Calculating Multidimensional Discrete Variable Representations from Cubature Formulas†

Ilan Degani* and David J. Tannor*

Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, Israel

Received: November 15, 2005; In Final Form: February 26, 2006

Finding multidimensional nondirect product discrete variable representations (DVRs) of Hamiltonian operators is one of the long standing challenges in computational quantum mechanics. The concept of a "DVR set" was introduced as a general framework for treating this problem by R. G. Littlejohn, M. Cargo, T. Carrington, Jr., K. A. Mitchell, and B. Poirier (*J. Chem. Phys.* **2002**, *116*, 8691). We present a general solution of the problem of calculating multidimensional DVR sets whose points are those of a known cubature formula. As an illustration, we calculate several new nondirect product cubature DVRs on the plane and on the sphere with up to 110 points. We also discuss simple and potentially very useful finite basis representations (FBRs), based on general (nonproduct) cubatures. Connections are drawn to a novel view on cubature presented by I. Degani, J. Schiff, and D. J. Tannor (*Num. Math.* **2005**, *101*, 479), in which commuting extensions of coordinate matrices play a central role. Our construction of DVR sets answers a problem left unresolved in the latter paper, namely, the problem of interpreting as function spaces the vector spaces on which commuting extensions act.

1. Introduction

The discrete variable representation, or DVR, is an important computational approach in quantum mechanics. Among other applications, it is used to calculate highly excited eigenfunctions and large amplitude dynamics of nuclei in molecules within the framework of the Born−Oppenheimer approximation. The motivation for introducing DVRs is the difficulty of calculating potential energy matrix elements. In a DVR algorithm, the basis functions are localized and the entire potential energy matrix is calculated at once, simply by evaluating the potential function on a diagonalized coordinate matrix. The potential matrix is then combined with the kinetic energy matrix to obtain a matrix representing the Hamiltonian operator. The eigenvalues and eigenfunctions of the Hamiltonian matrix give approximate solutions of the time independent Schrödinger equation, while quantum mechanical time evolution is approximated by using the Hamiltonian matrix in the time dependent Schrödinger equation. Comprehensive reviews of the DVR approach are given in refs 2 and 3.

Although one-dimensional DVRs are well understood, the construction of multidimensional DVRs beyond the obvious "direct product" type is a subject of ongoing research. The first step is to introduce a set of suitable, d variable, basis functions $\phi_1, \ldots, \phi_n$, called the finite basis representation (FBR) functions.[2] Typically, these are the set of all eigenfunctions of a simple Hamiltonian up to a given energy. Suppose for a moment that the coordinate matrices $(X_i)_{ab} = \langle \phi_a | \hat{x}_i | \phi_b \rangle$, $i = 1, \ldots, d$, are commuting. Then, their joint eigenfunctions form a DVR basis of $\mathcal{J} = \mathrm{span}\{\phi_1, \ldots, \phi_n\}$, and DVR points in $\mathbf{R}^d$ are formed by concatenating the eigenvalues of the X_i, $i = 1, \ldots, d$, corresponding to each DVR basis function to form the vector $(\lambda_{a1}, \ldots, \lambda_{ad})$. Each DVR basis function is typically localized in a neighborhood of the corresponding DVR point. The main obstacle to devising DVRs on $\mathcal{J}$ is that the coordinate matrices X_i, $i = 1, \ldots, d$, do not generally commute.

To avoid this problem of noncommuting coordinate matrices, Littlejohn et al.[4] introduced a general framework for multidimensional DVRs which does not explicitly invoke coordinate matrices. Their approach is based on the concept of "DVR sets", which consist of an N-dimensional function space $\tilde{\mathcal{J}}$ together with N points in the configuration space possessing the following property: the projections to $\tilde{\mathcal{J}}$ of the δ functions at the N points are orthogonal. These points are then regarded as DVR points, and normalizing the projected delta functions gives the DVR basis functions. However, no general method for constructing multidimensional DVR sets was given in ref 4 or later publications, apart from two special cases relying on symmetry.[5,6]

Littlejohn and Cargo made two observations[5] which form the basis for our development. The first is that usual choices of function spaces (e.g., those spanned by typical FBR functions) are generally too restrictive; we therefore need to carefully extend them to obtain the space $\tilde{\mathcal{J}}$ in a DVR set. The second is that DVR sets correspond to cubatures (multidimensional quadratures) evaluating exactly inner products on $\tilde{\mathcal{J}}$: the DVR points correspond to the cubature nodes, and the normalization factors used to obtain DVR basis functions correspond to cubature weights. Therefore, the construction of a DVR set can begin from constructing (or receiving) an N point cubature formula that evaluates exactly inner products on an $n \leq N$-dimensional space $\mathcal{J}$ and then extending $\mathcal{J}$ appropriately to an N-dimensional space $\tilde{\mathcal{J}} \supseteq \mathcal{J}$. The symmetry methods used in refs 5 and 6 to obtain DVR sets are very elegant and important in relevant cases; however, they are also restrictive. For example, the approach to calculating DVRs on the sphere in ref 5 relies on rotation groups of the regular solids; therefore, the number of nodes must belong to a specific set of integers whose maximal member is 60. More generally, we would like to have DVRs that are suited to problems with no special symmetries.

† Part of the special issue "John C. Light Festschrift".

* To whom correspondence should be addressed. E-mail: ilan.degani@weizmann.ac.il (I.D.); david.tannor@weizmann.ac.il (D.J.T.).

10.1021/jp056587r CCC: $33.50
Published on Web 04/20/2006

Here, we assume that a cubature formula is given and formulate the problem of constructing the extension space $\tilde{\mathcal{J}}$ as a linear algebra problem, which is solved in full generality. In this way, we construct eight new nonproduct DVR sets for the plane and sphere based on cubature formulas with no special symmetries. We also discuss $n \times n$ cubature FBRs of Hamiltonians, obtained by projecting $N \times N$ cubature DVR Hamiltonian matrices to the $\phi_1, \ldots, \phi_n$ basis of $\mathcal{J}$ ($n \leq N$). Our results indicate that if suitable cubature formulas were available then such FBRs may outperform DVRs (see also ref 7). Ideally, we would like to have DVRs and FBRs based on high degree cubatures whose nodes are concentrated in relevant regions of configuration space (e.g., low potential regions). However, available cubatures are limited and the field is waiting for new methods for constructing cubature formulas.

A new approach to the cubature construction problem was presented in refs 8−10. It is based on *commuting extensions* of coordinate matrices, which are formed by adding rows and columns to noncommuting coordinate matrices X_i. References 8−10 show that the eigenvalues and eigenvectors of commuting extensions of coordinate matrices give the nodes and weights of cubature formulas. Conversely, it is shown there that the nodes of a known cubature formula give the eigenvalues of commuting extensions of coordinate matrices, and the weights participate in determining their joint eigenvectors. Thus, the problem of calculating cubature formulas is equivalent to the problem of calculating appropriate commuting extensions. Initial attempts at solution yielded several new cubatures;[8,9] however, this approach is still largely unexplored.

Although DVR sets were introduced by Littlejohn et al. to avoid relying on noncommuting coordinate matrices, it turns out that appropriately defined coordinate matrices on the DVR function space $\tilde{\mathcal{J}}$ are actually commuting. This is so if $\tilde{X}_1, \ldots, \tilde{X}_d$, the coordinate matrices on $\tilde{\mathcal{J}}$, are calculated using the associated cubature formula, rather than the exact inner product. Suppose that $\mathcal{J}$ is a space of weighted degree q polynomials and that the DVR is associated with a cubature formula of degree $2q + 1$. Then, in a suitable basis of $\tilde{\mathcal{J}}$, the $\tilde{X}_i$ are commuting extensions of the noncommuting coordinate matrices X_i on $S \subset \tilde{\mathcal{J}}$. This actually solves a problem that was left open in refs 8 and 9. It was not known there how to interpret as a function space the vector space on which commuting extensions act. Here, the $\tilde{X}_i$ act on the *function* space $\tilde{\mathcal{J}}$. This observation puts cubature DVRs in the same framework together with one-dimensional quadrature DVRs. In one-dimensional quadrature DVRs, the eigenvalues of the coordinate matrix X are the nodes of a quadrature formula;[11,12] in multidimensional cubature DVRs, the joint eigenvalues of the $\tilde{X}_i$ are the nodes of a cubature formula.

Apart from refs 5 and 6, we know only one other previous publication on "nondirect product" multidimensional DVRs, given by Dawes and Carrington in ref 13. The idea of ref 13 is to find a basis of $\mathcal{J}$ in which the coordinate matrices are almost diagonal, that is, in which they have small off-diagonal entries. Then, commuting approximations of the coordinate matrices are obtained by discarding the small off-diagonal entries. The resulting commuting matrices are regarded as the new coordinate matrices. Their n joint eigenvectors give the DVR basis functions in $\mathcal{J}$, and the d eigenvalues corresponding to each eigenvector give the DVR nodes, which are points in $\mathbf{R}^d$. An important advantage of the algorithm in ref 13 is that it can be conveniently applied for general $\mathcal{J}$ with large dimension; however, the main limitation is the loss of accuracy associated with discarding the off-diagonals. Note that the DVRs of ref 13 present an alternative to the framework given in ref 4; as far as we can see, the DVR functions in ref 13 are generally not projected δ functions.

We now give a brief overview of the contents of this paper. Section 2 reviews some preliminaries on which our subsequent development is based: the basics of one-dimensional DVRs, the DVR set framework introduced in ref 4, and some basic facts from cubature theory including the relation with commuting extensions described in refs 8−10. In section 3, we show how to calculate multidimensional DVRs and FBRs based on general, nonproduct, cubature formulas, and we show the connection with the commuting extension formalism. In section 4, we show how our ideas can be used for obtaining cubature DVRs and FBRs on the plane, and on the sphere. In section 5, we review the existing types of multidimensional DVRs and study their relations with our approach. In section 6, we give numerical results obtained using cubature DVRs and FBRs. Section 7 ends this paper with a summary of our main findings and directions for future work.

2. Preliminaries

We begin by setting notation and terminology. Let Ω be a region in $\mathbf{R}^d$, and let $\mathcal{H}$ be the Hilbert space of square integrable functions on Ω, $\mathcal{H} = L^2(\Omega)$. The Hamiltonian operator on $\mathcal{H}$ is $\hat{H} = \hat{T} + \hat{V}$, where $\hat{T}$ and $\hat{V}$ are the kinetic and potential energy operators, respectively. The potential operator is determined by a potential function $V(x)$; then, $\hat{V} = V(\hat{x})$, or in the time dependent case, $\hat{V} = V(\hat{x}, t)$. Ω, which is called the configuration space, can be quite general. Particularly, in section 6, we give numerical examples for $\Omega = \mathbf{R}^2$ and $\Omega = S^2$, the surface of the unit sphere in $\mathbf{R}^3$. We are interested in solving the Schrödinger eigenproblem, that is, finding $\psi \in \mathcal{H}, E \in \mathbf{R}$, such that $\hat{H}\psi = E\psi$, and the time dependent Schrödinger equation (TDSE) $i\hbar(\partial/\partial t)\psi = \hat{H}\psi$, whose solutions describe the dynamics of a quantum mechanical system with Hamiltonian $\hat{H}$.

An important approach for numerical solution of these problems is based on projection to a finite dimensional subspace of $\mathcal{H}$, thereby replacing the full Hamiltonian operator with a finite matrix. Introducing suitably chosen orthonormal functions $\phi_1, \ldots, \phi_n$ in $\mathcal{H}$, we obtain the n-dimensional subspace $\mathcal{J} = \mathrm{span}\{\phi_1, \ldots, \phi_n\}$. We can then construct the $n \times n$ matrix H with entries $H_{ab} = \langle\phi_a|\hat{H}|\phi_b\rangle$. The Schrödinger eigenproblem is thus approximated by the problem of finding the eigenvalues and eigenvectors of H, and the TDSE is approximated by the ODE $i\hbar\dot{u} = Hu$, where $u \in \mathbf{C}^n$ is the coordinate vector of a function in $\mathcal{J}$. A technique widely used in the calculation of H is based on splitting the Hamiltonian $\hat{H}$. Write $\hat{H} = \hat{H}_0 + \hat{V} - \hat{V}_0$, where $\hat{H}_0 = \hat{T} + \hat{V}_0$. Thus, the matrix H can be decomposed to the sum $H_0 + V - V_0$, where $(H_0)_{ab} = \langle\phi_a|\hat{H}_0|\phi_b\rangle$ and $(V - V_0)_{ab} = \langle\phi_a|(\hat{V} - \hat{V}_0)|\phi_b\rangle$. If they are known, eigenfunctions of $\hat{H}_0$ can be chosen as the basis functions ϕ_a; thus, H_0 is a diagonal matrix with diagonal entries equal to eigenvalues of $\hat{H}_0$. In other cases, the eigenfunctions of $\hat{H}_0$ are not used; still, the functions ϕ_a are chosen so that calculation of the matrix H_0 (or an approximation) is not too difficult. Moreover, for a particular choice of $\mathcal{J}$ and $\hat{H}_0$, the matrix H_0 is calculated once and is then used for different problems given by different potentials $\hat{V}$.

The difficulty lies in calculating the matrix $V - V_0$ involving costly, generally multidimensional, integrals which are specific for each problem. Note that in our notation V and V_0 are $n \times n$ matrices, $V(x)$ and $V_0(x)$ are potential functions, and $\hat{V} = V(\hat{x})$ and $\hat{V}_0 = V_0(\hat{x})$ are operators on $\mathcal{H}$. For simplicity, we hence-

forth replace all appearances of $V - V_0$ by V; similiarly, $V(x) - V_0(x)$ is replaced by $V(x)$ and $\hat{V} - \hat{V}_0$ is replaced by $\check{V}$. The problem of calculating the matrix H is essentially the problem of calculating (or approximating) the matrix V

$$(V)_{ab} = \langle \phi_a | \hat{V} | \phi_b \rangle = \int_\Omega \phi_a^*(x)\, V(x)\, \phi_b(x)\, \mathrm{d}x \qquad a, b = 1, \ldots, n \quad (1)$$

2.1. One-Dimensional DVRs. Here, we summarize the basics of one-dimensional DVRs which were introduced by Light et al.[14] based on earlier work by Harris et al.[1] and Dickinson and Certain.[12] Shizgal and Blackmore have independently considered similiar methods.[15] Our point of view is similiar to that of Kanfer and Shapiro[16] who emphasized the role of the coordinate matrix on general spaces $\mathcal{S}$.

To address the difficulty of approximating the potential matrix V, one-dimensional DVRs replace the operator $\hat{x}$ with the $n \times n$ matrix X defined by $X_{ab} = \langle \phi_a | \hat{x} | \phi_b \rangle$. X is Hermitian, and there exists a unitary $n \times n$ matrix Q and a diagonal $n \times n$ matrix Λ such that

$$X = Q \Lambda Q^\dagger \quad (2)$$

We can then define the $n \times n$ matrix $\check{V} = V(X) = QV(\Lambda)Q^\dagger$ or

$$\check{V} = Q \begin{pmatrix} V(\lambda_1) & 0 & \cdots & 0 \\ 0 & V(\lambda_2) & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & V(\lambda_n) \end{pmatrix} Q^\dagger \quad (3)$$

where $\lambda_1, \ldots, \lambda_n$ are the eigenvalues of X. $\check{V}$ is an approximation of V defined in eq 1 and the matrix

$$\check{H} = H_0 + \check{V} \quad (4)$$

is an approximation of the Hamiltonian in the basis $\{\phi_1, \ldots, \phi_n\}$ of $\mathcal{S}$. $\check{V}$ and $\check{H}$ correspond to what is often called in the literature V^{FBR} and H^{FBR}.

