Generalized discrete variable approximation in quantum mechanics[a)]

J. C. Light, I. P. Hamilton, and J. V. Lill[b)]
The James Franck Institute and The Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

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The formal definition of the generalized discrete variable representation (DVR) for quantum mechanics and its connection to the usual variational basis representation (VBR) is given. Using the one dimensional Morse oscillator example, we compare the "Gaussian quadrature" DVR, more general DVR's, and other "pointwise" representations such as the finite difference method and a Simpson's rule quadrature. The DVR is shown to be accurate in itself, and an efficient representation for optimizing basis set parameters. Extensions to multidimensional problems are discussed.

I. INTRODUCTION

One of the most common approaches to the solution of quantum mechanical problems is the variational matrix representation method in which an orthonormal basis of N functions is used, and the variational coefficients are determined by diagonalization. We will denote this variational basis representation by VBR. In the VBR, the operators are represented in terms of their projections onto the basis of L^2 functions. The eigenvalues and eigenfunctions of a truncated $(N \times N)$ matrix representation are then usually determined by diagonalization.

For the Hamiltonian operator and an appropriate truncation of a complete basis $\{\phi\}_N$ this procedure leads monotonically to the exact eigenvalues and eigenfunctions as $N \rightarrow \infty$, provided an exact (integral) inner product is used to define the matrix representation. The effort depends on the complexity of the Hamiltonian matrix evaluation and the size of the matrix representation required for adequate accuracy.

We have recently shown[1-3] that an approximate discrete variable representation (DVR) may be useful for representing the internal degrees of freedom in scattering problems. In the DVR the approximate solutions are not expressed as coefficients (or amplitudes) of basis functions, but rather as the amplitudes of the approximate solutions at a well defined set of coordinate points. Obviously such pointwise representations have been used for many years in the solution of differential equations, the most common being the method of finite differences[4] and finite element methods.[5] These approaches have usually had the advantage that the determination of the representation of the Hamiltonian is greatly simplified, but had the disadvantage that a large increase in number of points (as opposed to basis functions) was required for comparable accuracy.

The DVR, on the other hand, is isomorphic to an approximate "finite basis representation" (FBR) in which some matrix elements of the Hamiltonian are determined by numerical quadrature over the DVR points. Thus the definition of a DVR requires both the definition of an appropriate set of N basis functions ($\{\phi\}_N$) and the definition of an appropriate quadrature over the DVR basis of points ($\{x\}_N$). Such relationships are, of course, not new—the theory of Gaussian quadratures[6] being well developed and widely used. Similarly, the transformational relationship between point and basis representations have been explored and used[7,8] for the approximate evaluation of matrix elements in the basis representation (FBR). Until recently, however, the DVR has not been exploited as a primary representation in which certain quantum problems may be treated more easily.[1,2] In both of our earlier applications[1,2] the DVR appropriate to the common, but specific, basis of Legendre functions was used, with considerable success.

The purpose of this article is to explore the formal properties of the DVR more fully as a general representation for quantum problems; to examine, for a single system, the relations between a variational basis representation and generalized DVR's; to compare (briefly) the DVR with other pointwise representations (finite difference methods); and to suggest areas and problems for which the DVR appears to offer significant advantages over the more exact VBR.

In the next section we define the generalized DVR and show that it may, indeed, be considered a proper representation, satisfying essentially all the formal characteristics expected. In the third section we present a numerical comparison of a number of possible generalized DVR's with the usual variational basis representation (VBR) and with a finite difference approximation for a simple Morse oscillator potential. We also present the (expectedly) poorer results obtained by degrading the DVR, and the (unexpectedly) accurate results obtained by using the DVR for efficient optimization of the basis function parameters. In the final section we discuss these

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[b)] Current address: Department of Chemistry, University of Houston, Houston, TX 77004.

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results and the probable utility of the DVR for a variety of problems. In particular, we have generalized the DVR such that it may easily be applied in the future to nonseparable multidimensional problems.

II. DISCRETE VARIABLE REPRESENTATIONS

In this section we shall discuss the formal properties associated with a set of coordinate points viewed as a "point space" representation much as an appropriate set of functions is viewed as a "function space" representation in quantum mechanics. We note at the outset that there is a significant difference between them, associated with the definition of the inner product which means, as explained later, that an N point DVR is not truly variational. Accepting this *caveat,* however, it appears that DVR's can be constructed which approximate variational basis representations (VBR's) and are isomorphic with what we define below as finite basis representations (FBR's).[1]

We first define what we mean by these representations, restricting our attention for simplicity to a real basis in one dimension, $\{\phi(x)\} = \{\phi\}$. For such a basis we have the normal definition of the inner product and metric, S (we assume the weight function, if any, to be included in the definition of ϕ):

$$(\mathbf{S})_{ij} = \langle \varphi_i | \varphi_j \rangle = \int dx\, \varphi_i^*(x)\varphi_j(x),\ i, j = 1, 2, \cdots \tag{2.1a}$$

with $x \in (0, \infty)$ or $(-\infty, \infty)$. Completeness is defined by

$$\delta(x - x') = \sum_{ij}^{\infty} |\varphi_i\rangle (\mathbf{S}^{-1})_{ij} \langle \varphi_j|. \tag{2.1b}$$

If the basis is orthonormal and complete, the metric or overlap matrix S is the unit matrix and we have the usual completeness and orthogonality relations

$$(\mathbf{S})_{ij} = \int dx\, \varphi_i^*(x)\varphi_j(x) = \delta_{ij}, \tag{2.2a}$$

$$\sum_{i=1}^{\infty} \varphi_i^*(x)\varphi_i(x') = \sum_{i}^{\infty} |\varphi_i\rangle\langle\varphi_i| = \delta(x - x'). \tag{2.2b}$$

Otherwise S is a positive semidefinite Hermitian matrix. Since methods of forming orthonormal bases are well known, we assume $\{\phi\}$ orthonormal from here on. We also assume the basis $\{\phi\}$ is composed of eigenfunctions of some zero order Hamiltonian operator h_0:

$$h_0 \varphi_i = \epsilon_i^0 \varphi_i \tag{2.3}$$

with eigenvalues $\{\epsilon^0\}$. The $\{\phi\}$ are then a basis of a Hilbert space.

