Accurate basis sets for the calculation of bound and continuum wave functions of the Schrödinger equation

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The major objective of this paper is to make some simple, but numerically useful generalizations of the classical orthogonal functions. The motivation for doing this is to develop accurate, orthornormal basis sets for the expansion of solutions of the Schrödinger equation in multichannel problems. The generalizations are needed for two reasons. First, it is often useful for the set to have a mathematical structure which is unrelated to the classical functions and second, the boundary conditions which need to be satisfied by the solutions to the Schrödinger equation are often not easily represented by the classical functions. In contrast to certain other techniques, such as those based on diagonalizing the overlap matrix, the method we propose is capable of generating very large, orthonormal subspaces in a numerically stable fashion. While it is not possible to demonstrate a one-to-one correspondence between this finite basis representation of the Hamiltonian and a representation based on the points and weights of a Gauss quadrature, the so-called discrete variable representation (DVR), as is true for the classical orthogonal functions, it is still possible to transform to a representation which preserves all of the essential features of the DVR. The method is illustrated by applying it to a few simple one- and two-dimensional problems. [S1050-2947(97)00205-9]

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I. INTRODUCTION

Most standard techniques for the numerical solution of the Schrödinger equation rely on discretization procedures in physical or function space. Grid-based methodologies [1] have the advantage that they often lead to structured matrices, which are easily adapted to a number of the iterative techniques [2,3] which have been developed for large, sparse linear systems [4]. The disadvantage of such approaches is that it is often difficult to approximate the derivatives that appear in the Schrödinger equation to a suffcent accuracy without resorting to high-order differences or very small step sizes. Expansions in function space (often called spectral methods [5]) typically do not suffer from this problem since it is possible to ''analytically'' differentiate and in many cases compute matrix elements of the representation without further approximation.

For a number of orthogonal systems, such as the classical orthogonal polynomials, there are one-to-one correspondences between the functional representation based on the polynomials and a set of grid points of the Gauss quadratures derived from the zeros of those polynomials. Thus, it is straightforward to transform freely between the two representations, and this has led to the application of the so-called discrete variable representation (DVR) to many problems in nonreactive and reactive collisions of importance in atomic physics and chemistry. What is attractive about the DVR is that the matrix representation of kinetic energy still has a fairly simple structure and the (here) local potential energy operator is diagonal. This preserves many of the features of grid-based techniques without having to numerically approximate derivatives. The simplicity of the matrix representation of the Hamiltonian in the DVR is fully exploited by solving the typically large linear systems that emerge from the discretization process by iterative techniques. Since these

methods are dominated by matrix-vector multiples, a structured and sparse matrix offers considerable computational savings. In addition, it is not necessary to compute complicated matrix elements of the potential energy operator in the DVR representation.

In Sec. II I will briefly review the classical theory and show how it is easily generalized to the nonclassical case. The generalization will preserve the three-term recursion relationship of the classical case but the recursion coefficients will be computed numerically. Once the functions have been determined, a simple transformation of the basis leads to a representation which preserves the diagonal character of local operators in coordinate space.

Section III of the paper will present a few illustrations of the method to the solution of simple and partial differential equations which are either analytically known or soluble by other approaches in order to show the accuracy attainable by the current technique.

II. CLASSICAL THEORY AND GENERALIZATION

All of the classical orthogonal polynomials are defined by a three-term recursion relation on the interval $a \leq x \leq b$ of the form,

$$\beta_j P_j(x) = (x - \alpha_j) P_{j-1}(x) - \beta_{j-1} P_{j-2}(x), \qquad (1)$$

with the properties

$$\int_a^b w(x) P_i(x) P_j(x) dx = \delta_{i,j}, \qquad (2)$$

where $w(x)$ is a non-negative weight function and $P_0(x) = $ const and where the coefficients α_j and β_j are known analytically for the classical case. The recursion relation provides a numerically stable procedure for generating

the polynomials for any value of x beginning with $P_0(x)$. For many of the classical polynomials there are analytic relations between the function and its first and/or second derivatives which may be used to generate the derivatives if needed. In the absence of such relationships, it is trivial to differentiate the recursion any number of times to obtain equations useful for computing derivatives. For example,

