Generalized pseudospectral methods with mappings for bound and resonance state problems

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Several extensions of the pseudospectral method are made and applied to the solution of bound and resonance state problems. First, an algebraic mapping is introduced to remove the singularity and the domain truncation error common to Coulomb problems. In addition, the conventional procedure is modified, leading to a more desirable symmetric eigenvalue problem instead of an unsymmetric or generalized one. The simplicity, efficiency, and accuracy of the procedures are illustrated by solving the one-electron Dirac equation. Finally a new complex-scaling pseudospectral method is introduced for resonance state problems and applied to the determination of the complex resonance energies for an anharmonic oscillator.

1. Introduction

Recently generalized Fourier-grid Hamiltonian (FGH) methods have been developed for accurate and efficient solution of shape resonances [1], laser-induced multiphoton quasi-energy resonances [2] and the relativistic Dirac–Coulomb problem [3] without the use of explicit basis set expansion. The FGH method [4] and its various generalizations [1–3] possess the simplicity of the direct discretization methods such as the finite difference (FD) and the finite element (FE) methods, and at the same time, maintain high accuracy and fast convergency of the finite basis set variational methods. The FGH methods do not require the computation of the potential matrix elements (which is usually the most time-consuming part of structure calculations using the basis set expansion methods), are simple to implement, and provide the values of the wavefunctions directly at the space grid points.

A natural extension of the FGH procedures is to use a set of orthogonal polynomial functions instead of the Fourier series. This is the pseudospectral method which has, in the last decade, been well studied in mathematics (see, e.g., ref. [5]) and been widely applied to many fields related to fluid dynamics [6], such as aerodynamics, meteorology, and oceanology. Like the FGH method, the general pseudospectral method also possesses both the simplicity of the direct FD and FE methods and the fast convergency of the finite basis set methods. As is rigorously proven [6], for any problem with smooth (i.e. infinitely differentiable) solution, which is generally the case in quantum chemistry, the exponential convergence (also called the “infinite-order convergence”) property is guaranteed provided that orthogonal (usually polynomial) functions of a common singular Sturm–Liouville problem are used. Here “exponential convergence” means that the error of the approximate solution decreases asymptotically faster than algebraic decay of any finite order. It is also shown [5] that a pseudospectral method with \(N+1\) or \(N+2\) grid points is usually equivalent in accuracy to the corresponding basis set expansion (more generally a spectral Galerkin) method with the use of \(N\) basis functions. These nice characteristics make the pseudospectral method a highly competitive alternative to the conventional finite basis methods and to the FD and FE direct discretization methods.

Little attention, however, has been paid to the usefulness of the method (at least in its most updated form) in the study of atomic and molecular structures and dynamics [7]. The purpose of this Letter is mainly to examine the usefulness of the pseudospectral method in treating quantum mechanical
problems. In doing this, we will first consider the one-electron Dirac–Coulomb problem in which a singularity at the origin is involved and the long-range potential has to be treated appropriately. These difficulties are common for three-dimensional Coulomb-field-involved problems when grid methods are used and need to be treated with great care. For this purpose, we will introduce an algebraic mapping which removes the singularity at the origin and avoid the truncation of the infinite domain. In addition, we will modify the procedure to obtain a symmetric eigenvalue problem instead of an unsymmetric or a generalized one. Finally we extend the complex-scaling transformation \[8\] to the pseudospectral formalism to solve efficiently the resonance state problems. Our results for the test cases consistently show the high accuracy of the pseudospectral results with the number of grid points comparable to that of the basis functions used in the conventional variational methods.

The Letter is arranged as follows: in section 2, the FGH formalism is rederived in a different way to illustrate the main procedures of the pseudospectral method. In section 3, a mapping is introduced and the pseudospectral method is modified and applied to solve the Dirac–Coulomb equation. This is followed in section 4 by the presentation and application of the complex-scaling pseudospectral method.

