an eigenvector matrix of a real symmetric matrix, $\mathbf{F}$ is an orthogonal matrix, and in addition to the orthogonality relation, Eq. (15), the orthogonality relation

$$\sum_{i=1}^{N} w_i^{1/2}\sigma_n(q_i)w_i^{1/2}\sigma_m(q_i)=\delta_{n,m}, \qquad (18)$$
$$n,m=0,1,\ldots,N-1,$$

also holds. By construction, the matrix that diagonalizes $\mathbf{Q}_T$ is $\mathbf{MT}$. Since we have shown that the matrix $\mathbf{F}$ given in Eq. (17) also diagonalizes $\mathbf{Q}_T$ we have $\mathbf{MT}\boldsymbol{\epsilon}=\mathbf{F}$ and thus Eq. (12) may be rewritten as

$$\begin{aligned} V_{m,n}^{\mathrm{VBR}} &= \int_a^b \psi_m^*(q)V(q)\psi_n(q)\rho(q)\mathrm{d}q \\ &\simeq V_{m,n}^{\mathrm{FBR}}=(\mathbf{MTVT}^\dagger\mathbf{M}^\dagger)_{m,n}=(\mathbf{FVF}^{\mathsf{T}})_{m,n} \\ &=\sum_{i=1}^{N} w_i\sigma_m(q_i)V(q_i)\sigma_n(q_i), \end{aligned} \qquad (19)$$

where the superscript T denotes transposition, $\boldsymbol{\epsilon}$ is a diagonal matrix with diagonal elements of unit magnitude, and it is also assumed that $\mathbf{T}$ is unitary, i.e., $\mathbf{TT}^\dagger=\mathbf{T}^\dagger\mathbf{T}=\mathbf{I}$ with $\mathbf{I}$ denoting the unit matrix of dimension $N\times N$. Note that $\mathbf{T}$ is unitary provided $\mathbf{Q}$ has no degenerate eigenvalues. If $\mathbf{Q}$ had degenarate eigenvalues $\mathbf{T}$ might not be unitary but it could be made unitary by orthogonalization of the eigenvectors belonging to degenerate eigenvalues.

Now, suppose that the potential energy function is given by a polynomial of degree K. Then, for $m+n+K<2N$,

$$\begin{aligned} &\int_a^b \psi_m^*(q)V(q)\psi_n(q)\rho(q)\mathrm{d}q \\ &=\sum_{i=1}^{N} w_i\sigma_m(q_i)V(q_i)\sigma_n(q_i) \\ &=\int_a^b \sigma_m(q)V(q)\sigma_n(q)u(q)\mathrm{d}q, \end{aligned} \qquad (20)$$

whereas for $m+n+K\geqslant 2N$ the signs of equality must be replaced by the sign of approximately equal. The first equality is a consequence of the tridiagonality of $\mathbf{Q}_T$.[3] The second equality holds provided that there exists a weighting function $u(q)$ making $\{\sigma_n(q)\}_{n=0}^{N-1}$ orthonormalized.

Thus, to show the Gaussian quadrature approximation property of the approximation in Eq. (19) we are left to show the existence of a function $u(q)$ such that the polynomials $\{\sigma_n(q)\}_{n=0}^{N-1}$ form an orthonormalized (normalized to unity) set and are orthogonal to $\tilde{\sigma}_N(q)$ with this $u(q)$ as a weight function.

One may prescribe additional properties that the weight function should satisfy. One may, for instance, restrict to positive weight functions and require that this weight function should approach a smooth function as $N\to\infty$. Although neither of these is neccessary to prove the Gaussian quadrature approximation property of the approximation in Eq. (19), they may be decisive in determining how fast the quadrature error decreases with increasing N, i.e., in determining the convergence properties of the calculations.

C. On the existence of a suitable weighting function $u(q)$

Suppose that the desired $u(q)$ function exists. Then $\mathbf{Q}_T$, i.e., the matrix of the coordinate operator given in the $\{\psi_n(q)\}_{n=0}^{N-1}$ basis, is identical to the matrix of the coordinate operator calculated in the polynomial basis $\{\sigma_n(q)\}_{n=0}^{N-1}$. The eigenvalues of $\mathbf{Q}_T$ correspond to Gaussian quadrature points, as shown below.