In what follows we wish to distinguish several representations, so we define the normal matrix representation of an operator [such as $H = h_0 + V(x)$] in a truncated basis, $\{\phi_i\}_N$ $i = 1, \ldots, N$ as the *variational basis representation* (VBR) with matrix elements defined by

$$(\mathbf{H}^{\mathrm{VBR}})_{ij} = \int dx\, \varphi_i^* H \varphi_j, \quad i, j = 1, \ldots, N. \tag{2.4}$$

Other isomorphic representations may be obtained by unitary transformations within the N dimensional function space. The designation "variational" applies because an N function representation of H always yields eigenvalues $\epsilon_i^{(N)} \geq \epsilon_i$, where $\{\epsilon_i\}$ are the true eigenvalues of H.

A discrete variable representation (DVR) corresponding to the VBR $\{\phi_i\}_N$ is an *approximate* pointwise representation on a set of N coordinate points, $\{x_i\}_N$. The points $\{x_i\}_N$ and the basis functions $\{\phi_i\}_N$ may be used together to define a generalized quadrature which replaces the inner product definition [Eq. (2.1a)]. The basis representation utilizing the functions $\{\phi\}_N$ and the general but finite quadrature inner product on $\{x\}_N$, is called the *finite basis representation* (FBR) and is isomorphic with the DVR, i.e., it represents the *same* approximation to the variational basis representation (VBR) in the set of basis functions $\{\phi\}_N$ as does the DVR on $\{x\}_N$. A properly defined DVR will satisfy discrete analogs of orthonormality and completeness [Eqs. (2.1) and (2.2)].

The approximation of a VBR by an FBR and the use of the isomorphism between the FBR and DVR for matrix element evaluation was proposed and used a number of years ago by Harris *et al.*,[7] and by Dickinson *et al.*[8] These applications, however, were restricted to the simplest cases of one-dimensional (or direct product) problems; to bases of classical orthogonal polynomials and weight functions and their related Gaussian quadratures; and, surprisingly, to the use of the FBR (vs DVR) as the primary representation. The DVR for one dimension based on the diagonalization of the coordinate operator (in the VBR) for an arbitrary one-dimensional orthonormal basis introduced by Harris *et al.*[7] was shown to be a Gaussian quadrature for orthogonal polynomial bases.[8]

In this section we briefly summarize the earlier results utilizing basis functions in one coordinate dimension and primarily, classical orthogonal polynomials and their related Gaussian quadratures. Viewing the pointwise representation, the DVR, as an approximate representation of a Hilbert space, we then formally generalize these results to arbitrary bases, arbitrary points, and many dimensions.

A. Classical orthogonal polynomials and Gaussian quadrature points

Dickinson *et al.*[8] showed that for bases of N classical orthogonal polynomials[9] times their appropriate weight functions $\{\phi_i^G\}_N$ an orthogonal transformation exists between representations in the N Gaussian quadrature points and representations in the N basis functions. The transformation is defined as (the superscript G stands for Gaussian)

$$\mathbf{T}_{i\alpha}^G \equiv \varphi_i^G(x_\alpha^G)\omega_\alpha^{G1/2}, \tag{2.5}$$

where $\{x_\alpha^G\}_N$ and $\{\omega_\alpha^G\}$ are the Gaussian points and weights for the classical polynomial basis functions $\{\phi_i^G\}_N$. Thus a potential matrix, diagonal on the points (a discrete variable representation)

$$(\mathbf{V})_{\alpha\beta} = V(x_\alpha^G)\delta_{\alpha\beta} \tag{2.6}$$

may be transformed to the approximate finite basis representation (FBR) by

$$(\mathbf{V}^{\mathrm{FBR}})_{ij} = (\mathbf{T}^G\mathbf{V}^{\mathrm{DVR}}\mathbf{T}^{GT})_{ij} = \sum_\alpha^N \varphi_i^G(x_\alpha^G)\omega_\alpha^{G1/2}V(x_\alpha^G)\varphi_j^G(x_\alpha^G)\omega_\alpha^{G1/2}. \tag{2.7}$$

Thus in the FBR the matrix elements are defined by numerical quadrature rather than by continuous integration as in the VBR [Eq. (2.1)]. Dickinson *et al.*[8] showed that discrete orthogonality and completeness relations are then given in finite matrix form by

$$(\mathbf{T}^G\mathbf{T}^{GT})_{ij} = \delta_{ij} = \sum_{\alpha=1}^N \varphi_i^G(x_\alpha^G)\omega_\alpha^G\varphi_j^G(x_\alpha^G), \tag{2.8a}$$

$$(\mathbf{T}^{GT}\mathbf{T}^G)_{\alpha\beta} = \delta_{\alpha\beta} = \sum_{i=1}^N \varphi_i^G(x_\alpha^G)\omega_\alpha^{G1/2}\varphi_i(x_\beta^G)\omega_\beta^{G1/2}. \tag{2.8b}$$

These relations mean that this DVR is isomorphic with the corresponding FBR in which the potential matrix elements are evaluated by the specified numerical quadrature.

It is interesting to note the entirely symmetric relationships between the FBR and DVR expressed in Eqs. (2.8a) and (2.8b). Equation (2.8a) is an orthonormality relation for the basis with respect to the N point inner product quadrature *and* a completeness relation for the coordinate points with respect to the N function basis. Conversely, Eq. (2.8b) is an orthonormality relation for the N quadrature points with respect to a sum over N basis functions as inner product, and a completeness relation of the N basis functions with respect to the N quadrature points. Thus the use of the N point Gaussian quadrature inner product with the N function classical orthogonal polynomial basis introduces complete symmetry between the DVR and the FBR analogous to the continuous coordinate and momentum representations related by Fourier transforms. In both cases operators may be evaluated in one representation and transformed to the other for convenience. The limitations of the DVR–FBR formulation as well as its advantage are discussed below.

B. General DVR motivation

Since the DVR based on Gaussian quadrature points and orthogonal polynomials offers significant advantages in terms of convenience and flexibility at a small loss in accuracy,[7,10] it is of interest to extend the formalism to more general cases, i.e., to bases and points for which standard Gaussian quadratures do not exist and/or to higher dimensions. The potential utility of such generalizations is clearly implied by the vibrational problem for triatomic molecules. The difficulty of obtaining a small number ($\sim$10) of accurate (error $\sim 10^{-3}$% or $\sim$3 cm^{-1}) eigenvalues from a large "CI" basis of direct product vibrational functions ($\sim$250–600) using even larger ($\sim$1000 point) quadratures (over the potential) is surprising.[11,12] One reason may be that the basis function space and the quadrature point space were both restricted to direct product form, and the function space was used for the Hamiltonian matrix representation, truncation, and diagonalization. We believe the results presented in Sec. III indicate that such problems may more easily be solved using the general DVR as the "primary" representation.