The eigenvectors of X correspond to the following eigenfunctions in $\mathcal{S}$: $f_a(x) = \sum_{b=1}^n Q_{ba}\phi_b(x)$, $a = 1, \ldots, n$. The f_a comprise an orthonormal basis of $\mathcal{S}$ which is called the DVR basis.[14] In this basis, X is represented by the diagonal matrix Λ and $\check{V}$ is represented by the diagonal matrix $V(\Lambda)$. This is the source of the DVR name (discrete variable representation): the "continuum variable" $\hat{x}$ is replaced by the "discrete variable" Λ to obtain the DVR approximation of the potential operator. The DVR basis functions f_a are typically peaked at the corresponding eigenvalue λ_a and decay as $|x - \lambda_a|$ grows. In the DVR basis, the Hamiltonian is represented by

$$H^{\mathrm{DVR}} = Q^\dagger \check{H} Q = Q^\dagger H_0 Q + V(\Lambda) \quad (5)$$

For a given $\mathcal{S}$, the matrix X can be calculated and diagonalized to obtain Λ and Q once and for all. Hence, calculating H^{DVR} or $\check{H}$ amounts to evaluating the potential function on a set of n points and calculating the matrix products $Q^\dagger H_0 Q$ in the DVR basis (eq 5) or $QV(\Lambda)Q^\dagger$ in the FBR basis (eq 4); direct evaluation of the integrals in eq 1 is avoided. The quality of the DVR/FBR approximations (note that in one-dimensional problems the DVR and FBR correspond to different bases of the same function space $\mathcal{S}$; thus, they lead to identical energy eigenvalues) depends on the choice of $\mathcal{S}$. Generally, the functions ϕ_a are chosen to satisfy the same boundary conditions, and possibly other properties (e.g., symmetry) of the exact eigenfunctions of $\hat{H}$. The question of convergence with increasing n is discussed in some detail in ref 4.

An important class of one-dimensional DVRs is based on orthogonal polynomials. Suppose we are given an interval, $\Omega \subseteq \mathbf{R}$, and a nonnegative weight function, w, such that the integrals $\int_\Omega w(x)x^m\, \mathrm{d}x$ exist for all natural m. Then, it is possible to construct a sequence of orthogonal polynomials e_a, $a = 1, 2, \ldots$, with degree $(e_a) = a - 1$, which satisfy $\int_\Omega w(x)\, e_a(x)\, e_b(x)\, \mathrm{d}x = \delta_{ab}$. The weighted polynomials $\phi_a = \sqrt{w} e_a$ are orthonormal with respect to the usual inner product in $\mathcal{H}$, $\langle \phi_a | \phi_b \rangle = \delta_{ab}$. One-dimensional DVRs are then constructed with $\mathcal{S} = \mathrm{span}(\phi_1, \ldots, \phi_n)$. Denoting the space of degree q polynomials on Ω by $\mathcal{P}_q^\Omega$, we see that $\mathcal{S} = \sqrt{w}\, \mathcal{P}_q^\Omega$ with $q = n - 1$ (recall that $n = \dim \mathcal{S}$). The weighted polynomial spaces to which we previously referred are obtained in this way. Zero boundary conditions are satisfied by a suitable choice of weight function $w(x)$.

There are intimate connections between polynomial DVRs in one dimension and Gaussian quadrature. It is shown in refs 11 and 12 that the n DVR points λ_a (eigenvalues of X) are the nodes in the degree $2n - 1$ $(=2q + 1)$ Gaussian quadrature formula for the interval Ω and weight function w and that the matrix Q from eq 2 is given by

$$Q_{ab} = \sqrt{\omega_b} e_a(\lambda_b) \quad (6)$$

where ω_b are the weights in the Gaussian quadrature formula. For a simpler proof of these facts, see ref 2; the discussion of Gaussian quadrature in refs 8, 9, and 18 is also very relevant. Due to these relations, this type of DVR is commonly called quadrature DVR. Note that eqs 3 and 6 imply that in this case the matrix element $(\check{V})_{ab}$ is the $2n - 1$ degree Gaussian quadrature approximation of the matrix element V_{ab}.

It is worth noting that the applied mathematics literature discusses the "sinc collocation method", of which sinc DVR (see ref 4 and references therein) is a particular case. Of particular interest are the results on convergence rates and on the passage from infinite to finite intervals (see Sugihara and Matsuo[19] and references therein).

2.2. Multidimensional DVR Sets. The basis for our discussion is the notion of DVR set as introduced in ref 4. Our interpretation of DVR sets emphasizes the extension of an initial function space $\mathcal{S}$ to a larger space $\tilde{\mathcal{S}}$ so that appropriately defined coordinate matrices on $\tilde{\mathcal{S}}$ are commuting. For clarity, we introduce the following index convention:

(i) Indexes a and b run from 1 up to $n = \dim \mathcal{S}$.

(ii) Indexes i, j, and k run from 1 up to d.

(iii) Indexes α, β, and γ run from 1 up to $N = \dim \tilde{\mathcal{S}}$, $N \geq n$.

In multidimensional problems, the potential is a function of the operators $\hat{x}_1, \ldots, \hat{x}_d$, with the associated $n \times n$ coordinate matrices $X_1, \ldots, X_d$, $(X_i)_{ab} = \langle \phi_a | \hat{x}_i | \phi_b \rangle$. Suppose, for the moment, that these matrices commute, $[X_i, X_j] = 0$ for all i, j. Defining $\hat{V} = V(X_1, \ldots, X_d)$ and simultaneously diagonalizing the commuting coordinate matrices $X_i = Q\Lambda_i Q^\dagger$, we can write $\hat{V}$ as in eq 3 but now the n points λ_a are vectors with d entries, $(\lambda_a)_i = (\Lambda_i)_{aa}$, that is, $\hat{V} = QV(\Lambda_1, \ldots, \Lambda_d)Q^\dagger$. If the λ_a are in Ω, then multidimensional DVRs could be constructed in this way (evaluation of $V(x)$ outside Ω is often meaningless). Direct product DVRs, which were until recently the only known multidimensional DVRs, can be formulated precisely in this way.

Working with a domain Ω and a space $\mathcal{S}$ which are not of the direct product type, we are faced with the problem that the X_i do not generally commute and therefore cannot be simultaneously diagonalized. This observation led Littlejohn et al.[4] to a generalized notion of DVR sets. Let $\mathcal{S}^{\sim}$ be an N-dimensional subspace of $\mathcal{H}$ such that $\mathcal{S} \subseteq \mathcal{S}^{\sim}$ and let $\phi_1, \ldots, \phi_N$ be orthonormal basis functions. Let $\lambda_1, \ldots, \lambda_N$ be points in Ω and define the projected delta functions $\Delta_\alpha \equiv \sum_{\gamma=1}^{N} |\phi_\gamma\rangle\langle\phi_\gamma|\delta(x - \lambda_\alpha)\rangle = \sum_{\gamma=1}^{N} \phi_\gamma^*(\lambda_\alpha)\phi_\gamma$. Note that

$$\langle\Delta_\beta|\Delta_\alpha\rangle = \Delta_\alpha(\lambda_\beta) \tag{7}$$

that is, the projection of Δ_α on Δ_β is obtained by evaluating it on λ_β.

Definition 1 (adapted from ref 4). *The space $\mathcal{S}^{\sim}$ and the points $\lambda_1, \ldots, \lambda_N$ are called a DVR set if*

$$\Delta_\alpha(\lambda_\beta) = \langle\Delta_\alpha|\Delta_\alpha\rangle\delta_{\alpha\beta} \tag{8}$$

In this case, we call $f_\alpha = (1/||\Delta_\alpha||)\Delta_\alpha$ DVR functions, and the λ_α are called DVR points.

The discussion of DVR approximation accuracy in ref 4 is based on the assumption that $\mathcal{S} = \mathcal{S}^{\sim}$ and consists of all eigenfunctions of $\hat{H}_0$ up to a given energy. Here, we retain the latter property of $\mathcal{S}$ but use "larger" spaces $\mathcal{S}^{\sim} \supset \mathcal{S}$.

Equation 8 implies that f_α is zero on all DVR points except its own, where $f_\alpha(\lambda_\alpha) = ||\Delta_\alpha||$. Therefore, eq 7 implies that the DVR functions are orthonormal; hence, they form an orthonormal basis of $\mathcal{S}^{\sim}$. Therefore, $\langle g|h\rangle = \sum_{\gamma=1}^{N} (1/||\Delta_\gamma||^2) g^*(\lambda_\gamma) h(\lambda_\gamma)$ for all $g, h \in \mathcal{S}^{\sim}$; that is, if $\mathcal{S}^{\sim}$ and $\lambda_1, \ldots, \lambda_N$ are a DVR set, then this sum is a cubature rule evaluating exactly inner products in $\mathcal{S}^{\sim}$. An important observation that was not discussed in refs 5 and 6 is that we can define d coordinate matrices on $\mathcal{S}^{\sim}$ using the cubature rule above rather than the exact inner product. In the DVR basis, they are $(\Lambda_i)_{\alpha\beta} = \sum_{\gamma=1}^{N} (1/||\Delta_\gamma||^2) f_\alpha^*(\lambda_\gamma)(\lambda_\gamma)_i\ f_\beta(\lambda_\gamma) = (\lambda_\alpha)_i\delta_{\alpha\beta}$. These matrices are simultaneously diagonal (in the DVR basis), and we can define $V(\Lambda_1, \ldots, \Lambda_d)$ as the DVR approximation of the potential operator. This is equal to $\mathrm{diag}(V(\lambda_1), \ldots, V(\lambda_N))$, the DVR potential matrix in ref 4, which is defined without invoking coordinate matrices.

2.3. Cubature Formulas and Commuting Extensions. Our discussion of cubature DVRs and FBRs will rely on some basic notation and facts of multivariable polynomials and cubature. *Commuting extensions* of coordinate matrices are particularly important for our discussion.

The degree of a monomial $x_1^{m_1} \cdot \ldots \cdot x_d^{m_d}$ in d variables is $m_1 + \ldots + m_d$, and the degree of a polynomial in d variables is the maximal of the degrees of the constituent monomials. We denote the space of polynomials with complex coeficients, in d variables restricted to Ω, and of degree up to q, by $\mathcal{P}_q^\Omega$. Generally, $\dim \mathcal{P}_q^\Omega \equiv n = \binom{d+q}{d}$; however, in some cases, the monomials are not independent and the dimension is smaller. Consider for example the space of polynomials in three variables on the surface of the sphere $\Omega = S^2$, where the relation $z^2 = 1 - x^2 - y^2$ holds. We later show that $\dim \mathcal{P}_q^{S^2} = (q+1)^2$ rather than $\binom{3+q}{3} = (q+3)(q+2)(q+1)/6$. By saying that $\mathcal{S}$ is a space of weighted polynomials, we mean that $\mathcal{S} = \sqrt{w}\,\mathcal{P}_q^\Omega$, where $w(x) \geq 0$ is an appropriate weight function.

Definition 2. *Suppose we have N points $\lambda_1, \ldots, \lambda_N \in \mathbf{R}^d$ and N weights $\omega_1, \ldots, \omega_N \in \mathbf{R}$ such that*

$$\sum_{\alpha=1}^{N} \omega_\alpha f(\lambda_\alpha) = \int_\Omega w(x) f(x)\, dx \tag{9}$$

for all $f \in \mathcal{P}_D^\Omega$ and such that there exist $f \in \mathcal{P}_{D+1}^\Omega$ for which eq 9 is not true. Then, the sum on the lhs is called a degree D cubature formula for the region Ω and weight function w(x).

The $\lambda_1, \ldots, \lambda_N$ are often called nodes (this term is justified, since the points of cubature formulas are common zeros of quasi-orthogonal multivariable polynomials; see Xu[10]); we consider only cubature formulas with positive weights whose nodes are in Ω. Estimates on the number of nodes are discussed in ref 8 and references therein. Particularly, the following estimate of N in a degree $2q+1$ formula is given there:

$$N \approx \left\lceil \frac{1}{d+1}\binom{d+2q+1}{d} \right\rceil \tag{10}$$

It is obtained by requiring that the number of parameters defining the formula will be the same as $\dim \mathcal{P}_{2q+1}^\Omega$. A similiar calculation for the sphere gives $N \approx \lceil (4/3)(q+1)^2 \rceil$. Note however that parameter counting just gives a guideline; generally, cubature formulas can have either a smaller or larger number of nodes.

Commuting extensions are a central object in cubature theory;

Definition 3 (from ref 8). *We say the $N \times N$ matrices $\tilde{X}_1, \tilde{X}_2, \ldots, \tilde{X}_d$ are $N \times N$ commuting extensions of the $n \times n$ matrices $X_1, \ldots, X_d$ ($N \geq n$) if the top left $n \times n$ block in $\tilde{X}_i$ is X_i, and the matrices $\tilde{X}_1, \ldots, \tilde{X}_d$ pairwise commute. If the X_i and $\tilde{X}_i$ are symmetric (Hermitian), we say that the $\tilde{X}_i$ are symmetric (Hermitian) commuting extensions of the X_i.*

Given a domain, Ω, and weight function, w, it is shown in refs 8−10 that knowing symmetric commuting extensions of coordinate matrices on $\mathcal{P}_q^\Omega$ is equivalent to knowing a degree $2q+1$ cubature formula for Ω and w (extension to the Hermitian case is trivial). However, refs 8−10 do not show how to interpret commuting extensions as operators on function spaces; our construction of DVR sets in the next section also solves this problem, thereby showing that cubature DVRs based on odd degree formulas are generalizations of one-dimensional quadrature DVRs.

For clearer notation, we define

$$\langle g|h\rangle_w \equiv \int_\Omega w(x)\, g^*(x)\, h(x)\, \mathrm{d}x \tag{11}$$

$$\langle g|h\rangle_c \equiv \sum_{\alpha=1}^{N} \omega_\alpha g^*(\lambda_\alpha)\, h(\lambda_\alpha) \tag{12}$$

3. Obtaining Multidimensional DVRs and FBRs from Cubature Formulas

Here, we give the general solution for the problem of calculating DVR sets from known cubature formulas. Furthermore, we consider the use of cubature formulas to obtain potentially very efficient FBRs of Hamiltonians (see also ref 7).

3.1. Calculating Multidimensional Cubature DVR Sets. In section 2.2, we saw that a DVR set generates a cubature formula giving exactly inner products in $\mathcal{S}^{\sim}$. The converse is also true; given such a formula, the Δ_α associated with the cubature points are orthogonal and therefore give a DVR set. The mathematical literature provides cubature formulas giving exactly inner products in spaces $\mathcal{S}$ of multivariable weighted polynomials. However, except for special cases, the number of cubature points N must be greater than $n = \dim(\mathcal{S})$. To generate a DVR set with the cubature points, we need to extend $\mathcal{S}$ to a larger space $\mathcal{S}^{\sim}$ on which the cubature formula still evaluates

inner products exactly. The full solution of this problem is given in ref 17; here, we give an outline.

Problem 1. *Suppose we are given (a) a degree 2q or 2q + 1 cubature formula with nodes* $\lambda_1, \dots, \lambda_N \in \Omega$ *and positive weights* $\omega_1, \dots, \omega_N$ *and (b) an* n_1*-dimensional function space* $\mathscr{B}$ *with the inner product* $\langle\cdot|\cdot\rangle_w$ *defined in eq 11, and such that* $\mathscr{P}_q^\Omega \subseteq \mathscr{B}$*. Find, or prove, that there do not exist, N functions* $u_1, \dots, u_N \in \mathscr{B}$ *such that*

1. $u_\alpha(\lambda_\beta) = \delta_{\alpha\beta}(1/\sqrt{\omega_\alpha})$
2. $\langle u_\alpha|u_\beta\rangle_w = \delta_{\alpha\beta}$
3. $\mathscr{P}_q^\Omega \subseteq \mathrm{span}\{u_1, \dots, u_N\}$

If a solution u_α, $\alpha = 1, \dots, N$, is found, then the DVR functions f_α of definition 1 are $f_\alpha = \sqrt{w}u_\alpha$ and the DVR function space is $\tilde{\mathscr{f}} = \sqrt{w}\ \mathrm{span}\{u_1, \dots, u_N\}$. A DVR set consisting of the nodes $\lambda_1, \dots, \lambda_N$ and the space $\tilde{\mathscr{f}}$ will be called a cubature DVR. Note that the u_α are generalizations of the familiar interpolation polynomials on Gaussian quadrature nodes: Item 1 specifies their values on the nodes so that $\langle u_\alpha|u_\beta\rangle_c = \delta_{\alpha\beta}$ (recall eq 12). Item 2 implies that $\langle u_\alpha|u_\beta\rangle_c = \langle u_\alpha|u_\beta\rangle_w$; that is, the cubature formula gives exactly inner products in span$\{u_1, \dots, u_N\}$. Note also that item 3 implies that $\tilde{\mathscr{f}}$ is an extension of $\mathscr{f} = \sqrt{w}\mathscr{P}_q^\Omega$, that is, $\mathscr{f} \subset \tilde{\mathscr{f}}$.

