Discrete Variable Representations and their Utilization

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Discrete variable representations (DVR's) have been widely used in chemical physics, in theoretical spectroscopy, quantum dynamics, and other areas. In this article we review the general types of DVR's, their definitions and properties, and their relation to some other pointwise coordinate representations. In addition we discuss the accuracy and efficiency of DVR's for multi- dimensional problems of quantum dynamics of small systems and indicate the most common modes of utilization.

I. INTRODUCTION AND HISTORY

A. Scope

The title of this article, Discrete Variable Representations or DVR's, suggests an oxymoron: spatial coordinate variables are not discrete, and, if discrete values are used, are not exact representations. A better description would be: a DVR is a representation whose associated basis functions are localized about discrete values of the variables. The name DVR also implies the use of an approximation: coordinate operators are assumed diagonal in this representation and are approximated by their values at the DVR points. DVR's have enjoyed great success as highly accurate representations for the solution of a variety of problems in molecular vibration-rotation spectroscopy and molecular quantum dynamics.

DVR's are highly advantageous for most of these problems for two reasons. First, they greatly simplify the evaluation of the Hamiltonian matrix: kinetic energy matrix elements are calculated simply, and potential matrix elements are merely the value of the potential at the DVR points, (*i.e.* no integral evaluations are required). Second, for direct product DVR's in multi-dimensional systems, the Hamiltonian is sparse and the operation of the Hamiltonian on a vector is always fast. DVR's provide simple and well defined representations which permit efficient and accurate numerical solutions to quantum dynamical problems of interest.

In this article we shall focus on three aspects of DVR's: what they are and how they compare with other "pointwise representations"; how they simplify solutions of multi-dimensional quantum dynamical problems, both in the time dependent and time independent frameworks; and their limitations, both in terms of their applicability to various coordinate systems and operators, and in terms of the accuracy of the solutions of the quantum problem at hand.

The objectives of this article are then

a) to review various definitions of DVR's, the differences between them, and their mathematical and physical foundations;

b) to note the basic advantages of DVR's in the solution of quantum dynamical problems in chemical physics;

c) to indicate the modes of solution for such problems;

d) to note the circumstances in which DVR's are **not** advantageous;

We hope this will remove confusion about DVR's and make their use both better understood and simpler.

We should note at the outset that the bias of this article is toward the solution of the Schrödinger equation , a *linear* second order partial differential equation with specified boundary conditions, primarily for nuclear dynamics, not electronic structure. This is a broad area encompassing theoretical molecular spectroscopy, dynamics, chemical reactions, etc. Although applications have been made to other non-linear systems, this article will not include these areas.

A fundamental problem in chemical physics is to solve the Schrödinger equation :

$$H\Psi = E\Psi \tag{1}$$

or

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi \tag{2}$$

which governs the properties and dynamics of matter at the atomic and molecular level. We will focus on nuclear motion on potential energy surfaces (PES's), and thus not be concerned with spin operators, etc., although non-adiabatic coupling between PES's may be included.

The above Hamiltonian, H, contains a second order differential (kinetic energy) operator in coordinate space, K({q}), and a potential energy operator, V({q}, t) which depends on coordinates and perhaps the time. {q} stands for the set of coordinates describing the system, and the Hamiltonian is

$$H(\{q\}) = K(\{q\}) + V(\{q\}, t). \tag{3}$$

We are interested in solutions both of molecular bound state and of scattering problems. In the bound state problems, the solutions, $\Psi(\{q\})$, of Eq. (1) are localized, and therefore are a discrete set of square integrable (L^2) eigenfunctions with discrete eigenvalues, E = ϵ_i. We usually take these eigenfunctions to be normalized over the coordinate range. Scattering solutions of the time independent Schrödinger equation are not square integrable, but the asymtotic forms of the solutions are known, and appropriate scattering boundary conditions may be applied. There is usually some finite range in which a numerical (versus analytical) solution is required, and this solution is then matched in some fashion to the known asymptotic form. Thus in both bound and scattering problems we may consider the numerical solution of the Schrödinger equation in only a finite coordinate range. For scattering solutions of the time dependent Schrödinger equation the use of absorbing potentials at finite ranges (or other techniques) also limits the range over which numerical solutions are required.

This has an enormously important consequence for the mathematical representation of Eqs 1 and 2. We need represent the solutions numerically only in a finite coordinate range, with boundary conditions either zero for bound states or permitting appropriate asymptotic matching for scattering states. An important consequence of this is that accurate dynamics, up to a specified energy, E, can be represented in a *finite* basis of N functions of the coordinates, $\{\theta_n(\{q\})\}_N$, (where, of course, N may be very large depending on the accuracy desired).

After a brief presentation of the historical context the article is divided into the following sections:

1) DVR's in 1-dimension: various types and comparisons;

2) Properties of multi-dimensional DVR's and methods used to solve the Schrödinger equation equation in DVR's;

3) Caveats: problems and resolutions; numerical quadratures, etc;

4) Conclusions

B. Historical Context

Unfortunately this description of the historical context of DVR's must be limited by the authors' knowledge and understanding. Since we are neither applied mathematicians nor historians there may be large gaps in our presentation, particularly with respect to the numerical analysis literature. We have, however, tried to be accurate as to the historical roots of these approaches in chemical physics.

The numerical solution of differential equations has been studied for centuries, presumably since the time of Newton. However, the restriction to linear equations such as the Schrödinger equation permits a variety of powerful approaches based on linear algebra, and the spectral properties of the Hamiltonians permit variational solutions. Thus for the Schrödinger equation a solution may be represented by an exact analytic functional form, $\Psi_l(\{q\})$; by values on a grid in coordinate (or momentum) space, $(\Psi_l)_i = \Psi_l(q_i)$; or by a representation in a complete basis,

$$\Psi_l(\{q\}) = \sum_j c_{jl}\phi_j(\{q\}) \tag{4}$$

Basis set representations started, of course, with Fourier series. More general Hilbert spaces and representations in terms of orthogonal basis expansions (due to Lord Rayleigh) were not developed until about 1900 (See Lanczos, [1]).

Discrete variable representations are representations in bases of continuous functions which are in some sense localized "on a grid" in coordinate space. In particular, to construct a DVR, a finite basis of "global" orthnormal functions is transformed to another orthnormal basis set (the DVR) in which each basis function is "localized" about one point of a coordinate space grid. The relationship is most clear for basis sets of orthogonal polynomials (with weight functions) and their associated grids of Gaussian quadrature points. This relationship may have been known earlier, but was pointed out for Chebyshev polynomials in the last section of Lanczos' book on Applied Analysis [1] published in 1956. Somewhat later (1966), L. Fox [2,3]. also noted that sets of orthogonal (Chebyshev) polynomials evaluated at the appropriate set of Gaussian quadrature points, formed an orthogonal transformation between the original polynomial representation and a more localized representation.

In chemical physics, Harris, Engerholm, and Gwinn [4] in 1965 generated the appropriate transformation via diagonalization of the coordinate operator. Their purpose was to evaluate approximately the matrix elements of coordinate (potential) functions in the basis by transformation of the diagonal matrix of the potential evaluated at the coordinate eigenvalues. In their specific case the basis functions were harmonic oscillator functions. In 1968 Dickinson and Certain [5] noted that the eigenvalues of the coordinate operator so obtained were, in fact, the Gaussian quadrature points for the (Hermite) polynomial used. This lent support to the accuracy of the matrix elements evaluated in this fashion.

In 1982 Lill, Parker, and Light [6,7] and and then Heather *et al.* [8] first explicitly used the transformed representation in which the coordinate operator is diagonal, the discrete variable representation, as a basis representation for quantum problems rather than only a means

for evaluation of matrix elements. The approach was introduced independently by Blackmore and Shizgal [9,10] in 1984 under the name "discrete ordinate method". In one dimensional problems, the use of a DVR may offer only a slight advantage. In higher dimensional problems with direct product basis sets, however, it becomes highly advantageous. This was noted when using a DVR in conjunction with a distributed Gaussian basis (DGB) by Bacic *et al.* [11–14] and for multi- dimensional DVR's by Whitnell *et al.* [15] and Light, Whitnell, Choi, and Park [16].

About 1990, discrete variable representations became increasingly widely used, and a number of variations and different prescriptions for their definition were presented by Manolopoulos and Wyatt [17], Echave and Clary [18], Wei and Carrington [19], Muckerman [20], and Colbert and Miller [21]. More recently Szalay [22] has proposed a generalized multi-dimensional DVR. Several earlier review articles on the definitions and uses of DVR's are in References [14,16,23,24].

II. "POINTWISE" REPRESENTATIONS IN ONE DIMENSION

A. Introduction to Types of DVR's

In the general variational approach to quantum problems, the unknown solution is represented exactly in a (usually infinite) basis, or, more properly, a Hilbert space. In practice, of course, the infinite basis is truncated, and the approximate solutions in this truncated representation are variational, *i.e.* the energy eigenvalues of the Hamiltonian in this truncated basis are all larger than or equal to the corresponding exact eigenvalues. We call the representation in which all Hamiltonian matrix elements are evaluated exactly the "variational basis representation" or VBR. In the VBR errors are due *only* to the truncation of the basis.

In general terms, DVR's are representations in terms of localized functions which are usually obtained by transformation from a truncated "global" basis. DVR's are generally used with the *approximation* that in the DVR the matrix representation of functions of the coordinate are diagonal and the diagonal matrix elements are values of the function at the DVR points. The term DVR in this paper implies that this approximation is made. It should be noted, however, that although the DVR functions are "focused" on the grid points, they are *not* perfectly localized. Each function extends throughout the range of the original basis. For example the infinite set of sinc functions $f_n(x) = \sin[\pi(x - x_n)/\Delta x]/\pi(x - x_n)$ with n = 0, ±1, ±2, ... and x_n = n Δx. is an infinite DVR basis with DVR points at x_n [21]. Each function, f_n is unity at x = x_n and zero at all other DVR points, but it is not zero for values of x between the DVR points. The sinc functions are symmetric about their DVR points but are infinite in extent, having an oscillatory shape typical of the "localized" DVR functions. The "focal points" (DVR points) of the DVR basis functions form a grid of points, and the Hamiltonian is then approximated as a matrix labeled by the grid points because DVR functions can be labeled by the grid point about which they are localized.

There are several ways to construct DVR's: one may establish a connection between a set of basis functions and an appropriate numerical quadrature; one may diagonalize a function of the coordinate operator in a basis set; or one may choose a basis of localized functions initially. In the approach based on numerical quadrature, the relationship between basis size and quadrature accuracy is direct. In the first two approaches, the transformation between DVR and global basis representation is known. In cases where this is a unitary or orthogonal transformation, operators in the global basis obtained by transformation from the DVR contain exactly the same approximations as the DVR. To distinguish this approximation from the VBR, we call it a "Finite Basis Representation" or FBR. Thus the VBR is an exact representation in terms of global basis functions, while the DVR and FBR are "local" and corresponding "global" representations in which an approximation has been made. We first will examine the different one dimensional DVR's and their relations to the FBR and VBR from the viewpoint of Gaussian quadrature, and then examine DVR's from the "product" point of view which is useful for complex kinetic energy operators.

B. Orthogonal Polynomial Bases and Gaussian Quadrature DVR's

The "standard" DVR's are defined in terms of classical orthogonal polynomials, weight functions, and their related Gaussian quadratures [6,25]. The approximations in these DVR's (and the corresponding FBR's) are related directly to the approximations of the Gaussian quadratures associated with the polynomials used. Classical orthogonal polynomials form many common one dimensional basis sets such as particle-in-a-box functions (Chebyshev polynomials), harmonic oscillator functions (Hermite polynomials), Legendre polynomials, Laguerre polynomials, etc. An excellent description of these polynomials is given in Dennery and Krzywicki [26] and concise definitions are given in Abramowitz and Stegun [27]. The basic property of classical orthogonal polynomials is that they are (normed) polynomials orthogonal with respect to integration over their range with a specific weight function, $\omega(x)$, *i.e.*

$$\int_{x=a}^{x=b} \omega(x) C_l(x) C_n(x) dx = \delta_{ln} \tag{5}$$

where $C_l(x)$ is a polynomial in x of l^{th} degree.

There are three general types of classical orthogonal polynomials based on the range of their argument, infinite, semi-infinite, or finite. These are summarized in the table below. Note that the arguments can be scaled and shifted so the mathematical ranges below correspond to the appropriate physical coordinates and ranges as desired.

Table 1. Ranges and Weight Functions for Classical Polynomials.

Range	Weight function	Name of Polynomial
(-∞, ∞)	exp(-x^2)	Hermite, $H_n(x)$ (harmonic oscillator functions)
[0 , ∞)	x^ν exp(-x) $\nu > -1$	Laguerre, $L_n^\nu(x)$
[-1, 1]	$(1-x)^\alpha(1+x)^\beta$ $\alpha, \beta > -1$	Jacobi, $P_n^{\alpha,\beta}$ (Legendre and Chebyshev polynomials)

One simple way to introduce the DVR is to use the well known properties of Gaussian quadratures [28] to generate the transformation between the FBR and the DVR. We show that the same transformation is obtained, following Harris, Engerholm and Gwinn [4], by diagonalizing the argument of the orthogonal polynomials. The argument might be the coordinate operator itself or a function of the coordinate operator. We emphasize that in this fashion DVR's can be easily constructed for most standard basis functions without explicit consideration of the properties (or points and weights) of Gaussian quadratures. The primary purpose of the section below is to show the relations which exist between the DVR and Gaussian quadrature and thus demonstrate the basis for the high accuracy of DVR's.