The discrete variable representation, however, has not been widely used, probably for several reasons. First, the use of an N point quadrature to evaluate H in an N basis function representation does not "look" very accurate, despite the published evidence.[7,8,10] Second, the point representation (DVR) was apparently always considered as a crutch—a means to approximate potential energy matrices in the FBR, and not as the best representation in which to carry out analyses and operations. Third, and probably most important, the techniques were not easily generalizable to more than one dimension (or direct product spaces). There are not, to our knowledge, general Gaussian quadrature techniques except for a restricted class of orthogonal polynomials in one dimension. In addition, there is in general no unique coordinate to be diagonalized in more than one dimension which would yield a coordinate diagonal representation. In the remainder of this section we examine the formal properties of the DVR, defining a general DVR which should remove the latter two objections above. In Sec. III we examine numerical models which should help to remove the first prejudice.

C. General DVR–FBR transformations

In this section we look at the formal properties of an N point inner product "quadrature" which permits us to treat the approximate DVR defined on a set of points $\{x_\alpha\}_N$ and the associated FBR defined on $\{\phi\}_N$ on equal footing. In what follows we assume the basis $\{\phi\}_N$ is orthonormal in the VBR, i.e., the overlap matrix $\mathbf{S} = \mathbf{I}$ with an exact (continuous integral) inner product as in Eq. (2.1a). To emphasize the fact that we are using a discrete set of points $\{x_\alpha\}_N$ as "basis vectors" in a representation, we adopt the bracket notation.

The set of basis functions $\{\phi_i\}_N$ define an orthonormal set of unit vectors in a Hilbert space (VBR):

$$\langle\varphi_i|\varphi_j\rangle \equiv \int \varphi_i^*(x)\varphi_j(x)dx = \delta_{ij} \tag{2.9}$$

with the unit projection operator on the N dimensional subspace

$$I_N = \sum_{i=1}^N |\varphi_i\rangle\langle\varphi_i|. \tag{2.10}$$

We now ask for an *approximate* representation in which the integrals such as are in Eq. (2.9) are replaced by a numerical "quadrature" on the points, $\{x_\alpha\}_N$.

The usual continuous coordinate representation is defined by the (infinite or continuous) transformation matrices:

$$\mathbf{Y}_{i\alpha}^+ \equiv \langle\varphi_i|x_\alpha\rangle = \varphi_i^*(x_\alpha) \tag{2.11}$$

with the unit operator in the coordinate representation

$$I = \int |x_\alpha\rangle dx_\alpha \langle x_\alpha|.$$

We now wish to discretize the continuum coordinate representation to a set of N points, $\{x_\alpha\}_N$, retaining the definition of the transformation in Eq. (2.11).

Since the coordinate basis $\{1x_\alpha\rangle\}_N$ is now discrete (and so far arbitrary), the finite dimensional transformation (2.11) will not in general remain orthogonal, i.e., the metrics of the finite dimensional spaces may be changed. Thus we use the general relations between the metrics S and Δ in two finite representations connected by an $N \times N$ transformation matrix Y:

$$\mathsf{Y}^+\Delta^{-1}\mathsf{Y} = \mathsf{S}, \tag{2.12a}$$

$$\mathsf{Y}\mathsf{S}^{-1}\mathsf{Y}^+ = \Delta. \tag{2.12b}$$

Since Eq. (2.12) does not define the metrics, we are free to choose either S or Δ and determine the other from Eq. (2.12). Choosing S = I (i.e., requiring that the functions remain orthonormal over the discrete quadrature), we have

$$\mathsf{S} = \mathsf{I} \Rightarrow \tilde{\Delta} = \mathsf{Y}\mathsf{Y}^+. \tag{2.13a}$$

Alternatively we may renormalize the functions over the simple quadrature by choosing Δ = I:

$$\Delta = \mathsf{I} \Rightarrow \tilde{\mathsf{S}} = \mathsf{Y}^+\mathsf{Y}. \tag{2.13b}$$

In *either* case we may define the *unique unitary* transformation between the orthonormal function basis and orthonormal point basis:

$$T^+ = \mathsf{Y}^+\tilde{\Delta}^{-1/2} = \tilde{\mathsf{S}}^{-1/2}\mathsf{Y}^+. \tag{2.14}$$

Using Eq. (2.13) it is easily seen that T is unitary. The two forms of the transformation are seen to be identical since the inverse of a matrix is unique and

$$\mathsf{T}^+\mathsf{T} = \mathsf{Y}^+\tilde{\Delta}^{-1/2}\mathsf{Y}\tilde{\mathsf{S}}^{-1/2} = \mathsf{Y}^+(\mathsf{Y}\mathsf{Y}^+)^{-1/2}\mathsf{Y}(\mathsf{Y}^+\mathsf{Y})^{-1/2} = \mathsf{I}.$$

The only formal restriction is that the points and functions be chosen such that the inverses of $\mathsf{Y}\mathsf{Y}^+$ and $\mathsf{Y}^+\mathsf{Y}$ exist.

Thus we have defined a general unitary transformation between representations in an N dimensional function space and an N dimensional point space. In the case of Gaussian quadratures the metrics $\tilde{\Delta}$ and $\tilde{\mathsf{S}}$ are diagonal and, with properly normalized functions, are unit matrices. As we shall show shortly, the use of Gaussian points is not only simpler but more accurate than the general relations with arbitrary (not Gaussian) points defined above. The purpose of defining the general relations is that they may be used for multidimensional systems for which Gaussian points cannot be chosen or, for example, when a potential is known only at an arbitrary set of points.

We now turn to the evaluation of operators using the DVR. We may proceed in two ways:

(a) To be exact, we may transform from the matrix representation in the variational basis; i.e., if

$$(\mathsf{A}^{\mathrm{VBR}})_{ij} = \langle\varphi_i|A|\varphi_j\rangle, \tag{2.15a}$$

then

$$\tilde{\mathsf{A}}^{\mathrm{DVR}} = \mathsf{T}\mathsf{A}^{\mathrm{VBR}}\mathsf{T}^+, \tag{2.15b}$$

where A is an arbitrary operator. We use the tilde to denote a DVR matrix obtained by exact transformation. Using this, a DVR is obtained which is isomorphic with the normal representation (VBR). This is useful, for example, to determine a coordinate function (such as a dipole function) from its matrix elements.