Xu considered a similiar problem obtained by dropping item 2 (see ref 10, p 45). His analysis does not give a full solution; however, it reveals additional properties (beyond the scope of this text) for the cases in which a solution is found. The approach described here is different: using only linear algebra techniques, problem 1 is solved fully.

Let $e_1, \dots, e_n, e_{n+1}, \dots, e_{n_1}$ be an orthonormal basis of $\mathscr{B}$ (with respect to $\langle\cdot|\cdot\rangle_w$) in which the first n elements form an orthonormal basis of $\mathscr{P}_q^\Omega$. We use boldface letters to denote the vector of coordinates $\mathbf{v}$ corresponding to the function v, while taking the liberty of denoting function spaces and the isomorphic spaces of coordinate vectors by the same symbol. As in ref 10, the starting point of our discussion is the sampling operator on the cubature nodes F: $\mathscr{B} \to \mathbf{C}^N$ defined by $F(f) = (f(\lambda_1), \dots, f(\lambda_N))^T$, $f \in \mathscr{B}$. The $N \times n_1$ matrix representing F in our chosen basis is

$$\Phi = \begin{pmatrix} e_1(\lambda_1) & \cdots & e_{n_1}(\lambda_1) \\ e_1(\lambda_2) & \cdots & e_{n_1}(\lambda_2) \\ \vdots & & \vdots \\ e_1(\lambda_N) & \cdots & e_{n_1}(\lambda_N) \end{pmatrix} \tag{13}$$

Given any vector $\mathbf{v} \in \mathscr{B}$, the vector $\Phi\mathbf{v} \in \mathbf{C}^N$ contains the values of the corresponding function v at the cubature nodes. Problem 1 is equivalent to the following.

Problem 2. *Find an* $n_1 \times N$ *matrix U such that*

1. $\Phi U = \omega^{-1/2}$, *where* $\omega = diag(\omega_1, \dots, \omega_N)$.
2. $U^\dagger U = I_{N\times N}$.
3. *There is an* $N \times n$ *matrix X such that* $UX = \begin{pmatrix} I_{n\times n} \\ O_{(n_1-n)\times n} \end{pmatrix}$.

Once a solution U of problem 2 is found, the corresponding solution of problem 1 is $u_\alpha = \sum_{\kappa=1}^{n_1} U_{\kappa\alpha}e_\kappa$. Note that item 3 simply means that the our first n basis vectors $\mathbf{e}_1, \dots, \mathbf{e}_n$ (on the rhs) are in the space spanned by the columns of U. We continue assuming $\mathrm{rank}(\Phi) = N$, which is a necessary condition for the existence of a solution.

Writing $\mathscr{Y} = (\mathscr{P}_q^\Omega \oplus \mathrm{null}(\Phi))^\perp$, we can decompose $\mathscr{B}$:

$$\mathscr{B} = \mathscr{P}_q^\Omega \oplus \mathscr{Y} \oplus \mathrm{null}(\Phi) \tag{14}$$

Let Y be an $n_1 \times (N - n)$ matrix whose columns form an orthonormal basis of $\mathscr{Y}$, and let $E = \begin{pmatrix} I_{n\times n} \\ O_{(n_1-n)\times n} \end{pmatrix}$ whose columns are an orthonormal basis of $\mathscr{P}_q^\Omega$. Then, $\Phi(E, Y)$ (this is the matrix product $\Phi\cdot(E, Y)$) is an invertible $N \times N$ matrix, and if W is the unique solution of

$$\Phi(E, Y)W = \omega^{-1/2} \tag{15}$$

then $U = (E, Y)W$ satisfies items 1 and 3 of problem 2. However, the columns of such a U will generally not be orthonormal. To resolve the problem, we introduce K, an $n_1 \times (n_1 - N)$ matrix whose columns form an orthonormal basis of null(Φ). Then $U = (E, Y + KC)W$ satisfies items 1 and 3 of problem 2 for any $(n_1 - N) \times (N - n)$ matrix C; that is, we can modify $\mathscr{Y}$ with any elements from null(Φ) without compromising a solution of items 1 and 3 in problem 2. To satisfy item 2, we require that $I_{N\times N} = U^\dagger U = W^\dagger(E, Y + KC)^\dagger(E, Y + KC)W$. Using the relations $E^\dagger E = I_{n\times n}$, $Y^\dagger K = O_{(N-n)\times(n_1-N)}$, $Y^\dagger E = O_{(N-n)\times n}$, $K^\dagger K = I_{(n_1-N)\times(n_1-N)}$, and $W^{-1} = \omega^{1/2}\Phi(E, Y)$, and using the fact that the cubature formula has a degree of at least $2q$, we obtain the following problem which is equivalent to problem 2.

Problem 3. *Find an* $(n_1 - N) \times (N - n)$ *matrix C satisfying the following equations:*

$$I + C^\dagger C = Y^\dagger\Phi^\dagger\omega\Phi Y \tag{16}$$

$$E^\dagger KC = E^\dagger\Phi^\dagger\omega\Phi Y \tag{17}$$

where I is the $(N - n) \times (N - n)$ *identity matrix.*

In our basis $e_1, \dots, e_{n_1}$ of $\mathscr{B}$, the bilinear form $\langle\cdot|\cdot\rangle_w$ is represented by the $n_1 \times n_1$ identity matrix, while $\langle\cdot|\cdot\rangle_c$ is represented by $\Phi^\dagger\omega\Phi$. Thus, eq 16 requires that $\langle f|g\rangle_w = \langle f|g\rangle_c$ if $\mathbf{f}$ and $\mathbf{g}$ are in the space spanned by the columns of $(Y + KC)$, while eq 17 requires the same when $\mathbf{f} \in \mathscr{P}_q^\Omega$.

The solution of eqs 16 and 17 is based on the singular value decomposition $C = LDR^\dagger$. Equation 16 determines D and R uniquely up to unitary transformations preserving the eigenspaces of $Y^\dagger\Phi^\dagger\omega\Phi Y$. Multiplying both sides of eq 17 by RD^{-1} (or an appropriate interpretation of D^{-1} in the case of zero singular values) gives an equation that L must satisfy. This generally has infinitely many solutions which all give $U = (E, Y + KC)W$, solutions of problem 2. Figure 11 gives pseudocode describing the full solution process; Matlab code can be downloaded from ref 17. In the special case that our cubature formula has degree $2q + 1$ and $\mathrm{rank}(\Phi) = N$ for $\mathscr{B} = \mathscr{P}_{q+1}^\Omega$, the solution of problem 3 is very simple. Equation 17 is automatically satisfied, with both sides equal to zero (in this case, eq 17 equates the integrals of polynomials of degree at most $2q + 1$ with their cubature evaluations, which are exact), and eq 16 is easily solved with a free choice of any L with orthonormal columns. The cubature formula used to calculate the DVR set in ref 5 (briefly reviewed in section 5.3) is of this type.

Let $H_0^{\mathscr{B}}$ be the projection of $\hat{H}_0$ to $\sqrt{w}\mathscr{B}$, $(H_0^{\mathscr{B}})_{\kappa\kappa'} = \langle\sqrt{w}e_\kappa|\hat{H}_0|\sqrt{w}e_{\kappa'}\rangle$, $\kappa, \kappa' = 1, \dots, n_1$. Then, the cubature DVR representation of the Hamiltonian operator on $\tilde{\mathscr{f}}$ is

$$H^{\mathrm{DVR}} = U^{\dagger} H_0^{\mathscr{B}} U + \begin{pmatrix} V(\lambda_1) & 0 & \cdots & 0 \\ 0 & V(\lambda_2) & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & V(\lambda_N) \end{pmatrix} \quad (18)$$

If the cubature formula has degree $2q + 1$, then the solution of problem 1 also solves a problem left open in ref 8: how to interpret the commuting extensions (see definition 3) associated with an odd degree positive weight cubature formula as operators on function spaces. Consider an orthonormal basis $\phi_1, \ldots, \phi_n, \phi_{n+1}, \ldots, \phi_N$ of $\tilde{\mathcal{J}}$ in which the first n functions are $\phi_a = \sqrt{w} e_a$, $a = 1, \ldots, n$; these functions form an orthonormal basis of $\mathcal{J} = \sqrt{w}\,\mathscr{P}_q^{\Omega}$. We define the diagonal DVR coordinate matrices by $(\Lambda_i)_{\alpha\beta} = \langle u_\alpha | \hat{x}_i | u_\beta \rangle_c$ $i = 1, \ldots, d$. In the basis $\{\phi_\alpha\}$, they are represented by the commuting matrices $\tilde{X}_1, \ldots, \tilde{X}_d$, defined by $(\tilde{X}_i)_{\alpha\beta} = \langle \phi_\alpha/\sqrt{w} | \hat{x}_i | \phi_\beta/\sqrt{w} \rangle_c$. Our choice of $\phi_1, \ldots, \phi_n$ and the fact that the cubature formula has degree $2q + 1$ imply that the upper left $n \times n$ block of each $\tilde{X}_i$ is X_i, the ith coordinate matrix on $\mathcal{J}$ defined by $(X_i)_{ab} = \langle \phi_a | \hat{x}_i | \phi_b \rangle$. That is, the $\tilde{X}_i$, which act on the DVR function space $\tilde{\mathcal{J}}$, are commuting extensions of the X_i.

Currently, our choice of the space $\mathscr{B}$ and the matrix L (from the singular value decomposition of C) used to construct cubature DVRs is arbitrary. However, the connection with commuting extensions of coordinate matrices suggests that the choice of $\mathscr{B}$ and L should minimize the difference between the extension blocks of the $\tilde{X}_i$ and the corresponding blocks of the exact coordinate matrices on $\tilde{\mathcal{J}}$. Where relevant symmetry can provide an additional approach to the choice of $\mathscr{B}$ and L, see ref 5.

It is interesting to compare the number of nodes in cubature DVR with that of direct product DVR. Equation 10 gives the typical number of nodes in a degree $2q + 1$ cubature formula giving a cubature DVR. The number of nodes in a DVR obtained from a product cubature formula of the same degree is $(q + 1)^d$. When q is large, the leading term of each is $(1/(d + 1))\binom{d + 2q + 1}{d} \sim 2^d q^d/(d + 1)!$ and $(q + 1)^d \sim q^d$. Thus, the ratio between the number of nodes of a cubature DVR obtained from a high degree nonproduct formula and that of the corresponding direct product DVR is expected to be approximately $2^d/(d + 1)!$.

3.2. Calculating Cubature FBRs. An important advantage of the DVR approach is the possibility of discarding DVR basis functions peaked in high potential regions. This is particularly true for direct product DVRs; their rectangular grids often cover unnecessary regions of configuration space. However, imagine that we could easily produce high degree cubature formulas for general domains and weight functions. We could then potentially tailor cubature DVRs to specific problems by an appropriate choice of Ω and w; discarding DVR basis functions would then become less important. Moreover, the higher part of the spectrum of H^{DVR} may contain large errors (see Figures 5 and 10) which can be avoided by projection to a low energy subspace. All of this leads us to define cubature FBRs that project the $N \times N$ DVR Hamiltonian matrix H^{DVR} to the $n \times n$ FBR Hamiltonian matrix $\check{H}$ ($n \leq N$) acting on the subspace $\mathcal{J} \subset \tilde{\mathcal{J}}$.

Suppose that for the region Ω and weight function w we have a degree $2q$ or $2q + 1$, N point, cubature rule with positive weights whose nodes are all in Ω. Let $\{e_a\}$, $a = 1, \ldots, n$, be any basis of $\mathscr{P}_q^{\Omega}$ such that the functions $\phi_a = \sqrt{w} e_a$ are an orthonormal basis of $\mathcal{J}$, and let f_α be DVR basis functions of $\tilde{\mathcal{J}}$ as calculated in section 3.1. Since $\langle f_\alpha | \phi_a \rangle = \langle u_\alpha | e_a \rangle_c = \sqrt{\omega_\alpha} e_a(\lambda_\alpha)$, the $n \times N$ projection matrix from the DVR representation of $\tilde{\mathcal{J}}$ to the $\{\phi_1, \ldots, \phi_n\}$ representation of $\mathcal{J}$ is

$$Q_{a\alpha} = \sqrt{\omega_\alpha} e_a^*(\lambda_\alpha) \quad (19)$$

Projecting the DVR potential matrix to $\mathcal{J}$, we obtain $\check{V}$, the cubature FBR potential matrix:

$$\check{V} = Q \begin{pmatrix} V(\lambda_1) & 0 & \cdots & 0 \\ 0 & V(\lambda_2) & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & V(\lambda_N) \end{pmatrix} Q^{\dagger}, \quad (n \times n) \quad (20)$$

The $n \times n$ cubature FBR Hamiltonian matrix is then

$$\check{H} = H_0 + \check{V} \quad (21)$$

Note that to calculate $\check{V}$ and $\check{H}$ we do not need to know DVR basis functions; the projection Q depends only on the cubature nodes and weights and on the FBR basis of $\mathcal{J}$. As far as we know, most existing FBRs (with the exception of ref 7) use only product cubature formulas; here, there is no such restriction. We can discard DVR basis functions also in cubature FBRs: if some of the cubature nodes are in high potential regions, we can reduce computational effort by deleting the corresponding diagonal entries from $V(\Lambda_1, \ldots, \Lambda_d)$, together with the corresponding columns of Q and rows of $Q^{\dagger}$. Similiar ideas have been used by Wang and Carrington[7] in an FBR calculation of the bend eigenfunctions of an HF trimer.

The dimension of $\mathcal{J}$ is generally $n = \binom{d + q}{q} \sim q^d/d!$. Recall that typically we expect $N = \dim(\tilde{\mathcal{J}}) \sim 2^d q^d/(d + 1)!$, while the leading term in the dimension of the corresponding direct product DVR is q^d. Thus, (n/dim DP DVR) $\sim 1/d!$ and $n/N \sim (d + 1)/2^d$. These estimations, the simplicity of cubature FBRs (no DVR functions needed), and the opening remarks of this section indicate that if high degree cubature formulas were available for relevant domains and weight functions then cubature FBR may be the method of choice.

3.3. Currently Available Cubature Formulas. Here, we survey existing cubature formulas for the domains relevant for nuclear Hamiltonians in molecular problems.

The spaces $\mathcal{J}$, and $\tilde{\mathcal{J}}$, should be large enough for convergence of eigenvalues and eigenfunctions within a given error tolerance. Speaking very generally, n and N should be at least several hundreds. Since $n = \binom{d + q}{d} \sim q^d/d!$ when $\mathcal{J} = \sqrt{w}\,\mathscr{P}_q^{\Omega}$, this implies that, to be useful for calculations involving nuclear Hamiltonians in molecular problems, cubature DVRs and cubature FBRs should be derived from formulas whose degree $2q$ or $2q + 1$ is at the very least several dozens or hundreds. The domains appearing in such problems are varied, but $\Omega = \mathbf{R}^d$, $\Omega =$ bounded rectangles in $\mathbf{R}^d$, $\Omega = S^2$ (the unit sphere), and Cartesian products of all of these domains are especially important, as they describe bond stretching and angular degrees of freedom. For example, in ref 20, the configuration space chosen for a methane molecule (CH_4) is $\Omega = \mathbf{R}^4 \times [0, \pi] \times S^2 \times S^2$ ($\mathbf{R}^4$ for the stretches and the rest for the bends). The boundary conditions are often zero for $\mathbf{R}^d$, while on spheres S^2 the functions are required to be continuous. At present, the largest molecules for which high energy nuclear eigenfunctions and large scale nuclear dynamics have been calculated are four or five atom molecules.[13] Counting degrees

TABLE 1: Degree and Number of Nodes in Known Cubature Formulas[a]

reference	$\Omega = \mathbf{R}^2$, $w(x) = e^{-\|\|x\|\|^2}$	$\Omega = \mathbf{R}^d$, $w(x) = e^{-\|\|x\|\|^2}$	$\Omega = S^2$, $w(x) = 1$
24	$D = 15$, $N = 44$	$D = 11$, $N = (4d^5 - 20d^4 + 140d^3 - 130d^2 + 96d + 15)/15$	$D = 14$, $N = 72$
23	$D = 31$, $N = 172$	$D = 11$, $N = (4d^5 - 20d^4 + 140d^3 - 130d^2 + 96d + 15)/15$	$D = 14$, $N = 72$
25			$D = 17$, $N = 110$
26			$D = 22$, $N = 117$
21			$D = 131$, $N = 5810$
22			$D = 191$, $N = 36\,864$

[a] The degree D and number of nodes N in the highest degree cubature formula in each reference is given here. Only formulas with positive weights and nodes inside Ω were considered. The regions and weight functions are $\mathbf{R}^2$ and $\mathbf{R}^d$ both with Gaussian weight function, and the sphere S^2 with unit weight function.

of freedom, we see that a DVR calculation with Ω a nine (or more)-dimensional domain would be at the present frontier of such quantum molecular computations.