$$\beta_j \frac{dP_j(x)}{dx} = (x - \alpha_j)\frac{dP_{j-1}(x)}{dx} - \beta_{j-1}\frac{dP_{j-2}(x)}{dx} + P_{j-1}(x) \tag{3}$$

may be used for the first derivative once the functions are known. The α and β coefficients may be regarded as the elements of a symmetric, tridiagonal matrix. It is easy to see from Eq. (1), that this is, in fact, the matrix representation of the coordinate operator x, in the basis. It is possible to show that the eigenvalues of this tridiagonal matrix are the points of an n-point Gauss quadrature corresponding to the n polynomials of the basis representation. It can also be demonstrated that the Gaussian weights for the quadrature may be obtained from the coefficient of the $P_0(x)$ polynomial in each eigenvector. This algorithim is used in one of the more popular codes, Gaussq [12], to get the points and weights of many Gauss quadratures. It is far more efficient than performing a search for the zeros of the nth polynomial using root search techniques. For the classical orthogonal polynomials, it is possible to show that there is a one-to-one correspondence between the n Gaussian quadrature points and the n orthonormal polynomials. This correspondence may be exploited numerically by transforming from the original polynomial basis to a representation based on the Gaussian quadrature points, i.e., the numerical grid. Thus, provided that it is numerically acceptable to represent a given function as a linear combination of the n orthonormal polynomials, it is also acceptable to evaluate to coefficients in that expansion by numerical quadrature over the Gaussian points and weights. When this is done, the entire problem may be recast in the grid representation. These ideas were first described by Dickinson and Certain [6], and extensively exploited by Light and co-workers [7], Kosloff and Kosloff [8], Marston and Balint-Kurti [9], Manolopoulos and Wyatt [10], and Muckerman and Lin [11].

For the purposes of generalizing the ideas of the preceding paragraph, another viewpoint, which focuses on the finite basis representation, is more useful. If we regard the coordinate x as an operator, the three-term recursion relationship for the orthogonal polynomials may also be obtained by the following procedure: (1) Starting from an arbitrary function $\chi_0(x)$ calculate,

$$\alpha_0 = \int_a^b dx \ w(x)\chi_0(x)\chi_0(x)dx \tag{4}$$

and then form the normalized $i=0$ function,

$$\psi_0(x) = \frac{\chi_0(x)}{\sqrt{\alpha_0}}. \tag{5}$$

(2) Form $\chi_1(x)$ as,

$$\chi_1(x) = (x - \alpha_1)\psi_0(x), \tag{6}$$

where

$$\alpha_1 = \int_a^b dx \ w(x)\psi_0(x)x\psi_0(x)dx$$

and then form the normalized $i=1$ function,

$$\psi_1(x) = \frac{\chi_1(x)}{\sqrt{\beta_1}}, \tag{7}$$

$$\beta_1 = \int_a^b dx \ w(x)\chi_1(x)\chi_1(x)dx. $$

(3) For $i=2$ to n, calculate

$$G(x) = x\psi_{i-1}(x), \tag{8}$$

$$\alpha_i = \int_a^b dx \ w(x)\psi_{i-1}(x)G(x)dx\chi_i(x)$$

$$= G(x) - \alpha_i\psi_{i-1}(x) - \beta_{i-1}\psi_{i-2}(x) \tag{9}$$

and form the normalized ith function,

$$\psi_i(x) = \frac{\chi_i(x)}{\sqrt{\beta_i}}, \tag{10}$$

$$\beta_i = \int_a^b dx \ w(x)\chi_i(x)\chi_i(x)dx. $$

Thus, a Gram-Schmidt process applied to the sequence of vectors defined in this manner, generates the desired three-term recursion relationship and the coefficients α and β needed to compute any member of the sequence as the procedure moves forward. The entire process may be regarded as an application of the Lanczos technique to the coordinate operator x. These α and β coefficients may be calculated using any quadrature capable of integrating the appropriate polynomial product with the given weight function over the desired interval. For the simple case where $w(x) = 1$ and the interval is finite, the integrals may be computed exactly using any number of standard quadratures. By computing the integrals numerically and as the calculation proceeds, one can avoid the instabilities associated with manipulating scalar products of x^n for large values of n. The entire procedure is trivial to program and is capable of generating numerically orthonormal sets for very large n.