Consider the integral

$$I=\int_a^b f(q)u(q)\mathrm{d}q=\int_a^b \sigma_0(q)f(q)u(q)\mathrm{d}q, \qquad (21)$$

[the limits of integration are those corresponding to the initial basis $\{\phi_n(q)\}_{n=0}^{N-1}$] and its quadrature approximation

$$I\simeq\sum_{i=1}^{N} w_i f(q_i). \qquad (22)$$

Simple arguments, that we shall recall, show that the quadrature approximation in Eq. (22) is exact to any polynomial $f(q)$ of degree less than $2N$. If $f(q)$ is a polynomial of degree less than N, then $f(q)=\Sigma_{n=0}^{N-1}\gamma_n\sigma_n(q)$ and $I=\gamma_0$. Due to Eq. (18) the quadrature approximation gives the exact I. Suppose $f(q)$ is a polynomial of degree less than $2N$. Then $f(q)=\sigma_N(q)s(q)+r(q)$, where $s(q)$ and $r(q)$ are polynomials of degree at most $N-1$, and $I=\int_a^b r(q)u(q)\mathrm{d}q$. Since the quadrature points are the zeros of $\sigma_N(q)$ and since the quadrature approximation has been shown to be exact for polynomials of degree less than N, the quadrature approximation is exact to polynomials of degree less than $2N$, i.e., it is a Gaussian quadrature approximation.

Therefore, provided a suitable function $u(q)$ exists, the approximation in Eq. (19) does correspond to the Gaussian quadrature approximation with quadrature points obtained by the diagonalization method. In addition, note that any further unitary transformation of the basis merely redistributes and scatters the quadrature error to many more matrix elements without affecting the accuracy of the representation, e.g., when solving the eigenvalue problem, Eq. (10).

We shall argue that a function $u(q)$ desired does exist.

Satisfying the $N(N+1)/2+1$ equations,

$$\int_a^b u(q)\sigma_n(q)\sigma_n(q)\mathrm{d}q=1, \quad n=0,1,\ldots,N-1; \qquad (23)$$

$$\int_a^b u(q)\sigma_n(q)q\sigma_n(q)\mathrm{d}q=\alpha_n, \quad n=0,1,\ldots,N-1; \qquad (24)$$

$$\int_a^b u(q)\sigma_m(q)q\sigma_{n-1}(q)\mathrm{d}q=0,$$
$$n=3,4,\ldots,N \quad \text{and} \quad m=0,1,\ldots,n-3, \qquad (25)$$

guarantees that $u(q)$ is suitable, i.e., the polynomials $\{\sigma_n(q)\}_{n=0}^{N-1}$ become an orthonormalized set and become orthogonal to $\tilde{\sigma}_N(q)$ with this $u(q)$. Let

$$u(q)=u(q,\{c_i\}_{i=1}^{N(N+1)/2+1}), \tag{26}$$

and determine the values of the parameters $\{c_i\}_{i=1}^{N(N+1)/2+1}$ by using Eqs. (23)–(25). We shall show that, in general, this sytem of equations can be solved, and a function $u(q)$ desired does exist. We show this by proving that the opposite statement, namely that *there is no function* $u(q)$ *satisfying Eqs. (23)–(25)*, cannot be valid.

If no function $u(q)$ can satisfy Eqs. (23)–(25), then these equations must contain at least one inconsistent statement. Note that the integrands [not including the function $u(q)$] in Eqs. (23)–(25) are polynomials.

Were a polynomial from Eq. (24) and another from Eq. (25) identical, inconsistency would arise since, in general, $\alpha_n \neq 0$ and no suitable $u(q)$ could be found. Similarly, no suitable $u(q)$ would exist if a polynomial in Eq. (23) were identical to a polynomial in Eq. (25). Given the origin and definition of the $\sigma_n(q)$ polynomials, the occurrence of such situations is, however, nongeneric and can be excluded from consideration.