Most very high order (i.e., more than a few dozen) formulas in the cubature literature for the domains above are of the product type. Notable exceptions are given by Lebedev and Laikov[21] and by Sloan and Womersley.[22] Lebedev and Laikov give cubatures for S^2 of degree up to 131, whose number of nodes is approximately $^2/_3$ the number of a product cubature of the same degree. Moreover, in contrast to product formulas where the nodes are concentrated at the poles, the nodes of Lebedev−Laikov cubatures are (nearly) evenly distributed. The FBR used in ref 7 is based on these cubatures. The nodes of the cubatures given by Sloan and Womersley in ref 22 are also evenly distributed over the sphere; however, their number is double that of a product formula of the same degree. Several other sources for existing cubature formulas are refs 23−26, and the references therein. Table 1 lists the degrees and number of nodes in the highest degree formulas in each of these references; apart from ref 21 (and possibly also ref 22), this is not sufficient for the needs of quantum molecular computations. The potential usefulness of cubature formulas for DVR and FBR calculations provides renewed motivation for finding new nonproduct high order formulas. As mentioned in section 3.1, this is equivalent (at least for odd degree formulas) to the problem of calculating commuting extensions of coordinate matrices.

4. Cubature DVRs and FBRs for the Plane and Sphere

Here, we describe cubature DVRs and FBRs for two particular configuration spaces, the plane and the sphere.

4.1. Cubature DVRs and FBRs on the Plane. Consider a quantum mechanical system whose configuration space is the plane $\Omega = \mathbf{R}^2$ with wave functions which satisfy the boundary conditions $\lim_{||x||\to\infty} \psi(x) = 0$. Orthonormal eigenfunctions of the two-dimensional isotropic harmonic oscillator Hamiltonian, $\hat{H}_0 = (^1/_2)(-\nabla^2 + ||x||^2)$, can provide a convenient basis. These are of the form $\phi_a(x_1, x_2) = \exp(-(^1/_2)(x_1^2 + x_2^2))\, h_{r_1}(x_1)\, h_{r_2}(x_2)$, where the h_{r_i} are Hermite polynomials of degree r_i, and the corresponding eigenvalue is $E_a = 1 + r_1 + r_2$. The mth eigenspace ($m = 0, 1, \ldots$) is the subspace spanned by all eigenfunctions of $\hat{H}_0$ whose eigenvalue is $m + 1$; its dimension is equal to $m + 1$. We choose $\mathcal{S} = \mathrm{span}\{\phi_a | E_a \le q + 1\}$, that is, all eigenspaces of $\hat{H}_0$ up to and including the qth eigenspace. It is easily seen that $\mathcal{S} = e^{-1/2||x||^2}\mathscr{P}_q^{\mathbf{R}^2}$, so given a positive weight degree $2q + 1$ cubature formula, $\int_{\mathbf{R}^2} e^{-||x||^2} f(x)\mathrm{d}x = \sum_{\alpha=1}^{N} \omega_\alpha f(x_\alpha)\ \forall f \in \mathscr{P}_{2q+1}^{\mathbf{R}^2}$, our prescriptions can be applied; this is a standard type of cubature formulas (see refs 23 and 24). To apply cubature DVR to a given Hamiltonian $\hat{H} = \hat{H}_0 + V(\hat{x}_1, \hat{x}_2)$, we chose $\mathscr{B} = \mathscr{P}_{q_1}^{\mathbf{R}^2}$, increasing q_1 until a solution U of problem 2 was found. Then, $(H_0^{\mathscr{B}})_{\kappa\kappa'} = \langle\phi_\kappa|\hat{H}_0|\phi_{\kappa'}\rangle = \delta_{\kappa\kappa'}E_\kappa$ for $\kappa, \kappa' = 1, \ldots, n_1 = \dim(\mathscr{P}_{q_1}^{\Omega})$ and $H^{\mathrm{DVR}} = U^\dagger H_0^{\mathscr{B}} U + V(\Lambda_1, \ldots, \Lambda_d)$ as in eq 18. Cubature FBR approximates $\hat{H}$ by $\check{H} = H_0 + Q^\dagger V(\Lambda_1, \ldots, \Lambda_d)Q$ as in eq 21. In section 6.1, this is applied to the Henon−Heiles problem.

4.2. Cubature DVRs and FBRs on the Sphere. Consider quantum mechanical systems whose configuration space is the unit sphere in $\mathbf{R}^3$, $\Omega = S^2$, with Hamiltonian

$$\hat{H} = \hat{L}^2 + V(\hat{\theta}, \hat{\varphi}) \tag{22}$$

Here, $\hat{L}^2 = (-1/(\sin\theta))(\partial/\partial\theta)(\sin\theta\ (\partial/\partial\theta)) - (1/(\sin^2\theta))\cdot(\partial^2/\partial\varphi^2)$ is the square of the angular momentum operator expressed in angular coordinates. The spherical harmonics are eigenfunctions of $\hat{L}^2$

$$\hat{L}^2 Y_l^m = l(l+1)Y_l^m \tag{23}$$

We wish to construct cubature DVRs and FBRs on spaces spanned by spherical harmonics with $\Omega = S^2$. Recall that in spherical coordinates the Y_l^m are given by

$$Y_l^m(\theta, \varphi) = \frac{N_{lm}}{\sqrt{2\pi}} \sin(\theta)^{|m|} P_l^m(\cos(\theta)) e^{im\varphi} \qquad 0 \le \theta \le \pi, -\pi \le \varphi \le \pi \tag{24}$$

where P_l^m is a degree $l - |m|$ polynomial. It is easily seen that in Cartesian coordinates the spherical harmonics Y_l^m are degree l polynomials:

$$Y_l^m(x_1, x_2, x_3) = \frac{N_{lm}}{\sqrt{2\pi}} P_l^m(x_3)(x_1 + ix_2)^m \qquad \text{if } m \ge 0$$

$$Y_l^m = (-1)^m (Y_l^{|m|})^* \qquad \text{if } m < 0 \tag{25}$$

The inner product on $\mathcal{S}$ is given by

$$\langle f|g\rangle = \int_{S^2} f^* g\, \mathrm{d}\sigma,\ \forall f, g \in \mathcal{S} \tag{26}$$

where $\mathrm{d}\sigma$ is the surface area measure, $\mathrm{d}\sigma = \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\varphi$. Using the fact that the spherical harmonics are orthonormal $\langle Y_l^m | Y_{l'}^{m'}\rangle = \delta_{ll'}\cdot\delta_{mm'}$, it follows that $\mathcal{S}$ is an $\sum_{l=0}^{q}(2l+1) = (q+1)^2$ dimensional subspace of $\mathscr{P}_q^{S^2}$, the space of degree q polynomials in x_1, x_2, x_3 on S^2. However, the relation $x_3^2 = 1 - x_1^2 - x_2^2$ implies that $\mathscr{P}_q^{S^2}$ is spanned by the monomials $\{x_1^\mu x_2^\eta x_3^\delta | \mu + \eta + \delta \le q,\ \delta = 0 \text{ or } 1\}$. Therefore, $\mathscr{P}_q^{S^2}$ is a direct sum of the following two subspaces: the space of all polynomials in x_1, x_2 of degree at most q and the space of all polynomials in x_1, x_2 of degree at most $q - 1$ multiplied by x_3, that is, $\mathscr{P}_q^{S^2} = \mathscr{P}_q^{\mathbf{R}^2} \oplus x_3\mathscr{P}_{q-1}^{\mathbf{R}^2}$. Thus, $\dim \mathscr{P}_q^{S^2} = \binom{2+q}{2} + \binom{1+q}{2} = (q+1)^2$. It follows that $\mathcal{S} = \mathscr{P}_q^{S_2}$ and that the spherical harmonics with $l \le q$ are an orthonormal basis of $\mathscr{P}_q^{S^2}$ (see also ref 7 and references therein). Following the

notation of sections 3.1 and 3.2, with $w(x) \equiv 1$ for $x \in S^2$, we relabel the spherical harmonics so

$$e_1 = \phi_1 = Y_0^0,\ e_2 = \phi_2 = Y_1^{-1},\ e_3 = \phi_3 = Y_1^0,$$
$$e_4 = \phi_4 = Y_1^1, \text{ etc.}$$

Given a Hamiltonian of the form of eq 22, we set $\hat{H}_0 \equiv \hat{L}^2$. To construct DVR functions corresponding to the nodes of a given cubature formula, we chose $\mathscr{B} = \mathscr{P}_{q_1}^{S^2}$, increasing q_1 until a solution U of problem 2 was found. The diagonal DVR representation of the angular coordinate matrices, Λ_θ, Λ_ϕ, is obtained by expressing the cubature nodes in angular coordinates. Cubature DVRs and FBRs for spherical problems are then given by eqs 18 and 21, as explained for $\Omega = \mathbf{R}^2$. Results for a double-well problem on the sphere are given in section 6.2.

5. Comparison with Other Multidimensional DVRs

Here, we briefly survey other types of multidimensional DVRs. In each case, we point out how coordinate matrices are defined so that they are commuting. As previously discussed, the DVR approximation of the potential is then obtained using the simultaneously diagonal forms of the commuting coordinate matrices.

5.1. Direct Product DVRs. Until the appearance of refs 5, 6, and 13, the only known multidimensional DVRs were of the direct product type. This type of DVR is widely used because of its simplicity and availability. However, the direct product function spaces often require very large dimension for accurate approximation of eigenfunctions (see, for example, ref 20 and Figure 5). This is a major computational bottleneck for current algorithms, and the quest for improved methods, particularly the quest for nonproduct DVRs, is an important theme in this field. A crucial aspect of direct product DVRs is the fact that the coordinate matrices on direct product function spaces commute. This is mentioned often in the literature (see, e.g., refs 2 and 13) but, as far as we know, not explicitly explained. The following discussion uses the language of tensor products to explain this fact.

Direct product DVRs are characterized by two properties:

1. The domain Ω is a (hyper) rectangular domain; that is, it is a product of one-dimensional, possibly infinite, intervals $\Omega = I_1 \times ... \times I_d$.

2. The space $\mathcal{S}$ is a tensor product of spaces of 1 variable functions defined on these intervals, that is, $\mathcal{S} = \mathcal{S}_1 \otimes ... \otimes \mathcal{S}_d$, where $\mathcal{S}_i \subset L^2(I_i)$.

In the following discussion, operators and matrices on the "small" spaces $\mathcal{S}_i$ are denoted by smaller font: $\hat{k}_i$ denotes an operator on $\mathcal{S}_i$, and k_i is its matrix representation in a given basis. On the "big" space $\mathcal{S}$, an operator and its matrix representation are denoted $\hat{K}$ and K.

Matrix representations of operators on $\mathcal{S}$ may be easily expressed as tensor products of smaller matrices. Let $\hat{k}_1, ..., \hat{k}_d$ be operators on the corresponding spaces $\mathcal{S}_1, ..., \mathcal{S}_d$, $\hat{k}_i: \mathcal{S}_i \rightarrow \mathcal{S}_i$. Write $n_i = \dim \mathcal{S}_i$ and let $\{\phi_l^{(i)}\}$, $l = 1, ..., n_i$, be an orthonormal basis of $\mathcal{S}_i$ in which the $n_i \times n_i$ matrix k_i represents $\hat{k}_i$. We assume that $(k_i)_{lm} = \langle \phi_l^{(i)} | \hat{k}_i | \phi_m^{(i)} \rangle$; other possibilities, which we avoid, arise from approximating these matrix elements. The set of all products $\phi_{l_1}^{(1)} \cdot ... \cdot \phi_{l_d}^{(d)}$ form an orthonormal basis for the tensor product space $\mathcal{S}$. It is immediately seen that $n = \dim \mathcal{S} = n_1 \cdot ... \cdot n_d$. Ordering the above basis functions lexicographically (e.g., if $d = 2$, then $\phi_1 = \phi_1^{(1)}\phi_1^{(2)}$, $\phi_2 = \phi_1^{(1)}\phi_2^{(2)}$, $\phi_3 = \phi_1^{(1)}\phi_3^{(2)}$, ..., $\phi_{n_2} = \phi_1^{(1)}\phi_{n_2}^{(2)}$, $\phi_{n_2+1} = \phi_2^{(1)}\phi_1^{(2)}$, etc.), we label them $\{\phi_1, ..., \phi_n\}$. The operators $\hat{k}_i$ naturally extend to operators $\hat{K}_i: \mathcal{S} \rightarrow \mathcal{S}$ with $n \times n$ matrix representations $(K_i)_{ab} = \langle \phi_a | \hat{K}_i | \phi_b \rangle$. However, properties 1 and 2 above imply that it is unnecessary to directly calculate these inner products. Knowing the matrices k_i, we have

$$K_i = I_{n_1 \times n_1} \otimes ... \otimes I_{n_{i-1} \times n_{i-1}} \otimes k_i \otimes I_{n_{i+1} \times n_{i+1}} \otimes ... \otimes I_{n_d \times n_d} \tag{28}$$

Now suppose that we are given a Hamiltonian $\hat{H} = \hat{H}_0 + V(\hat{x})$ and that evaluation of the matrix $(H_0)_{ab} = \langle \phi_a | \hat{H}_0 | \phi_b \rangle$ is easy with the tensor product basis functions ϕ_a described above. For example, this is so if $\hat{H}_0$ is a sum of 1-d Hamiltonians $\hat{H}_0 = \hat{h}_1 + ... + \hat{h}_d$, with each $\hat{h}_i$ depending just on the operators $\hat{p}_i = -i\hbar(\partial/\partial x_i)$ and $\hat{x}_i$. Then, $H_0 = H_1 + ... + H_d$ with each H_i obtained from h_i as in eq 28. To construct a direct product DVR approximation of the potential energy matrix, we need to compute the coordinate matrices $(X_i)_{ab} = \langle \phi_a | \hat{x}_i | \phi_b \rangle$; these are obtained from the matrices $(x_i)_{lm} = \langle \phi_l^{(i)} | \hat{x}_i | \phi_m^{(i)} \rangle$, as prescribed in eq 28. The following properties of tensor products of matrices are necessary to continue the discussion:

1. $(A_1 \otimes B_1) \cdot (A_2 \otimes B_2) = (A_1 \cdot A_2) \otimes (B_1 \cdot B_2)$ if A_1, B_1 and A_2, B_2 can be multiplied.

2. $(A_1 \otimes A_2)^\dagger = A_1^\dagger \otimes A_2^\dagger$.

By property 1, the matrices X_i in a direct product DVR are commuting, $[X_i, X_j] = 0$. Let Q_i be the unitary $n_i \times n_i$ matrix such that $Q_i^\dagger X_i Q_i = \Lambda_i$ is diagonal. Then, by properties 1 and 2, the matrix $Q = Q_1 \otimes ... \otimes Q_d$ is unitary and the matrices $\Lambda_i = Q^\dagger X_i Q = I_{n_1 \times n_1} \otimes ... \otimes I_{n_{i-1} \times n_{i-1}} \otimes \Lambda_i \otimes I_{n_{i+1} \times n_{i+1}} \otimes ... \otimes I_{n_d \times n_d}$ are diagonal. Thus, product structure generates commuting coordinate matrices which give rise to a DVR approximation of the potential energy operator $V(\Lambda_1, ..., \Lambda_d)$. Here, the joint eigenvectors of the X_i are naturally interpreted as DVR functions, which are products of the eigenfunctions of the x_i (one variable DVR functions). Note that if $\mathcal{S}_i = \sqrt{\omega_i(x_i)}\,\mathscr{P}_q^{I_i}$, then the nodes $\lambda_\alpha = ((\Lambda_1)_{\alpha\alpha}, ..., (\Lambda_d)_{\alpha\alpha})$ in the direct product DVR are those of a degree $2q + 1$ product cubature formula.

