Some useful discrete variable representations for problems in time-dependent and time-independent quantum mechanics

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We develop a simple, yet powerful approach to constructing discrete variable representations for the solution of quantum mechanical problems by focusing on properties of the underlying basis set. Two examples, one involving fixed-node boundary conditions and the other periodic boundary conditions, are explicitly derived and applied to a problem in spherical polar coordinates with azimuthal symmetry. These two DVRs have equally spaced points and equal weights.

1. Introduction

Light and coworkers [1,2] have pioneered the use of so-called discrete variable representations (DVRs) in quantum mechanical problems. The basic idea of a DVR is applicable whenever two conditions are satisfied: (1) there is a basis set $\{\psi_n(x); n=1, N\}$ in which to expand the wavefunction for a system, and (2) a (Gaussian) quadrature rule consisting of a set of quadrature points $\{x_n; n=1, N\}$ and weights $\{w_n; n=1, N\}$ is used to compute matrix elements in this basis [1]. When these conditions are satisfied, there exists an isomorphism, originally pointed out by Dickinson and Certain [3], between the finite basis representation (FBR) in $\{\psi_n\}$ and a discrete representation of coordinate eigenfunctions based on the quadrature points. This isomorphism is the result of the existence of a unitary transformation between the two representations; the quadrature points are the eigenvalues of the FBR (employing the Gaussian quadrature rule) of the coordinate operator [4], so that the corresponding eigenvector matrix specifies the transformation between the "coordinate eigenfunctions" and the original basis functions [1,3].

While Dickinson and Certain [3] explored the use of this transformation to a DVR for the facile evaluation of matrix elements in the context of the FBR, Light and coworkers [1,2] have focused on the use of the DVR as the primary representation. While most of the work of Light's group has been applied to grid-method solutions to time-independent problems, the popular FFT (fast Fourier transform) method of Kosloff and Kosloff [5] for propagating wavepackets may be viewed as a discrete variable representation for time-dependent problems. Marston and Balint-Kurti [6] have also recently applied the FFT method to time-independent problems.

The types of Gaussian quadrature rules employed by Light and coworkers do not include the end points of the integration variable as quadrature points. This makes it difficult to apply explicit boundary conditions at the end points of the interval. Manolopoulos and Wyatt [7], however, employed the Gauss–Lobatto quadrature rule, which explicitly includes the end points of the integration interval as quadrature points, in the context of a solution to the time-independent Schrödinger equation. Instead of focusing on the "points" per se, they constructed "Lobatto shape functions", as they termed the set of Lagrange polynomials defined by these quadrature points, which they used as the primary representation. These basis functions have by construction the Kronecker delta property at the quadrature points, and they can be differentiated analytically to evaluate the action of momentum operators on the wavefunction.

Lin and Muckerman [8–10] have extended the approach of Manolopoulos and Wyatt to time-de-

pendent problems and to the use of more general classes of Gaussian quadrature rules which include the end points of the integration interval in solving both the time-dependent and time-independent Schrödinger equations. Here the wavefunction was approximated by the Lagrange interpolating polynomial from its values at the grid points. This approach thus employs the Lagrange polynomial as the primary representation. Control over the spacing of grid points is achieved by selecting different members of the Gauss–Bouzitat or Gauss–Markov classes of quadrature. The sets of Lagrange polynomials defined by the points of the quadrature rule selected were used as the basis for expanding the wavefunction describing either a time-dependent or time-independent system. These basis functions also have the Kronecker delta property at the grid points, and can be written in analytical form without diagonalizing the matrix representation of the coordinate. The implicit "original" basis in this approach is the particular set of orthogonal polynomials underlying the quadrature rule selected.

The advantages of this so-called LGB (Lagrange–Gauss–Bouzitat) [8,9] or LGM (Lagrange–Gauss–Markov) [8,10] approach to time-dependent problems over the FFT method are: (1) it is not necessary to transform of the wavefunction into momentum space at each step in the propagation; (2) there is no noise level limiting the accuracy of the evaluation of the action of either the kinetic or potential energy operators; (3) it is more convenient for the application of fixed-node boundary conditions at the end points; (4) there are no special requirements pertaining to the optimum number of grid points; and (5) non-Cartesian coordinate systems, which have kinetic energy operators involving both coordinate and momentum operators in a single term, can be straightforwardly handled. The principal disadvantages of this approach are: (1) it scales as N^2 rather than $N \log N$, however all the overhead of stuffing and unstuffing the input and output arrays of numerical FFT routines is totally avoided; and (2) the relevant quadrature rules tend to bunch the points near the end points, which may be "wasteful", while the FFT method employs equally spaced points.

