Discrete variable representation for singular Hamiltonians

Barry I. Schneider*
Physics Division, National Science Foundation, Arlington, Virginia 22230, USA
and Electron and Optical Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

Nicolai Nygaard†
Chemical Physics Program, University of Maryland, College Park, Maryland 20742-2431, USA
and Electron and Optical Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

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We discuss the application of the discrete variable representation (DVR) to Schrödinger problems which involve singular Hamiltonians. Unlike recent authors who invoke transformations to rid the eigenvalue equation of singularities at the cost of added complexity, we show that an approach based solely on an orthogonal polynomial basis is adequate, provided the Gauss-Lobatto or Gauss-Radau quadrature rule is used. This ensures that the mesh contains the singular points and by simply discarding the DVR functions corresponding to those points, all matrix elements become well behaved, the boundary conditions are satisfied, and the calculation is rapidly convergent. The accuracy of the method is demonstrated by applying it to the hydrogen atom. We emphasize that the method is equally capable of describing bound states and continuum solutions.

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I. INTRODUCTION

The discrete variable representation (DVR) [1–6] is one of the most effective and widely used methods for discretizing the Schrödinger equation. In its most elemental form, it has the virtues of maintaining the locality of operators which are local in space, and the rapid convergence of a spectral method. In addition, for multidimensional problems it leads to a sparse matrix representation of the Hamiltonian, which may be used quite effectively when coupled to iterative techniques designed to solve large sets of linear equations or to extract the lowest eigenvalues of large matrices. A recent variant of the method, which combines the DVR with a finite element method [7], has been used to solve one of the most intractable problems in atomic scattering theory, the impact ionization of the hydrogen atom. Lately, the technique has been combined with the Arnoldi/Lanczos approach to produce an extremely efficient method for the solution of the time-dependent Schrödinger equation [8].

The purpose of this note is to correct some misconceptions concerning the application of the method to problems involving singular potentials. These issues appear to arise when it is apparent that the boundary conditions satisfied by the solution to the Schrödinger equation should not lead to any numerical difficulties. A number of authors [3,9–11] have provided "remedies" to remove the singularities and to transform the original Schrödinger equation into a more tractable and rapidly converging form. Unfortunately, these transformations often destroy the natural symmetry of the original equations and lead to more complex algebraic solution methods than is really necessary. Here we present an alternative approach, which addresses the problem more transparently, leading to a simpler numerical procedure with no loss of accuracy. Section II is a summary of the key elements of the DVR method, and in Sec. III we present our approach for applying this methodology to singular Hamiltonians. We end in Sec. IV with a brief conclusion.

II. DISCRETE VARIABLE REPRESENTATION

Since the DVR has been discussed extensively [1–6] in the literature, we provide only the essentials here. A DVR exists when there is both a spectral basis of N functions, $\phi_i(x)$, orthogonal over a range $[a,b]$ with weight function $w(x)$

$$\int_a^b w(x)\phi_n^*(x)\phi_m(x)dx = \delta_{m,n}, \tag{1}$$

and an associated quadrature rule with N points x_i and weights w_i which enable a set of coordinate eigenfunctions $u_i(x)$ to be defined with the following properties:

$$u_i(x) = \sqrt{w(x)}\sum_{n=0}^{N-1} c_n\phi_n(x), \tag{2a}$$

$$u_i(x_j) = \sqrt{\frac{w(x_i)}{w_i}}\delta_{i,j}. \tag{2b}$$

Using the quadrature rule to evaluate c_n gives

$$c_n = \int_a^b \sqrt{w(x)}\phi_n^*(x)u_i(x)dx = \sum_{k=1}^{N} w_k\phi_n^*(x_k)\frac{u_i(x_k)}{\sqrt{w(x_k)}}$$
$$= \sqrt{w_i}\phi_n^*(x_i), \tag{3a}$$

$$u_i(x) = \sqrt{w_i w(x)}\sum_{n=0}^{N-1} \phi_n^*(x_i)\phi_n(x), \tag{3b}$$

*Electronic address: bschneid@nsf.gov
†Electronic address: nicolai.nygaard@nist.gov

$$\langle u_i|x|u_j\rangle = \delta_{i,j}x_i. \tag{3c}$$

There are two important features to note. First, the coordinate eigenfunctions are defined as continuous functions of the spectral basis. When this basis is polynomial the sum in Eq. (3b) can be carried out exactly, and the coordinate eigenfunctions can be expressed as

$$u_i(x) = \sqrt{\frac{w(x)}{w_i}} \prod_{k=1}^{N}{}' \frac{x - x_k}{x_i - x_k}, \tag{4}$$