Let N_k denote the number of different polynomials of degree k appearing in Eq. (25). If $N_k > k$ for a given k held then any polynomial of degree k could be written as a linear combination of these k-degree polynomials. Then, depending on the parity of k, either Eq. (24) with $2n+1=k$ and $\alpha_n \neq 0$ or Eq. (23) with $2n=k$ would lead to contradiction and would prove that no $u(q)$ can satisfy Eqs. (23)–(25). However, such situations, unless deliberately created, can hardly occur in practice. Indeed, even when assuming that all the polynomials of degree k given in Eq. (25) are different, one obtains that

$$N_k=\begin{cases}(k-1)/2, \\ \text{if } k \text{ is odd and } 3\leqslant k\leqslant N; \\ (k-2)/2, \\ \text{if } k \text{ is even and } 3\leqslant k\leqslant N; \\ (2N-k-1)/2, \\ \text{if } 2N-k \text{ is odd and } N<k\leqslant 2N-3; \\ (2N-k-2)/2, \\ \text{if } 2N-k \text{ is even and } N<k\leqslant 2N-3; \end{cases} \tag{27}$$

i.e., N_k is less than k, which could be reversed only under special assumptions about the entries in $\mathbf{Q}_T$. Therefore, the $N(N+1)/2+1$ equations, Eqs. (23)–(25), are, in general, consistent and may be solved for the $N(N+1)/2+1$ unknown parameters given in Eq. (27) defining $u(q)$.

Thus, we have shown the equivalence of the transformation method and the Gaussian quadrature approximation for the case of general bases.

III. THE TRANSFORMATION METHOD AND THE OPTIMAL GENERALIZED DVR

Given a truncated, general orthonormal basis set, $\{\phi_n(q)\}_{n=0}^{N-1}$, and a set of grid points and weights, $\{q_i,w_i\}_{i=1}^{N}$, one can set up[5] a FBR for the eigenvalue equation of $\hat{H}$ as

$$(\mathbf{K}+\boldsymbol{\mathcal{F}}\boldsymbol{\Delta}^{-1}\mathbf{V}\boldsymbol{\mathcal{F}}^{\dagger})\mathbf{C}=\mathbf{C}\mathbf{E}, \tag{28}$$

where $\boldsymbol{\Delta}=\boldsymbol{\mathcal{F}}^{\dagger}\boldsymbol{\mathcal{F}}$, and $\boldsymbol{\mathcal{F}}$, $\mathbf{K}$, $\mathbf{V}$, and $\mathbf{C}$ are defined in Eqs. (2), (5), (6), and (7), respectively. This FBR may be transformed into an equivalent representation,

$$(\boldsymbol{\mathcal{F}}^{\dagger}\mathbf{K}\boldsymbol{\mathcal{F}}\boldsymbol{\Delta}^{-1}+\mathbf{V})(\boldsymbol{\mathcal{F}}^{\dagger}\mathbf{C})=(\boldsymbol{\mathcal{F}}^{\dagger}\mathbf{C})\mathbf{E}, \tag{29}$$

called the optimal generalized DVR.[5] The optimal GDVR is defined, although it may not be equally efficient, with any set of grid points and weights. It was shown to have exponential convergence.[8]

Were the basis functions standard orthogonal polynomials and the grid points and weights were those of the associated Gaussian quadrature, $\boldsymbol{\mathcal{F}}$ would be equal to $\mathbf{T}$, $\boldsymbol{\Delta}$ would be equal to the unit matrix, and the optimal GDVR would reduce to the standard DVR derivable by the transformation method. With general basis functions and with the corresponding grid points derived by the diagonalization method, however, $\boldsymbol{\mathcal{F}}$ is not equal to $\mathbf{T}$, $\boldsymbol{\Delta}$ is not the unit matrix, and the optimal GDVR given in Eq. (29) does not simplify to the DVR-like representation, Eq. (9), obtained by the transformation method. Thus, we have two distinct representations apparently employing the same basis functions and grid points. While in the GDVR one has to solve the eigenvalue problem of an asymmetric matrix, in the transformation method one has to solve the eigenvalue problem of a symmetric matrix. While the ith element of the nth eigenvector obtained by the GDVR method is proportional to the value of the nth eigenfunction taken at the ith grid point,[5] an advantageous property that may be used to contract the basis set by throwing away grid points where the wave function is known to be small, one cannot establish a similar relationship concerning the eigenvectors obtained by the transformation method.