We explore here another approach to the construction of DVRs for both time-dependent and time-independent problems in quantum mechanics which focuses primarily on incorporating convenient properties of the *original* basis $\{\psi_n\}$ into the basis used for the primary representation. A secondary consideration, which turned out to be easily satisfied, was to obtain more evenly spaced grid points than in the LGB or LGM methods without loss of accuracy.

2. Approach

We begin by specifying a basis set, which need not consist of orthogonal polynomials, that has certain desired properties such as fixed nodes at the end points of the coordinate interval. As above, we will denote this basis by $\{\psi_n;\ n=1, N\}$. What we seek is a basis of "coordinate eigenfunctions" $\{u_j;\ j=1, N\}$, *and* a generalized quadrature rule consisting of a set of points $\{x_k;\ k=1, N\}$ and weights $\{w_k;\ k=1, N\}$ such that the $\{u_j\}$ satisfy the Kronecker delta property

$$u_j(x_k)=\delta_{jk} \tag{1}$$

at the quadrature (grid) points. Let us assume the existence of such a quadrature rule, so that the points and weights are implicitly defined. At a later stage of the development, we will have to define it explicitly.

We may construct a projection operator from the $\{\psi_n\}$,

$$\mathscr{P} \equiv \sum_{n=1}^{N} |\psi_n\rangle\langle\psi_n| = 1 , \tag{2}$$

where the second equality in eq. (2) is a statement of closure in the space spanned by the basis $\{\psi_n\}$. We then project our unknown functions $\{u_j\}$ onto this space:

$$u_j(x) = \sum_{n=1}^{N} \psi_n(x)\langle\psi_n|u_j\rangle . \tag{3}$$

Eq. (3) would be nothing more than a tautology if it were not for two features of the matrix element on its right-hand side. The first is that it is in the spirit of a DVR to evaluate this matrix element by quadrature [1],

$$\langle\psi_n|u_j\rangle \approx \sum_{k=1}^{N} w_k\, \psi_n^*(x_k)\, u_j(x_k) \tag{4}$$

and the second is that, while the continuous function $u_j(x)$ is unknown, its values at the quadrature points

are by definition given by eq. (1). Thus we may write

$$\langle \psi_n | u_j \rangle = w_j \psi_n^*(x_j) \tag{5}$$

or

$$u_j(x) = w_j \sum_{n=1}^{N} \psi_n(x)\, \psi_n^*(x_j)\,. \tag{6}$$

Eq. (6) is the central result of this approach. Once an appropriate quadrature rule is specified, which will depend upon the choice of basis functions $\{\psi_n\}$, the $u_j(x)$ are analytical functions which can readily be differentiated and tabulated at the grid points. They are constructed without recourse to numerical matrix diagonalization and are not subject to any inaccuracies associated with numerical eigenvectors.

2.1. Example 1: a fixed-node DVR

As a concrete example of the use of the present approach to the construction of a DVR, consider the application of fixed-node boundary conditions to the solution of the Schrödinger equation. In the FFT method this would require special procedures: one must either use a sine transform, which is less efficient than the general transform, or "force" the general transform to be a sine transform by doubling the number of grid points and making the wavefunction antisymmetric over the doubled interval [11]. In the present approach, we simply choose the original basis $\{\psi_n\}$ to be particle-in-a-box eigenfunctions

$$\psi_n(x) = \sqrt{\frac{2}{\pi}} \sin nx \tag{7}$$

for $0 \leqslant x \leqslant \pi$ and $n = 1, N$. The desired nodal structure is built into this basis.

With this choice of basis, eq. (6) becomes

$$u_j(x) = \frac{2w_j}{\pi} \sum_{n=1}^{N} \sin nx \sin nx_j\,. \tag{8}$$

The specification of an appropriate quadrature rule in this case is guided by the fact that $\sin(N+1)x$ is the lowest-order function not included in the original basis, and has evenly spaced zeros

$$x_k = \frac{k\pi}{N+1}, \quad k = 1, N\,. \tag{9}$$

By defining $g(x) = f(x)/\sin^2 x$ and $y = \cos x$, we have

$$\int_0^{\pi} f(x)\,\mathrm{d}x = \int_0^{\pi} g(x) \sin^2 x\,\mathrm{d}x$$

$$= \int_{-1}^{1} g(\cos^{-1} y)\sqrt{1-y^2}\,\mathrm{d}y\,. \tag{10}$$

The second line of eq. (10) is in the form of a Gauss–Chebyshev quadrature of the second kind, with points given by eq. (9) and adjusted weights $w_k = \pi/(N+1)$ [12],