Despite their shortcomings, direct product DVRs are particularly useful for Hamiltonians of the form $\hat{H} = \hat{H}_0 + \epsilon V(\hat{x})$, where ϵ is small and $\hat{H}_0 = \hat{h}_1 + ... + \hat{h}_d$ is a sum of "sub-Hamiltonians" acting on spaces $\mathcal{S}_i$ of functions in one variable. In this case, $\hat{H}$ is a small perturbation of $\hat{H}_0$ and a space $\mathcal{S}$ spanned by eigenfunctions of $\hat{H}_0$, which are products of eigenfunctions of the $\hat{h}_i$, is a very natural choice. This is the idea of "potential optimized" DVR:[2] it is a direct product DVR with a sufficient number (typically a few dozen) of the eigenfunctions of each $\hat{h}_i$ chosen as the basis functions $\phi_l^{(i)}$. These are obtained numerically, to machine accuracy, using one-dimensional DVRs with a few hundred basis functions. This step is called "contraction" in the DVR literature. Where applicable, the potential optimized DVRs are orders of magnitude more efficient (i.e., $\dim \mathcal{S}$ is much smaller without compromising accuracy) compared to general direct product DVRs. As in all direct product DVRs, the coordinate matrices in potential optimized DVR are commuting, a fact that allows the convenient evaluation of the potential matrix.

5.2. Dawes−Carrington Commuting Approximations DVR. The idea of potential optimized DVR was extended by Dawes and Carrington to the case of multidimensional sub-Hamiltonians.[13] As in the discussion of direct product DVRs, we use small fonts to denote operators and matrices on small spaces and large fonts to denote operators and matrices on tensor product spaces. The algorithm in ref 13 is described in the following setting, which can be naturally generalized. Suppose that $\hat{H} = \hat{h}_{12} + \hat{h}_{34} + \epsilon V(\hat{x}_1, \hat{x}_2, \hat{x}_3, \hat{x}_4)$, where $\hat{h}_{ij}$ is composed of

the operators $\hat{x}_i$, $\hat{x}_j$, $\partial/\partial x_i$, $\partial/\partial x_j$ for $i, j = 1, 2$ or 3, 4. Similar to the case of potential optimized DVR, we choose $\mathcal{J} = \mathcal{J}_{12} \otimes \mathcal{J}_{34}$ where $\mathcal{J}_{ij}$ is spanned by eigenfunctions of $\hat{H}_{ij}$. The $n_{ij} \times n_{ij}$ ($n_{ij} = \dim \mathcal{J}_{ij}$) coordinate matrices on $\mathcal{J}_{ij}$ are generally noncommuting, $[X_i, X_j] \neq 0$. Using the simultaneous diagonalization algorithm from ref 27, it is possible to find a unitary $n_{ij} \times n_{ij}$ matrix R_{ij} so that the sum of squares of the off-diagonal entries in both $R_{ij}^{\dagger} x_i R_{ij}$, $R_{ij}^{\dagger} x_j R_{ij}$ is small (hopefully minimal). The diagonal matrices $\Lambda_i = \mathrm{diag}(R_{ij}^{\dagger} x_i R_{ij})$, $\Lambda_j = \mathrm{diag}(R_{ij}^{\dagger} x_j R_{ij})$ are obtained by setting the off-diagonals to zero and then the (nondiagonal) matrices $x_i^{\mathrm{DC}} = R_{ij} \Lambda_i R_{ij}^{\dagger}$, $x_j^{\mathrm{DC}} = R_{ij} \Lambda_j R_{ij}^{T}$ are commuting approximations of x_i, x_j. Commuting coordinate matrices are then defined on $\mathcal{J}$ by $X_i^{\mathrm{DC}} = x_i^{\mathrm{DC}} \otimes I_{n_{34} \times n_{34}}$, for $i = 1, 2$, and $X_i^{\mathrm{DC}} = I_{n_{12} \times n_{12}} \otimes x_i^{\mathrm{DC}}$ for $i = 3, 4$. The fact that $[X_i^{\mathrm{DC}}, X_j^{\mathrm{DC}}] = 0$ for all $i, j = 1, 2, 3, 4$ allows convenient evaluation of the potential matrix on $\mathcal{J}$ in Dawes−Carrington DVR.

It is very natural to consider replacing the commuting approximations x_i^{DC}, x_j^{DC} of the Dawes−Carrington DVR with commuting extensions $\hat{x}_i$, $\hat{x}_j$ (see definition 3). Recall that the cubature DVR coordinate matrices on $\tilde{\mathcal{J}}$ are in fact commuting extensions of the coordinate matrices on $\mathcal{J}$. Therefore, Figures 4 and 9 indicate that commuting extensions may give better accuracy than commuting approximations. This possibility further motivates future research on computing commuting extensions.

5.3. The Littlejohn−Cargo Approach. Apart from ref 13, the only other published nondirect product multidimensional DVRs are given, to the best of our knowledge, by Littlejohn and Cargo in refs 5 and 6. These are based on the notion of DVR sets,[4] reviewed here in section 2.2. An important observation made in ref 5 is that there is a correspondence between DVR sets and cubature formulas. Particularly, if an n point cubature formula with positive weights gives exactly all inner products in an n-dimensional function space $\mathcal{J}$, then the nodes and $\mathcal{J}$ form a DVR set. It is also observed there that if such a cubature formula has N points with $N > n = \dim(\mathcal{J})$, then a DVR set may be obtained by extending to an N-dimensional space $\tilde{\mathcal{J}} \supset \mathcal{J}$ for which the formula still gives exactly inner products. Therefore, the task of constructing a DVR set for a given function space $\mathcal{J}$ is decomposed in ref 5 to the problem of finding a suitable cubature formula, and then extending $\mathcal{J}$ to a larger space $\tilde{\mathcal{J}}$.

A severe obstacle to finding DVR sets is that there are $O(n^2)$ equations to satisfy (orthogonality of projected delta functions) and only $O(n)$ variables (coordinates of DVR points); note that this corresponds to the difficulty of constructing cubature formulas. Thus, refs 5 and 6 suggest to seek DVR sets in which the nodes are an orbit of a discrete group of transformations, and in which the DVR basis functions are an orbit of a unitary representation of the same group. Then, the number of orthogonality conditions is reduced to n, since orthogonality of one DVR basis function to all others implies orthogonality of any two. We stress that the correspondence between cubature and DVR is general, while DVR sets in which the DVR functions are obtained as an orbit of a group are a special case.

These ideas are combined in ref 5 to obtain a 12 point DVR set on the sphere: a degree 5 cubature formula is found whose 12 nodes are the vertices of an icosahedron invariant under the action of a tetrahedral group and whose weights are equal. In fact, this formula can be obtained by rotating the nodes of formula U_3: 5−1 from ref 24. These formulas evaluate exactly all inner products in the nine-dimensional space $\mathcal{P}_2^{S^2}$ spanned by spherical harmonics with $l \leq 2$. A three-dimensional extension $\mathcal{F}$ is needed to obtain a DVR set, and it is argued in ref 5 that since their cubature formula is tetrahedrally invariant it makes sense to seek an extension which is an irreducible invariant subspace of the same tetrahedral group. There are many such extensions, but we need those for which the cubature formula evaluates all inner products exactly. Such an extension $\mathcal{F}$ is found within the space of spherical harmonics with $l = 3$, thus giving a DVR set whose nodes are those of the cubature formula and whose function space is $\tilde{\mathcal{J}} = \mathcal{P}_2^{S^2} \oplus \mathcal{F}$.

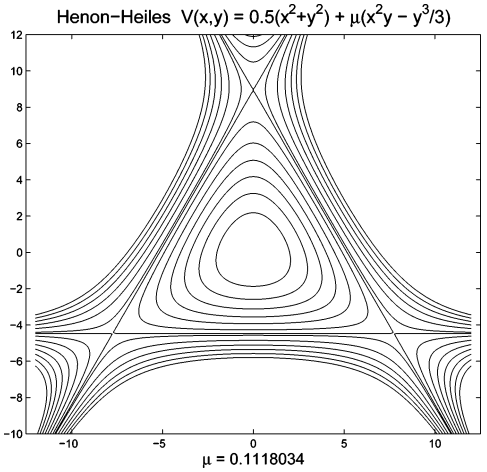

Figure 1. Level sets of the Henon−Heiles potential; the sets $V(x, y) = 0, 2, 4, \ldots, 24$ and $V(x, y) = 13.333\,333$ (straight lines) are shown. The triangle is a well and each of its vertices a saddle point.

Our approach to the calculation of DVR sets differs in two main points: First, as described in section 3.1, we consider only the problem of extending $\mathcal{J}$ to $\tilde{\mathcal{J}}$ when a cubature formula is given. The problem of constructing cubature formulas is left to future work. Second, the algebraic approach of our solution to the extension problem can accommodate symmetry considerations but is not restricted by them.

6. Numerical Examples

6.1. Cubature DVRs and FBRs for the Plane. In section 4.1, we explained how to apply cubature DVRs and FBRs to problems whose configuration space is $\mathbf{R}^2$ with zero boundary conditions. Here, this is applied to the Henon−Heiles Hamiltonian[28]

$$\hat{H} = \frac{1}{2}\left(-\frac{\partial^2}{\partial {x_1}^2} - \frac{\partial^2}{\partial {x_2}^2} + {\hat{x}_1}^2 + {\hat{x}_2}^2\right) + \mu\left({\hat{x}_1}^2\hat{x}_2 - \frac{1}{3}{\hat{x}_2}^3\right) \quad (29)$$

with $\mu = 0.111\,803\,4$. A contour plot of the potential appears in Figure 1. It is a triangular well whose minimum is at the origin and whose maximum value of 13.333 333 is attained at the straight line level sets (this is the maximal value of the well, not of the potential). Each vertex of the triangle is a saddle point. Note that $\hat{H} = \hat{H}_0 + V(\hat{x}_1, \hat{x}_2)$, where $V(\hat{x}_1, \hat{x}_2) = \mu({\hat{x}_1}^2\hat{x}_2 - {\hat{x}_2}^3/3)$, and $\hat{H}_0$ is the isotropic harmonic oscillator Hamiltonian.

The cubature formulas used to construct the cubature DVRs and FBRs are the degree $2q + 1$ formulas from refs 8 and 9, where $q = 5$, 6, 7, and 8 and the number of nodes in each is 26, 35, 46, and 57, respectively. The node locations are illustrated in Figures 2 and 3 together with the squared absolute value of typical DVR functions, note the nondirect product layout. The function spaces used for the cubature FBRs are $\mathcal{J} = \exp(-({}^1/_2)(x_1^2 + x_2^2))\mathcal{P}_q^{\mathbf{R}^2}$, $q = 5$, 6, 7, 8, whose dimension is $(q + 1)(q + 2)/2$. In the cubature DVRs, $\mathcal{J}$ was extended to spaces $\tilde{\mathcal{J}}$, as explained in section 4.1.

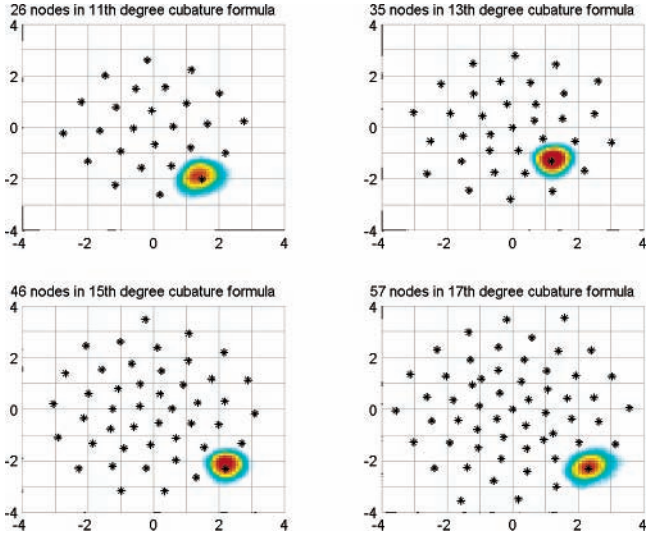

Figure 2. Cubature DVR nodes and functions for $\mathbf{R}^2$; this figure illustrates the nodes in the cubature DVRs used for the Henon−Heiles problem, together with the squared absolute value of typical DVR basis functions. The nodes are those of the 11, 13, 15, and 17 degree cubature formulas constructed in refs 8 and 9 for $\Omega = \mathbf{R}^2$, $w(x_1, x_2) = \exp(-x_1^2 - x_2^2)$. DVR basis functions were obtained by solving problem 1 of section 3.1 for these cubature formulas.

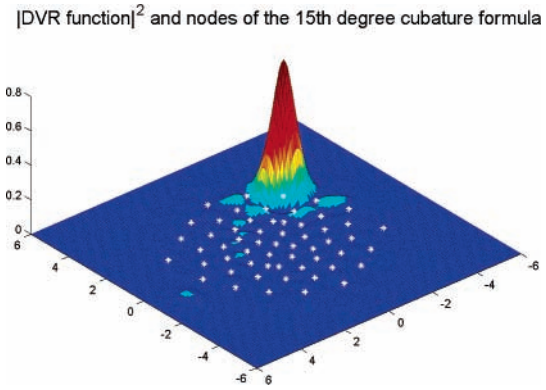

Figure 3. Typical DVR function; the squared absolute value $|f_\alpha|^2$ of a typical DVR basis function f_α is shown here, together with the nodes of the corresponding degree 15 cubature formula used for the Henon−Heiles problem.

The results are compared to those of two other methods, direct product DVR obtained from one-dimensional Gauss−Hermite quadrature (DP DVR) and the algorithm given by Dawes and Carrington in ref 13 (DC DVR); see section 5 (but bear in mind that here we have only $\hat{H}_{12}$, so the combination of $\hat{H}_{12}$ with $\hat{H}_{34}$ should be ignored now). The function spaces used in DP DVR are the product spaces $\exp(-(1/2)x_1^2)\mathscr{P}_q^{\mathbf{R}} \otimes \exp(-(1/2)x_2^2)\mathscr{P}_q^{\mathbf{R}}$, $q = 5, 6, 7, 8$, whose dimension is $(q+1)^2$. The function spaces used in DC DVR were the same as those used in the cubature FBRs.

Table 2 lists the exact eigenvalues together with errors in their approximation by the four methods. The exact eigenvalues were computed using DP DVR with $q = 45$ for which the first 45 eigenvalues were observed to converge to 10 decimal digits, and the remaining eigenvalues up to the 81st were converged to 4 decimal digits (the table shows only 50 eigenvalues). The 81st eigenvalue is 12.065 039; note that it is below the barrier energy of 13.333 333. Recall that for each $q = 5, 6, 7, 8$ the space $\mathcal{S}$ is spanned by all harmonic oscillator eigenfunctions with energy $E \le q + 1$. It is interesting to observe the abrupt error increase in the cub DVR and, to a lesser extent, in the DP

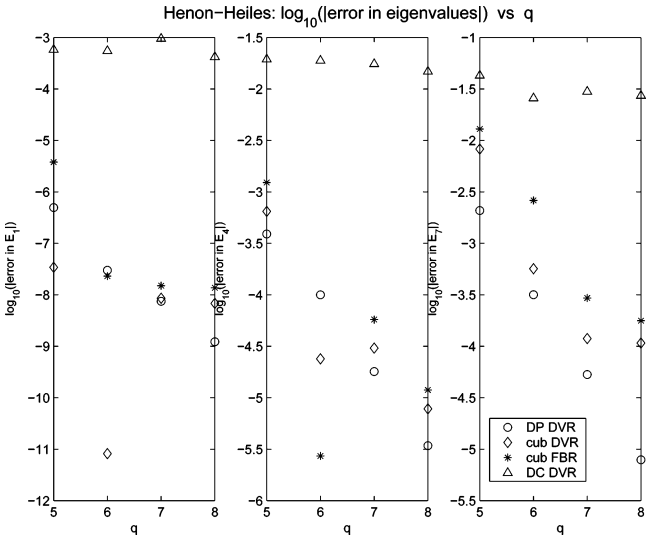

Figure 4. Performance comparison; eigenvalues in the Henon−Heiles problem were approximated using DP DVR (direct product), cubature DVR, cubature FBR, and DC DVR. This figure shows log(|error|) in approximating the first, fourth, and seventh eigenvalues (vertical axis) versus q (horizontal axis). Note the rapid decay of error with increasing q in DP DVR, cubature DVR, and FBR but not in DC DVR.