(b) We may also *approximate* coordinate operators directly in the DVR by their values at the DVR points, $\{x_\alpha\}$. Since a major purpose of a DVR is to permit the direct and simple approximation of such coordinate operator matrix elements in this fashion, we shall define this approximate representation to be the DVR. Thus we set for a coordinate operator V the DVR matrix elements to be

$$(\mathsf{V}^{\mathrm{DVR}})_{\alpha\beta} = V(x_\alpha)\delta_{\alpha\beta} \approx (\mathsf{T}\mathsf{V}^{\mathrm{VBR}}\mathsf{T}^+)_{\alpha\beta}. \tag{2.16}$$

This equation, together with Eqs. (2.13) and (2.14), defines a numerical quadrature over the DVR points ($\{x_\alpha\}_N$)

$$\mathsf{V}^{\mathrm{VBR}} \approx \mathsf{T}^+\mathsf{V}^{\mathrm{DVR}}\mathsf{T}. \tag{2.17}$$

By construction the quadrature is exact for those components of $V\phi_i$ which remain in the Hilbert space defined by $\{|\phi_i\rangle\}_N$. The error in the quadrature is due to those components of $V\phi_i$ which do not lie in $\{|\phi_i\rangle\}_N$ but which contribute (garbage) to the approximate quadrature.

This is easily seen by evaluating (formally) the projected potential

$$V(x)\varphi_i(x) = \sum_{j=1}^{N} V_{ij}^N\varphi_j + \sum_{j=N+1}^{\infty} V_{ij}^Q\varphi_j = V^N\varphi_i + V^Q\varphi_i. \tag{2.18}$$

Since $V_{ij}^N = V_{ji}^N$, for $k, i = 1, N$,

$$\varphi_k^* V^N\varphi_i = \sum_{j=1}^{N} \varphi_k^* V_{ij}^N\varphi_i = \sum_{j=1}^{N} V_{kj}^N\varphi_j^*\varphi_i. \tag{2.19}$$

Integrating Eq. (2.19) leaves V_{ki}, the exact matrix element, whereas summing over the points $\{x_\alpha\}_N$ yields

$$\sum_\alpha \varphi_k^*(x_\alpha)V^N(x_\alpha)\varphi_i(x_\alpha) = \sum_{j,\alpha} \varphi_k^*(x_\alpha)\varphi_j(x_\alpha)V_{ij}^N = \sum_{j,\alpha} V_{kj}^N\varphi_j^*(x_\alpha)\varphi_i(x_\alpha). \tag{2.20}$$

In matrix form this is

$$\mathsf{Y}^+\mathsf{V}^{N,\mathrm{DVR}}\mathsf{Y} = \tilde{\mathsf{S}}\mathsf{V}^{N,\mathrm{VBR}} = \mathsf{V}^{N,\mathrm{VBR}}\tilde{\mathsf{S}}. \tag{2.21}$$

Since this implies that $\tilde{\mathsf{S}}$ and $\mathsf{V}^{N,\mathrm{VBR}}$ commute, we have

$$\mathsf{Y}^+\mathsf{V}^{N,\mathrm{DVR}}\mathsf{Y} = \tilde{\mathsf{S}}^{1/2}\mathsf{V}^{N,\mathrm{VBR}}\tilde{\mathsf{S}}^{1/2} \Rightarrow \mathsf{V}^{N,\mathrm{VBR}} = \mathsf{T}^+\mathsf{V}^{N,\mathrm{DVR}}\mathsf{T}. \tag{2.22}$$

Thus the quadrature (2.17) is exact (as might be expected) for the portion of $V\phi$ projected onto $\{|\phi_i\rangle\}_N$. However, the functions $|\phi_p\rangle p > N$ (which are orthogonal to $\{|\phi_i\rangle\}_N$ using exact integrals) are *not* orthogonal to the $\{|\phi_i\rangle\}_N$ using the numerical quadrature. Therefore components of $V\phi$ lying outside $\{|\phi_i\rangle\}_N$ "contaminate" the numerical quadrature (2.17). Gaussian quadratures gain extra accuracy by the choice of quadrature points at the zeros of ϕ_{N+1}, thus eliminating contamination from this component of all $V\phi_i$. This suggests that "arbitrary" points

$\{x_\alpha\}_N$ be chosen such that $\phi_{N+1}(x_\alpha)$ at least be small, if not zero.

Finally we note that the approximation inherent in Eq. (2.16) destroys the usual variational principle for operators bounded from below (such as H) when the DVR is used. Although we shall show in the next section that this is not necessarily serious, numerically, we must be cognizant of it.

One major advantage of the general DVR–FBR presented in this section is that it applies automatically to higher dimensions. Equations (2.11)–(2.17) have obvious generalizations to points and functions defined on m dimensional coordinate spaces. One of the penalties we pay for this additional freedom is the lack of a general definition of optimal quadratures, i.e., a prescription for choosing the points given the basis ($\{\phi\}_N$). Although one could attempt to choose the points such that $\tilde{\Delta}$ is diagonal we do not believe this is possible in general for higher dimensional systems and an arbitrary (not direct product) basis. Thus we assume a satisfactory point basis is provided by a set $\{x\}$ for which $\tilde{\Delta}$ has *no small* eigenvalues ($\ll 1$), i.e., for which there is no approach of linear dependence. This uncomfortable uncertainty can be relieved somewhat by numerical examples.

In the next section we present numerical results using the general DVR–FBR formulation which verify the utility of the formal approach taken here. We also compare with the results of application of a simple finite difference approach to our model problem.

III. COMPARISON FOR ONE-DIMENSIONAL MORSE OSCILLATOR

The one dimensional Morse oscillator has often served as a model problem for testing new approaches, and for good reason. It is a flexible asymmetric problem for which the exact analytic eigenfunctions and eigenvalues are known and for which accurate variational solutions are reasonably difficult to obtain. Shore,[10] for example, recently used it to test about a dozen numerical approaches. It is, therefore, instructive to use this model to examine the flexibility and accuracy of the general DVR's just defined.

In this section we shall first define the model problem, its analytic eigenvalues, and a "standard" variational result using appropriate harmonic oscillator basis functions. We shall then present and compare the results from a sequence of other pointwise representations. These include, in order of decreasing accuracy, the Gaussian DVR based on the standard harmonic oscillator basis and associated standard Gaussian quadrature points; a DVR with the standard harmonic oscillator functions and shifted points; a DVR with shifted harmonic oscillator functions and the standard Gaussian points; three calculations based on one set of equally spaced points (the DVR for the standard harmonic oscillator functions, a finite differences calculation, and an FBR using Simpson's rule quadrature).