$$\int_0^{\pi} f(x)\,\mathrm{d}x \doteq \sum_{k=1}^{N} w_k f(x_k)\,. \tag{11}$$

Using this quadrature rule, we have

$$u_j(x) = \frac{2}{N+1} \sum_{n=1}^{N} \sin nx \sin nx_j \tag{12}$$

with equally spaced points and equal weights. Fig. 1a shows $u_1(x)$ for the case of $N = 13$, and fig. 1b shows that complete set of the $u_j(x)$ for that case. The Kronecker delta property is obviously satisfied.

2.2. Example 2: a periodic DVR

In this second example we will employ a Fourier basis similar to that used in the FFT method [5]. Here we take as the original basis

$$\psi_n(x) = \frac{1}{\sqrt{2\pi}} \exp(\mathrm{i}k_n x) \tag{13}$$

with $-\pi \leqslant x \leqslant \pi$ and $k_n = \frac{1}{2}(2n - N - 1)$ for $n = 1, N$ where N is any *odd* integer. Using this basis of (complex) plane waves, the $u_j(x)$ become the *real* functions

$$u_j(x) = \frac{w_j}{2\pi} \sum_{n=1}^{N} \cos[k_n(x - x_j)]\,. \tag{14}$$

Further, we define $y = \cos[\frac{1}{2}(x+\pi)]$ and write

$$\int_{-\pi}^{\pi} f(x)\,\mathrm{d}x = \int_{-\pi}^{\pi} \frac{f(x)}{\sin x} \sin x\,\mathrm{d}x$$

$$= 2 \int_{-1}^{1} \frac{f(x(\cos^{-1} y))}{\sqrt{1-y^2}}\,\mathrm{d}y\,, \tag{15}$$

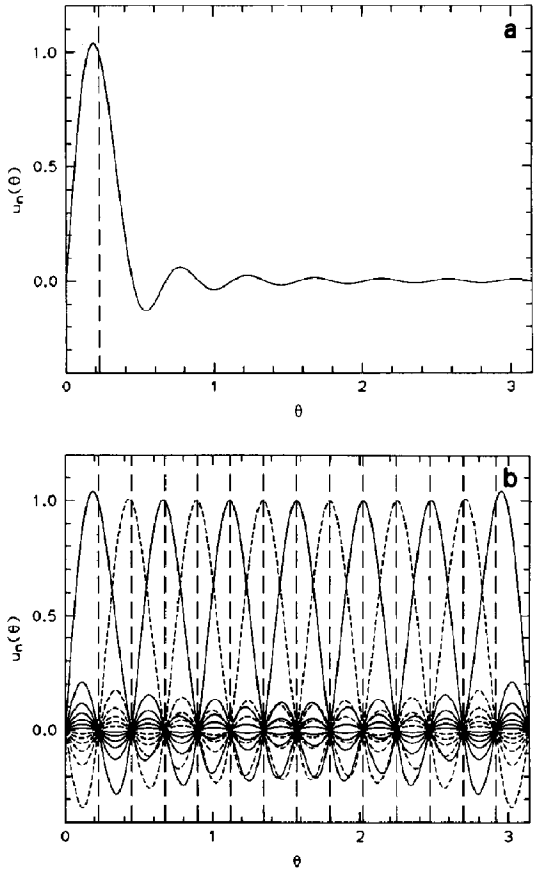

Fig. 1. Continous "coordinate eigenfunctions", $u_j(\theta)$, of a fixed-node DVR derived from a basis of 13 particle-in-a-box eigenfunctions: (a) $u_1(\theta)$ alone; and (b) the entire set $\{u_j(\theta); j=1, 13\}$. Dashed vertical lines indicate the positions of the equally spaced grid points, θ_k. The Kronecker delta property of the functions is apparent.