the Lagrange interpolating functions at the quadrature points. With either representation, they may be easily differentiated analytically. Second, the expansion coefficients c_n are computed using the quadrature rule. Implicit in using the quadrature rule for the evaluation of c_n is that the result is accurate. This is not guaranteed except for certain cases. For example, when $\phi_i(x)$ is one of the classical orthogonal functions, there is an associated Gauss quadrature [12] which guarantees that Eq. (3) is exact when the integrand is a polynomial of degree $(2N-1)$ or less. There are other examples such as particle-in-a-box or Fourier functions, which are not polynomials, but which can be shown to exactly satisfy Eq. (3) with an appropriately chosen quadrature rule. In all of these cases there exists a unitary transformation between the original spectral and the coordinate basis. Since the coordinate functions diagonalize the coordinate operator, any function of the coordinates is also diagonal. This is very convenient for actual calculations and gives the DVR calculation many of the desirable properties of a grid based method with few of the disadvantages. It should also be noted that matrix elements of the kinetic energy operator while not diagonal in the coordinate basis may be evaluated simply and exactly using the quadrature rule or analytically. Since the kinetic energy part of the Hamiltonian matrix is a separable sum over particle and coordinate variables, a product DVR basis leads to a sparse representation. When the interval $[a,b]$ is infinite or semi-infinite, the weight function $w(x)$ ensures that the wave function will decay properly at large distances. For finite intervals, boundary conditions may be enforced by requiring that the wave function or its derivative behave correctly at the left and/or right boundary.

There is a simple, but quite useful generalization of Gauss quadratures that will be needed in what follows. It is possible to specify in advance that some of the points are fixed. When these points are either or both of the end points of a finite interval, the quadrature rule is termed a Gauss-Radau or Gauss-Lobatto quadrature, respectively. The remaining Gauss points may be determined by a simple modification of the original procedure [12]. Since one or two points are now fixed, the quadrature is of lower accuracy than the full Gauss quadrature, but the great advantage of being able to satisfy specific boundary conditions at the end points far outweighs this disadvantage.

III. SINGULAR HAMILTONIANS

Consider the radial Schrödinger equation

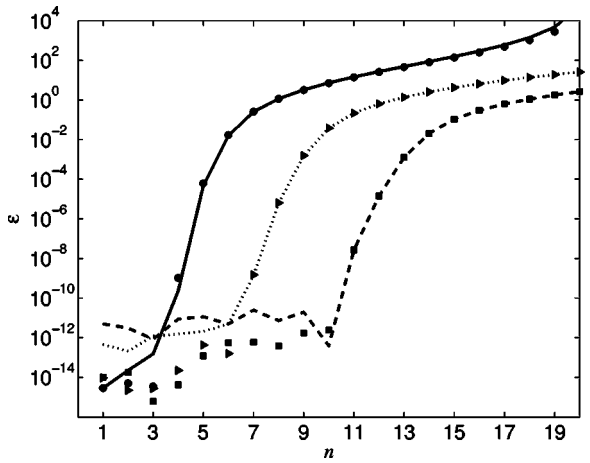

FIG. 1. Relative error on the first ten $l=0$ eigenstates of hydrogen using a Gauss-Laguerre basis with no scaling ($h=1$). The points indicate the results obtained using the method of this paper for $N=20$ (●), $N=50$ (▶), and $N=100$ (■). The lines represent the relative error obtained using the regularized Lagrange mesh method of Vincke et al. [9] for $N=20$ (solid), $N=50$ (dotted), and $N=100$ (dashed).

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v(r) - E\right]\psi(r) = 0 \tag{5}$$

where we assume that $v(r)$ vanishes for large r and is singular at the origin. The radial function satisfies the boundary condition $\psi(0)=0$, and either exponentially decays or oscillates for large r. Here we will offer two alternative approaches to solving Eq. (5). To motivate the discussion, recall that Baye and Heenen [3] suggest that for the case of exponentially decaying boundary conditions, one very natural choice for the spectral functions is

$$\phi_n(r) = r^{l+1}\exp(-r/2)L_n^{2l+2}(r) \tag{6}$$

where $L_n^{\alpha}(r)$ are the generalized Laguerre polynomials. When this basis is used for the Coulomb potential, the results are quite disappointing. The relative error in the ground state energy with ten basis functions is about 5×10^{-3}. This appears to be simply related to the choice of $r^2\exp(-r)$ as the weight function. While this choice does result in a set of coordinate functions that satisfy both boundary conditions, it gives rise to a potential energy matrix element that does not behave as a polynomial times the weight function. In fact,

TABLE I. *s*-wave eigenvalues of hydrogen atom in Legendre basis; $R=50$ a.u.

n	$N=10$	$N=20$	$N=40$	Exact
1	−0.39428839	−0.49997882	−0.50000000	−0.50000000
2	−0.11142228	−0.12500000	−0.12500000	−0.12500000
3	−0.05165408	−0.05555555	−0.05555555	−0.05555555
4	−0.02957707	−0.03120434	−0.03120434	−0.03120434
5	−0.01651543	−0.01786476	−0.01786476	−0.01786476
6	−0.00060937	−0.00226590	−0.00226590	−0.00226590