The basic property of Gaussian quadratures for these polynomials is that for each type of polynomial a quadrature defined on N specified points $\{x_\alpha\}_N$ with particular weights $\{\omega_\alpha\}_N$ is exact for integrals of the weight function $\omega(x)$ times polynomials up to order 2N - 1. Thus if our basis functions are normalized orthogonal polynomials times the square root of the weight functions, $\omega(x)$

$$\phi_n(x) = \sqrt{\omega(x)} C_n(x) \tag{6}$$

then the orthonormality relations are given exactly by the quadrature

$$\begin{aligned}\delta_{ln} &= \int_{x=a}^{x=b} \phi_l^*(x)\phi_n(x)dx \\ &= \sum_{\alpha=1}^{N} \frac{\omega_\alpha}{\omega(x_\alpha)} \phi_l^*(x_\alpha)\phi_n(x_\alpha)\end{aligned} \tag{7}$$

and the matrix elements of the coordinate x are also given exactly by

$$\begin{aligned}\mathbf{X}_{ln} &= \int_{x=a}^{x=b} \phi_l^*(x) x \phi_n(x)dx \\ &= \sum_{\alpha=1}^{N} \frac{\omega_\alpha}{\omega(x_\alpha)} \phi_l^*(x_\alpha) x_\alpha \phi_n(x_\alpha)\end{aligned} \tag{8}$$

Both relations are exact for $0 \le l$,n $\le$ N-1 since the N basis functions contain only powers of x from x^0 to x^{N-1}.) The polynomial basis functions, $\phi_n(x)$, are frequently chosen so that they are eigenfunctions of an operator H_0, where $H = H_0 + V$, with $H_0 = K + V_0$. K is the kinetic energy operator and V_0 is the part of the potential (if any) included in the definition of the basis functions.

We may now write the above equations in matrix form if we identify the elements of the transformation matrix, $\mathbf{T}$, as

$$\mathbf{T}_{\alpha j} = \sqrt{\frac{\omega_\alpha}{\omega(x_\alpha)}}\, \phi_j(x_\alpha). \tag{9}$$

Note that $\mathbf{T}$ is a *square* matrix; there are the same number of points as basis functions. Then Eqs (7) and (8) are equivalent to the matrix relations

$$\mathbf{I} = \mathbf{T}^\dagger\, \mathbf{I}^{DVR}\, \mathbf{T} \tag{10}$$

$$\mathbf{X} = \mathbf{T}^\dagger\, \mathbf{X}^{DVR}\, \mathbf{T} \tag{11}$$

where $\mathbf{T}^\dagger$ is the Hermitian transpose of $\mathbf{T}$, $\mathbf{I}^{DVR}$ is a unit matrix labeled by the quadrature points and $\mathbf{X}^{DVR}$ is the *diagonal* matrix of values of x at the quadrature points $\{x_\alpha\}$, *i. e.* the DVR points.

Since Eq (10) demonstrates that $\mathbf{T}$ is orthogonal (or unitary), we can multiply Eq. (11) by $\mathbf{T}$ on the left and by $\mathbf{T}^\dagger$ on the right and find that $\mathbf{T}^\dagger$ is the matrix which diagonalizes the exact coordinate matrix, $\mathbf{X}$:

$$\mathbf{T}\mathbf{X}\mathbf{T}^\dagger = \mathbf{X}^{DVR}(diagonal) \tag{12}$$

Thus we see that the diagonalization of $\mathbf{X}$ generates the Gaussian quadrature points as the eigenvalues, and the transformation matrix related to the Gaussian weights and points given by Eq (9). Thus the Gaussian quadrature points are the DVR "points" and $\mathbf{T}$ is the DVR-FBR transformation. Obviously it can be generated either from the polynomials themselves via Eq. (9) or by diagonalization of $\mathbf{X}$. The tridiagonal coordinate matrix $\mathbf{X}$ is easily generated from the three term recursion relations satisfied by all classical orthogonal polynomials [27,26]. DVR's are most commonly and most easily determined by diagonalization of the exact coordinate matrix, and no explicit reference to quadrature points and weights is then required.

If we label the DVR eigenvalues by Greek letters, then the basis function localized at x_α is

$$\theta_\alpha(x) = \sum_j \mathbf{T}^*_{\alpha j} \phi_j(x) \tag{13}$$

An important property of these functions is that each function is non-zero at the DVR point about which it is "localized", but is zero at the remaining N - 1 points. This is easily seen by evaluating Eq. (13) at a DVR point:

$$\begin{aligned}\theta_\alpha^{DVR}(x_\beta) &= \sum_j \mathbf{T}^*_{\alpha j}\phi_j(x_\beta) \\ &= \sum_j \sqrt{\frac{\omega_\alpha}{\omega(x_\alpha)}}\phi_j^*(x_\alpha)\phi_j(x_\beta) \\ &= \sqrt{\frac{\omega(x_\beta)}{\omega_\beta}}(\mathbf{T}\mathbf{T}^\dagger)_{\alpha\beta} \\ &= \sqrt{\frac{\omega(x_\beta)}{\omega_\beta}}\delta_{\alpha\beta} \end{aligned} \tag{14}$$

Note that this also yields the normalization of the DVR functions over the quadrature:

$$\begin{aligned}\int_a^b \theta_\alpha^2(x)dx &= \sum_\beta \theta_\alpha^2(x_\beta)\frac{\omega_\beta}{\omega(x_\beta)} \\ &= \sum_\beta \delta_{\alpha\beta} \\ &= 1 \end{aligned} \tag{15}$$

The equations $\mathbf{T}\ \mathbf{T}^\dagger = \mathbf{I}$ and $\mathbf{T}^\dagger\ \mathbf{T} = \mathbf{I}$ are the discrete orthonormality relations of DVR's.

In practice the simplest procedure to define a Gaussian quadrature DVR is to generate the exact tridiagonal coordinate matrix implicit in the three term recursion relation satisfied by the appropriate orthogonal polynomials and then to diagonalize this matrix. The only care required is that the normalization of the polynomials must generate an orthonormal basis from Eq. (6). After determining the Gaussian quadrature points, they must be scaled to the appropriate physical range via a linear transformation.

Viewed from the Gaussian quadrature viewpoint it is clear that a Gaussian DVR is as accurate as an FBR with potential matrix elements evaluated by a Gaussian quadrature with an equal number of DVR quadrature points and basis functions. An alternate view is to view the DVR as a "product approximation" described below.

C. Product Approximation and Potential Optimized DVR's (PODVR)

We have discussed three representations: the VBR, the FBR, and the DVR. In a VBR all matrix elements are computed exactly; errors with a VBR occur only because the VBR basis is finite. The FBR and the DVR are unitarily equivalent and an FBR may be thought of in two ways. If the underlying basis for the DVR is a classical orthogonal polynomial basis, then a "quadrature" FBR is the representation obtained by evaluating the residual potential matrix elements by Gaussian quadrature and taking exact, analytic kinetic energy (or H_o) matrix elements. (If it is not possible to write down analytic kinetic energy matrix elements an FBR is constructed as explained below in the section on complicated kinetic energy operators). However, a "product" FBR can be generated from any representation in which the kinetic energy matrix (or $\mathbf{H}_o$) and the transformation to the representation in which the coordinate matrix is diagonal are known. The FBR for such a *product approximation* is obtained for a Hamiltonian by using the exact, analytic kinetic energy matrix and replacing the matrix representations of products of the coordinate in the potential with products of the matrix representation of the coordinate.

Thus the matrix representation of a function of x is approximated as the function of the matrix representation of x (assuming the function has a Taylor series expansion in x):

$$[\mathbf{V}(x)]_{ij} \approx [\mathbf{V}(\mathbf{X})]_{ij} \tag{16}$$

However, in order for a product of operators to be evaluated exactly as a product of matrices, a complete basis must inserted between the operators:

$$[\mathbf{AB}]_{ij} = \sum_n^\infty \mathbf{A}_{in}\mathbf{B}_{nj} \tag{17}$$

Thus the above expression containing products of the operator, x, is only an approximate evaluation of the potential matrix in a finite representation. However, as the dimension, N, of the basis increases, matrix elements for a given {i,j} become more exact.

Errors (if any) in results computed with a quadrature FBR (or its corresponding DVR) occur because the VBR (from which the FBR is obtained) is finite and because some potential matrix elements are not computed perfectly by quadrature. Errors (if any) in results computed with a product FBR occur because the VBR is finite and because the product approximation is not perfect. If the matrix representations of the factors of the products are banded matrices the error introduced by the product approximation is restricted to the bottom right hand corner of the matrix. [19]).

If the VBR basis functions are orthogonal polynomials as discussed above and one chooses as many quadrature points as basis functions, the quadrature FBR and the product FBR are identical (the matrix element errors are also identical). Since a DVR matrix is unitarily equivalent to its FBR counterpart, errors (if any) in results computed with a DVR are the same as the errors which would be obtained with the corresponding FBR. They may equally well be thought of as being due to the finiteness of the VBR basis and either (i) the quadrature error or (ii) the product approximation error.

Obviously one wants to make the errors as small as possible. If one uses a Gaussian quadrature FBR, errors are minimized by choosing good VBR basis functions (basis functions which represent wavefunctions compactly) and

using many functions such that the quadrature error for the residual potential is minimal.

If one uses a basis not associated with a Gaussian quadrature, then product FBR errors would be minimized by choosing VBR basis functions which both represent wavefunctions accurately and compactly (i.e. decrease the size of off-diagonal matrix elements) *and* improve the accuracy of the product approximation. However, it is often (but not always) the case that basis functions that render the Hamiltonian matrix more diagonal (good VBR basis functions) will decrease the accuracy of the product approximation since the coordinate matrix, from which the product approximation FBR is built, will be far from diagonal. If one is willing to accept this degradation of the accuracy of the product approximation one can optimise the VBR. This leads to the potential optimised DVR (PODVR).

In 1992 Echave and Clary [18] and Wei and Carrington [19] introduced a means of generating a DVR which concentrates the DVR points in the region of space where they do the most good and which minimizes the residual potential. The approach is useful only in multidimensional problems where it may greatly reduce the size of the basis required for each coordinate, but is easily described for one coordinate.

If one wants a *small* DVR for an arbitrary one dimensional bound potential, then an advantageous DVR (with a good distribution of points in x and a smaller residual potential) may be obtained by using a DVR determined from eigenfunctions of a model potential in x. The procedure is simply that of Harris *et al.* [4] outlined above, except that eigenfunctions of a model Hamiltonian are used as the basis.

A PODVR with N points is obtained by first defining a good model potential for the coordinate in question, and then solving accurately for N eigenfunctions. (This may require a basis size considerably larger than N whether using a DVR or not.) The coordinate matrix is then diagonalized in the N eigenfunctions to yield the DVR-FBR transformation and the DVR points. In constructing the Hamiltonian in the PODVR (e.g. for multi-dimensional problems), the N eigenvectors are transformed to the DVR and the *residual* potential is evaluated in the DVR. This *product approximation* is found to be very useful in multi-dimensional problems, permitting a much smaller DVR in the dimension for which the PODVR is constructed.

In a multidimensional problem one defines a PODVR basis for each coordinate in a similar fashion using an appropriate model potential. Then products of the the PODVR functions for each coordinate are used as direct product basis functions for the full problem. Although DVR points for a single degree of freedom will be strewn between the limiting values of the coordinate, PODVR points are concentrated in regions where the amplitude of the wavefunction is significant.

PODVRs are most advantageous when coupling between degrees of freedom is weak. If there were no coupling products of solutions of one-dimensional Hamiltonians would be solutions of the Schrödinger equation equation for the multidimensional Hamiltonian. If the coupling is weak such products (and the associated PODVR functions) are very good basis functions. If, however, the coupling is strong PODVR functions will be less useful.

PODVR's share some of the properties of Gaussian DVRs. The transformation matrix $\mathbf{T}$ is composed of the eigenvectors of the coordinate function diagonalized and is orthogonal but because PODVR's are not derived from a Gauss quadrature scheme it is not possible to write the PODVR transformation matrix as Eq. (13). PODVR functions will, therefore, not exactly satisfy Eq. (14) but this does not necessarily limit the quality of the results obtained with a PODVR: the accuracy of PODVR results is determined by the accuracy of the associated product approximation and the minimization of the residual potential.