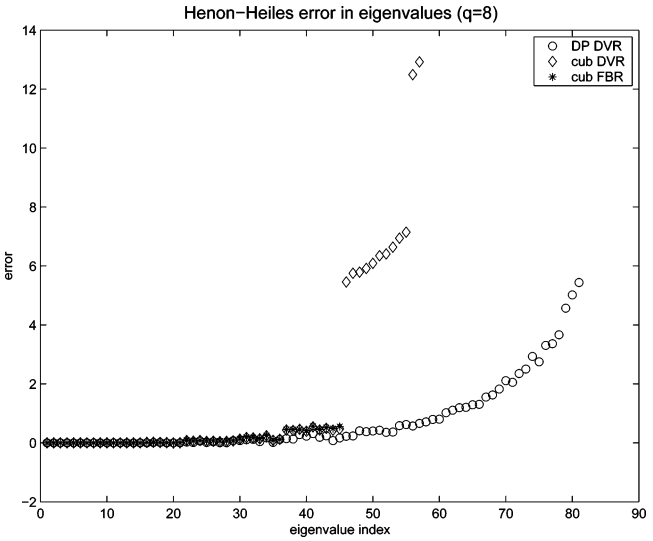

Figure 5. Large errors in high DVR eigenvalues; the error in approximating Henon−Heiles eigenvalues using cubature DVR, cubature FBR, and DP DVR with $q = 8$ is shown. The steep increase of error restricts DP DVR and cubature DVR to calculation of lower eigenvalues. However, for this part of the spectrum, the accuracy of the cubature FBR is similiar at a significantly smaller computational cost.

DVR approximations of eigenvalues which are significantly above $q + 1$ (see also Figure 5).

Figure 4 shows the log of the absolute value of errors in approximating the first (lowest), fourth, and seventh eigenvalues in the Henon−Heiles problem using the four methods. Note the (approximately) linear decrease in log(|error|) for DP DVR, cub DVR, and cub FBR (see also Figure 9). This is a manifestation of the "exponential convergence" discussed in ref 4; that is, the error in a given eigenvalue seems to decrease exponentially with increasing q. Although further tests are required, it seems that DC DVR based on commuting approximations has a much slower convergence rate.

Figure 5 gives the errors in all Henon−Heiles eigenvalues calculated by DP DVR, cubature DVR, and FBR, with $q = 8$.

TABLE 2: Results for the Henon−Heiles Problem[a]

	error, q = 5				error, q = 6				error, q = 7				error, q = 8			
exact	DPDVR	cubDVR	cubFBR	DCDVR	DPDVR	cubDVR	cubFBR	DCDVR	DPDVR	cubDVR	cubFBR	DCDVR	DPDVR	cubDVR	cubFBR	DCDVR
0.998595	0.000000	0.000000	0.000004	-0.000583	0.000000	0.000000	0.000000	0.000548	0.000000	0.000000	0.000000	0.000948	0.000000	0.000000	0.000000	0.000418
1.990077	0.000002	-0.000020	-0.000018	0.003238	0.000000	-0.000003	0.000016	0.000958	0.000000	0.000000	0.000001	0.003651	0.000000	0.000000	0.000000	0.001992
1.990077	0.000029	0.000011	0.000015	0.004465	0.000005	0.000011	0.000017	0.007186	0.000001	0.000001	0.000001	0.003752	0.000000	0.000000	0.000000	0.004129
2.956243	0.000390	0.000646	0.001235	0.019416	0.000100	-0.000024	-0.000003	0.018893	0.000018	0.000030	0.000057	0.017488	0.000003	0.000008	0.000012	0.014750
2.985326	0.000021	0.000096	0.000205	-0.007941	0.000007	-0.000080	-0.000046	0.006673	0.000001	0.000001	0.000065	-0.000627	0.000000	-0.000000	0.000001	0.004717
2.985326	0.000385	0.000397	0.000439	0.021110	0.000101	0.000033	0.000044	0.006768	0.000018	0.000049	0.000069	0.012380	0.000004	0.000007	0.000008	0.005310
3.925964	0.002085	0.008247	0.012930	0.042783	0.000316	0.000567	0.002612	0.025720	0.000053	0.000119	0.000294	0.029820	0.000008	0.000107	0.000177	0.027242
3.925964	0.009038	0.013202	0.015156	0.047230	0.002167	0.002609	0.003520	0.037305	0.000631	0.000727	0.000829	0.030480	0.000140	0.000183	0.000234	0.030645
3.982417	0.003544	0.002335	0.017583	0.006217	0.000896	0.000503	0.001053	0.008038	0.000247	0.000299	0.000441	0.007600	0.000053	0.000168	0.000258	-0.004051
3.985761	0.000953	0.013542	0.015087	0.004630	0.000069	0.000120	0.000164	0.005433	0.000013	-0.000001	0.000047	0.005534	0.000002	0.000066	0.000150	0.016010
4.870144	0.033902	0.022212	0.023024	-0.034251	0.010767	0.015073	0.024217	0.039863	0.003521	0.005985	0.009152	0.053823	0.001157	0.001762	0.001997	0.052571
4.898644	0.012103	0.062193	0.067121	0.058173	0.002472	0.013088	0.022299	0.029489	0.000554	0.002333	0.006797	0.025995	0.000115	-0.000243	0.000040	0.033590
4.898644	0.063453	0.083364	0.084776	0.101734	0.019065	0.020845	0.026372	0.047154	0.005634	0.007465	0.008489	0.049508	0.001703	0.002738	0.002845	0.034745
4.986251	0.007590	0.018426	0.018788	0.031302	0.001705	0.004797	0.026918	-0.034654	0.000371	-0.000159	0.000901	0.004759	0.000082	0.000168	0.000394	0.004980
4.986251	0.041604	0.035273	0.036168	0.206281	0.004043	0.025306	0.027824	0.086615	0.001246	0.002157	0.002502	0.005723	0.000374	0.000496	0.000581	0.005035
5.817019	0.074343	0.169759	0.183062	0.093524	0.038010	-0.016327	-0.000006	-0.031627	0.010861	0.019547	0.044865	0.079910	0.002508	0.016256	0.020598	0.067069
5.817019	0.088449	0.184125	0.189228	0.098149	0.050402	0.065039	0.074163	0.005318	0.026626	0.046871	0.052892	0.086146	0.013211	0.019715	0.022655	0.077801
5.867015	0.131959	0.141751	0.144499	0.145074	0.035440	0.043405	0.048259	0.120179	0.017951	0.023990	0.043697	0.043001	0.011326	0.016940	0.020914	0.030988
5.881446	0.125710	0.169670	0.183892	0.139033	0.091741	0.074274	0.075243	0.111737	0.020381	0.030349	0.043649	0.055245	0.000947	0.007142	0.009268	0.066545
5.991327	0.024169	0.087208	0.094521	0.139699	0.008859	0.026177	0.026267	0.234206	0.001267	0.008610	0.042805	-0.051163	0.000548	-0.001632	-0.000042	0.003661
5.991327	0.054513	0.156798	0.181447	0.143149	0.060769	0.052299	0.052776	0.245441	0.006363	0.033717	0.043550	0.091950	0.002021	0.005755	0.005920	0.004035
6.737916	0.129690	1.460453			0.103292	0.244322	0.263010	0.151273	0.063844	0.015767	0.038018	0.015192	0.029002	0.079671	0.087365	0.129075
6.764867	0.126945	2.183174			0.083200	0.229370	0.237373	0.137574	0.040484	0.006456	0.025891	-0.004370	0.012644	0.057740	0.065547	0.103478
6.764867	0.234379	2.539693			0.205699	0.248368	0.254481	0.167889	0.095193	0.113151	0.120286	0.212621	0.061615	0.082028	0.087563	0.128020
6.853431	0.211197	2.655938			0.125617	0.239564	0.259603	0.185466	0.039408	0.085167	0.116495	0.147852	0.012770	0.050167	0.066336	0.069126
6.853431	0.225570	2.879236			0.165573	0.278270	0.303799	0.299759	0.134080	0.145834	0.150598	0.180184	0.040152	0.058500	0.071238	0.069971
6.998932	0.856438				0.056185	0.194247	0.239916	0.172583	0.010062	0.050151	0.052812	0.308977	0.004160	0.041230	0.062553	-0.075123
6.999387	0.928360				0.066091	0.244404	0.326441	0.210546	0.085883	0.069605	0.071375	0.309626	0.006010	0.051016	0.064820	0.089984
7.659485	0.450972				0.139632	2.743188			0.119957	0.268973	0.303157	0.200509	0.075454	0.065939	0.072652	0.051978
7.659485	0.462141				0.181354	2.988359			0.120481	0.326403	0.347711	0.232315	0.078070	0.124968	0.134088	0.052207
7.697721	1.268657				0.281562	3.054962			0.230206	0.324308	0.363308	0.215646	0.108347	0.178693	0.191378	0.253357
7.736885	1.280679				0.256186	3.343254			0.200339	0.310083	0.351203	0.314408	0.119821	0.167053	0.176641	0.281055
7.832735	1.333181				0.261015	3.762126			0.183422	0.318941	0.407662	0.243146	0.041470	0.138161	0.140757	0.225554
7.832735	2.320738				0.277888	4.105353			0.209372	0.371660	0.420817	0.392391	0.170434	0.240532	0.245858	0.229214
8.009425	2.271808				0.782532	4.130564			0.056054	0.230082	0.258994	0.252006	0.014698	0.087779	0.090166	0.379132
8.009425	3.083438				0.825866				0.105268	0.350205	0.398974	0.286901	0.115704	0.122653	0.122935	0.379204
8.554023					0.434060				0.192347	1.991762			0.146083	0.437525	0.449110	0.301778
8.576351					0.582125				0.178296	2.186544			0.131562	0.420779	0.449360	0.280145
8.576351					0.588688				0.356606	2.530373			0.280127	0.459297	0.464017	0.329332
8.677929					1.113288				0.296154	2.765010			0.228276	0.395689	0.415854	0.424285
8.677929					1.256393				0.355155	2.933068			0.316883	0.541364	0.561665	0.426548
8.811327					1.402949				0.315470	3.094330			0.191449	0.438750	0.461031	0.304290
8.815188					1.399100				0.321572	3.407805			0.239771	0.495176	0.517503	0.519255
9.021723					1.948624				0.671814	3.602606			0.078285	0.434931	0.487885	0.312895
9.021723					2.050122				0.743266	3.819408			0.166246	0.476680	0.553556	0.379001
9.444055					1.848686				0.522405	3.958890			0.224253	5.457143		
9.444055					2.818157				0.532827				0.235971	5.753576		
9.466773					3.017031				0.744734				0.410656	5.791812		
9.552382					3.620778				0.663102				0.378695	5.917146		
9.629394									1.099355				0.402723	6.090892		

[a] This table gives exact eigenvalues and errors (approximate − exact) of the four different methods applied to the Henon−Heiles problem. DP DVR stands for direct product DVR, cub DVR and cub FBR stand for cubature DVR and FBR, and DC DVR stands for the Dawes−Carrington algorithm. All numbers were rounded to six decimal digits.

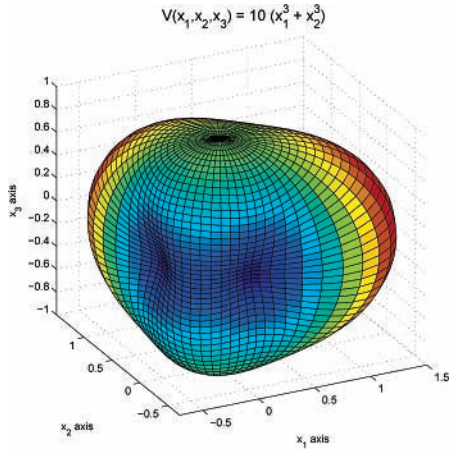

Figure 6. Potential on sphere; illustration of the potential $V(\theta, \varphi) = 10 \sin^3 \theta(\cos^3 \varphi + \sin^3 \varphi)$, which in Cartesian coordinates reads $V(x_1, x_2, x_3) = 10(x_1^3 + x_2^3)$. The plotted surface consists of the points $(0.05V(x_1, x_2, x_3) + 1)$ (x_1, x_2, x_3); that is, standing at any point (x_1, x_2, x_3) on S^2 and looking up (or down) at the plotted surface, its height above (or below) the sphere's surface is the normalized value of the potential function, $0.05V(x_1, x_2, x_3)$.

Thus, 81 eigenvalues are calculated by DP DVR, 57 are calculated by cub DVR, and 45 by cub FBR. For the first 45 eigenvalues, the errors of the three methods are similiar. However, the error steeply rises in the additional eigenvalues provided by DP DVR and cub DVR. These results support our discussion of section 3.2 in favor of cubature FBRs; the additional information calculated by DVRs (eigenvalues 46−81 in this example) may contain large errors. However, cubature DVRs may possibly overcome this problem in the future. Presently, DVR basis functions are arbitrarily chosen from the solutions of problem 3; a refinement is certainly needed.

6.2. DVRs for the Sphere S^2. We now turn to problems on the sphere $\Omega = S^2$ discussed in section 3.2. Consider the Hamiltonian $\hat{H} = \hat{L}^2 + \hat{V}$ where $V(\theta, \varphi) = 10 \sin^3 \theta(\cos^3 \varphi + \sin^3 \varphi)$; in Cartesian coordinates, $V(x_1, x_2, x_3) = 10(x_1^3 + x_2^3)$. Figure 6 gives a plot of this double-well potential; the well centered at the point (−1, 0, 0) is due to negative x_1 values, and the well centered at (0, −1, 0) is due to negative x_2 values.

The results of cubature DVRs and FBRs obtained from nonproduct cubature formulas were compared to those of product cubature FBRs (PC FBR) and to the Dawes−Carrington method (DC DVR). For the latter three methods, the corresponding function spaces are $\mathcal{J} = \mathscr{P}_q^{S^2}$, with $q = 5, 6, 7, 8$, of dimension $(q + 1)^2$, and in each case, spherical harmonics were used as basis functions. In cub DVR, the space $\mathcal{J}$ was extended to $\tilde{\mathcal{J}}$, as explained in section 4.2. The cubature formulas used in cubature DVR and FBR were the 11th degree formula U_3: 11−3 from ref 24 with 62 nodes, and the 13, 15, 17, degree formulas U_3: 13−2.1(1, 0, 1, 0, 2, 0) − 78, U_3: 15−1.1(1, 0, 1, 1, 2, 0) − 86, U_3: 17−1.1(1, 0, 1, 1, 3, 0) − 110, from ref 25 with 78, 86, and 110 nodes, respectively. The nodes of these formulas together with typical DVR functions are illustrated in Figures 7 and 8. The product formulas used for PC FBR were obtained as follows: The θ coordinates of the nodes in a degree $2q + 1$ product formula on S^2 are $\cos^{-1}$ of the $q + 1$ nodes in the degree $2q + 1$ Gauss−Legendre formula on [−1, 1]. The φ coordinates are $m(2\pi/(2q + 2))$, $m = 1, \ldots, 2q + 2$; thus, there are $2(q + 1)^2$ nodes. The weights are products of Gauss−Legendre weights with the constant $1/(2q + 2)$. The product cubature FBRs used here were obtained from such product cubature formulas with $q = 5, 6, 7$, and 8, and the number of nodes in each is 72, 98, 128, and 162, respectively. In ref 30, several methods are compared for constructing representations of spherical Hamiltonians, among which is PC FBR. The conclusion there is that this method is the most accurate and efficient among the alternatives tested. The DC DVR was applied in Cartesian coordinates; that is, commuting approximations of the X_1, X_2, X_3 coordinate matrices were found by discarding small off-diagonal entries, as explained in section 5.2. In all of our numerical examples, the DC DVR points $((\Lambda_1)_{aa}, (\Lambda_2)_{aa}, (\Lambda_3)_{aa})$ were on the sphere S^2; it is not clear at present if this is generally true.