For the classical polynomical bases, one begins the recursion procedure with the function one. The so generated orthonormal basis, is capable of expanding any arbitrary function in the interval (a,b). However, if the desired function is required to satisfy some boundary conditions at the end points of the interval, it may be far more efficient and convenient to build those boundary conditions into the basis at the outset. It is essential to be able to do this if the orthogonal functions are being used to expand the solution of a differential equation where there are essential singularities at the end points. A simple example will clarify this. Suppose one is trying to solve a second order differential equation

where the desired solution is required to be zero at the left end point. Since the classical orthogonal polynomials must contain a constant in order to be complete for the expansion of all functions, a large cancellation of terms would be necessary to satisfy the required boundary condition. This is very dangerous, since even a small admixture of the irregular solution to the second-order equation could lead to disasterous results. The problem is easily solved by starting the recursion with x instead of a constant.

A discrete variable representation

One of the nicest features of the classical orthogonal functions is their relationship to Gauss quadratures. As we have noted above, the coefficients of the three-term recursion relation may be viewed as a tridiagonal matrix whose eigenvalues and eigenvectors provide the points and weights of an n point Gauss quadrature. Since these functions are polynomials, the properties of the Gauss quadratures assure us that an orthonormality relation of the form,

$$\sum_{q=1}^{n} w_q P_i(x_q) P_j(x_q) = \delta_{i,j} \tag{11}$$

exists and in addition, it can be demonstrated that a completeness relation of the form,

$$\sum_{i=1}^{n} P_i(x_q) P_i(x_{q'}) = \frac{\delta_{q,q'}}{w_q} \tag{12}$$

also holds. The latter is a consequence of the Christoffel-Darboux identity [13]. For the nonclassical case, there is no one-to-one correspondence between the functions and the points of any Gauss quadrature and the Christoffel-Darboux identity has no meaning. However, by diagonalizing the tridiagonal matrix of coefficients, it is still possible to generate a new basis in which the coordinate operator is diagonal, and that is all that is required. In the new basis, any local function (operator) of x, is diagonal and the matrix element consists of the function evaluated at the eigenvalue. This enables us to use a representation having all the simple features of the usual DVR but unrelated to any quadrature scheme.

III. NUMERICAL RESULTS

I have applied the ideas of the previous sections to a few one-dimensional and one two-dimensional problem. The one-dimensional problems examine the eigenvalue spectrum for the s-wave radial Schrödinger equation for a free particle, a particle in a potential well and the hydrogen atom. In each case the problem is solved by placing the system in a box of appropriate dimension, generating the set of polynomials and then forming and diagonalizing the Hamiltonian in the representation defined by that basis. In the case of the free particle and potential well, the box size and the physical region were taken to be 1.0 a.u. For the Coulomb potential, the box size was set at 1000.0 a.u. in order to be able to make comparisons between numerically generated and exact eigenvalues for a high principal quantum number. The results for the free-particle case for two different boundary conditions are

TABLE I. Eigenvalues of s-wave free particle Hamiltonian for different size basis sets (n_b). The box size$=1.0$ a.u. and the boundary condition is zero derivative at $r=1.0$ a.u.

N	Energy ($n_b=25$)	Energy ($n_b=50$)[a]
1	1.233 700 55	1.233 700 55
2	11.103 304 95	11.103 304 95
3	30.842 513 75	30.842 513 75
4	60.451 326 96	60.451 326 96
5	99.929 744 56	99.929 744 56
6	149.277 766 57	149.277 766 57
7	208.495 392 97	208.495 392 97
8	277.582 623 78	277.582 623 78
9	356.539 459 00	356.539 458 **99**
10	445.365 900 00	445.365 **898 60**
11	544.062 030 93	544.06**1 942 61**
12	652.630 590 51	652.62**7 591 02**
13	771.121 294 21	771.**062 843 84**
14	900.045 405 57	**899.367 701 05**
15	1042.371 469 69	103**7.542 162 66**