D. Hamiltonian evaluation

We now look briefly at the consequences of approximating the Hamiltonian in the DVR. The choice of the underlying basis for the DVR is based on the Hamiltonian, the boundary conditions on the wave functions, and the domains of the coordinates. It would be ideal to have the spacing of the quadrature points proportional to the nodal spacing of the highest eigenfunctions of interest, and to have the basis satisfy the appropriate boundary conditions. Chebyshev polynomials (particle in the box functions) yield DVR's with equally spaced points in x $= \cos^{-1}\theta$; Legendre and associated Legendre polynomials (with x = cos(θ))are appropriate for angular functions on $\theta = (0, \pi)$ satisfying boundary conditions of unity and zero respectively, etc. Using the Jacobi polynomials with differing α and β shifts the DVR points away from x = 1 and -1.

Given an exact evaluation of the Hamiltonian matrix in the VBR the Hamiltonian could be evaluated exactly in the DVR by transformation from the exact VBR Hamiltonian:

$$\tilde{\mathbf{H}}^{DVR} = \mathbf{T}\mathbf{H}^{VBR}\mathbf{T}^{\dagger} \tag{18}$$

where

$$\mathbf{H}^{VBR} = \mathbf{H_0}^{VBR} + \mathbf{V}^{VBR}. \tag{19}$$

Here $\mathbf{V}^{VBR}$ is the exact representation of the *residual* potential, the portion of the potential not included in $\mathbf{H_0}$. $\mathbf{H_0}^{VBR}$ is transformed from the VBR where it is usually simple to determine. Szalay [29] has given analytic formulae for the differential operators, d/dq and the second order differentials, $\frac{d^2}{dq^2}$ for all orthogonal polynomial DVR's of Gaussian quadrature accuracy. It is therefore often easy to evaluate $\mathbf{T}\mathbf{H_0}^{VBR}\mathbf{T}^{\dagger}$ (see sectionIII C for alternative methods). However, to obtain $\tilde{\mathbf{H}}^{DVR}$ the

residual potential matrix, $\mathbf{V}^{VBR}$, would have to be evaluated exactly in the VBR beforehand, and this eliminates any advantage of the DVR. The potential matrix evaluated exactly as above in the DVR is diagonally dominant, but is not exactly diagonal.

The power and simplicity of the DVR comes from approximating the residual potential matrix in the DVR. The matrix representation of $\mathbf{V}$, the residual potential energy, is, however, *approximated* by the quadrature of the DVR itself. Thus

$$H^{DVR} = H_0^{DVR} + V^{DVR} \tag{20}$$

where

$$\mathbf{H}_0^{DVR} = \mathbf{T}\mathbf{H}_0^{VBR}\mathbf{T}^\dagger. \tag{21}$$

and we approximate the residual potential as

$$\mathbf{V}_{\alpha,\beta}^{DVR} = V(x_\alpha)\delta_{\alpha\beta} \tag{22}$$

Thus the DVR approximation is equivalent to approximating the exact residual potential matrix, $\mathbf{V}$ as:

$$\mathbf{V} \approx \mathbf{T}^\dagger\mathbf{V}^{DVR}\mathbf{T} \equiv \mathbf{V}^{\mathbf{FBR}} \tag{23}$$

The DVR with an underlying orthogonal polynomial basis is exactly equivalent to evaluating potential matrix elements using the Gaussian quadrature appropriate to the basis, with N quadrature points. The disadvantage of this is that the eigenvalues resulting from evaluating the Hamiltonian in the DVR are *not* variational; the quadrature error may cause some eigenvalues to be below their true value. (For a recent discussion, see Wei [30]). However, the advantage of DVR's based on the classical orthogonal polynomials is that the convergence of the Gaussian quadratures to the exact integrals is excellent. For smooth potentials as the basis size is increased (and the number of DVR points is increased), the quadrature error quickly disappears at least for lower levels. The convergence of these eigenvalues is then limited by the basis set in a variational fashion.

E. Other DVR's

Alternate grid representations have been proposed as DVR's by Muckerman [20], Manolopoulos and Wyatt [17], Colbert and Miller [21] and others. These all share the characteristic that in representing the Hamiltonian, coordinate functions are represented by their values at grid points. However, all differ from Gaussian DVR's in that not all of the equations of orthonormality, exact quadrature for the coordinate and the definition of the DVR-FBR transformation in terms of the basis functions and quadrature points hold exactly (Eqs. (7), (8), and (9)). All three approaches define the DVR functions directly as Lagrange interpolating polynomials or by analytic transformation and summation. Of these DVR's we will discuss only the Lobatto quadrature DVR and the "sinc" DVR of Colbert and Miller as these have seen the most frequent application.

1. Lobatto DVR

The Lobatto quadrature/function DVR was introduced by Manolopoulos and Wyatt [17] for scattering problems in which simple evaluation of non-zero boundary conditions was desired. The Lobatto shape functions are Lagrange interpolating polynomials over the Lobatto quadrature points. These *are* the DVR functions. Lobatto quadratures are well known [27]. Lobatto shape functions satisfy the pointwise orthogonality relations on the quadrature points as in Eq. (14) and are orthogonal over the quadrature, but their squares are not themselves integrated exactly by the quadrature. The kinetic energy operator can be determined exactly in this DVR.

Manolopoulos *et al.* demonstrated that their DVR provided a simple L^2 basis for scattering when L^2 methods requiring log derivative evaluation at the boundary are used. Since most basis sets fix the log derivative at the end points, they do not have sufficient flexibility to be used. Although Jacobi polynomials could be used, the Lobatto functions have the advantage that the log derivative is simple to evaluate in this basis as only one function is non-zero (unity) at the boundary.

2. Sinc DVR

In 1992 Colbert and Miller [21] introduced a "novel universal" DVR in which they evaluated the kinetic energy operators by infinite order finite differences on infinite uniform grids. The kinetic energy representation on the grid was derived using particle-in-a-box functions, which are, of course, Chebyshev polynomials, and the number of functions was permitted to go to infinity as the range became infinite, with $\Delta x = L / N$ finite. (In the finite and semi-infinite range cases, discussed [21] the functions are not as appropriate or accurate as, for example, Legendre polynomials, and these cases have rarely, if ever, been used.) We therefore discuss only the $(-\infty, \infty)$ range case in which case the basis becomes the infinite set of sinc functions.

In the infinite range case the kinetic energy operator becomes, of course, translationally invariant, depending only on the distance between the grid points in question. This DVR corresponds to an infinite basis of sinc functions,

$$s_n(x) = \frac{sin(\pi(x - x_n)/\Delta x)}{\pi(x - x_n)} \tag{24}$$

where $x_n = n\Delta x$, and $n = 0, \pm1, \pm2, ...$

On the surface, these DVR functions and the associated quadrature would seem ideal since the kinetic energy matrix elements are given analytically, on the DVR points; the basis can be orthonormal, both analytically and on the uniform quadrature; the discrete orthonormality holds (Eq. 14); and the coordinate operator, x, is given exactly in this localized basis by $\mathbf{X}^{DVR}{}_{ij} = x_i$

δ_{ij}. The problem, however, is that in application one cannot use an infinite basis. For a finite set of points, the kinetic energy is *not* given exactly by the truncated representation *and* as with all DVR's, the potential energy is also not given exactly. The sinc DVR is usually truncated by limiting it to regions in which the potential energy is less than some maximum value. It has, however, the advantage of great simplicity (equally spaced points and analytic kinetic energy matrices) and has been quite widely used.

F. Generalized DVR's?

As noted above and discussed in Section III, DVR's are useful primarily for multi-dimensional problems. If direct product bases are used for the multi-dimensional system, the basis for each dimension may be separately transformed to the DVR. In this representation, the multi-dimensional potential energy is diagonal, and the kinetic energy terms may be evaluated simply from the one-dimensional representations of each momentum or second derivative operator. In the case of orthogonal coordinates, this leads to very sparse Hamiltonian matrices in the multi-dimensional DVR.

However, there exist coordinate systems, spherical polar coordinates being the most familiar, where eigenfunctions of the kinetic energy operators do not form direct product bases, *e.g.* the spherical harmonics. For multi-dimensional coupled bases such as the two dimensional spherical harmonics, an accurate quadrature and DVR-FBR transformation cannot be generated by diagonalization of a coordinate. Thus no simple 1:1 mapping of an arbitrary number of basis functions to DVR type functions by unitary or orthogonal transformations exists.

A few attempts to overcome this difficulty have been made without great success. In particular the collocation method generates a non-orthogonal transformations between the basis and a set of points, but leads to a generalized eigenvalue problem with attendant problems of some complex eigenvalues. Light *et al.* [25] generated an orthogonal transformation using the metrics of the collocation matrix. Although this is briefly described below, the accuracy is greatly dependent on the choice of points and this avenue has not been used for real problems.

If the N basis functions $\{\phi_n\}$ are evaluated at N "independent" points, $\{q_\alpha\}$ a square collocation matrix may be formed:

$$\mathbf{R}_{n\alpha} = \phi_n(q_\alpha) \tag{25}$$

If one takes the collocation matrix to define the DVR-FBR transformation, then the metrics of the two representations are related by:

$$\mathbf{S} = \mathbf{R}(\Delta)^{-1}\mathbf{R}^t \tag{26}$$

where $\mathbf{S}$ and Δ are the metrics in the FBR and DVR respectively.

Thus if the functions are orthonormal and we want to maintain the orthonormality over the quadrature implied in the DVR, then $\mathbf{S}$ is the unit matrix, and Δ must be chosen accordingly:

$$\mathbf{\Delta} = \mathbf{R}^t\mathbf{R} \tag{27}$$

If Δ is a diagonal and positive definite, then a good quadrature is defined using the diagonal values of δ^{-1}. For general points and basis sets this will not be true. If Δ^{-1} exists, however, an orthogonal transformation can still be defined by

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

However, in multi-dimensional systems not only is Δ not diagonal, but it often has very small eigenvalues indicating that on the set of points chosen, the set of functions is not independent (or vice versa). In this case the attempt to represent the Hamiltonian accurately in the DVR fails disastrously.

Recently Szalay [22] has investigated this problem further and has shown that with careful choice of points a mixed representation of the Hamiltonian can be used which yields some eigenvalues with quite acceptable accuracy. The final GDVR method proposed is in essence a collocation method and impressive accuracy was obtained for 1-D problems. (The accuracy was much higher than for the GDVR described above.) The costs, however, are similar to those encountered in collocation methods which include dealing with the generalized eigenvalue problem. In the two dimensional example given, complex eigenvalues were encountered before all bound state eigenvalues were determined.

It has become apparent from a number of studies [31–35] that such non-direct product multi-dimensional bases are best treated by direct product quadratures, with enough points in each dimension to assure accurate evaluation of the matrix elements. (The basis representation is used.) The use of direct product quadratures (i.e. the points and weights in each dimension are independent of the other dimensions) greatly simplifies the transformations between the basis and grid representations. In addition, one can choose the quadratures sufficiently large that all matrix elements are evaluated accurately. These can, of course, be combined with DVR's in other coordinates in a direct product fashion. This is discussed more fully in the section on applications below.

III. MULTI-DIMENSIONAL DVR'S AND APPLICATIONS

A. Introduction

In the previous section we defined and discussed various DVR's. In this section we consider how the favorable properties of DVR's facilitate solving the Schrödinger

equation . Many problems of interest in chemical dynamics and spectroscopy involve large amplitude motions of polyatomic systems. For such problems numerical representations are required and standard harmonic normal mode approximations are not adequate. If one is to solve the Schrödinger equation accurately for such systems, it is important to have

a) accurate potential energy surface(s);

b) an appropriate coordinate system for the Hamiltonian operator;

c) an adequate and efficient basis in which to represent the Hamiltonian; and

d) appropriate means of extracting the desired information.

To extract the desired information the first thing one must do is to write down equations for the matrix elements of the Hamiltonian. This is addressed in subsections B and C. In subsection D we present procedures for exploiting symmetry. In subsections E and F, we discuss ideas for coping with the huge number of basis functions required to obtain converged solutions for polyatomic large amplitude motion problems. Even for total angular momentum zero there are $3n$ - 6 degrees of freedom for an n atom system and it is therefore imperative that one either devise schemes to minimise the number of basis functions or employ iterative methods that depend only on matrix-vector products. Explicit sequential diagonalization truncation schemes for obtaining a compact, high-quality basis from a multidimensional direct product DVR are treated in subsection E. The use of iterative methods with DVRs and basis sets obtained from DVRs is considered in subsection F.

B. Orthogonal coordinates

Orthogonal coordinates are coordinates in terms of which the kinetic energy operator has no mixed second derivatives (no cross terms). Because the kinetic energy operator is simpler in orthogonal coordinates they are often preferable (however, it is possible that basis functions which are functions of coordinates which simplify the kinetic energy will be poorer basis functions and that the trade-off to simplify the kinetic energy operator is an increase in the size of the Hamiltonian matrix).

DVR's are useful primarily for multi-dimensional problems. If a direct product basis is used for the multi-dimensional system, the basis for each dimension may be separately transformed to the DVR. In this DVR the multi-dimensional potential energy is diagonal. In the case of orthogonal coordinates, the kinetic energy terms may be evaluated simply from the one-dimensional representations of each momentum or second derivative operator. this leads to very sparse Hamiltonian matrices in the multi-dimensional DVR.