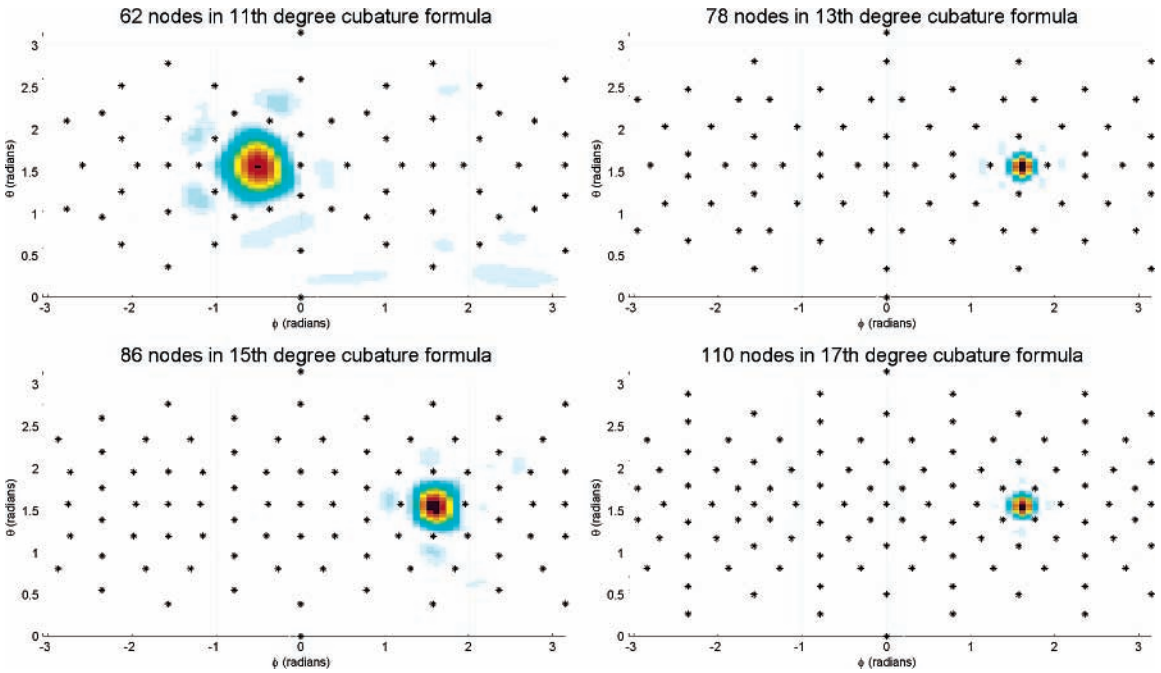

Figure 7. Cubature DVR nodes and functions for S^2; this figure illustrates the nodes in the cubature DVRs used for the double-well problem on the sphere, together with the squared absolute value of typical DVR basis functions. The nodes are those of the 11, 13, 15, and 17 degree cubature formulas from refs 24 and 25 which are specified in the text. DVR basis functions were obtained by solving problem 1 of section 3.1 for these cubature formulas.

TABLE 3: Results for Problem on the Sphere

	error, q = 5				error, q = 6				error, q = 7				error, q = 8			
exact	cubDVR	PCFBR	cubFBR	DCDVR	cubDVR	PCFBR	cubFBR	DCDVR	cubDVR	PCFBR	cubFBR	DCDVR	cubDVR	PCFBR	cubFBR	DCDVR
-4.564174	-0.003017	-0.000680	-0.001801	2.777245	0.000301	0.000159	0.000358	2.503076	-0.000014	0.000028	0.000017	-0.065542	0.000001	0.000000	0.000001	-0.164797
-2.522768	-0.001794	0.008865	0.004725	2.581197	0.000848	0.000092	0.000899	2.387476	0.000018	0.000062	0.000043	1.694697	0.000002	0.000005	0.000005	1.639890
0.255758	0.005581	-0.001080	0.006241	1.159641	-0.000102	0.000655	0.000090	1.026775	0.000049	0.000022	0.000068	-1.069600	0.000002	0.000004	0.000003	-1.125076
2.229091	0.019354	0.026248	0.023769	0.804582	-0.000784	0.000962	-0.000241	0.831997	0.000266	0.000335	0.000314	0.245911	0.000007	0.000018	0.000017	0.214493
4.051134	0.021141	0.014149	0.028142	0.949941	-0.000157	0.002185	0.000711	0.936394	0.000174	0.000069	0.000196	0.324692	0.000011	0.000022	0.000018	0.280967
4.162917	-0.002494	0.016540	0.006038	1.244494	0.001238	0.000536	0.001553	0.980747	0.000068	0.000294	0.000209	0.248456	0.000003	0.000009	0.000011	0.190775
5.873425	0.011223	0.008838	0.015069	0.093475	0.000147	0.001695	0.000235	0.121953	0.000104	0.000004	0.000136	0.120009	0.000004	0.000013	0.000009	0.135917
6.176480	0.004456	0.040351	0.035203	0.274049	0.004089	0.005251	0.006763	0.352457	-0.000819	-0.000674	-0.000754	-0.161189	0.000020	0.000022	0.000030	-0.160582
7.847146	0.000101	0.018945	0.012182	-1.129376	-0.000034	0.000082	0.000769	-0.988807	-0.000043	0.000232	0.000018	-0.040065	0.000005	0.000006	0.000010	0.006304
10.571264	0.038190	0.117508	0.085275	0.770191	0.002520	0.009553	0.008982	0.754284	-0.000672	0.000781	-0.000435	0.425390	0.000017	0.000041	0.000027	0.382957
10.631898	0.045632	0.070075	0.072090	0.944880	0.009650	0.011536	0.011800	0.746239	0.001014	0.000256	0.001227	0.405675	0.000033	0.000066	0.000077	0.356732
11.853191	-0.171764	-0.200608	-0.136266	-0.014278	0.022975	0.017304	0.027232	0.182729	-0.000452	0.002703	0.002323	-0.030994	0.000054	0.000021	0.000088	-0.039996
11.911442	0.053243	0.033762	0.070444	0.137484	-0.000498	0.013246	0.006962	0.198296	0.000703	0.000175	0.000989	-0.050380	0.000007	0.000072	0.000026	-0.021757
12.370341	0.042599	0.011566	0.051707	-0.231977	0.006962	0.009194	0.008679	-0.119824	0.000762	-0.000532	0.000795	0.150429	0.000018	0.000061	0.000036	0.197124
12.840853	-0.018759	0.023166	0.003669	-0.520800	-0.000371	0.004399	0.004079	-0.547168	-0.000340	0.000989	0.000120	-0.283441	0.000004	-0.000005	0.000015	-0.264316
13.294078	0.063419	0.156144	0.087558	-0.831434	0.007459	0.010276	0.010934	-0.772051	0.000346	0.001411	0.000668	-0.357129	0.000023	-0.000002	0.000035	-0.313026
19.020923	-0.287322	-0.068052	-0.248045	0.057002	0.002951	0.039765	0.027313	0.341056	-0.000639	0.005183	0.007110	0.294504	-0.000500	0.000301	-0.000415	0.270952
19.024855	-0.072801	-0.013467	-0.047415	0.220960	0.056286	0.048597	0.067714	0.415566	0.001480	0.005694	0.003662	0.355260	0.000759	0.000199	0.000879	0.302535
19.706739	0.009821	-0.026511	0.086776	-0.279062	0.042739	0.021645	0.059564	0.115867	0.009762	0.014299	0.013485	0.057640	0.000040	0.000471	0.000334	0.036512
19.783650	0.135000	0.246471	0.177195	-0.077819	-0.005447	0.052586	0.008870	0.182823	0.003942	0.007278	0.007635	0.034047	0.000364	0.000459	0.000544	0.032131
20.286198	-0.258738	-0.058256	-0.201283	-0.369555	0.019760	0.030235	0.035207	-0.188756	0.003193	0.002000	0.004044	-0.184861	0.000083	0.000409	0.000120	-0.118286
20.298254	0.116085	0.063482	0.178037	0.098241	0.024167	0.029564	0.028594	-0.041049	-0.002912	0.005800	0.002827	-0.097637	0.000069	-0.000325	0.000109	-0.083819
20.356430	0.229890	0.019675	0.244418	0.206082	0.030366	0.048716	0.048972	-0.085554	0.006179	0.004559	0.007890	0.053645	0.000006	0.000464	0.000093	0.041167
20.643964	0.119021	0.110057	0.145382	0.055894	0.042474	-0.037022	0.049740	-0.315185	-0.008107	0.004014	0.004359	-0.206027	0.000526	0.000696	0.000816	-0.168348
20.726590	0.379144	0.807376	0.552623	0.057697	-0.019070	0.064421	-0.010097	-0.382565	0.004940	0.010904	0.008608	-0.213559	0.000277	0.000311	0.000507	-0.171699
29.291987	0.220238	0.714643	0.719833	-1.611612	-0.095765	-0.134730	-0.067421	-0.572556	-0.008360	0.024100	0.015474	0.149463	0.001784	0.003325	0.003869	0.193949
29.293494	0.401238	0.715092	0.728574	-1.269847	-0.078555	0.128371	-0.062293	-0.127194	0.022947	0.038626	0.046412	0.287199	0.002179	0.003587	0.003059	0.238158
29.703363	0.652310	0.857810	0.887823	-1.247244	-0.309156	-0.209834	-0.272630	-0.403942	0.026646	0.055488	0.056112	-0.000382	0.002267	0.005802	0.005076	0.018911
29.716363	0.793485	1.085193	1.077708	-0.910398	0.106220	0.051102	0.123477	-0.095118	0.034110	0.065303	0.059864	0.096105	0.004259	0.005472	0.006181	0.046921
30.159471	0.467864	0.908975	0.714926	-1.284536	-0.282942	-0.256963	-0.274360	-0.302555	-0.047467	-0.006274	-0.015417	-0.224864	0.003560	0.004786	0.005352	-0.167637
30.161245	0.632057	0.915777	1.061430	0.208173	-0.216089	-0.155044	-0.196536	-0.066898	0.017685	0.025514	0.044366	-0.151029	0.002308	0.004751	0.004396	-0.079888
30.183635	0.659771	0.967518	1.123667	1.611845	0.101631	-0.008325	0.148786	0.165940	0.015771	0.034557	0.023711	-0.068470	0.001178	0.001271	0.002063	-0.044017
30.212557	0.731718	1.105261	1.310408	1.642066	0.297594	0.157076	0.301701	0.255993	0.002651	0.022108	0.018470	-0.060481	0.001138	0.002830	0.002323	0.059788
30.296161	0.954175	1.385575	1.293847	2.310786	0.316863	0.270404	0.334886	0.365316	0.036816	0.023252	0.042476	-0.026534	0.001971	0.003917	0.003375	0.021111
30.445755	0.990548	1.309871	1.479880	2.214337	0.182603	0.135351	0.217110	0.277405	-0.051823	-0.025790	-0.037363	-0.045445	0.003046	0.004622	0.005386	-0.106846
30.477131	2.304622	2.838875	2.579330	3.082443	0.467866	0.831508	0.511291	0.539226	0.050823	0.086658	0.082243	0.054070	0.004183	0.006355	0.006494	-0.039562
41.468987	11.446208				0.389748	0.533924	0.534017	-2.246029	-0.272715	-0.117400	-0.259694	-0.106246	0.013345	0.031063	0.025825	0.074512
41.469564	13.052851				0.484496	0.539181	0.538542	-1.512979	-0.095061	-0.016215	-0.070150	0.003935	0.025196	0.033665	0.037057	0.154610
41.718463	14.883231				0.647509	0.713718	0.688002	-1.521911	-0.296306	-0.132207	-0.277001	-0.201697	0.025125	0.035462	0.034078	-0.073519
41.721214	17.521087				0.686920	0.863687	0.911428	-1.357439	-0.059477	-0.078312	-0.034349	-0.160790	0.026694	0.041992	0.047171	0.041393
42.036347	18.618229				0.420139	0.704447	0.673379	-1.339846	-0.251891	-0.200957	-0.198651	-0.329795	0.023579	0.025127	0.037671	-0.157994
42.042876	23.434579				0.534692	0.773143	0.738087	-1.120236	-0.082176	-0.147873	-0.055794	-0.300314	0.019595	0.037450	0.032918	-0.085514
42.123245	25.407586				0.544753	0.874102	0.734173	-0.112610	-0.158897	-0.050573	-0.110860	-0.275247	0.015416	0.019094	0.024355	-0.059058
42.125840	26.612733				0.575418	0.917106	0.762259	1.681443	-0.073350	0.072505	-0.052369	-0.190838	0.014228	0.025511	0.022333	0.008119
42.173999	27.237635				0.794832	1.081393	0.958162	1.934344	0.060507	0.051243	0.092434	0.007816	0.022116	0.023972	0.031251	-0.013244
42.214949	30.233350				0.980636	1.076810	1.133215	2.090458	0.040785	0.056097	0.073506	0.167649	0.015273	0.027856	0.024859	0.011924
42.215904	32.449262				1.639584	1.185489	1.839535	2.577004	0.312548	0.235297	0.319804	0.289688	0.016078	0.028956	0.027901	0.055575
42.324108	34.916290				1.592439	1.146159	1.760840	3.131057	0.282828	0.158473	0.285438	0.260174	0.021705	-0.015940	0.029153	0.062986
42.338642	36.011735				1.593863	2.651312	1.813688	3.322794	0.659065	0.805566	0.769089	0.424136	0.012881	0.061838	0.023535	0.121911
55.588705	23.937626				47.222084				-0.159746	0.413655	0.413714	-3.470509	-0.409245	-0.235364	-0.399986	-0.360051
55.588871	26.407265				48.749309				0.179722	0.418190	0.417597	-3.232754	-0.122594	0.001943	-0.112019	-0.185121
55.745631	26.868760				54.368934				0.206709	0.601606	0.570245	-2.496484	0.149842	-0.091311	0.151177	-0.290863

[a] This table gives exact eigenvalues and errors (approximate − exact) of the four methods applied to the double-well Hamiltonian $\hat{H} = \hat{L}^2 + 10 \sin^3 \theta(\cos^3 \varphi + \sin^3 \varphi)$ on the sphere. PC FBR stands for product cubature FBR, cub DVR and cub FBR stand for cubature DVR and FBR, and DC DVR stands for the Dawes−Carrington algorithm. All numbers are rounded to six decimal digits.

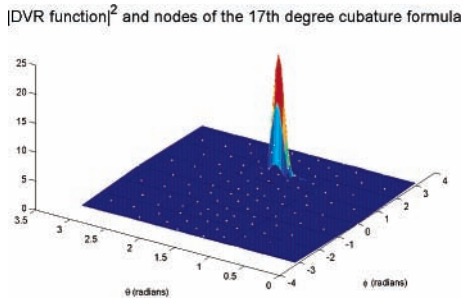

Figure 8. Typical DVR function; the squared absolute value $|f_\alpha|^2$ of a typical DVR basis function f_α is shown here, together with the nodes of the corresponding degree 17 cubature formula used for the double-well problem on the sphere.

The results for the four methods applied to the double-well problem above are given in Table 3 and Figures 9 and 10. The "exact" values of the E_i were obtained using PC FBR with $q = 19$, a value for which the first 81 eigenvalues were converged to 11 decimal digits (Table 3 gives the first 52 eigenvalues). Note that here PC FBR is not associated with a tensor product function space. Rather, the same spherical harmonics function space that is used in cub FBR and DC DVR is also used in PC FBR. This is the reason that the corresponding columns in Table 3 have equal length whereas in Table 2 the DP DVR column is longer. Examination of Table 3 shows that, as in the Henon−Heiles problem, an abrupt cub DVR error increase occurs at the first eigenvalue which is significantly greater than $q(q+1)$. For each $q = 5, 6, 7, 8$, this is the maximal $\hat{L}^2$ eigenvalue of the spherical harmonic basis functions of $\mathcal{J}$.

Similiar to the Henon−Heiles problem, the results in Figures 9 and 10 and Table 3 illustrate the good performance of cubature DVRs and FBRs relative to PC FBR and to DC DVR. Moreover, Figure 9 indicates that the error in DC DVR decays comparatively slowly with increasing q. However, the steep increase of error in the *additional* eigenvalues produced by cubature DVR (see Figure 10) suggests that the arbitrary choice of DVR functions in the solution of problem 3 should be refined.