To illustrate the convergence of the DVR procedure, we then compare (columns I, J) the 25 point finite differences approximation with the 25 point DVR based on the Gaussian quadrature using the standard basis. The latter is several orders of magnitude superior in accuracy for the lowest eight eigenvalues.

Next we examine briefly the problem of truncation in the DVR (Table II). It is common to use many more points in numerical quadratures than basis functions. Therefore, viewing the DVR and FBR in reverse [see Eq. (2.21)], we asked if it is advantageous to use more functions than points with the DVR as the "primary" representation. The answer appears to be negative.

Finally (Table III) we show the results of exploiting the simplicity of the DVR in order to obtain more accurate results with a fewer number of points or basis functions. Since the trace of the Hamiltonian may be evaluated very simply in the DVR for given basis set parameters, it is easier to minimize the trace with respect to the parameters in the DVR than in the FBR (or VBR). After choosing the basis set parameters to minimize the trace of H, using this basis (in the DVR, FBR, or VBR) yields excellent results. It appears that the simplicity afforded by the DVR will be most useful in this "optimization" process.

A. Morse oscillator and standard harmonic oscillator basis

We take a one dimensional Morse oscillator which roughly represents the ($J = 0$) HF molecule as the model. The Hamiltonian is given by [$V(r \to \infty) = 0$]

$$H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + D(e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)}) = T + V \tag{3.1}$$

with $r_e = 1.75a_0$, $\mu = 19/20$ amu, $D = 5.726$ eV, and $\alpha = 1.22a_0^{-1}$. The analytic solutions for the eigenvalues yield the bound state energies:

$$\epsilon_n = \hbar\omega(n + \tfrac{1}{2}) - \hbar\omega x_e(n + \tfrac{1}{2})^2, \quad n = 0, 1, \ldots, 22 \tag{3.2}$$

with $x_e = 0.022\,468\,85$.

For our comparisons we chose to focus on the lowest eight eigenvalues using an $N = 12$ harmonic oscillator basis as standard. The basis $\{\phi\}$ is defined by the zero order harmonic oscillator Hamiltonian,

$$h_0 \equiv -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\kappa}{2}(r - r_0)^2, \tag{3.3a}$$

$$h_0\varphi_n = \hbar\omega(n + \tfrac{1}{2})\varphi_n = \epsilon^0\phi_n. \tag{3.3b}$$

The parameters $\omega = 5.001\,209\ S^{-1}$ [or $\beta = (\mu k/\hbar^2)^{1/4} = 4.6a_0^{-1}$) and $r_0 = 2.18a_0$ were chosen, after some variation, to yield good agreement of the variational eigenvalues ϵ_i^v with the exact eigenvalues ϵ_i for $i = 1, 8$. The Morse potential energy levels, and h.o. potential for the standard basis are shown in Fig. 1.

The exact eigenvalues are shown in Table I, second column, together with the errors $\epsilon_i^v - \epsilon_i$ in various approximation (columns A–J). The errors in column A

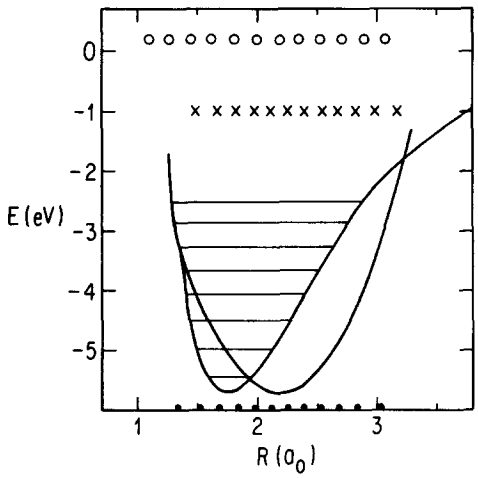

FIG. 1. Morse potential, eight energy levels of interest, and harmonic oscillator potential of standard basis: · · · Gauss–Hermite points for standard basis; × Gauss–Hermite points for shifted basis; ○ equally spaced points.

(to the accuracy shown) are due entirely to the truncation of the harmonic oscillator basis to $N = 12$, since the Hamiltonian was evaluated essentially exactly in this basis with a 500 point Simpson's rule integration used to evaluate ΔV in the standard ($N = 12$) harmonic oscillator basis representation:

$$\mathbf{H}^{\mathrm{VBR}} = \epsilon^0 + \Delta\mathbf{V}^{\mathrm{VBR}}, \tag{3.4a}$$

$$(\Delta V)_{ij} = \int_{-\infty}^{\infty} \varphi_i(r)\left[V - \frac{\kappa}{2}(r - r_e)^2\right]\varphi_j(r)dr. \tag{3.4b}$$

This 12-function harmonic oscillator basis is not optimum, but is quite close. This basis is referred to in the following as the standard harmonic oscillator basis and the results as the standard variational ($N = 12$) results.

B. A Gaussian DVR based on the standard harmonic oscillator representation

As Harris *et al.*,[7] Dickinson *et al.*,[8] and Shore[10] showed, the replacement of the exact ΔV matrix in Eq. (3.4a) by the $\Delta\mathbf{V}^{\mathrm{FBR}}$ [computed by Gaussian quadrature over the N (=12) Gauss–Hermite points corresponding to the N (=12) standard harmonic oscillator basis functions] is really a very accurate approximation. Since this (FBR) representation is isomorphic with the N (=12) point Gaussian DVR, the results below in Table I, column B, apply to both. We now face a (minor) ambiguity in presentation—do we wish to judge the DVR–FBR results vs the exact results or vs the results of the corresponding N function standard harmonic oscillator variational calculation? Since no information is lost, we present only the errors compared with the exact ϵ_i in Table I. As can be seen, there is no significant loss of accuracy in using the DVR in this case, i.e., all errors are comparable to those of the standard variational harmonic oscillator in magnitude. We note, however, that the DVR–FBR results do *not* provide an upper bound on the individual eigenvalues.

An illustration of the accuracy of the DVR is given in Fig. 2 in which the exact values of ΔV at the DVR points (ΔV^{DVR}) are compared with the diagonal elements and the eigenvalues of $\mathbf{T}^{+}\Delta\mathbf{V}^{\mathrm{VBR}}\mathbf{T}$. Even though ΔV is quite large (>1.5 eV) in the coordinate range of interest, the DVR approximation is of comparable accuracy to the standard VBR result.