The great simplification of Hamiltonians using direct product DVR's are most easily demonstrated for a three dimensional Cartesian system. In a three dimensional Cartesian DVR where the DVR points for x, y, and z are labeled by α, β and γ respectively, the Hamiltonian matrix elements would be:

$$\mathbf{H}_{\alpha,\alpha',\beta,\beta',\gamma,\gamma'} = \mathbf{K}_{\mathbf{x}\alpha,\alpha'}\delta_{\beta,\beta'}\delta_{\gamma,\gamma'} + \mathbf{K}_{\mathbf{y}\,\beta,\beta'}\delta_{\alpha,\alpha'}\delta_{\gamma,\gamma'} + \mathbf{K}_{\mathbf{z}\gamma,\gamma'}\delta_{\alpha,\alpha'}\delta_{\beta,} + V(x_\alpha, y_\beta, z_\gamma)\delta_{\alpha,\alpha'}\delta_{\beta,\beta'}\delta_{\gamma,\gamma'}$$

where $\mathbf{K}_i$ is the kinetic operator for the i coordinate.

For triatomic molecules orthogonal coordinate systems such as Jacobi coordinates, Radau coordinates, and hyperspherical coordinates all permit one to avoid mixed second derivatives. If kinetic energy singularities are unimportant (unimportant singularities are singularities for which all wavefunctions are extremely small where the kinetic energy operator is infinite), they can always be dealt with by simply not putting quadrature points close to the singularity. It is straightforward to construct a direct product DVR for the triatomic Jacobi, and Radau Hamiltonians.

For coordinates with more complex kinetic energy operators, direct product DVR's are still highly advantageous for iterative methods in some cases. For four-atom molecules it is not possible to choose coordinates to eliminate all terms with mixed second derivatives from the kinetic energy operator and one is forced (if the calculation is to be exact) to deal with complicated kinetic energy operators.

C. Complicated kinetic energy operators

A quadrature FBR is defined above as the representation obtained by evaluating potential matrix elements by Gauss quadrature and taking exact, analytic kinetic energy matrix elements. One transforms from the FBR to the DVR using a transformation matrix which may be obtained by diagonalizing a matrix representation of a coordinate function. If exact (FBR) kinetic energy matrix elements are known it is easy to determine the DVR of a kinetic energy operator. However, obtaining an hermitian FBR (or DVR) of a complicated kinetic energy operator, whose terms involve both (noncommuting) derivatives and functions of coordinates is somewhat tricky because analytic kinetic energy matrix elements are generally not available. We denote a kinetic energy operator as "complicated" if either i) it is factorizable and matrix elements of a factor which involves derivatives must be calculated numerically, or ii) it is not factorizable and matrix elements of a term must be evaluated numerically, or iii) matrix representations of derivatives are not antihermitian.

One way to obtain an hermitian FBR for a complicated kinetic energy operator is to use Gauss quadrature to compute kinetic energy matrix elements. A DVR matrix can then be obtained by transforming the FBR matrix whose elements are computed by quadrature. As originally defined, for simple kinetic energy operators, one can

compute matrix elements of the DVR Hamiltonian matrix without calculating integrals by quadrature. DVR matrices for coordinate functions are obtained directly from values of the functions at the DVR points and not by first computing an FBR matrix which is then transformed to the DVR. Not having to compute integrals makes the DVR simple and convenient. It would be advantageous not to have to evaluate quadratures even for complicated kinetic energy operators. Quadrature may be avoided only by using some sort of product approximation. We refer to replacing the matrix representation of a product of operators with a product of representations as a product approximation (see II.C). Unfortunately, a simple product approximation Hamiltonian matrix may be nonhermitian. In this section we show how the product approximation can be used to construct an hermitian DVR of a general kinetic energy operator without evaluating quadratures.

Consider a one-dimensional (1d) Hamiltonian (in atomic units) with a complicated kinetic energy operator:

$$H = K + V, \qquad K = -(1/2)\frac{d}{dx}G(x)\frac{d}{dx}, \quad x \in (x_1, x_2) \tag{31}$$

with a unit weight factor so that orthogonal basis functions are normalized as

$$\int_{x_1}^{x_2} dx \theta_m(x)^* \theta_n(x) = \delta_{mn}, \tag{32}$$

where G and V are real and G is positive and bounded. If G satisfies the boundary condition

$$G(x_j) = 0 \tag{33}$$

then even if $\theta_n(x_j)$ and $\frac{d}{dx}\theta_n(x_j)$ are nonzero at the boundary point x_j, the $\theta_n(x)$ matrix representation of the Hamiltonian is hermitian. The matrix representing the derivative with respect to x is not antihermitian if the "surface term" $\theta_m(x)^*\theta_n(x)|_{x_1}^{x_2}$, obtained by integrating by parts, does not vanish. Despite the fact that the derivative matrix is not antihermitian the kinetic energy matrix is hermitian, *if matrix elements are evaluated exactly*. We now show that, with care, the product approximation can be used to construct an hermitian DVR of the KEO.

To define a prescription for building DVR matrices for complicated kinetic energy operators without evaluating quadratures it would be natural to use a product approximation and to replace representations of products with products of representations. Applying the product approximation in this way yields an "ordinary" FBR for the 1d kinetic energy operator above,

$$K_{mn}^{oFBR} = -(1/2)\sum_{j,k=0}^{N-1} D_{mj}\langle j|G|k\rangle D_{kn}, \tag{34}$$

where

$$D_{mn} = \int_{x_1}^{x_2} dx \theta_m(x)^* \frac{d}{dx}\theta_n(x) \tag{35}$$

and $\langle j|G|k\rangle$ is evaluated by quadrature,

$$\langle j|G|k\rangle = G_{jk}^{FBR} = \sum_{\alpha=0}^{N-1} \theta_j(x_\alpha)^* G(x_\alpha)\theta_k(x_\alpha) w_\alpha / w(x_\alpha) = (\mathbf{T}^\dagger \mathbf{G}^{DVR} \tag{36}$$

with

$$T_{\alpha j} = \sqrt{w_\alpha / w(x_\alpha)}\,\theta_j(x_\alpha)^*, \qquad G_{\alpha\beta}^{DVR} = G(x_\alpha)\delta_{\alpha\beta} \tag{37}$$

and w_α a quadrature weight.

With a unit weight factor the derivative matrix $\mathbf{D}$ is antihermitian if the basis functions $\theta_n(x)$ are zero at x_1 and x_2, the largest and smallest allowed values of the coordinate. If $\mathbf{D}$ is antihermitian the product FBR Hamiltonian matrix $\mathbf{K}^{oFBR}$ is hermitian. However, if $\mathbf{D}$ is not antihermitian the product FBR Hamiltonian matrix is not hermitian. Although an exact variational basis representation (VBR) matrix (with no product and no quadrature approximation) is hermitian, $\mathbf{H}^{oFBR}$ is not.

To obtain an hermitian FBR kinetic energy matrix by invoking the product approximation one must write the kinetic energy operator in the explicitly hermitian form [36]).

$$\breve{K} = (1/2)(\frac{d}{dx})^\dagger G(x)\frac{d}{dx} \tag{38}$$

with

$$\breve{K}_{mn} = \langle m|\breve{K}|n\rangle = (1/2)\int_{x_1}^{x_2} dx \theta_m(x)^* \left(\frac{d}{dx}\right)^\dagger G(x)\frac{d}{dx}\theta_n(x), \tag{39}$$

where $(\frac{d}{dx})^\dagger = \overleftarrow{\frac{d}{dx}}$ and the arrow denotes differentiation to the left. If integrals are evaluated exactly then

$$K_{mn} = \breve{K}_{mn} \tag{40}$$

because at x_1 and x_2 either $G(x_j) = 0$ or $\theta_n(x_j) = 0$ or $\frac{d}{dx}\theta_n(x_j) = 0$ and the surface term obtained when one integrates by parts is zero. It is clear, therefore, that one may replace K with $\breve{K}$. We define the FBR of $\breve{K}$ as

$$\breve{\mathbf{K}}^{FBR} = (1/2)\mathbf{D}^\dagger \mathbf{G}^{FBR}\mathbf{D}, \tag{41}$$

where $\mathbf{G}^{FBR}$ is the matrix of G with elements evaluated by quadrature. Both the exact VBR matrix $\breve{\mathbf{K}}$ *and the FBR matrix* $\breve{\mathbf{K}}^{FBR}$ *obtained via the product approximation are hermitian.*

The DVR matrix is obtained from $\breve{\mathbf{K}}$ by premultiplying by $\mathbf{T}$ and postmultiplying by $\mathbf{T}^\dagger$

$$\mathbf{K}^{DVR} = \mathbf{T}\check{\mathbf{K}}^{FBR}\mathbf{T}^\dagger = (1/2)\mathbf{T}\mathbf{D}^\dagger\mathbf{G}^{FBR}\mathbf{D}\mathbf{T}^\dagger$$
$$= (1/2)\mathbf{T}\mathbf{D}^\dagger\mathbf{T}^\dagger\mathbf{G}^{DVR}\mathbf{T}\mathbf{D}\mathbf{T}^\dagger = (1/2)(\mathbf{D}^{DVR})^\dagger\mathbf{G}^{DVR}\mathbf{D}^{DVR}, \quad (42)$$

where

$$\mathbf{D}^{DVR} = \mathbf{T}\mathbf{D}\mathbf{T}^\dagger. \quad (43)$$

Here $\mathbf{K}^{DVR}$ is an explicitly hermitian operator. To calculate the DVR of $\check{K}$ it is not necessary to first calculate $\check{\mathbf{K}}^{FBR}$. $\mathbf{K}^{DVR}$ is computed without calculating $\mathbf{G}^{FBR}$, without quadratures, without differentiating G matrix elements, from the values of $G(x)$ at the DVR points and $\mathbf{D}^{DVR}$. Note that although no quadratures are evaluated to obtain the DVR, the quadrature approximation is implicit in our assumption that $\mathbf{G}^{DVR}$ is diagonal. For a multidimensional application of this DVR for complicated kinetic energy operators see reference [36].

D. Symmetry Adapted DVR's

It is almost always advantageous to block diagonalize the Hamiltonian matrix by exploiting symmetry. (Note that for floppy molecules the permutation inversion groups are more appropriate than space groups although isomorphisms exist.) If basis functions are chosen so that they transform like irreducible representations of the group of the molecule being studied, matrix elements in off-diagonal blocks, connecting basis functions of different symmetries, are zero. Block diagonalizing the Hamiltonian matrix reduces the size of the matrices one works with and aids assignment of energy levels. In this section we shall discuss how to construct DVRs which take advantage of such symmetry.

It is simplest to construct DVR basis functions adapted to symmetry operations which affect just one coordinate. Examples of such symmetry operations are: (i) the permutation of homonuclear diatom nuclear labels in the triatomic Jacobi Hamiltonian for a X_2Y molecule (affecting only θ), (ii) space fixed inversion of a four-atom molecule (affecting only the out-of-plane coordinate) (iii) permutation of the identical nuclei of a X_2Y molecule (affecting only the antisymmetric Radau coordinate). For such symmetry operations a method of devising a symmetry adapted DVR was suggested by Whitnell and Light [15]. They chose VBR functions which have the desired symmetry properties and defined separate sets of DVR functions for each symmetry by diagonalizing the VBR of a symmetric operator. For example (i) above, one designs a symmetry adapted DVR for the operation having the effect $\theta \rightarrow \pi - \theta$ by separating symmetric ($j - |m|$ even) and antisymmetric ($j - |m|$ odd) associated Legendre functions and diagonalizing $cos^2(\theta)$ separately in the symmetric and antisymmetric basis sets to obtain separate sets of points (in the half-range $(0, \pi/2)$ for the symmetric and antisymmetric blocks. For example (ii) one diagonalizes $cos\phi$ in a basis of $cos(m\phi)$ functions and a basis of $sin(m\phi)$ to generate points (in the half-range $(0, \pi)$) for each symmetry block.

Another (perhaps better) method to devise symmetry adapted DVRs was first used by McNichols and Carrington [37] and Wei and Carrington [36]. Rather than constructing symmetry adapted DVR functions as linear combinations of symmetry adapted VBR functions they suggested taking symmetry combinations of DVR functions which do not have the desired symmetry properties. For example (i) one would construct symmetry adapted DVR functions by taking symmetric and antisymmetric combinations of the DVR functions obtained by diagonalizing $cos(\theta)$ in a Legendre basis. For example (ii) one takes symmetric and antisymmetric combinations of the DVR functions obtained by diagonalizing $sin(\phi/2)$ in the $[cos(m\phi), sin(m\phi)]$ basis. This method of devising symmetry adapted DVRs has the advantage that the symmetry adapted DVR functions for both symmetry blocks are localized about the same values of the coordinate. This simplifies calculating integrals of antisymmetric operators between symmetric and antisymmetric functions. The second method can also be used to to construct DVR basis functions adapted to symmetry operations which affect more than one coordinate. One simply takes linear combinations of 1d DVR functions (without the symmetry properties) to obtain new DVR functions with the symmetry properties [36].