2. Pseudospectral methods for bound state eigenvalue problems

Trial functions are essential in distinguishing different types of spectral methods \[9\]. The most frequently used trial functions in pseudospectral methods are trigonometric polynomials, Chebyshev polynomials, and Legendre polynomials \[5,6\]. The trigonometric polynomials are distinct from the others as they are, strictly speaking, useful only for periodic boundary value problems. Also they are more familiar to us. Hence we will illustrate the procedures of pseudospectral methods by first considering the trigonometric (Fourier) polynomials.

The central part of the spectral method is to approximate the exact solution \(\psi(x)\) by order \(N\) or \(N+1\) polynomial \(\psi_N(x)\). In the Fourier spectral methods, it is equivalent to

\[
\psi(x) \approx \psi_N(x) = \sum_{l=-N/2}^{N/2} a_l \exp(ilx) .
\]  

The pseudospectral method further requires that the approximation be exact, i.e. \(\psi_N(x_j) = \psi(x_j)\), at \(N\) grid (collocation) points \(x_j (j = 0, 1, ..., N-1)\). In this case \(x_j = 2\pi j/N\) for \(x\) defined in \([0, 2\pi]\). Due to the orthogonality of the Fourier series \(\exp(ilx)\), the expansion coefficients can be written as

\[
a_l = \frac{1}{Nc_l} \sum_{j=0}^{N-1} \psi(x_j) \exp(-ilx_j) ,
\]  

where \(c_l = 1\) for \(|l| < \frac{1}{2}N\) and \(c_l = 2\) for \(l = \pm \frac{1}{2}N\). The approximate function \(\psi_N(x)\) can now be represented by the exact function values at \(N\) collocation points,

\[
\psi_N(x) = \sum_{j=0}^{N-1} \psi(x_j) g_j(x) ,
\]  

where

\[
g_j(x) = \sum_{l=-N/2}^{N/2} \frac{1}{Nc_l} \exp[i(x-x_j)]
\]

\[
= \frac{1}{N} \sin[\frac{1}{2} \left(N(x-x_j)\right)] \cot[\frac{1}{2} (x-x_j)] .
\]  

For a given periodic function \(\psi(x)\), the \(N\) point approximation of eq. (3) can be shown to be of exponential convergence.

Now let us consider the eigenvalue problem \(\hat{H} \psi(x) = E \psi(x)\), with \(\hat{H}\) being a linear differential operator. Under the polynomial approximation eq. (3), the eigenvalue problem becomes

\[
\sum_{j=0}^{N-1} \left[ \hat{H} g_j(x) - E g_j(x) \right] \psi(x_j) = 0 ,
\]  

where the differentiation \(\hat{H} g_j(x)\) can be performed exactly. One of the key points of the pseudospectral method is to require the equation to be satisfied exactly at all collocation points. This leads to the \(N \times N\) matrix form eigenvalue problem

\[
H \Psi = E \Psi ,
\]  

where

\[
H_j = \hat{H} g_j(x) \big|_{x=x_i} ,
\]

\[
\Psi = (\psi(x_0), \psi(x_1), ..., \psi(x_{N-1}))^T .
\]  

Take the one-dimensional Schrödinger equation as an example, we have
\[ H_0 = -\frac{1}{2\mu} (D_x)_0 + V(x) \delta_0, \]  

(9)

where \( \mu \) is the reduced mass of the system, \( V(x) \) is the potential, and \((D_x)_0\) is the matrix element of the second derivative

\[
(D_x)_0 = g_j'(x_j) = -\frac{1}{2} (N^2+2), \quad \text{if } i=j.
\]

\[
(D_x)_0 = g_j'(x_j) = (-1)^{j+i+1} x (2 \sin^2 \left[ \pi (i-j)/N \right])^{-1}, \quad \text{otherwise}. \quad (10)
\]

Diagonalization of eq. (6) provides both the bound state energies and the values of the wavefunctions directly at the mesh points. Note in eq. (9) the potential energy matrix is always diagonal and the kinetic energy matrix elements are of simple analytical forms. The Fourier pseudospectral method given above, though derived in a different fashion, is identical to the Fourier-grid Hamiltonian (FGH) method [4]. The power of the FGH and its generalized methods has been recently demonstrated [1-4].