7. Discussion and Conclusion

The concept of DVR sets was introduced in ref 4 as a general framework for future development of multidimensional nonproduct DVRs (the Dawes−Carrington DVRs[13] present an alternative framework; as far as we can see, the DC DVR functions are not projected δ functions) (see section 2.2). However, except for cases which are simplified by symmetry (see refs 5 and 6), the calculation of DVR sets remained an open problem. In section 3.1, we formulated the problem of calculating DVR sets based on cubature formulas as a linear algebra problem and solved it in full generality. Our solution can give families of DVR sets associated with any known cubature formula; previously, only a few nonproduct DVR sets were known. As an illustration, we calculate four new nonproduct cubature DVRs with up to 110 points for the sphere and 4 for the plane.

We show that cubature formulas can also give cubature FBRs (see section 3.2). In contrast to the one-dimensional and direct product cases, the multidimensional cubature FBRs we suggest do not use the same function space as the corresponding DVRs. Rather, cubature FBRs include a projection to a low energy subspace. The accurate results produced by cubature FBRs, the relatively low dimensional function spaces used, and the ease of application all suggest that cubature FBRs can be useful. This observation is supported by the work of Wang and Carrington,[7] which use an FBR based on Lebedev−Laikov cubature[21] to find bend eigenfunctions of an HF trimer.

Except for product cubature formulas and for refs 5 and 7, the connection between DVRs, FBRs, and multidimensional integration formulas has been largely overlooked. Our findings

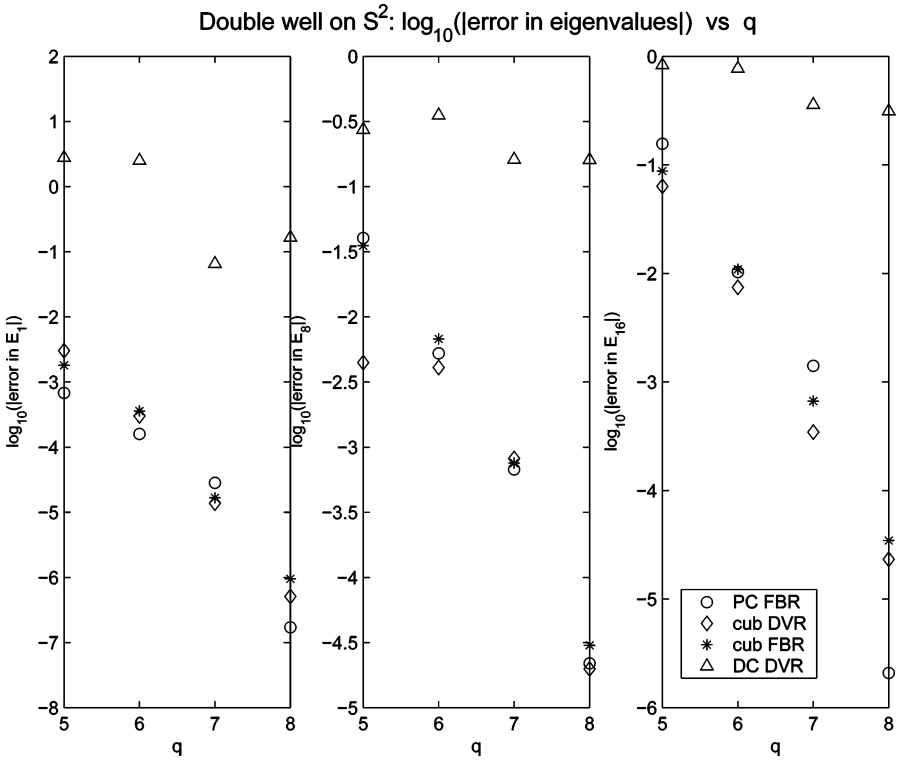

Figure 9. Performance comparison; this figure shows the log of the error in approximating the 1st, 8th, and 16th eigenvalues vs q of the double-well problem with $V(\theta, \varphi) = 10 \sin^3\theta(\cos^3\varphi + \sin^3\varphi)$. Note the rapid decay of error with increasing q in cub DVR, cub FBR, and PC FBR but not in DC DVR. Note that the errors in PC FBR and cub FBR are similar, although the latter requires significantly less computational effort.

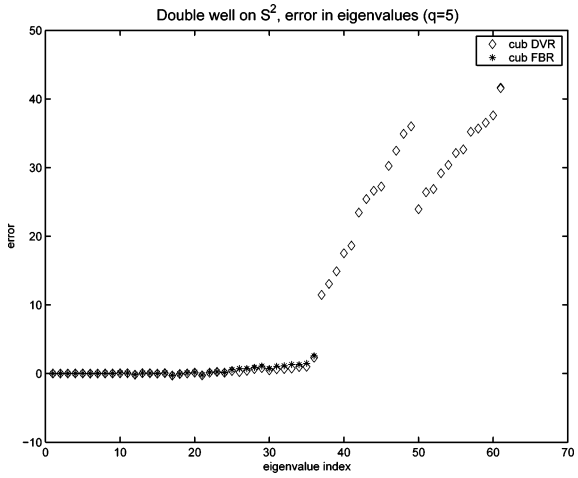

Figure 10. Large error in high DVR eigenvalues; here, we show the error in eigenvalues calculated by cubature DVR, and cubature FBR, for the double-well problem with $V(\theta, \varphi) = 10 \sin^3 \theta(\cos^3 \varphi + \sin^3 \varphi)$. Both cub DVR and cub FBR were based on the degree 11 cubature formula specified in the text. The steep increase of error in cubature DVR may be due to the arbitrary choice of solution in problem 3.

establish general relations between nonproduct cubature formulas and multidimensional DVRs and FBRs. This opens the door to using any member in the menagerie of existing (positive weight) cubature formulas for DVR and FBR calculations.

Multidimensional DVR algorithms are inextricably connected with commuting matrix representations of coordinate operators. This connection is recognized and explicitly used in ref 13 and in direct product DVRs; as explained here in section 2.2, this connection is also implicit in refs 5 and 6. In section 3.1, we showed that the coordinate matrices in cubature DVRs derived from an odd degree formula are *commuting extensions* of noncommuting coordinate matrices. This draws another connection to cubature theory, where an equivalence was shown to exist between cubature formulas and commuting extensions of coordinate matrices on weighted polynomial spaces.[8−10]

Several issues in our approach are presently open and call for further research.

With the exceptions of refs 21 and 22, there are not that many high degree nonproduct cubature formulas available. DVR and FBR calculations would benefit from finding new, very high order (of at least several dozen), cubature formulas for relevant domains and weight functions. It should be examined whether the methods used by Lebedev and Laikov to calculate cubatures on the sphere, of degree up to 131, can be extended to other domains and higher degrees. Additionally, a fresh and almost unexplored point of view on the problem of calculating cubatures is offered by their equivalence to commuting extensions of coordinate matrices on spaces of weighted polynomials, as described in refs 8−10.

The problem of constructing cubature DVR sets based on a known cubature rule was formulated here in problem 3 and was solved in section 3.1. The solution allows some freedom in the choice of cubature DVR sets. Figures 5 and 10 indicate that criteria for optimizing the choice of DVR sets from among the full family of solutions should be introduced. One possible approach is to require that the DVR coordinate matrices, whose matrix elements are calculated using the cubature formula, will be as close as possible to coordinate matrices calculated with the exact inner product. In an appropriate basis, this is equivalent to requiring that the extension blocks in the commuting extensions associated with a cubature DVR will be as close as possible to the same blocks in the exact coordinate matrices. However, it should be kept in mind that our understanding of nonproduct multidimensional DVRs is still preliminary; it may turn out that the results in Figures 5 and 10 are a manifestation of an inherent problem in the DVR approach.

Molecular Hamiltonians are often composed of a sum of several sub-Hamiltonians and a coupling potential term. It is often desirable to represent the problem in spaces spanned by products of eigenfunctions of the sub-Hamiltonians. This is the idea of potential optimized DVR which is extended to multidimensional sub-Hamiltonians in ref 13. The basic step in ref

```
[nodes,wts] = input nodes and weights of a degree 2q or 2q+1 cubature formula;
q = input q;
n = dim𝒫q^Ω; N = length(wts);
ω = diag(wts); ω^1/2 = sqrt(ω);

q1 = q;
for k = 1:a sufficiently large integer     % increase q1 till solution is found
   n1 = dim(𝒫q1^Ω);
   Φ = construct_Φ(n1,nodes);
   if rank(Φ) == N
      K = null(Φ);
      E = [eye(n); zeros(n1 - n, n)];
      Y = null([E, K]');
      B1 = E'*Φ'*ω*Φ*Y;
      K1 = E'*K;
      if norm(K1*(pinv(K1)*B1) - B1) < 0.00001     % check that eq (??) is solvable
         [dummy,cY] = size(Y);
         [dummy,D,R] = svd( Y'*Φ'*ω*Φ*Y - eye(cY) );
         if min(diag(D)) > 0.00001                 % find r = rank(D)
            r = N-n;
         else
            for r = 1:(N-n)
               if D(r,r) < 0.00001
                  r = r-1;
                  break
               end
            end
         end
         Δ = sqrt(D(1:r,1:r));
         B = B1 * R(:,1:r)*inv(Δ);
         κ = null(K1);
         κ⊥ = null(κ');
         C1 = pinv(K1*κ⊥)*B;
         if (max(svd(C1)) < 1)
            break     % if I-C1*C1 is positive semi-def then we have a solution
         end
      end
   end
   q1 = q1+1;
end
```

```
if rank(Φ) != N
   'no solution with tried values of q1:  rank Φ != N'
   return
elseif norm(K1*κ⊥*C1*[Δ, zeros(r, N-n-r)]*R' - B1) > 0.000001
   'no solution with tried values of q1:  K1*C1 != B1'
   return
elseif max(svd(C1)) > 1.000001
   'no solution with tried values of q1:  singular vals of C1 are too big'
   return
end

[dummy, cC1] = size(C1);
[dummy,D1,R1] = svd(eye(cC1) - C1'*C1);
[dummy,ckappa] = size(κ);
L1 = [eye(cC1); zeros(ckappa - cC1,cC1)]; % choose any L1 with orthonormal columns
C0 = L1*sqrt(D1) * R1';

L = (κ⊥*C1 + κ*C0);
C = L * [Δ, zeros(r, N-n-r)] * R';

 W = (Φ*[E,Y]) \ inv(ω^1/2);
 U = [E,Y + K*C]*W;

ErrInprodU = U'*U - eye(N);     % check that U solves problem 2
errUU = norm(ErrInprodU(:),inf)
ErrValsU = norm(Φ*U - inv(ω^1/2),inf)

X = U \ E;
errX = U*X - E;
ErrReproduce𝒫q^Ω = norm(errX(:),inf)
```

Figure 11. Matlab code for constructing DVR sets. This figure gives the code implementing the construction of DVR sets explained in section 2.2. Note that we use (mostly) Matlab syntax; particularly, A' means A transpose conjugate. However, "not equal" is denoted "!=" which is different from the Matlab "∼=".

13 is forming commuting approximations of coordinate matrices on spaces spanned by eigenfunctions of the sub-Hamiltonians. It would be interesting to check the possibility of replacing these commuting approximations with commuting extensions. To do this, the problem of computing commuting extensions on such spaces of functions (which are not spaces of weighted polynomials) needs to be addressed.

Acknowledgment. This work grew from our earlier paper[8] done jointly with Jeremy Schiff. We thank Ronny Hadani, Jeremy Schiff, and Gal Zahavi for useful discussions and the anonymous referees for their useful remarks. We thank Robert McLachlan for bringing to our attention the literature on spherical designs,[31] which are high symmetry cubature rules for spheres.

References and Notes

(1) Harris, D. O.; Engerholm, G. G.; Gwinn, W. D. *J. Chem. Phys.* **1965**, *43*, 151.
(2) Light, J. C.; Carrington, T., Jr. *Adv. Chem. Phys.* **2000**, *114*, 263.
(3) Light, J. C. Discrete variable representations in quantum dynamics. In *Time-dependent quantum molecular dynamics*; Plenum Press: 1992.
(4) Littlejohn, R. G.; Cargo, M.; Carrington, T., Jr.; Mitchell, K. A.; Poirier, B. *J. Chem. Phys.* **2002**, *116*, 8691.
(5) Cargo, M.; Littlejohn, R. G. *J. Chem. Phys.* **2002**, *117*, 59.
(6) Littlejohn, R. G.; Cargo, M. *J. Chem. Phys.* **2002**, *116*, 7350.
(7) Wang, X. G.; Carrington, T., Jr. *J. Theor. Comput. Chem.* **2003**, *2*, 599.
(8) Degani, I.; Schiff, J.; Tannor, D. J. *Num. Math.* **2005**, *101*, 479. Download cubature formulas from http://www.math.biu.ac.il/∼schiff/commext.html.
(9) Degani, I. RCMS−Right Correction Magnus Schemes For Oscillatory ODEs and Cubature Formulae and Commuting Extensions. Ph.D. Thesis, Feinberg Graduate School, Weizmann Institute of Science, 2004.
(10) Xu, Y. *Common zeros of polynomials in several variables and higher dimensional quadrature*; Pitman research notes in mathematics; Longman: Essex, U.K., 1994.
(11) Golub, G. H.; Welsch, J. H. *Math. Comput.* **1969**, *23*, 221.
(12) Dickinson, A. S.; Certain, P. R. *J. Chem. Phys.* **1968**, *49*, 4209.
(13) Dawes, R.; Carrington, T., Jr. *J. Chem. Phys.* **2004**, *121*, 726.
(14) Light, J. C.; Hamilton, I. P.; Lill, J. V. *J. Chem. Phys.* **1985**, *82*, 1400.
(15) Shizgal, B.; Blackmore, R. *J. Comput. Phys.* **1984**, *55*, 313.
(16) Kanfer, S.; Shapiro, M. *J. Phys. Chem.* **1984**, *88*, 3964.
(17) Degani, I. *Hilbert spaces of functions and cubature formulae*, in preparation. Matlab code for the solution of problem 2 is available at http://www.weizmann.ac.il/chemphys/ilan.
(18) Tannor, D. J. *Introduction to Quantum Mechanics: A Time Dependent Perspective*; University Science Books: Sausalito, CA, 2005.
(19) Sugihara, M.; Matsuo, T. *J. Comput. Appl. Math.* **2004**, *164*−*165*, 673.
(20) Wang, X. G.; Carrington, T., Jr. *J. Chem. Phys.* **2003**, *119*, 101.
(21) Lebedev, V. I.; Laikov, D. N. *Dokl. Math.* **1999**, *59*, 477.
(22) Sloan, I. H.; Womersley, R. S. *Adv. Comput. Math.* **2004**, *21*, 107. Download formulas from Womersley's site http://web.maths.unsw.edu.au/rsw/sphere/.
(23) Cools, R. *J. Complexity* **2003**, *19*, 445. Internet site http://www.sc.kuleuven.ac.be/∼nines/ research/ecf/ecf.html.
(24) Stroud, A. H. *Approximate Calculation of Multiple Integrals*; Prentice Hall: Englewood Cliffs: New Jersey, 1971. Download formulas from J. Burkardt's site http://www.csit.fsu.edu/∼burkardt/f src/stroud/stroud.html.
(25) De Wit, D. arXiv:math.NA/0003018, 2000.
(26) Heo, S.; Xu, Y. *J. Comput. Appl. Math.* **1999**, *112*, 95.
(27) Bunse-Gerstner, A.; Byers, R.; Mehrmann, V. *SIAM J. Matrix Anal. Appl.* **1993**, *14*, 927. Cardoso, J. F.; Souloumiac, A. *SIAM J. Matrix Anal. Appl.* **1996**, *17*, 161.
(28) Feit, M. D.; Fleck, J. A., Jr.; Steiger, A. *J. Comput. Phys.* **1982**, *47*, 412.
(29) Schiff, J.; Degani, I.; Tannor, D. J. http://www.math.biu.ac.il/∼schiff/commext.html.
(30) Sharafeddin, O.; Light, J. C. *J. Chem. Phys.* **1995**, *102*, 3622.
(31) Hardin, R. H.; Sloane, N. J. *Discrete and Computational Geometry* **1996**, *15*, 429. De La Harpe, P.; Pache, C. 2005 ariXiv:math.CO/0502312.