E. Sequential diagonalization/truncation or adiabatic reduction

The DVR is a powerful tool because it facilitates multidimensional calculations [13,14,38]. The simplest multidimensional DVR basis is a basis each of whose functions is a product of 1-d DVR functions for the separate degrees of freedom. This is a direct product DVR. Direct product DVRs are useful for several reasons: (i) the potential and functions of coordinates in the kinetic energy operator are diagonal in the DVR and hence very easy to construct (no integrals are computed) and use (for example with iterative methods); (ii) for many molecules the direct product DVR basis may be used to efficiently construct more compact basis functions using the sequential diagonalization/truncation method.

The structured sparseness of the DVR Hamiltonian matrix can be exploited to generate in a sequential fashion good contracted basis sets in an increasing number of dimensions. The final result is a Hamiltonian matrix expressed in an optimized contracted basis for all dimensions. This approach, known as the "sequential diagonalization/truncation method" or "sequential adiabatic reduction (SAR) method" was applied to large amplitude vibrational motions of polyatomic molecules

by Bacic *et al.* [11–14] and has since been used in numerous studies. It has the advantage that a relatively large number of accurate eigenvalues and eigenfunctions can be evaluated, even for "floppy" molecules in which a basis of harmonic oscillator functions, for example, is inadequate. It has the disadvantage that at each stage of reduction the Hamiltonians for the reduced dimension problems must be diagonalized.

The approach is most easily understood in terms of adiabatic decompositions of the degrees of freedom, although the SAR method does not actually use adiabatic approximations. If we consider two orthogonal degrees of freedom, and the motions in one coordinate, say y, are much lower frequency than those in x, then one is tempted to use an approximate adiabatic decomposition of the Hamiltonian and the solutions.

The approximate (not the SAR) adiabatic procedure is as follows. Let the exact Hamiltonian be

$$H(x,y) = K_x + K_y + V(x,y) \tag{44}$$

and find the solutions for x for fixed values of y:

$$h(x;y) = K_x + V(x,y) \tag{45}$$

$$h(x;y)\phi_n(x;y) = \epsilon_n(y)\phi_n(x;y) \tag{46}$$

Then the adiabatic approximation for the solutions is obtained by solving for the y motion in the potentials defined by the $\epsilon_n(y)$'s:

$$(K_y + \epsilon_n(y))\theta_m^n(y) = \lambda_m^n \theta_m^n(y) \tag{47}$$

and the full wave function for an n,m state is *approximated* by

$$\Theta_{n,m}(x,y) = \theta_m^n(y)\phi_n(x;y) \tag{48}$$

with energy λ_m^n. The error in this procedure, of course, is that the kinetic energy operator in y is not allowed to operate on the $\phi_n(x:y)$. However, if we use a DVR for y, these terms may be included exactly (within the basis), and simply.

If we are using a DVR for y and an arbitrary basis for x, then at each y_α the solutions for x of Eq. 46 are obtained as a matrix of eigenvectors (a transformation matrix), $\mathbf{T}^\alpha$. The full Hamiltonian matrix can now be transformed *exactly* to this basis:

$$H^{2D}_{\alpha,n;\alpha',m} = (\mathbf{T}^{\alpha T}\mathbf{T}^{\alpha'})_{n,m}(K_y)_{\alpha,\alpha'} + \epsilon_n^\alpha \delta_{n,m}\delta_{\alpha,\alpha'} \tag{49}$$

The adiabatic *reduction* is easily accomplished by *eliminating* from this basis some of the eigenvectors of $h(x;y_\alpha)$ at some (or all) of the y_α. This makes the transformation matrices, T^α *rectangular* of dimension n_x x n_x^α where n_x is the number of basis functions in x, and n_x^α is the number of eigenvectors *retained* at y_α. A minimum number of eigenvectors of $h(x;y_\alpha)$ are retained at each y_α (those with lowest energy). Some of the remaining eigenvectors of $h(x;y_\alpha)$ are usually eliminated on the basis of energy; with an energy cut-off of $E_{max,1d}$, those vectors with $\epsilon_n^\alpha > E_{max,1d}$ are discarded. It has been found empirically and repeatedly [12,13,39] that convergence of the final eigenvalues of multi-dimensional problems is greatly enhanced by keeping *all* the localized DVR basis functions available to the final states. If the energy criterion alone is used to eliminate eigenvectors (of $h(x,y_\alpha)$ in this case), then for some y_α all the eigenvalues of $h(x,y_\alpha)$ may lie above the cut-off, and the DVR function corresponding to y_α would be eliminated from the basis. This has unfortunate consequences for accuracy. A better basis for the 2-D Hamiltonian is obtained by keeping 3 to 10 eigenvectors at each y, and using a lower cut-off energy to limit the size of the resulting Hamiltonian matrix.

Obviously this process may be extended to higher dimension, and is used frequently for three dimensional problems. In this case H^{2D} would be evaluated as above for each value of the third coordinate, say z_γ, the two dimensional basis vectors would be truncated by an $E_{max,2d}$ cut-off again keeping a minimum number at each z point. The form of H^{3D} is identical to that of H^{2D} above, with obvious substitution of the K_z for K_y and the 2D eigenvectors and eigenvalues for those of the 1D Hamiltonian in Eq. (49).

Although the CPU requirements and scaling depend on the actual reductions used, one can get a general picture of the scaling with n, the number of basis functions per dimension (assumed equal for all dimensions), and the truncation fraction, q = (1 - f), 0 < f < 1 (f = 1 means no truncation). In d dimensions the basis size would be n^d, and the diagonalization time would scale as n^{3d}. In the SAR method, there are n^{d-1} diagonalizations of the first coordinate, which itself scales as n^3. Thus the time for this scales as n^{d+2}. After truncation, there are n^{d-2} diagonalizations of average dimension n^2f. Thus the time for this second set of diagonalizations scales as $n^{d+4}f^3$, and so on. For 3-D, the CPU time for the third (and last) diagonalization would scale as n^9f^6. The transformations (see Eq. (49)) also require amounts of computer time comparable to the diagonalizations themselves. A substantial savings in time can also be obtained if diagonalizations are carried out only at every third point in some dimensions, and that basis, suitably truncated, is used for neighboring points. The residual potential is, of course, retained and transformed to the reduced basis [39].

It should be noted that the general approach above is not restricted to DVR bases. First, the representation for the initial diagonalizations (of coordinate, x, above) can be in any basis, one or higher dimensional. In a number of problems coupled angular bases must be used for some degrees of freedom, and, after diagonalization of this basis at each DVR point, the adiabatic reduction may be carried out as above. The initial SAR implementations [11,12] were with a distributed Gaussian basis coupled with a DVR. In the 6-D rigid water dimer problem, as an extreme example, a 5-D coupled angular basis is used together with a 1D DVR in the water-water

distance [40–42] to calculate the bound states accurately.

Bowman and Gazdy [43] noted that direct product bases of any sort may lend themselves to a reduction procedure as above; merely diagonalize the block diagonal components of the Hamiltonian corresponding to one or more fixed basis functions (ϕ_i(y) say), truncate the eigenvector bases for each, and transform the Hamiltonian to this truncated basis. The reduced Hamiltonian may then be diagonalized. In this approach (without a DVR), however, the full potential matrix must be evaluated.

F. Iterative methods

Methods for solving the time-independent Schrödinger equation equation (whether designed to calculate S matrix elements or spectra) are often impeded by the number of basis functions required for convergence. For example, using a conventional time-independent method one calculates a spectrum by diagonalizing a matrix representation of the Hamiltonian; energy levels converge from above (in the VBR) as the basis set is enlarged. To calculate highly excited states of triatomic molecules or more than a few levels for four-atom molecules one has to diagonalize large matrices. Large matrices are difficult to deal with for two reasons: (i) conventional diagonalization algorithms explicitly modify the matrix as it is being diagonalized and therefore require that it be stored in the core memory of the computer (we presently know of no conventional diagonalization calculations with matrices larger than about 10000 × 10000); (ii) the cost of conventional diagonalization algorithms scales as N^3, where N is the size of the matrix. [44]

To alleviate these problems one may either (i) devise good basis functions which represent wavefunctions compactly to minimize the number of basis functions (and the size of the matrix) required to obtain converged energy levels; (ii) use simple product basis functions and an iterative method which exploits the simplicity of the basis; or (iii) use good (and therefore not simple) basis functions and an iterative method. In the previous sections we discussed in detail sequential diagonalization/ truncation methods for devising good basis functions which enable one to use conventional algorithms for solving the time-independent Schrödinger equation equation. In this section we shall discuss using DVRs with iterative methods.

To use an iterative method to compute eigenvalues and eigenvectors of a matrix representation of the Hamiltonian, **H**, one does not need to store **H**; one merely needs to store vectors and to evaluate the product of **H** with a vector at each iteration of the recursion. If the basis is a product basis (option (ii) above) each matrix-vector product may be evaluated with a cost scaling as n^{f+1} where n is a representative number of basis functions for a single degree of freedom, and f is the number of degrees of freedom. Most of the best methods for solving the time-dependent Schoedinger equation also obviate the need to store **H** and allow one to propagate by computing matrix-vector products. [45]

1. *Efficient matrix-vector products*

If the basis is a product basis, each of whose functions is a product of functions of a single coordinate, and the Hamiltonian is factorizable, i.e., it can be written in the form,

$$\hat{H} = \sum_{l=1}^{g} \prod_{k=1}^{f} \hat{h}^{(k,l)}(q_k), \tag{50}$$

a sum of g terms each with f factors (for a single term no more than two of the factors contain derivatives), then it is always possible to evaluate matrix-vectors products so that their cost scales as n^{f+1}. Almost all kinetic energy operators have this factorizable form, and most have fewer than f factors in each term. Owing to the factorizability of $\hat{H}$ and the product structure of the basis, a matrix-vector product $\mathbf{Hu} = \mathbf{u}'$ is evaluated most efficiently by doing sums sequentially [46–48] ,

$$\sum_{l=1}^{g} \sum_{i_1} h^{(1,l)}_{i'_1,i_1} \sum_{i_2} h^{(2,l)}_{i'_2,i_2} \cdots \sum_{i_f} h^{(f,l)}_{i'_f,i_f} u_{i_1,i_2,\cdots,i_f} = u'_{i'_1,i'_2,\cdots,i'_f} \tag{51}$$

where $h^{(k,l)}_{i'_k,i_k}$ is an element of the $n \times n$ matrix representation of the factor $\hat{h}^{(k,l)}(q_k)$ (involving a single coordinate) and for simplicity we have assumed that the basis is a direct product basis, i.e.,

$$\Phi_{i_1,i_2,\cdots,i_f} = \phi_{i_1}(q_1)\phi_{i_2}(q_2)\cdots\phi_{i_f}(q_f). \tag{52}$$

Note that for notational simplicity we have assumed that there are n basis functions for each degree of freedom but that this is not necessary. If the lth term has c_l non-identity $\mathbf{h}^{(k,l)}$ matrices the number of multiplications required to evaluate the matrix-vector product for that term is $c_l n^{f+1}$

The favorable n^{f+1} scaling relation is not due the sparsity of the Hamiltonian matrix or to the sparsity of the $\mathbf{h}^{(k,l)}$ matrices, it is not due to the absence of mixed second-order differential operators, and it is not due to choosing special single coordinate functions from which to build the product basis functions. The n^{f+1} scaling relation is a result of using a product basis and having a factorizable operator. [46] Note that if one evaluates matrix-vector products by doing sums sequentially one never actually calculates (or stores) matrix elements of the Hamiltonian (not even on the fly): one uses matrix elements of the factors of the terms of the Hamiltonian to build up the Hamiltonian matrix-vector product. One

stores only (small) one-dimensional representations of the factors.

Although matrix-vector products can be evaluated so that their cost scales as n^{f+1} regardless of whether one chooses FBR or DVR single coordinate functions it is often advantageous to choose DVR functions for three reasons. First, if one uses DVR functions some of terms in the Hamiltonian can be combined before computing matrix-vector products so that the effective number of terms for which matrix-vector products must be computed is reduced. This is most obvious for the potential. If matrix-vector products were evaluated for each term in the potential separately the total cost of an iterative calculation would depend on the number of potential terms but in the DVR the entire potential can be treated as one term, the number of terms is irrelevant and the cost of the potential matrix-vector product scales as only n^f. In general, if two terms share the same non-diagonal $\mathbf{h}^k$ matrices (i.e., the same differential operators) they can be added together prior to the matrix-vector multiplication. Second, if one uses the DVR, multiplicative operators need not be factorizable to attain n^{f+1} scaling. Third, since functions of coordinates the kinetic energy operator are also diagonal in the DVR, then for each term there are at most two non-diagonal $\mathbf{h}^{(k,l)}$ matrices. Neglecting n^f compared to n^{f+1}, evaluating a DVR matrix-vector product for a kinetic energy term costs either n^{f+1} or $2n^{f+1}$ depending on whether the term has derivatives with respect to one or with respect to two coordinates.