The FBR of the potential energy operator in the transformation method involves, implicitly, an orthogonal polynomial basis, the $\{\sigma_n(q)\}_{n=0}^{N-1}$ set, and is of Gaussian quadrature accuracy. The FBR of the potential energy operator in the optimal GDVR, however, is hard to relate (except in the case of a standard orthogonal polynomial basis) to the Gaussian quadrature approximation. This suggests that the optimal GDVR might give less accurate eigenvalues than the DVR-like representation derived by the transformation method. At first glance this might be surprising, since the optimal GDVR has been shown to be the most accurate representation among all representations employing the same basis functions and quadrature points.[5] Note, however, that the transformation method employs (implicitly) two different bases. The $\{\phi_n(q)\}_{n=0}^{N-1}$ basis is used to form the matrix elements of the kinetic energy operator, while the $\{\chi_n(q)\}_{n=0}^{N-1}$ basis, where $\chi_n(q)=\Sigma_{m=0}^{N-1}M_{m,n}\sigma_m(q)$, is used to form the FBR of the potential energy operator. The optimal GDVR relies exclusively on the $\{\phi_n(q)\}_{n=0}^{N-1}$ basis. The optimal

TABLE I. Eigenvalues of the Hamiltonian of Eq. (30) as calculated with a basis set consisting of the first 15 eigenfunctions of the Hamiltonian of Eq. (31) and using different matrix representations.

	Transformation method	GDVR[a]	VBR[b]	Accurate[c]
1	1.614895064	1.614895069	1.614894252	1.614894082
2	5.656442162	5.656442160	5.656449635	5.656437055
3	11.107339593	11.107339940	11.107378164	11.107353336
4	17.637339719	17.637339395	17.638218119	17.637771274
5	25.064086745	25.064096710	25.069886577	25.068670563
6	33.278734997	33.278733648	33.297180465	33.293463662
7	42.189692496	42.189824402	42.252156070	42.236728714
8	51.981066951	51.980962039	51.904267355	51.841299964
9	62.668918878	62.676853057	62.137428525	62.061885955
10	69.738392060	69.729540448	77.251252657	72.861434123
11	70.693718739	70.693291637	92.555156459	84.208891006
12	122.467368704	122.465864484	144.539895982	96.077734785
13	125.321983645	125.322120603	173.930211698	108.444967253
14	293.849155740	293.851435172	332.706607268	121.290394935
15	296.504025194	296.504421925	388.866395065	134.596100534

[a]GDVR=generalized discrete variable representation.
[b]VBR=variational basis representation.
[c]Accurate eigenvalues converged up to the last digit quoted. They were obtained by comparing the results of two VBR calculations with basis sizes 55 and 75, respectively.

GDVR and the DVR-like representation derived by the transformation method become identical once the same bases are employed in their derivations, since then, the matrix $\boldsymbol{\mathcal{F}}$ is defined by the equation $\boldsymbol{\mathcal{F}}=\mathbf{M}^{\dagger}\mathbf{F}$ and not by Eq. (2).

A comparison of numerical results obtained by the optimal GDVR (using a single basis), Eq. (29), with those obtained by the transformation method, Eq. (9), tests the accuracy of the approximation of the potential matrix elements in Eq. (28).