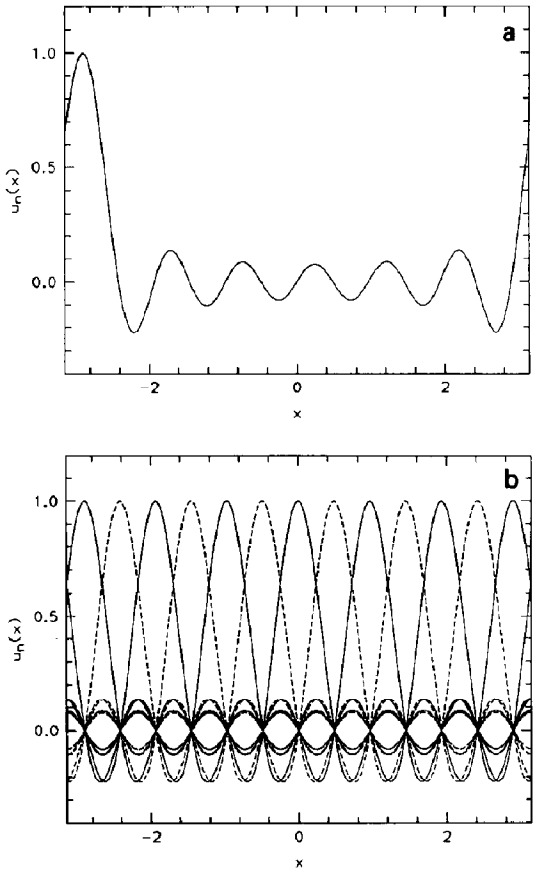

Fig. 2. Same as fig. 1 except for a periodic DVR derived from a basis of 13 plane waves: (a) $u_1(x)$ alone; and (b) the entire set of $\{u_j(x); j=1, 13\}$. The periodicity of the functions is obvious from panel (a), and the Kronecker delta property from panel (b).

which is the form of the Gauss–Chebyshev quadrature of the first kind with equally spaced points

$$x_k = \frac{(2k-N-1)\pi}{N} \tag{16}$$

and equal scaled weights $w_k=2\pi/N$ [12]. Fig. 2a shows $u_1(x)$ for this periodic basis for the case of $N=13$, and fig. 2b shows the complete set of $u_j(x)$. The periodicity is obvious from fig. 2a, and the Kronecker delta property is apparent in fig. 2b.

3. Applications

The two example DVRs constructed in section 2 are useful in the solution of a wide variety of quantum mechanical problems. We will demonstrate this usefulness by solving a two-dimensional, time-dependent problem in which one of the variables is treated with the periodic DVR and the other with the fixed-node DVR.

Lin and Muckerman have applied the LGM method to the multiphoton excitation of a rotating Morse oscillator representing the HF molecule by an intense infrared laser [10]. This model was studied by quasiclassical trajectory techniques by Noid and Stine [13]. Related quantum mechanical investigations have been carried out by Walker and Preston [14], Leasure and Wyatt [15], and Dardi and Gray [16]. We repeat here one of the cases studied by Lin and Muckerman corresponding to resonant

(0,0)→(1,1) excitation [10] using the DVRs constructed above instead of those of the LGM type. We also consider the effect of simultaneous irradiation by a second, red-shifted laser with parallel polarization. Two-laser irradiation of HF has been studied classically by Stine and Noid [17,18].

Following the development of Lin and Muckerman [10], we represent the Hamiltonian and the wavefunction in correspondence rule form [19,20] in spherical polar coordinates. For an HF molecule initially in the rotational ground state, the Hamiltonian has azimuthal symmetry

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}\right) + \hat{V_M}(r) - \frac{\hbar^2}{8mr^2}\left(1 + \frac{1}{\sin^2\theta}\right) + \mu(r)\varepsilon_0 \cos\theta\cos\omega t\,. \quad (16)$$

Here the volume element is $dr\,d\theta$ and the wavefunction is the "usual" one multiplied by $r\sin^{1/2}\theta$, hence the fixed-node DVR seems appropriate for treating the θ coordinate. The radial coordinate will be treated with the periodic DVR. Further details of the calculation are described elsewhere [10].

We expand the time-dependent wavefunction, $\Psi(r, \theta, t)$, in the orthogonal (but not normalized) direct product DVR basis

$$\Psi(r,\theta,t) = \sum_{j=1}^{N_r}\sum_{k=1}^{N_\theta} \Psi(r_j,\theta_k,t)\,u_j(r)\,v_k(\theta)\,, \quad (17)$$

where we have used the symbol v_k to distinguish the θ basis from the r basis, u_j. In a time-independent calculation of energy eigenvalues and eigenfunctions, it is more convenient to use the orthonormal basis $\{w_j^{-1/2}u_j(r)\}$, which we have done to obtain the initial values of the wavefunction on the spatial grid employed. Eq. (17) has the advantage in time-dependent problems that the expansion coefficients are the values of the wavefunction at the grid points. We (somewhat arbitrarily) employ a grid of 45 points in r and 17 points in θ.