C. General DVR–FBR results

We now wish to test numerically the general DVR–FBR formulation of the last section. In doing so, we introduce a new degree of freedom in that the points of the DVR are chosen independently from the basis functions. This extra degree of freedom means that one can, if one so desires, choose a disastrously poor set of points (one could, also, choose an equally disastrous set of functions). The purpose of this section, therefore, is not to find the best set of points (those were explored in Sec. B, above), but to examine, at least semiquantitatively, what happens when the choice of points and basis functions is decoupled. This is important to investigate because (a) in multidimensional systems Gaussian-type quadratures are nontrivial to find[13] and are limited in order or

TABLE I. Comparison of exact eigenvalues (n = 1–8) with various approximate eigenvalues for a Morse oscillator. A–H $N = 12$; I, J $N = 25$. Deviations from exact results are shown. A: Standard harmonic oscillator basis. Variational calculation ($r_0 = 2.18a_0$). B: Standard DVR-Gauss–Hermite points corresponding to A. C: Shifted h.o. basis ($r_0 = 2.32a_0$), corresponding to Gauss–Hermite DVR points. D: Shifted h.o. basis ($r_0 = 2.32a_0$), Gauss–Hermite points corresponding to A. E: Standard h.o. basis, shifted Gauss–Hermite points corresponding to C. F–H: Equally spaced points. F: DVR with standard h.o. basis. G: First order finite differences. H: Simpson's rule quadrature. I: Finite differences, $N = 25$ points. J: DVR-Standard h.o. basis and points, $N = 25$.

		$\epsilon_n^{\mathrm{approx}} - \epsilon_n$					$\epsilon_n^{\mathrm{approx}} - \epsilon_n$				
n	Analytic ϵ_n (eV)	A	B	C	D	E	F	G	H	I	J
1	−5.4620	0.0000	0.0000	−0.0001	−0.0001	−0.0001	0.0000	−0.0165	−0.0795	−0.0033	0.0000
2	−4.9714	0.0003	0.0004	+0.0026	−0.0003	+0.0026	−0.0084	−0.0998	−0.0881	−0.0166	0.0000
3	−4.5038	0.0014	−0.0015	+0.0076	−0.0077	+0.0078	+0.0284	−0.2793	−0.1321	−0.0421	0.0000
4	−4.0594	0.0033	−0.0125	−0.0396	−0.0416	−0.0433	−0.0143	−0.2194	−0.1308	−0.0774	0.0000
5	−3.6380	0.0095	−0.0126	−0.0931	−0.0612	−0.1063	−0.0231	−0.5082	−0.0641	−0.1204	0.0000
6	−3.2397	0.0312	+0.0296	−0.0306	−0.0122	−0.0453	+0.0876	−0.4534	−0.3532	−0.1601	0.0000
7	−2.8645	0.0689	0.0914	+0.0753	−0.0283	+0.0600	+0.0986	−0.2571	+0.0031	−0.2217	−0.0001
8	−2.5123	0.1131	−0.0057	+0.1795	−0.2782	+0.1628	+0.2256	−0.0914	−0.2143	−0.2769	0.0000
rms error:		0.0482	0.0346	0.0784	0.1024	0.0753	0.0935	0.2904	0.1671	0.1475	0.0000
Avg. error:		0.0285	0.0114								

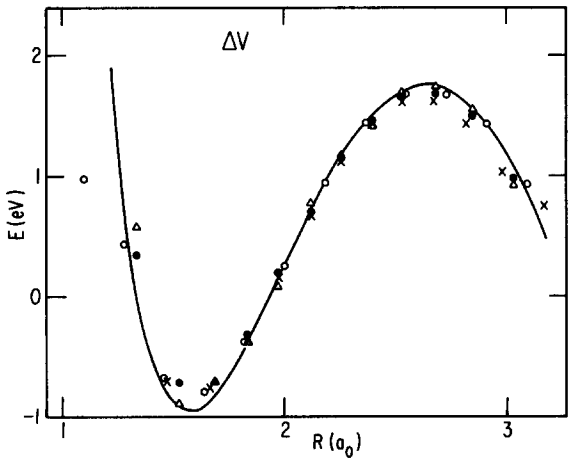

FIG. 2. ΔV(—) and approximations to it. $(T^{+}\Delta V^{\mathrm{VBR}}T)_{\alpha\alpha}$ for: ● standard Gauss–Hermite DVR points; × G-H points for shifted basis; O equally spaced points. Δ are eigenvalues of ΔV^{VBR} plotted at nearest standard G-H points.

function type, and (b) the potential information known, on which to base the Hamiltonian evaluation, may not be at appropriate points. Therefore in this section we examine what happens when the basis and point representations do *not* have a Gaussian quadrature relationship, and the general formulas of Sec. II must be used.

In Table I, columns C–E, we present the results using less than optimal bases and points. In column C a poorer $N = 12$ harmonic oscillator basis ($r_0 = 2.32a_0$ vs $2.18a_0$ for the previous results) is used with its associated Gauss–Hermite points. In columns D and E the general DVR is used since for D, the original G–H points (for the basis with $r_0 = 2.18a_0$) were used with the shifted basis ($r_0 = 2.32a_0$) and vice versa in column E. In this first example we note that the errors using the general DVR (columns D and E) are comparable in magnitude to those using the appropriate Gaussian quadrature with the degraded basis (column C) and thus comparable in magnitude to the errors of the variational calculation using the degraded basis. This implies that the additional error incurred by using the general DVR is small.

The Morse potential and energy levels and the standard harmonic potential are shown in Fig. 1. Also shown are the 12 standard G–H points, the 12 shifted G–H points, and the 12 equally spaced points used.

In columns F–H of Table I we briefly compare the DVR using 12 evenly spaced points (between $r_1 = 1.08a_0$, $r_{12} = 3.04a_0$). In column F the standard harmonic oscillator basis and the general DVR is used. In column G, the first order finite differences result on the same points is shown. In column H the same points and functions were used with a Simpson's rule quadrature of the potential. Finally, in column I a 25 point finite differences result is shown, and compared, in column *J*, with a 25 point Gaussian DVR using the standard basis.