TABLE II. *s*-wave eigenvalues of hydrogen atom in Legendre basis; $R=100$ a.u.

n	$N=20$	$N=40$	$N=50$	Exact
1	−0.48882286	−0.50000000	−0.50000000	−0.50000000
2	−0.12481146	−0.12500000	−0.12500000	−0.12500000
3	−0.05554641	−0.05555556	−0.05555556	−0.05555556
4	−0.03124909	−0.03125000	−0.03125000	−0.03125000
5	−0.01999983	−0.01999997	−0.01999997	−0.01999997
6	−0.00959636	−0.01386848	−0.01386848	−0.01386848

the integrand has terms that behave as inverse powers of r. Vincke, Malegat, and Baye [9] propose a simple procedure to remedy the problem. They regularize the problem by multiplying the Schrödinger equation by $\rho(r)$, where $\rho(r)$ is chosen so that $\rho(r)v(r)=\text{const}$ as $r=0$. Using, for example, $\rho(r)=r^2$, leads to a generalized eigenvalue problem with a modified kinetic energy matrix based on Laguerre polynomials with $\alpha=0$. Here we suggest a more direct attack. First, we do not transform the Schrödinger equation. We use the Laguerre polynomials with $\alpha=0$, that is, with a weight function $\exp(-r)$, but choose the points and weights of the quadrature by the Gauss-Radau rule with $r=0$ as the fixed point. The set of resulting DVR functions all satisfy the boundary conditions at infinity and due to the Kronecker δ function property (2b) all but the first DVR function also satisfy the boundary condition at the origin, that is, they lead off as r. The first basis function is then simply dropped from the expansion. The resulting matrix elements of the Hamiltonian are all exactly integrated by the quadrature rule and quite well behaved.

We have applied our method to the spectrum of the hydrogen atom. In Fig. 1 we show the relative error ε on the first ten eigenstates with $l=0$ for various basis set sizes. For comparison we also plot the results obtained when using the regularized mesh technique of Vincke *et al.* (with scaling factor $h=1$, see Ref. 9). In addition to its greater simplicity the accuracy of our method is equal or superior to that of the regularized mesh technique. Moreover, since all basis functions vanish at the origin, our method works equally well for finite values of the angular momentum, as long as the wave function is well localized within the interval.

A second approach, which works for both the bound and continuous spectrum, places the system in a large box of radius, $r=a$. The DVR basis is defined using the Gauss-Legendre-Lobatto quadrature rule. By ensuring that the two end points are part of the quadrature, it becomes trivial to satisfy the boundary conditions. Dropping the DVR function

TABLE III. *s*-wave eigenvalues of hydrogen atom in Legendre basis; $R=200$ a.u.

n	$N=40$	$N=50$	Exact
1	−0.49997974	−0.49999999	−0.50000000
2	−0.12500000	−0.12500000	−0.12500000
3	−0.05555556	−0.05555556	−0.05555556
4	−0.03125000	−0.03125000	−0.03125000
5	−0.0200000	−0.02000000	−0.02000000
6	−0.01388889	−0.01388889	−0.01388889
7	−0.01020408	−0.01020408	−0.01020408
8	−0.00781238	−0.00781238	−0.00781238

at the origin guarantees that the solution will vanish at $r=0$. If the DVR function at the last point is dropped, the solution will go to zero at $r=a$ and simulate exponentially decaying solutions. By retaining the DVR function at the last point and adding a Bloch operator

$$L=\frac{\hbar^2}{2M}\left[\delta(x-a)\frac{d}{dx}\right] \tag{7}$$

to the Hamiltonian, it is possible to deal with nonfixed node boundary conditions at the right end point and simulate scattering boundary conditions. For long range potentials, such as the Coulomb potential, it is necessary to make sure that the results are not box size dependent. Stated differently, one must examine the convergence of the eigenvalues with respect to basis set and box size. This is clearly evidenced in Tables I–III where one sees convergence to eigenvalues of the truncated Coulomb potential when the size of the box is too small. By systematically increasing the box size and the basis, it is possible to obtain the eigenvalues to arbitrary accuracy.

IV. CONCLUSIONS

Previous researchers have developed DVR techniques that require special treatment of singular potentials or nonpolynomial based quadratures. Here we have demonstrated that a judicious use of the orthogonal polynomial approach, using the Gauss-Lobatto quadrature rule, avoids the need to transform the Schrödinger equation into a form which is numerically less tractable. In addition, the method is applicable to all types of boundary conditions and is able to treat the bound and continuous spectra on equal footing. As a final note, using the finite element DVR enables one to treat singularities or even discontinuities [7] at interior points, if they are known in advance, by choosing the boundaries of the elements at those points.

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