2. *Efficient FBR matrix-vector products*

Sometimes it is preferable (see the section on nondirect product FBRs below) to use an FBR rather than a DVR basis. In the previous section we explained that using a DVR basis enables one to combine all the terms of the potential before evaluating matrix vector products. It would be very costly to compute matrix-vector products for each potential term separately but even in the FBR this is not necessary. The best way to evaluate matrix-vector products in the FBR is to use quadratures and to evaluate sums sequentially. This technique is sometimes referred to as the psuedospectral method. [49] Using the psuedospectral method one can evaluate matrix vector products for terms which are not factorizable at a cost which scales as n^{f+1}.

Consider the matrix-vector product for the two-degree of freedom (unfactorizable) term,

$$h = \frac{1}{a^2 + q_1^2 + q_2^2}. \tag{53}$$

The above operator cannot be written as a product (or a simple sum of products) of functions of a single coordinate and it might therefore appear that the cost of the corresponding matrix-vector product

$$\sum_{i_1}\sum_{i_2} h_{i'_1 i'_2, i_1 i_2} u_{i_1,i_2} = u'_{i'_1,i'_2} \tag{54}$$

should necessarily scale as n^{f+2} (in this case n^4). However, if one introduces sums over the quadrature points which would be required to compute the $h_{i'_1 i'_2, i_1 i_2}$ integral and then does all of the sums sequentially one can achieve n^{f+1} scaling.

The integral

$$h_{i'_1 i'_2, i_1 i_2} = \int dq_1 dq_2 \phi_{i'_1}(q_1)\phi_{i'_2}(q_2)\frac{1}{a^2 + q_1^2 + q_2^2}\phi_{i_1}(q_1)\phi_{i_2}(q_2) \tag{55}$$

$$\approx \sum_\alpha \sum_\beta \sqrt{\frac{\omega_\alpha}{w(q_1)_\alpha}}\sqrt{\frac{\omega_\beta}{w(q_2)_\beta}}\phi_{i'_1}(q_1)_\alpha \phi_{i'_2}(q_2)_\beta \frac{1}{a^2 + (q_1)_\alpha^2 + (q_2)_\beta^2} \tag{56}$$

$$\times \phi_{i_1}(q_1)_\alpha \phi_{i_2}(q_2)_\beta \sqrt{\frac{\omega_\alpha}{w(q_1)_\alpha}}\sqrt{\frac{\omega_\beta}{w(q_2)_\beta}} \tag{57}$$

where $(q_1)_\alpha$ and $(q_2)_\beta$ are quadrature points for the q_1 and q_2 coordinates, ω_α and ω_β are the corresponding quadrature weights and $w(q_1)$ and $w(q_2)$ are the corresponding weight functions (which together with the coordinate ranges determine the quadrature points and weights).

In terms of the $\mathbf{T}$ matrices,

$$h_{i'_1 i'_2, i_1 i_2} \approx \sum_\alpha \sum_\beta (T^\dagger)_{i'_1,\alpha}(T^\dagger)_{i'_2,\beta}\frac{1}{a^2 + (q_1)_\alpha^2 + (q_2)_\beta^2}(T)_{\alpha,i_1}(T)_{\beta,i_2}. \tag{58}$$

The matrix-vector product can now be written,

$$\sum_{i_1}\sum_{i_2}\sum_\alpha\sum_\beta (T^\dagger)_{i'_1,\alpha}(T^\dagger)_{i'_2,\beta}\frac{1}{a^2 + (q_1)_\alpha^2 + (q_2)_\beta^2}(T)_{\alpha,i_1}(T)_{\beta,i_2}u_{i_1,i_2} \tag{59}$$

and doing the sums sequentially,

$$\sum_\alpha (T^\dagger)_{i'_1,\alpha}\sum_\beta (T^\dagger)_{i'_2,\beta}\frac{1}{a^2 + (q_1)_\alpha^2 + (q_2)_\beta^2}\sum_{i_1}(T)_{\alpha,i_1}\sum_{i_2}(T)_{\beta,i_2}u_{i_1,i_2} \tag{60}$$

the matrix vector-product is evaluated at a cost of $4n^3$ which scales as n^{f+1}. Note that the $h_{i'_1 i'_2, i_1 i_2}$ integrals are never actually computed.

Provided the basis is a product basis all matrix-vector products can therefore be evaluated at a cost which scales as n^{f+1} (regardless of whether or not the Hamiltonian or its terms are factorizable) using the pseudospectral method or a combination of the pseudospectral method and the DVR.

3. *Efficient matrix-vector products for nondirect product and non-product representations*

For some problems a direct product basis,

$$\Phi_{i_1,i_2,\cdots,i_f} = \phi_{i_1}(q_1)\phi_{i_2}(q_2)\cdots\phi_{i_f}(q_f), \tag{61}$$

for which matrix-vector products were discussed above, is adequate. Often, however, it will be advantageous to use either a product basis which is not a direct product basis or to use a basis each of whose functions is not a product of functions of a single coordinate. In this section we discuss evaluating matrix-vector products for such basis sets.

Before we explain how the matrix-vector products are done efficiently we briefly address the question: why is it useful to choose nondirect product or non-product basis sets? The Lanczos algorithm is the most useful iterative method for calculating a large number of energy levels. The number of Lanczos iterations required to converge energy levels of interest is strongly correlated to the spacing of the close energy levels relative to the spacings of the most widely separated eigenvalues of the Hamiltonian matrix: widely spaced energy levels are converged first whereas bunches of closely spaced eigenvalues are converged slowly. The Lanczos algorithm also tends to preferentially converge eigenvalues at the top and at the bottom of the spectrum of the matrix. For both these reasons the Lanczos algorithm converges enthusiastically for systems with very large, widely spaced energy levels. Convergence is also poorer if the spectral range (the difference between the largest and the smallest eigenvalues) of the matrix is large. [50] (The number of Chebyshev polynomials and hence the number of matrix-vector products required to accurately propagate a wavepacket using a Chebyshev series also directly depends on the spectral range of the Hamiltonian matrix. [51])

If the Lanczos algorithm is used, as suggested by Cullum and Willougby [50], without reorthogonalization of Lanczos vectors, to calculate energy levels, the highest (and usually widely spaced) eigenvalues of the Hamiltonian matrix converge first and as one iterates further they are wastefully reproduced. Unfortunately the eigenvalues computed most easily by the Lanczos algorithm (the largest) are often those one cares least about since they may not be converged with respect to the basis size and may not have physical significance. For many molecules this problem is not really debilitating but it is exacerbated by any important singularities in the kinetic energy operator. An important singularity is one for which the wavefunctions one wishes to calculate have significant amplitude at points in configuration space at which the kinetic energy operator is infinite. Because they magnify the spectral range, singularities also make application of most iterative propagation methods more difficult.

4. *Nondirect product representations*

To deal with important singularities one chooses basis functions to reduce the size of the kinetic energy matrix elements and thereby reduce the spectral range of the Hamiltonian matrix. Optimal basis functions may be nondirect product functions which are eigenfunctions of part of the Hamiltonian which includes the kinetic energy term(s) with the singularity. We use the term nondirect product function to mean a function which is a product of functions of different coordinates but for which at least one of the single coordinate functions is labeled not only by the index for its coordinate but also by the index for another coordinate, i.e., there is a shared index. The most familiar example of a nondirect product basis function is a spherical harmonic: $Y_{lm} = \Theta_l^m(\theta)\Phi_m(\phi)$ with m being the shared index. Singularities occur whenever one coordinate takes a limiting value and another becomes undefined. If there is an important singularity good basis functions are always nondirect product functions which are products of functions (one with a shared index) of the coordinate which becomes undefined and the coordinate which takes a limiting value.

To evaluate the matrix-vector product efficiently for basis functions which have the form $f_n^m(q_1)g_m(q_2)$ (m is the shared index and the singularity occurs when q_1 takes a limiting value and q_2 becomes undefined) one uses the pseudospectral sequential summation method described above. There are two issues which require some thought. (i) How should one order the factors in the nondirect product equivalent of equation (59). (ii) Should one use different sets of q_1 quadrature points for different values of the shared index m or is it better to use the same set of q_1 quadrature points for all values of m. If one chooses to use different points for different values of m it is clear that one should use the appropriate (m dependent) Gauss quadrature points for the polynomial associated with $f_n^m(q_1)$. If, on the other hand, one choose to use the same q_1 quadrature points for all values of m what points should one choose?

The nondirect product basis functions will usually be eigenfunctions either of part of the kinetic energy operator or of the sum of part of the kinetic energy operator and part of the potential and therefore the only nontrivial matrix-vector product will be for the potential or for part of the potential. One may always attain n^{f+1} scaling by choosing the same set of q_1 quadrature points for all values of m.

If one chooses m independent points the quadrature approximation for the integral

$$V_{n'm',nm} = \int dq_1 dq_2 f_{n'}^{m'}(q_1)g_{m'}(q_2)V(q_1,q_2)f_n^m(q_1)g_m(q_2) \tag{62}$$

$$= \sum_\alpha \sum_\beta \sqrt{\frac{\omega_\alpha}{w((q_1)_\alpha)}}\sqrt{\frac{\omega_\beta}{w((q_2)_\beta)}} f_{n'}^{m'}((q_1)_\alpha)g_{m'}((q_2)_\beta) \tag{63}$$

$$\times V((q_1)_\alpha,(q_2)_\beta) f_n^m((q_1)_\alpha) g_m((q_2)_\beta) \sqrt{\frac{\omega_\alpha}{w((q_1)_\alpha)}} \sqrt{\frac{\omega_\beta}{w((q_2)_\beta)}} \tag{64}$$

where $(q_1)_\alpha$ and $(q_2)_\beta$ are quadrature points for the q_1 and q_2 coordinates, ω_α and ω_β are the corresponding quadrature weights and $w(q_1)$ and $w(q_2)$ are the corresponding weight functions. In terms of the **T** matrix elements,

$$({}^{[q_2]}T)_{\beta,m} = \sqrt{\frac{\omega_\beta}{w((q_2)_\beta)}} g_m((q_2)_\beta), \tag{65}$$

$$({}^{[q_1]}T^m)_{\alpha,n} = \sqrt{\frac{\omega_\alpha}{w((q_1)_\alpha)}} f_n^m((q_1)_\alpha), \tag{66}$$

the potential integral is,

$$V_{n'm',nm} \approx \sum_\alpha \sum_\beta (({}^{[q_1]}T^{m'})^\dagger)_{n',\alpha} ({}^{[q_2]}T^\dagger)_{m',\beta} V((q_1)_\alpha,(q_2)_\beta) ({}^{[q_1]}T^m)_{\alpha n} ({}^{[q_2]}T)_{\beta,m}, \tag{67}$$

where for clarity we have indicated at the left of each T whether it is for q_1 or q_2. As the notation implies there is a different ${}^{[q_1]}T^m$ for each value of m (because there is a different set of q_1 functions for each m).

The matrix-vector product can now be written,

$$\sum_\alpha (({}^{[q_1]}T^{m'})^\dagger)_{n',\alpha} \sum_\beta ({}^{[q_2]}T^\dagger)_{m',\beta} V((q_1)_\alpha,(q_2)_\beta) \sum_m ({}^{[q_2]}T)_{\beta,m} \sum_n ({}^{[q_1]}T^m)_{\alpha,n} u_{nm} = u'_{n'm'} \tag{68}$$

Note that because u_{nm} on the left hand side is indexed by m the fact that the matrix elements $({}^{[q_1]}T^m)_{\alpha,n}$ are indexed not only by α and n but also by m does not mean that the result of the summation $\sum_n ({}^{[q_1]}T^m)_{\alpha,n} u_{nm}$ is labelled by more indices than would be necessary if the T matrix elements were independent of m. The sum over n yields a vector labelled by α, and m (and costs n^3). If the ${}^{[q_2]}T$ matrix were placed to the right of the ${}^{[q_1]}T^m$ matrix the matrix-vector product would be more costly because one could not sum over the elements of one T matrix, store the result, and then sum over the elements of the second T matrix (because both are labelled by m). To attain n^{f+1} scaling the T matrices whose elements are labelled by three indices should therefore be on the outside.

We must still consider the choice of the m independent q_1 quadrature points. For each value of m the f_n^m functions are products of polynomials and the square root of a weight function and the polynomials are associated with Gauss quadrature points. What (fixed) value of m should one choose to determine the m independent points? Clearly the value of m should be chosen so that the associated quadrature accurately approximates the potential and overlap integrals. Regardless of what m is chosen it will almost always be true that some potential integrals will not be exact but it is important to choose the fixed value of m for which q_1 Gauss quadrature points are determined so that all overlap integrals (for all values of m) are exact. If overlap integrals were not exact one would have to take a non-unit overlap matrix into account.