In the first order finite differences method, the second order differential operator is approximated by

$$\frac{d^2}{dr^2}f(r) \rightarrow [f(r_{i-1}) + f(r_{i+1}) - 2f(r_i)]h^{-2},$$

where $h = r_{i+1} - r_i$. In all cases only the potential values at the points were used, resulting in effective trapezoid rule quadratures for the finite differences method. Although the choice of points and the low order method is clearly not optimal for the determination of the lowest few eigenvalues by the finite difference, the qualitative results are in accord with previous experience[10]—the low order finite differences method requires several times the number of points as are required for reasonably chosen global basis functions in variational methods. The DVR appears to require only a number of points comparable to the number of basis functions. (For comparison purposes we show the 25 point Gaussian DVR for 25 standard harmonic oscillator basis functions in column J.)

D. Truncation in the DVR

We now very briefly examine a procedure which is not useful for 1D problems but is quite relevant to extensions to higher dimensions, and that is the effect of truncation of an N point, N function DVR–FBR to an M point DVR, $M < N$. The converse, using many more points for numerical quadrature than basis functions, is, of course, very common. Here we define an N point DVR and the full $N \times N$ DVR Hamiltonian, $\mathsf{H}_N^{\mathrm{DVR}}$,

$$\mathsf{H}_N^{\mathrm{DVR}} = \mathsf{T}^{+}\mathsf{h}_0\mathsf{T} + \Delta\mathsf{V}^{\mathrm{DVR}},$$

and then *truncate* the matrix representation to $M \times M$, with $M < N$, where the M retained points lie in low regions of the potential energy. This may be useful in multidimensional problems where some direct product bases are normally truncated because their diagonal matrix elements of H are very large. The corresponding direct product DVR will have some points, e.g., (X_n, Y_n) which lie in very high regions of the potential energy. If we are interested in low energy eigenfunctions, we should be able to truncate these points from the DVR with little loss in accuracy. A brief 1D illustration of this is presented here.

We illustrate this by choosing an optimized (with respect to ω_0, r_0, as discussed in the next section) 13 point DVR using Gaussian points and harmonic oscillator functions. The optimization was carried out by minimizing the sum of the seven lowest energy diagonal elements in the 13×13 DVR Hamiltonian. The DVR Hamiltonian matrix was then truncated and diagonalized keeping, sequentially, 7, 9, 11, and all 13 points. The results are shown in Table II.

The results show two things:

(a) Optimization of the basis for a small number (7) of points yields remarkably good results for 5 of the 7 eigenvalues.

(b) The lower eigenvalues converge to the full 13×13 results quite quickly (e.g., the fifth eigenvalue changes only in the third decimal place as the number of points retained increases from 9 to 13, all lower eigenvalues changing much less).

This is at least a preliminary indication that for a

TABLE II. Results for truncated DVR: 13 point DVR with basis optimized over the trace for the center seven points. DVR truncated to $N = 7, 9, 11, 13$. n = number of eigenvalue. Errors from exact are shown $\epsilon_n^{DVR} - \epsilon_n^{EXACT}$.

n \ N	13	11	9	7
1	−0.0001	−0.0001	−0.0001	−0.0001
2	0.0000	0.0000	0.0000	0.0000
3	+0.0054	0.0054	0.0054	0.0065
4	−0.0139	−0.0139	−0.0137	−0.0043
5	−0.0572	−0.0572	−0.0545	−0.0067
6	+0.0245	+0.0245	+0.0568	0.3987
7	+0.1720	+0.1870	+0.3724	0.4713
8	+0.0521	+0.0548	+0.1806	···

fixed basis and DVR transformation, the lower eigenvalues are relatively insensitive to truncation of the DVR.

E. Optimization using the DVR

In this section we present the first evidence that, because of the ease of evaluation of matrix elements in the DVR, it may provide a simple means of determining an optimum *basis* for variational calculations. For the model problem and, in particular, the harmonic oscillator basis we are using, the procedure is particularly simple: we vary the two parameters of the harmonic oscillator basis (ω and the minimum, r_0) to minimize the *trace* of the truncated Hamiltonian in the (Gaussian) DVR. Since, for complicated (or even Morse) potentials, the trace is much easier to evaluate in the DVR than the FBR (or the usual variational representation) the basis optimization, although a nonlinear process, is easy to carry out.

Specifically, if we choose a harmonic oscillator basis and the associated Gauss–Hermite points for the FBR–DVR, the Hamiltonian in the DVR has the form

$$\mathsf{H}^{DVR} = \hbar\omega\epsilon^0 + \Delta\mathsf{V}^{DVR}(r; r_0, \omega),$$

where ϵ^0 is a *constant* matrix (independent of ω, r_0) and $\Delta\mathsf{V}$ is the *diagonal* difference potential matrix evaluated at the DVR points, which depends on the parameters of the harmonic oscillator basis (r_0 and ω). For a given basis size, the trace of H^{DVR} can very easily be evaluated and minimized with respect to r_0 and ω. The results of optimizing the basis in this fashion and then diagonalizing H^{DVR} for DVR–FBR's with $N = 7, 9, 11, 12, 13$ (columns B–F) are shown in Table III, compared with the standard $N = 12$ variational results (column A). It can be seen that the optimized basis DVR for $N = 12$ is significantly better than our "standard basis" variational calculation.

In order to assure that the optimized basis for the DVR is, indeed, an optimized (or at least very good) variational basis, we used the $N = 12$ DVR optimized basis in a standard variational calculation. The results are shown in Table III (column G). The utilization of the optimized basis results in about a factor of 3 reduction of error from the standard basis results for the first eight eigenvalues. Although this optimization could have been carried out in the VBR, it is rarely done because it is so much more difficult.

It is also interesting to note, from Table III that an optimized $N + 1$ point DVR appears to be comparable or better than a variational optimized N function calculation. From our other calculations this appears to be true for a variety of N's, although the variational calculations retain the advantage of converging to the true values from above only.

IV. SUMMARY AND DISCUSSION

In the last two sections we have defined a general discrete variable representation for quantum mechanical problems which is a dual space of normal truncated variational basis representations, i.e., it is related by orthogonal (or unitary) transformations. Although the Hamiltonian could, of course, be evaluated in the usual variational representation, transformed to the DVR, and manipulated there, this is not the purpose of establishing the DVR. The DVR is established in order to simplify the *approximate* evaluation and manipulation of the Hamiltonian operator. In particular, the h_0 operator, easily evaluated in the variational basis representation, is transformed (exactly) to the DVR, whereas the remaining potential (coordinate) operators, which are difficult to evaluate in the basis representation, are approximated directly (and simply) in the DVR.