[a]Bold numbers indicate where differences in energy begin.

shown in Tables I and II. Similarly, I show in Table III the results for a potential well with zero derivative condition at $r=1.0$ a.u. In both the free-particle and potential well calculations for the eigenvalue spectrum for zero derivative boundary conditions, the polynomial basis was not forced to satisfy the condition at $r=1.0$ a.u. Instead, I added a Bloch operator, L, [14–16] to the Hamiltonian, H, and diagonalized $H+L$ in the basis. Comparison of the numerical results for the larger of the two basis sets in Tables I–III with exact values indicates essentially perfect agreement.

In Table IV I present the results for the hydrogen atom. Here the boundary condition of zero value at $r=1000.0$ a.u. was imposed directly on the basis set. The results for the larger basis sets agree perfectly with the exact spectrum except for the highest values of the principal quantum number n. In order to remove any questions of the finite size of the

TABLE II. Same as Table I for the boundary condition zero wave function at $r=1.0$ a.u.

N	Energy ($n_b=25$)	Energy ($n_b=50$)[a]
1	4.934 802 20	4.934 802 20
2	19.739 208 80	19.739 208 80
3	44.413 219 80	44.413 219 80
4	78.956 835 21	78.956 835 21
5	123.370 055 01	123.370 055 01
6	177.652 879 22	177.652 879 22
7	241.805 307 83	241.805 307 83
8	315.827 340 83	315.827 340 83
9	399.718 978 25	399.718 978 2**4**
10	493.480 222 52	493.480 22**0 05**
11	597.111 084 72	597.111 0**66 27**
12	710.615 952 61	710.61**1 516 88**
13	833.998 829 84	833.9**81 571 89**
14	968.128 523 99	967.**221 231 31**
15	1112.477 531 34	1110.**330 495 12**

[a]Bold numbers indicate where differences in energy begin.

TABLE III. Same as Table I for a potential well of -1.0 a.u.

N	Energy ($n_b=25$)	Energy ($n_b=50$)[a]
1	.233 700 55	.233 700 55
2	10.103 304 95	10.103 304 95
3	29.842 513 75	29.842 513 75
4	59.451 326 96	59.451 326 96
5	98.929 744 56	98.929 744 56
6	148.277 766 57	148.277 766 57
7	207.495 392 97	207.495 392 97
8	276.582 623 78	276.582 623 78
9	355.539 459 00	355.539 458 **99**
10	444.365 900 00	444.365 **898 60**
11	543.062 030 93	543.061 **942 61**
12	651.630 590 51	651.627 **591 02**
13	770.121 294 21	770.**062 843 84**
14	899.045 405 57	898.**367 701 05**
15	1041.371 469 69	103**6.542 162 66**

[a]Bold numbers indicate where differences in energy begin.

box on the eigenvalue spectrum, the Hamiltonian was rediagonalized in a box of $r=2000.0$ a.u. This caused the higher lying eigenvalues to come into perfect agreement with the exact values, showing that the box size not the basis set was responsible for the small differences in the original calculation.

The results of the final calculation, which treats the hydrogen atom as if it were a diatomic molecule, is shown in

Table V. The objective of this calculation was to give some indication of the performance of the method in a two-dimensional problem. By placing the proton 1.0 a.u. from the origin of the coordinate system, the problem can be reduced to a two-dimensional partial differential equation in the variables (r,θ). Here I examine only the $m=0$ symmetry solutions. The basis set is taken to be the product of Legendre polynomials in θ and radial polynomials in r, satisfying the boundary condition of zero value at $r=10.0$ a.u. A point worth noting is that by expanding the solution away from the Coulomb singularity, one is faced with the additional difficulty of converging the electron-nuclear interaction potential in the basis set. It is well known that this is not an optimal approach to multicenter systems and I am currently investigating alternatives that retain the essentials of the polynomial basis sets but do not suffer from the convergence problems of single-center expansions. In the last row of Table V I present the results of the calculation when the nuclear singularity and the origin of the coordinate system are coincident. This calculation did not impose spherical symmetry on the system. It was performed using the diatomic code with a trivial one line modification to place the proton at the origin. All of the calculations used the representation where r and θ were diagonal. Thus, only diagonal matrix elements of the Coulomb interaction are computed and these are trivially related to the eigenvalues of r and $\cos(\theta)$ for the polynomial basis sets. By not explicitly enforcing spherical symmetry, there is a lack of exact degeneracy in eigenvalues of the same (n,l) quantum numbers. This arises for two reasons; first, the radial basis set does not satisfy the exact r^{l+1}

TABLE IV. Energy levels of hydrogen atom for different size basis sets (n_b). The box size is 1000.0 a.u.