Examples of important $f_n^m(q_1)$ functions are Jacobi basis functions and spherical oscillator functions. Each function is proportional to the product of a polynomial and the square root of a weight function,

$$f_n^m(q_1) \propto \sqrt{w^m(q_1)} p_{n,m}(q_1), \tag{69}$$

where $w^m(q_1)$ is the weight function with respect to which the polynomials $p_{n,m}(q_1)$ are orthogonal. In the Jacobi case with $a = b = m$, $w^m(q_1) = (1-(q_1)^2)^m$ and $p_{n,m}(q_1) = P_{n-m}^{(m,m)}$, a Jacobi polynomial. In general, the overlap integral is,

$$\int dq_1 dq_2 f_n^m(q_1) g_m(q_2) f_{n'}^{m'}(q_1) g_{m'}(q_2). \tag{70}$$

$$= \int dq_1 f_n^m(q_1) f_{n'}^m(q_1) \delta_{m,m'} \tag{71}$$

which is proportional to

$$\int dq_1 w^m(q_1) p_{n,m}(q_1) p_{n',m}(q_1) \delta_{m,m'} \tag{72}$$

It is simple to rewrite the above integral as

$$\int dq_1 w^{m_{fix}}(q_1) [\frac{w^m(q_1)}{w^{m_{fix}}(q_1)}] p_{n,m}(q_1) p_{n',m}(q_1) \delta_{m,m'} \tag{73}$$

where m_{fix} is a chosen, fixed value of m. This integral can be evaluated exactly by the Gauss quadrature associated with $p_{n,m_{fix}}(q_1)$ if $[\frac{w^m(q_1)}{w^{m_{fix}}(q_1)}] p_{n,m}(q_1) p_{n',m}(q_1)$ is a polynomial of finite degree. Therefore, if the weight function ratio $R = [\frac{w^m(q_1)}{w^{m_{fix}}(q_1)}]$ can be written as a polynomial of finite degree, i.e., if m_{fix} is the smallest possible value of m, the overlaps integrals can be evaluated exactly with the q_1 quadrature appropriate for $m = m_{fix}$. If polynomials are chosen so that the degree of the weight function ratio, R, increases by the same amount that the degree of $p_{n,m}(q_1) p_{n',m}(q_1)$ decreases as m is increased (so that the degree of the integrand of Eq. (73). does not depend on the value of m) then the quadrature for $m_{fix} = m_{smallest}$ will do all of the overlap integrals correctly. Corey and Lemoine [33] were the first to point out the importance of choosing the points for $m_{smallest}$ if m independent points are used.

Note that although it is possible to choose one set of quadrature points to evaluate all the overlap integrals exactly it may not, in general, be possible to use one set of quadrature points to evaluate overlap integrals and all the potential matrix elements accurately. For example, if

one uses spherical harmonic basis functions up to j_{max}, all the 2-D overlap integrals are evaluated exactly using $(2j_{max}+1)$ Fourier points in ϕ and $j_{max}+1$ Gauss Legendre ($m=0$) points in θ. (Note that $(2j_{max}+1)(j_{max}+1)$ points are required to compute the overlap integrals for $(j_{max}+1)^2$ basis functions.) However, if one wishes to calculate a potential integral such as ($z=\cos(\theta)$,

$$\int dz d\phi \Theta_{lm}(\theta)\cos(m\phi)\cos(\phi)\cos(m'\phi)\Theta_{l'm'}(\theta) \quad (74)$$

it is necessary to calculate,

$$\int dz \Theta_{lm}(\theta)\Theta_{l'm+1}(\theta) \quad (75)$$

which is difficult to evaluate accurately with a Gauss Legendre quadrature because

$$\int dz \Theta_{lm}(z)\Theta_{l'm+1}(z) \propto \int dz (1-z^2)^{(1/2)}(1-z^2)^m P_{j-m}^{(m,m)} P_{j-m-1}^{(m+1,m+1)} \quad (76)$$

and $(1-z^2)^{(1/2)}$ is not a polynomial in z. To evaluate such an integral (off-diagonal in m) one would need a Gauss Jacobi (with $a=b=1/2$) quadrature. With spherical harmonic basis functions an $a=b=1/2$ Gauss Jacobi quadrature will be required to evaluate integrals of $\cos(n\phi)\sin(n'\theta)$ where $n+n'$ is odd.

Consider now the question: is it necessary to choose m independent q_1 points to attain n^{f+1} scaling? To calculate $V_{n'm',nm}$ one might, for example, choose either different q_1 quadrature points for each (m,m') pair or different q_1 quadrature points for each m'. In either case at least one q_1 $\mathbf{T}$ matrix would depend on both m and m' and to calculate the matrix-vector product one would be obliged to evaluate sums such as,

$$\sum_n ({}^{[q_1]}T^{m,m'})_{\alpha,n} u_{nm} = w'_{n'm'm} \quad (77)$$

the cost of which scales as n^4 (and in general as n^{f+2}). If, however, $V_{n'm',nm} \propto \delta_{mm'}$ one can use different q_1 quadrature points for each value of m without jeopardizing the n^{f+1} scaling relation. This is the case, for example, for the bending basis functions for a triatomic molecule. The bending basis functions depend on the index for the body-fixed component of the angular momentum but the potential does not depend on the Euler angles and one may therefore use different sets of q_1 quadrature points with impunity.

The use of the underlying direct product angular DVR (based on Legendre (m=0) polynomials and a Fourier grid in ϕ) instead of spherical harmonics was examined by Dai *et. al.* [52]. In the direct product DVR with the above set of points the j^2 operator was diagonalized. As expected from the above analysis, the lowest eigenvalues for even values of m are given exactly since the exact associated Legendre eigenfunctions (m even) can be represented exactly by Legendre polynomials (m = 0). For odd m values, however, the eigenvalues converge to the exact values slowly (m = 1 being the slowest to converge). The exact eigenfunctions for m odd cannot be given exactly in a finite basis of Legendre polynomials. For angular scattering problems, however, this direct product angular DVR was shown to be quite accurate.

5. Using Lanczos with sequential diagonalization/truncation

We have discussed in detail evaluating matrix-vector products because the efficacy of several of the best methods for solving the time-dependent (e.g., Chebyshev and Lanczos propagation schemes) and the time-independent (e.g., Lanczos's and Davidson's algorithm [53]) methods for solving the Schrödinger equation equation is contingent on the efficiency of matrix-vector products. If one uses a product basis (it may be either a nondirect or a direct product basis) matrix-vector products can always be evaluated at a cost which scales as n^{f+1}. The n^{f+1} scaling relation is attained by exploiting the special structure of the product basis and evaluating summations (over basis set or quadrature indices) sequentially. If one were not able to exploit the structure of the basis and had to do the sums sequentially, the cost of the matrix-vector product (for an $n^f \times n^f$ matrix) would scale as n^{2f}. Although n^{f+1} is certainly favourable compared to n^{2f} it is nevertheless clear that as f (or n) increases the cost of the matrix-vector product calculation will become prohibitive. In addition, although iterative methods obviate the need to store a Hamiltonian matrix one does need to store vectors, with as many components as there are basis functions, and eventually, as f (or n) is increased, one finds that the core memory of the computer is not large enough to do so. To mitigate both these problems it is natural to consider using iterative methods with basis functions which represent wavefunctions or wavepackets more compactly (so that one will require fewer basis functions than would be needed if product basis functions were used). If fewer basis functions are required one will surely have less to store and it might appear that the cost of each matrix-vector product should also be reduced. Basis functions obtained from the sequential diagonalization/ truncation method of Light and co-workers are excellent and might fruitfully be combined with iterative methods. In this section we discuss using DVRs to evaluate matrix-vector products for non-product basis functions.

It is clear that using a more compact basis will reduce storage requirements. Although one might expect that using a compact basis should somehow reduce n and hence the cost of each matrix-vector product, compact-basis matrix-vector products are actually more and not less expensive than product-basis matrix-vector products. They are more expensive because the n^{f+1} scaling relation is due to the simplicity of the product basis: bet-

ter basis functions are necessarily more complicated (the structure of the basis is less simple) and the corresponding matrix-vector products are more costly. The memory advantage of better basis functions is manifest but, if one considers only the cost of a single matrix-vector product it appears that using better basis functions may increase (and not decrease) the computer time required. However. the cost of an iterative calculation depends not only on the cost of a matrix-vector product for a single term but also on the number of times the Hamiltonian must be applied to a vector (either to converge a series representation of the evolution operator or to converge the desired energy levels) and the effective number of terms for which matrix-vector products must be evaluated for each application of the Hamiltonian. For energy level calculations, sequential diagonalisation/truncation basis functions will, in general, not only reduce memory requirements but also make Lanczos calculations more efficient. This was first exploited by Wu and Hayes [54,55]. For many molecules a sequential diagonalisation/truncation basis Lanczos calculation is more efficient than its product basis counterpart because (i) using a better basis reduces the spectral range of the Hamiltonian matrix and uniformizes the gaps between neighbouring eigenvalues and thus decreases the number of iterations required to converge the energy levels of interest and (ii) sequential diagonalisation/truncation basis functions can be chosen so that only one term in the Hamiltonian is not diagonal and therefore so that only one nontrivial matrix vector product must be evaluated.

We define the primary representation as the representation in which the iteration is performed (i.,e, the representation in which the wavepacket is propagated or the representation in which wavefunctions are computed). To efficiently evaluate matrix-vector products for a sequential diagonalisation/truncation primary representation one uses matrices (much like the quadrature T matrices of section) to transform between the sequential diagonalisation/truncation representation and a representation in which matrix elements of Hamiltonian terms can be computed easily and inexpensively. For this (secondary) representation it is usually best to choose a DVR. The number of labels on the transformation matrices and the number of values each label assumes determine the cost of the sequential diagonalisation/truncation matrix-vector products. The more refined the sequential diagonalisation/truncation basis is the greater the number of labels on the transformation matrices.

Consider first the matrix-vector product for a triatomic sequential diagonalisation/truncation basis of the type discussed in section . We label functions of q_1 and q_2 obtained by diagonalizing a two-dimensional Hamiltonian for each DVR point γ for coordinate q_3 by the index j. If the two-dimensional Hamiltonian is diagonalized in a direct product q_1 q_2 basis and α and β are DVR labels for q_1 and q_2 DVR basis functions then the matrix of eigenvectors is the transformation matrix, $C^{\gamma}_{\alpha\beta,j}$. (Instead of diagonalizing the two-dimensional Hamiltonian in a direct product DVR basis one might use products of optimised 1d functions for q_1 and DVR functions for q_2 reference our paper.) In a basis of functions labelled by j and γ the Hamiltonian (written in Radau, symmetrized Radau, or Jacobi coordinates) matrix elements are,

$$\langle j'\gamma'|\hat{H}|j\gamma\rangle = E^{\gamma}_{j}\delta_{j'j}\delta_{\gamma\gamma'} + \sum_{\alpha\beta} C^{\gamma'}_{\alpha\beta,j'}\mu(r_{1\alpha}r_{2\beta})l_{\gamma'\gamma}C^{\gamma}_{\alpha\beta,j} \tag{78}$$

where, μ is an inverse moment of inertia function and $l_{\gamma'\gamma}$ is a DVR matrix element of an operator proportional to $\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta}$.

In this representation applying the Hamiltonian to a vector implicates only one non- trivial matrix-vector product. When sums are evaluated sequentially the cost of the matrix- vector product,

$$\sum_{\alpha\beta} C^{\gamma'}_{\alpha\beta,j'}\mu(r_{1\alpha}r_{2\beta})\sum_{\gamma} l_{\gamma'\gamma}\sum_{j} C^{\gamma}_{\alpha\beta,j}v_{\gamma j} \tag{79}$$

scales as $2(n_j n_\alpha n_\beta n_\gamma)+n_\gamma^2 n_\alpha n_\beta + n_\alpha n_\beta n_\gamma$. If $n_\alpha = n_\beta = n_\gamma = n$ and it were necessary to retain all n^2 eigenvectors of the two-dimensional Hamiltonians then the cost would scale as n^5 (and in general as n^{2f-1}). This should be compared to the cost of the product-basis matrix-vector product, n^{f+1}. Clearly, if at each stage of the sequential diagonalisation procedure it were necessary to retain all the eigenvectors of the reduced dimensional Hamiltonians the sequential-diagonalisation and the product matrices would have the same eigenvalues (same spectral range, same gap structure) and the same number of iterations would be required for both representations and it would be much more expensive to use the sequential diagonalisation basis. However, the utility of the sequential-diagonalisation basis is derived from the truncation and if it is truncated one reduces *both* the cost of each individual matrix-vector product and the number of iterations required. For the three dimensional example, if n_j is reduced from n^2 to n (by retaining only n of the n^2 eigenvectors of the two-dimensional Hamiltonians) the cost of each matrix-vector product is reduced from n^5 to n^4. The cost of product-basis matrix-vector product also scales as n^4 but because the spectral range and/or gap structure of the sequential-diagonalisation basis are much more favourable the number of required iterations is reduced and the calculation is less costly. If the number of required iterations is large and truncation enables one to reduce n_j significantly it might be advantageous to multiply the **C l C** matrices prior to iterating. Although it is not possible to know *a priori* how effective the sequential diagonalisation procedure will be (how much one will be able to truncate) it seems clear that for Lanczos calculations of energy levels the sequential diagonalisation-Lanczos method will, for many, but not all, triatomic molecules, be more efficient than the product basis-Lanczos method. [56,57]

For molecules with four or more atoms the advantages of the sequential diagonalisation basis are even more convincing: as the number of degrees of freedom increases it becomes more and more important to reduce the size of the product basis and to exclude poor (unimportant) functions from the basis.