As an example, we have calculated the eigenvalues of the Hamiltonian,

$$\hat{H}=-\frac{\mathrm{d}^2}{\mathrm{d}q^2}+q^2+q^4+q^6, \tag{30}$$

in three different representations of the same dimension. For basis functions we used the eigenfunctions of the quartic oscillator Hamiltonian,

$$\hat{H}_0=-\frac{\mathrm{d}^2}{\mathrm{d}q^2}+q^2+q^4, \tag{31}$$

that we derived by solving the Schrödinger equation for $\hat{H}_0$ using a large Gauss–Hermite DVR. We have calculated three different representations for the Schrödinger equation for $\hat{H}$ in this basis: the VBR, the DVR-like representation, Eq. (9), obtained by the transformation method, and the optimal GDVR. In the GDVR we used the same grid as in the transformation method and set the quadrature weights to one. (The results of optimal GDVR calculations do not depend on the values of the quadrature weights; see Ref. 5.) For the calculation of the VBR of the potential energy operator we used Gauss–Hermite quadrature. The VBR results served as a reference of comparison.

The numerical results presented in Table I and Fig. 1 show that the results by the optimal GDVR method are almost as accurate as those obtained by the transformation method. The same has been observed when employing polynomial potentials different from those given in Eq. (30) and Eq. (31). It follows that in the examples considered the approximation of the potential matrix elements in Eq. (28) is of nearly Gaussian quadrature accuracy when the grid points are derived by the diagonalization method.

It must be noted that since the Hamiltonian matrix given in the GDVR, Eq. (29), is asymmetric, one, in principle, may obtain complex eigenvalues. In the sample calculation whose results are presented in Table I, no complex eigenvalues were obtained. In other calculations we did obtain complex eigenvalues. Then, in fact, all eigenvalues obtained were complex numbers having exactly the same imaginary part, whereas all eigenvectors were real. Under such circumstances, however, the real part of an eigenvalue is also an eigenvalue. This can be seen by adding Eq. (29) to its complex conjugate and by noting that both the Hamiltonian matrix and the eigenvector matrix is real. As to the real parts of the eigenvalues it was

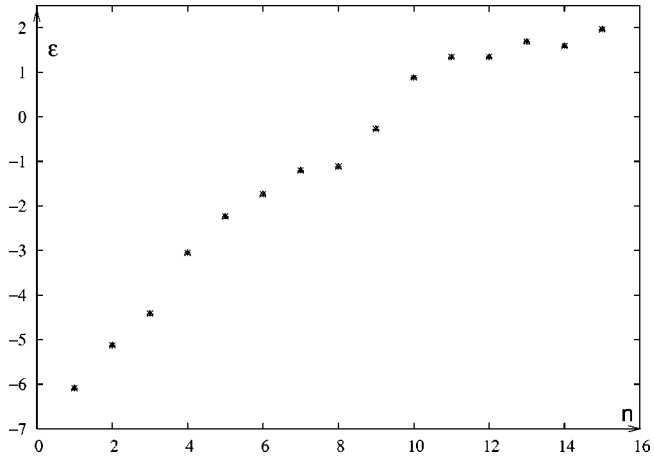

FIG. 1. Deviations of the GDVR eigenvalues from the VBR ones (triangles) are compared with the deviations of the eigenvalues obtained by using the transformation method from those obtained by the VBR (crosses). The deviations (ϵ) are given as the ten base logarithm of the absolute value of the differences of the eigenvalues obtained by the different methods, while n on the abscissa numbers the eigenvalues.

found that they agreed with the variationally obtained eigenvalues (the VBR results) just as well as the eigenvalues obtained by the transformation method.

In these calculations we used the subroutine DECRG of the IMSL[9] to find the eigenvalues of our asymmetric Hamiltonian matrices. When repeating the calculations by employing the subroutine DGEEV of LAPACK[10] we did not obtain complex eigenvalues, but the real parts of the eigenvalues obtained by DECRG and DGEEV, respectively, agreed to within numerical precision.

Thus, again, one may conclude that the quadrature approximation to the potential matrix elements in Eq. (28) is of nearly Gaussian quadrature accuracy when the grid points are derived by the diagonalization method. The somewhat curious results observed ocassionally when employing DECRG might be caused by algorithmical, numerical problems in this subroutine.