The DVR's corresponding to Gaussian quadrature

TABLE III. Results using bases of size N with parameters optimized to minimize $\mathrm{Tr}(\mathsf{H}^{DVR})$. $\epsilon_i - \epsilon_i^{EXACT}$ are shown.[a]

n \ N	A 12 (Standard variational)	B 7 Optimized DVR	C 9 Optimized DVR	D 11 Optimized DVR	E 12 Optimized DVR	F 13 Optimized DVR	G 12 (Variational, optimized basis)
1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2	0.0003	0.0002	0.0001	0.0000	0.0000	0.0000	0.0000
3	0.0014	−0.0044	0.0007	−0.0001	−0.0001	−0.0001	0.0003
4	0.0033	−0.0128	−0.0007	0.0006	−0.0001	−0.0002	0.0022
5	0.0095	0.0229	−0.0141	0.0020	0.0010	0.0002	0.0072
6	0.0312	0.2186	−0.0149	0.0001	+0.0042	0.0025	0.0129
7	0.0689	0.0998	0.0689	−0.0148	+0.0038	0.0054	0.0183
8	0.1131	···	0.4185	0.0092	−0.0025	0.0043	0.0369

[a] A: $N = 12$, standard basis variational calculations. B–F: basis optimized in the DVR. G: variational calculation using the $N = 12$ basis optimized in the DVR.

points for classical orthogonal polynomial bases have been implicitly defined and used before.[7,8,10–12] Because the potential operators in these Gaussian DVR's are approximated to well known (and high) accuracy by their diagonal DVR matrix elements, such Gaussian DVR's should be widely and freely used. The examples of their accuracy in Sec. III and by others[7,8,10–12,14] are impressive. In Sec. III we also showed that the simplicity of evaluation of the Hamiltonian matrix in the DVR may permit simple improvement of the basis functions, i.e., by the choice of parameters of the basis to minimize the *trace* of the Hamiltonian in the truncated basis in the DVR.

For other orthogonal bases in 1D, the eigenvalues of the VBR of the position operator x form an excellent DVR (and the eigenvectors form the DVR–FBR transformation) for the approximation of potential matrix elements by their diagonal DVR values. This has been discussed and used effectively elsewhere.[15]

Because of the limitations of the above techniques to 1D or direct product bases, however, we felt it useful to define the dual space relation between a truncated set of orthonormal basis, functions $\{\phi\}_N$ and an arbitrary set of points ($\{x\}_N$). This was accomplished by defining the metric of the DVR, Δ. Using this, a dual space $\{|q\rangle\}_N$ to the function space $\{|\phi\rangle\}_N$ could be established on the "primitive" nonorthogonal points $\{|x\rangle\}_N$.

The approximate representation of the potential by its diagonal elements $V(x_\alpha)$ in the general DVR was tested and found to be a reasonably good approximation; much better, certainly, than a finite differences approximation to H on the same points and much better than the approximation via a standard Simpson's rule quadrature on the same points. There appear to be several reasons for this. First, the use of the DVR transformation for the evaluation of h_0 in the DVR preserves an exact representation, i.e., the eigenvalues of h_0 are unchanged in contrast to the approximate evaluation of h_0 using finite differences. In addition, the dual space representation appears to define a quadrature on the given points $\{x\}_N$ which is appropriate for the basis $\{\phi\}_N$ at least insofar as this is possible for arbitrary $\{x\}_N$. It is clear that the accuracy of the diagonal approximation to $V(x)$ in the DVR depends on the points $\{x\}_N$ chosen. Although where possible the Gaussian points should be used for highest accuracy, the choice of other points apparently leads to reasonably good results, and the DVR prescription appears clearly superior to finite difference methods and simple quadratures (such as Simpson's rule) when restricted to N points.

The use of arbitrary points $\{x\}_N$ rather than Gaussian points appears to be deliberately choosing a less than optimal basis for the DVR. One reason for doing this in 1D problems would be that a nonpolynomial basis is used for which standard Gaussian quadratures are not available. In this case the choice of the eigenvalues of the coordinate operator x as the point basis appears to be appropriate and quite accurate.[7,15]

For systems defined in higher dimensional spaces (2, 3 or higher), however, it appears that the general DVR may be most useful. For this article preliminary investigations of three desirable characteristics have been carried out, with promising results reported here. First, and most important, we have shown that reasonable (but not Gaussian quadrature) sets of points yield reasonable results. Since simple Gaussian quadrature techniques do not seem to be available in higher dimensions (except as direct products),[13] one may be required to choose somewhat arbitrary points in higher dimensions. The general DVR procedure provides a prescription for using such points.

Second, the relative ease of Hamiltonian evaluation in the DVR (vs the VBR) may be much larger in higher dimensions. Specifically, since the h_0 portion of the Hamiltonian is usually separable (or may be chosen to be) while the potential often is not, the multidimensional integrals required to evaluate V in the VBR are often difficult to evaluate. In the DVR, on the other hand, the h_0 portions can be obtained simply by direct product transformations (using the separate DVR transformations), and the potential is merely evaluated at the DVR points, by determining the (diagonal) discrete variable representation of V.

This simplicity of evaluation of $\mathsf{H}^{\mathrm{DVR}}$ may be used in higher dimensions, as in 1D, to facilitate the determination of an optimized basis. As shown in the last section (III E), the optimized basis can be used directly in the DVR or in a standard variational calculation.

Finally, in multidimensional problems direct product bases are often truncated such that the basis used is no longer a full direct product basis. If, for example, N_x and N_y basis functions in the coordinates x and y are used, the full $(N_x + N_y)$ direct product basis may be truncated to include only functions with $n_x + n_y \leq M < N_x + N_y$. We have shown, at least in 1D, that the DVR may also be truncated with only comparable loss of accuracy. We note that the truncated DVR is not dual to the truncated basis function representation. It would be interesting to see if a truncated direct product DVR using M Gaussian points is more or less accurate than a general DVR based on M reasonably chosen points which is dual to the M function representation.

The last major use of the DVR, explored elsewhere,[15–17] appears to be the application to coordinate function inversion problems. A major problem has been the determination of coordinate function operators given their matrix elements or eigenvalues. In a recent paper[16] we show that the DVR provides a very simple and flexible approach to the determination of the dipole function of diatomic molecules given a portion of the dipole matrix in the energy eigenfunction representation. Although somewhat less direct, we have also used the DVR to determine the potential function for surface–molecule interactions given the energy eigenvalues.[17] The application of the DVR to these problems for multidimensional systems would also appear to be promising.[15]

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