The best contracted basis functions are obtained from a contraction scheme which involves diagonalizing reduced dimensional Hamiltonians whose dimension is almost as large as the original Hamiltonian. Unfortunately the larger the dimension of the reduced dimensional Hamiltonian the more costly the matrix-vector product for the associated contracted basis. This has motivated Antikainen *et al.* [58] to develop a sequential diagonalization/ truncation Lanczos method using less than optimal basis functions but basis functions which allow one to evaluate matrix-vector products efficiently. Each of the contracted basis functions of Antikainen *et al.* is obtained by diagonalizing a one-dimensional Hamiltonian for fixed values of indices of other basis functions. Because their basis functions are eigenfunctions of one- (and not multi-)dimensional reduced Hamiltonians the cost of each matrix-vector product is reduced. Such a scheme seems very promising for molecules with more than three atoms.

The cost of the sequential diagonalisation matrix-vector product can also be reduced (at the price of decreasing the quality of the basis functions and hence increasing the number of basis functions and the number of iterations required to converge), while using multidimensional basis functions, if eigenfunctions of the reduced dimension Hamiltonian are not recomputed for all the values of the DVR index for the lowest-frequency degree of freedom. [57,39] For example, for a triatomic molecule, rather than choosing a new set of (r_1, r_2) functions for every θ DVR function one could use one set of (r_1, r_2) functions computed for (say) the equilibrium value of θ. This reduces the number of integrals to calculate in the contracted basis, but more importantly it reduces the number of labels on the C matrix and hence allows one to construct (explicitly) a matrix representation of μ labelled by only two indices so that the cost of the matrix-vector product is reduced. Alternatively, for every third value of θ one might compute the contracted basis in (r_1, r_2) and use this basis also for the two neighboring values of θ. Please see references [57,39] for details and numerical tests.

IV. CAVEATS

In any approach to the numerical solution of complex problems, many opportunities for subtle errors exist, and DVR methods are no exception. Since DVR's are basis representations, the common problems of convergence with basis size, etc. all occur in DVRs. There are additional somewhat subtle problems, however, associated with DVR's which are usually not encountered with normal basis representations and which must be considered. They are associated with quadrature error versus convergence (variational) error; criteria for basis set reduction (particularly in the sequential adiabatic reduction approach), and questions of boundary conditions and ranges which may not be so obvious in DVR's.

A. Boundary conditions and ranges, symmetries

In general, all DVR's are defined in terms of some basis set which spans some range and satisfies certain boundary conditions. The underlying basis for the DVR should be appropriate to the problem and to the operators being used. As discussed below, the use of DVR's corresponding to bases satisfying the wrong boundary conditions can lead to substantial and persistent quadrature errors.

Since DVR's are useful primarily for multi-dimensional problems in which solutions spanning a rather large region of space are desired, assuring that the DVR's span the appropriate range with an appropriate density of points is a major concern. In particular, if the range of interest in one coordinate varies substantially with the value of another coordinate, then the range of the DVR basis must span the entire range. One way of assuring this is to find the minimum of the potential for one coordinate (say x) as the others (say y and z) are varied. This defines a one dimensional "global minimum" potential for x, $V_g(x)$. The same can be done for the other coordinates. These "global minimum" potentials define the ranges required for each coordinate in order to represent the system up to given energies, and DVR's can be chosen in each coordinate to satisfy this. These "global minimum" potentials are also the potentials of choice in defining potential optimized DVR's (PODVR's) since the PODVR points will then span the appropriate range.

When convergence of DVR bases is checked, both the density of DVR points (which affects the quality of the quadratures) and the range of the DVR points (if it can vary) must be considered separately.

B. Quadrature error and variational error

Since DVR's are closely related to numerical quadratures and contain inherent quadrature approximations, their accuracy depends on the size of the DVR basis (for a given range) in two ways: the accuracy of the quadrature increases (the quadrature error decreases) as the basis is increased, and the variational error due to the finite basis size also decreases. The variational error is always positive, i.e. the convergence to eigenvalues of the Hamiltonian is from above. However, the quadrature error can be of either sign, depending on the potential and the type and size of the DVR, but should decrease in magnitude as the basis size is increased.

We have often observed that the quadrature error causes *negative* errors in the calculated energies. (The sign may be due to the common existence of regions of large repulsive non-polynomial potentials.) If this is the case, then one often observes first increases in the energy levels with basis size as the quadrature error decreases faster than the variational error, then for some range of basis size, increases in the basis size make changes of comparable magnitude in the quadrature error and the variational error, leading to very stable, but not quite accurate results, and finally the quadratures become very accurate and the reduction of variational error causes convergence from above for very large basis size.

Another tempting, but questionable, practice is to replace infinite integrals with finite quadrature results. Kinetic energy and effective potential terms often contain repulsive singularities; the repulsive effective potentials from angular momentum are the most common. Since these singularities exclude the wave functions in any case, one is tempted to use a DVR for which the quadrature points miss the singularity and thus ignore the problem. This may lead to *very* slow convergence and not necessarily to the correct answer. The best way to treat such situations is to use as a basis functions which have the correct boundary conditions and in which the singular operators are treated exactly.

The most common example is the singularity of the angular momentum operator in polar coordinates at $\theta = 0, \pi$. The matrix elements of the angular momentum operator are finite in a basis of spherical harmonics, containing associated Legendre polynomials. If only Legendre polynomial (m=0) basis functions are used the exact matrix elements of the angular momentum operator are infinite. However, because a Legendre polynomial DVR has no points at 0,π, the quadrature approximations to the integrals are always finite, *i. e.* the quadrature error is infinite! If the wavefunction amplitude is very small near the singularities, then the error in energy may not be large, but it will be persistent, *e.g.* for m = 1 the eigenvalues of the j^2 operator converge very slowly as the Legendre DVR basis size is increased. Thus it may be better to forego the pleasures of a DVR in these cases, and use (usually non-direct product) variational bases for these degrees of freedom. The use of both the DVR and non-direct product bases were discussed above.

C. Truncation of primitive DVR's

Another, perhaps more subtle, problem has to do with the truncation of primitive DVR's in multi-dimensional problems. In using direct product DVR's in several dimensions, there are always DVR points located in regions of space where the wave functions of interest will be very small; regions of very large repulsive potentials being the most common. It is tempting to eliminate such points from the DVR basis in order to reduce both the size of the basis and the spectral range of the Hamiltonian operator. However, DVR basis functions are not truly localized, and kinetic energy operators in DVR bases give long range coupling. Thus, as indicated above, it is best *not* to eliminate DVR points themselves, but to permit all DVR points to mix in the eigenfunctions (at a given level) and then to eliminate high energy functions if desired to reduce the basis size. This means that in sequential reduction procedures, an energy criterion alone should not be used to eliminate functions at intermediate levels, but a minimum number of functions should be kept at each of the DVR points being considered explicitly in the basis. In the case of the sinc function DVR's, however, explicit truncation must be made since the basis is always infinite.

V. SUMMARY AND CONCLUSIONS

The DVR has had an enormous impact on the way we calculate vibrational spectra, rate constants, state-to-state transition probabilities, and other properties which characterize the motion of atoms in or between molecules. To calculate spectra, rate constants, etc one almost always proceeds by choosing basis functions, calculating integrals, and solving a linear algebra problem. The most important and the most striking advantage of the DVR is that it drastically simplifies the calculation of integrals: in the DVR matrix elements of functions of coordinates do not need to be calculated at all because matrix representations of functions are diagonal and the diagonal elements are simply values of the function. Because the DVR obviates the need to calculate integrals it significantly simplifies most dynamical calculations.

It is easy to construct a DVR Hamiltonian matrix for a one-dimensional problem. There is no need to master the details of Gauss quadrature or finite difference methods to use the DVR. To construct a DVR Hamiltonian matrix one must merely (i) choose a VBR basis set, $\theta_k(z)$ (e.g., harmonic oscillator functions with $z = x - x_e$ or Legendre functions with $z = \cos(\theta)$); (ii) diagonalize z in the VBR basis set; (iii) form the potential matrix by building a diagonal matrix whose diagonal elements are $V(z_\alpha)$, where the z_α are the eigenvalues of the VBR z matrix; (iv) form the kinetic energy matrix by transforming the VBR kinetic energy matrix with the eigenvectors of the z matrix. It is easy! The most straightforward way to handle multidimensional problems is with direct-product DVRs.

To use the DVR is one thing; to understand why it works is another. The DVR Hamiltonian matrix is NOT unitarily equivalent to the VBR Hamiltonian matrix. VBR and DVR eigenvalues are not equal. Instead, the DVR Hamiltonian matrix is unitarily equivalent to the FBR Hamiltonian matrix. FBR and DVR eigenvalues are equal. Since one would like to have the VBR eigenvalues, but the advantages of the DVR enables one to

compute DVR eigenvalues easily, one wants to know why the DVR and VBR eigenvalues are different and how different they are. DVR and VBR eigenvalues are different simply because the FBR and the VBR are not identical. The FBR may be thought of in two ways. If the VBR basis functions are classical polynomial functions (e.g., simple harmonic oscillator functions) the FBR may be thought of as the representation in which potential matrix elments are computed with a Gauss quadrature with as many quadrature points as basis functions. The FBR may also be thought of as the representation obtained by replacing matrix representations of products with products of matrices. The difference between DVR (or FBR) and VBR eigenvalues becomes smaller and smaller as the size of the basis is increased. In general, near the top of the spectrum a few of the DVR eigenvalues will be significantly in error but most eigenvalues are essentially exact.

The DVR is simply an alternative representation. A matrix representation is obtained from a set of basis functions. Like any representation the DVR is associated with a set of basis functions. The DVR basis functions are linear combinations of the VBR basis functions, chosen so that the DVR functions diagonalize the coordinate matrix. The basis functions are localized about the eigenvalues of the coordinate matrix, the "DVR points".

The most obvious and striking advantage of the DVR is that it eliminates the calculation of integrals. It has other advantages. (i) The use of the DVR facilitates the construction of good contracted basis functions. For example for a triatomic molecule one can devise an excellent basis using the sequential diagonalization truncation method. Although it is possible to use other (non-DVR) functions to build a contraction schemes it is often true that it is best to form different functions of q_2, q_3, $\cdots$ for each DVR function localized about a q_1 point. (ii) Because DVR functions are localized it is sometimes possible to discard DVR functions localized about points in configuration space for which the potential is high (see however the discussion in reference [46]). (iii) The DVR facilitates the use of iterative methods (e.g., Chebyshev expansions of the time evolution operator or the Lanczos method to calculate spectra) because it reduces the effective number of terms in the Hamiltonian and increases the number of diagonal terms.

One potential disadvantage of the DVR is that it works best if the VBR basis functions are classical polynomial functions but it might not always be efficient to choose such functions. The accuracy of the DVR eigenvalues is equivalent to the accuracy of FBR eigenvalues which is determined by the accuracy of the product approximation used to construct the FBR potential matrix. If one uses N classical polynomial functions as a basis, FBR matrix elements $\langle\theta_k(z)|z^d|\theta_{k'}(z)\rangle$ with $k = 0, 1, \cdots N$ are exact if $k + k' + d \leq 2N + 1$. If one uses VBR functions which are not classical polynomial functions one will increase the number of FBR matrix elements which are not exact. Nonetheless it is often worth accepting this disadvantage in order to decrease the dimension of the matrices. If classical polynomial basis functions are poor in the sense that many of them are required to represent the wavefunctions one wishes to calculate it is better to use basis functions adapted to the potential. For example, rather than using Legendre functions and the associated DVR for a bending angle it is often better to use eigenfunctions of the one-dimensional bending problem and a PODVR.

As is the case with any representation it is useful to have basis functions which transform as irreducible representations of the appropriate symmetry group. Two ways of obtaining symmetrized DVR functions have been described in this article: one can obtain symmetrized DVR functions either (i) by taking linear combinations of symmetrized VBR functions or (ii) by taking symmetrized linear combinations of DVR functions obtained from VBR functions which do not transform like irreducible representations.

Despite the benefits of the DVR it is sometimes true that it is better to use the FBR. This is true for example if (multidimensional) non-direct product VBR functions are ideal basis functions. In this case it is difficult to devise a good DVR and one is better off using direct product or product quadratures.

The DVR will continue to dominate the way theorists calculate spectra, photodissociation cross sections, rate constants etc. Earlier theoretical methods were mostly based on models for which matrix elements could be computed analytically. More and more, at least for small molecules, it is possible to use realistic but complicated potential functions or interpolations for which matrix elements cannot be computed analytically. The DVR enables one to use such potentials without needing to compute difficult integrals. New methods which will be developed to couple exact quantum calculations and approximate classical or semi-classical approaches to handle more complex problems will also surely exploit the advantages of the DVR.

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