IV. SUMMARY

For the case of standard orthogonal polynomial bases the question of accuracy of the matrix elements of the potential energy operator derived via the transformation method has been made clear by Dickinson and Certain,[4] who showed the relation of the transformation method and the Gaussian quadrature associated with the polynomial basis employed. Little is known, however, about the accuracy of these matrix elements when a general, i.e., nonpolynomial or nonstandard orthogonal polynomial, basis is used. Here we have extended the proof of Dickinson and Certain and shown that the transformation method gives matrix elements of Gaussian quadrature accuracy even in the case of general bases. This explains, at least partially, the success of the potential optimized DVR method[11,12] where the transformation method is employed in deriving a DVR corresponding to the potential optimized (therefore usually not standard orthogonal polynomial) basis functions.

In our analysis the Christoffel–Darboux identity plays a fundamental role. It has been introduced for a general basis set by replacing the general basis functions with an appropriate set of polynomials [the $\sigma_n(q)$'s]. Recently a semiclassical generalization for the Christoffel–Darboux identity has been derived by Littlejohn and Wright.[13] It is valid in the asymptotic sense (large N) directly (i.e., without introducing a polynomial basis) for general bases.

The optimal generalized DVR offers an alternative to the DVR-like representation derivable by the transformation method. Our numerical calculations have shown that the optimal GDVR gives results nearly of Gaussian quadrature accuracy when using grid points obtained by the transformation method. Obviously, the optimal GDVR contains, as its special case, the DVR derivable by the transformation method with a standard orthogonal basis. But even for general bases, the optimal GDVR becomes identical to the DVR derived by the diagonalization method provided the same basis sets (and grid) are used in constructing the GDVR as used in the transformation method.

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APPENDIX: PROOF OF EQS. (15) AND (16)

Consider the recurrence relations

$$\beta_n\sigma_{n+1}(q)=(q-\alpha_n)\sigma_n(q)-\beta_{n-1}\sigma_{n-1}(q) \tag{A1}$$

and

$$\beta_n\sigma_{n+1}(q')=(q'-\alpha_n)\sigma_n(q')-\beta_{n-1}\sigma_{n-1}(q'). \tag{A2}$$

Multiply the first equation by $\sigma_n(q')$, multiply the second equation by $\sigma_n(q)$ and add them together. Following some rearrangement the resulting equation is

$$\begin{aligned}\sigma_n(q)\sigma_n(q')=\frac{1}{q-q'}\{&\beta_n\sigma_{n+1}(q)\sigma_n(q')\\&-\beta_n\sigma_{n+1}(q')\sigma_n(q)\\&+\beta_{n-1}\sigma_{n-1}(q)\sigma_n(q')\\&-\beta_{n-1}\sigma_{n-1}(q')\sigma_n(q)\}.\end{aligned} \tag{A3}$$

Then simply adding the terms on the left and right side in Eq. (A3) one obtains the Christoffel–Darboux identity:

$$\sum_{n=0}^{N-1}\sigma_n(q)\sigma_n(q')=\frac{\beta_{N-1}\sigma_N(q)\sigma_{N-1}(q')-\beta_{N-1}\sigma_N(q')\sigma_{N-1}(q)}{q-q'}, \tag{A4}$$

for $q\neq q'$. The result for $q=q'$ is obtained by applying the L'Hospital rule:

$$\begin{aligned}\sum_{n=0}^{N-1}\sigma_n(q)\sigma_n(q)=&\beta_{N-1}\left(\frac{d\sigma_N(q)}{dq}\right)_{q=q'}\sigma_{N-1}(q')\\&-\beta_{N-1}\sigma_N(q')\left(\frac{d\sigma_{N-1}(q)}{dq}\right)_{q=q'}.\end{aligned} \tag{A5}$$

Finally, since by definition the x_i's are the zeros of $\tilde{\sigma}_N(q)=\beta_{N-1}\sigma_N(q)$, Eqs. (15) and (16) follow.

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