N	Energy ($n_b=50$)	Energy ($n_b=75$)	Energy ($n_b=100$)	Energy ($n_b=500$)
1	−0.431 725 32	−0.499 085 26	−0.499 999 62	−0.500 000 00
2	−0.118 899 63	−0.124 999 05	−0.125 000 00	
3	−0.054 332 93	−0.055 555 55	−0.055 555 56	
4	−0.030 903 54	−0.031 250 00		
5	−0.019 880 44	−0.020 000 00		
6	−0.013 841 87	−0.013 888 89		
7	−0.010 183 73	−0.010 204 08		
8	−0.007 803 00	−0.007 812 50		
9	−0.006 172 84	−0.006 172 84		
10	−0.004 997 53	−0.005 000 00		
11	−0.004 130 87	−0.004 132 23		
12	−0.003 471 45	−0.003 472 22		
13	−0.002 958 12	−0.002 958 58		
14	−0.002 550 74	−0.002 551 02		
15	−0.002 222 04	−0.002 222 22		
16	−0.001 953 01	−0.001 953 13		
17	−0.001 730 03	−0.001 730 10		
18	−0.001 543 16	−0.001 543 21		
19	−0.001 385 00	−0.001 385 04		
20	−0.001 249 94	−0.001 249 96		
21	−0.001 132 64	−0.001 132 66		
22	−0.001 022 18	−0.001 022 20		
23	−0.000 901 48	−0.000 901 50		
24	−0.000 762 78	−0.000 762 79		
25	−0.000 606 56	−0.000 606 57		

TABLE V. Lowest eigenvalues of the hydrogen atom treated as a diatomic molecule as a function of radial (n_r) and angular (n_θ) basis. The nucleus is placed 1.0 a.u. from the coordinate center and the box size is 10.0 au

n_r	n_θ	root 1	root 2	root 3	root 4	root 5	root 6
10	10	−0.494 910 47	−0.128 874 35	−0.122 037 58	−0.054 011 00	−0.051 926 93	−0.049 862 49
20	10	−0.463 632 43	−0.125 050 11	−0.120 256 85	−0.053 995 17	−0.051 709 26	−0.047 290 98
30	10	−0.490 605 19	−0.124 971 14	−0.123 796 91	−0.053 994 04	−0.051 701 78	−0.048 924 36
40	10	−0.480 290 82	−0.124 993 94	−0.122 473 67	−0.053 994 26	−0.051 666 95	−0.048 364 58
50	10	−0.482 830 44	−0.124 985 16	−0.122 802 72	−0.053 994 25	−0.051 680 48	−0.048 497 08
70	10	−0.482 374 66	−0.124 987 05	−0.122 743 66	−0.053 994 25	−0.051 676 86	−0.048 474 89
70	20	−0.494 296 71	−0.124 993 51	−0.124 267 95	−0.053 995 02	−0.051 762 58	−.049 082 15
70	30	−0.496 453 55	−0.124 994 74	−0.124 539 32	−0.053 995 16	−0.051 781 65	−0.049 184 98
70	40	−0.496 974 67	−0.124 995 28	−0.124 604 47	−0.053 995 19	−0.051 786 53	−0.049 209 39
		−0.499 885 8	−0.124 994 62	−0.124 972 81	−0.053 967 56	−0.051 611 43	−0.049 911 71

boundary condition at the origin *separately* for each partial wave and second, the finite sized region of 10.0 a.u. has a slightly different effect on the eigenvalues for each angular momentum. All of these effects contribute to the differences between the atomic and molecular calculation.

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