The application of any coordinate operator to the wavefunction of eq. (17) followed by evaluation at a grid point yields a diagonal representation

$$(f(r,\theta)\,\Psi(r,\theta,t))|_{r_j,\theta_k} = f(r_j,\theta_k)\,\Psi(r_j,\theta_k,t) \quad (18)$$

and the kinetic energy operations (such as that for radial motion) may be evaluated as follows

$$\left(\frac{\partial^2}{\partial r^2}\Psi(r,\theta,t)\right)\Big|_{r_j,\theta_k} = \sum_{n=1}^{N_r}\sum_{l=1}^{N_\theta}\Psi(r_n,\theta_l,t)\,u_n''(r_j)\,v_l(\theta_k) = \sum_{n=1}^{N_r}\Psi(r_n,\theta_k,t)\,u_n''(r_j)\,, \quad (19)$$

where (in this case) we have used the Kronecker delta property of $v_l(\theta_k)$. As in all DVR methods, the

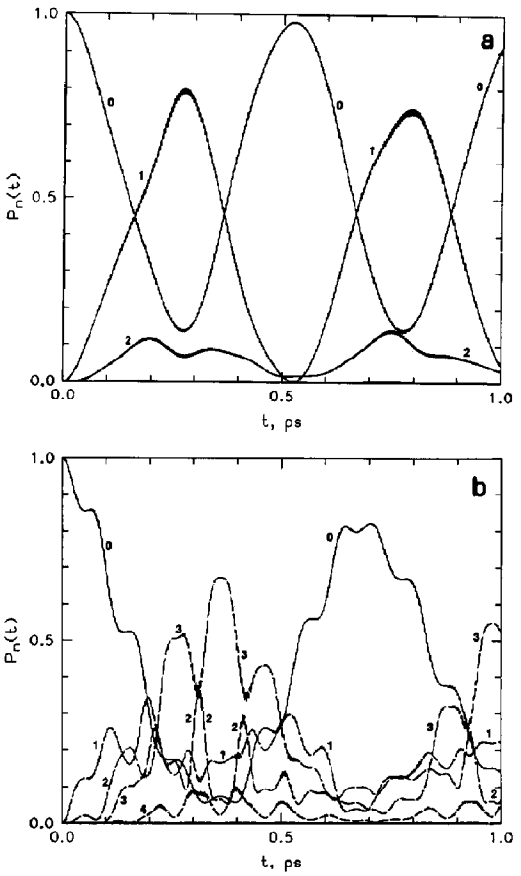

Fig. 3. Population of various HF vibrational states, summed over rotational states, as a function of time during irradiation by: (a) a single laser of frequency 757.4363 ps^{-1} and electric field strength 78.86×10^6 V cm^{-1}; and (b) the same laser as in (a) plus a second laser with the same field strength and polarization and of frequency 696.4801 ps^{-1}. The molecule is initially in its ground rovibrational state. Other parameters of the model are specified elsewhere [10,13].

Hamiltonian matrix is thus very sparse [1,2].

Fig. 3a shows the time evolution of the vibrational populations of the HF molecule during a 1 ps irradiation by a laser with a frequency resonant with the $(0,0)\rightarrow(1,1)$ transition. Except for a longer irradiation time, fig. 3a is identical to the result obtained by Lin and Muckerman using the LGM method [10]. The population primarily oscillates between the ground state and the resonant first excited vibrational state at a frequency close to the (idealized, two-level) Rabi frequency. The rapid oscillations arise from the dipole moment of the molecule oscillating at the frequency of the applied field. Fig. 3b shows the effect of a second laser, with the same field strength and polarization, simultaneously irradiating the HF molecule at a frequency resonant in *two* photons with the $(1,1)\rightarrow(3,1)$ transition. Here the population primarily oscillates between the ground state and $v=3$ at a frequency lower than the Rabi frequency for resonant excitation of $v=1$.

4. Summary

We have described an approach to the construction of discrete variable representations that focuses on properties of the underlying basis functions, and have used this approach to construct two useful DVRs for time-dependent and time-independent problems in quantum mechanics. This approach is simple to execute and produces accurate "coordinate eigenfunctions" and their spatial derivatives. An added bonus to this approach was obtaining DVRs with equally spaced points and equal weights. These features recommend them for general use.

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