For general nonperiodic boundary value problems defined in \([-1, 1]\), naturally other orthogonal polynomials should be used. Again the solution can be approximated as linear combinations of the basis functions \( u_i(x) \). Similar to eq. (1), we have

\[ \psi(x) = \sum_{j=0}^{N} a_j u_j(x). \quad (11) \]

If the collocation points are appropriately chosen, the orthogonality of the polynomials \( u_i(x) \) is maintained in the sense of discrete inner product, i.e.

\[ (u_i, u_k)_N = \sum_{j=0}^{N} u_i(x_j) u_k(x_j) w_j = \gamma_k \delta_{ik}, \quad (12) \]

where \( w_j \) is the weighting factor, and \( \gamma_k \) is the normalization constant depending on the choice of the basis set. As a result, the expansion coefficients can also be expressed in terms of the function values at all the mesh (collocation) points and the approximate function \( \psi_N(x) \) at arbitrary coordinate can be written the same as eq. (3). The only difference is that the cardinal functions \( g_j(x) \) are now given by

\[ g_j(x) = w_j \sum_{i=0}^{N} u_i(x_j) u_i(x)/\gamma_i, \quad (13) \]

with the property \( g_j(x_i) = \delta_{ij} \). Now the general eigenvalue problem is again converted to the matrix form of eq. (6) and the Hamiltonian matrix element in the case of one dimension is of the form of eq. (9). In general, the second derivative matrix elements \((D_x)_0\) possess simple analytical forms [5]. In addition, no computation of the potential matrix elements are required. The eigenvectors provide directly the values of wavefunctions at collocation points. Notice its differences from the basis set expansion technique. While global orthogonal basis functions are also used in pseudospectral method to approximate the solution, the expansion coefficients are used only as an intermediate step. The resultant linear equations are with respect to the unknown function values at a set of specific (usually unevenly spaced) collocation points rather than to expansion coefficients. In this sense, the pseudospectral method can be viewed as another direct numerical discretization technique (spectral discretization).

3. The pseudospectral method with mappings for the Dirac equation

To illustrate the usefulness of the general pseudospectral method, let us consider the solution of the Dirac equation for one-electron Coulomb field [3,10,11]. This is a problem typical in the atomic structure calculations, as both the singularity and the long-range potential need to be dealt with.

In its most general form, the four-component Dirac equation under consideration is written as

\[ (c\alpha \cdot p + \beta mc^2 - Ze^2/r)\psi = E\psi, \quad (14) \]

where \( p \) is the momentum operator, \( \alpha \) and \( \beta \) are the usual \( 4 \times 4 \) Dirac matrices. After factoring out the two-component spherical spinor, the Dirac equation is reduced to the following coupled radial equations [3,10,11]

\[
\begin{pmatrix}
-Z\alpha/r & k/r - d/dr \\
 k/r + d/dr & -(2mc + Z\alpha/r)
\end{pmatrix}
\begin{pmatrix}
g(r) \\
h(r)
\end{pmatrix} = \frac{E}{c} \begin{pmatrix}
g(r) \\
h(r)
\end{pmatrix}, \quad (15)
\]

where \( \alpha = 1/c \), \( k \) is the Dirac quantum number \( k = l \pm j \pm \frac{1}{2} \) for \( l = j \pm \frac{1}{2} \), and \( g(r) \) and \( h(r) \) are respectively the large and small radial functions. Note
the boundary conditions of the problem are 
\( \psi(0) = \psi(\infty) = 0 \), and the normalization condition is

\[
\int_0^\infty dr \left[ |g(r)|^2 + |h(r)|^2 \right] = 1 ,
\]  
(16)

where \( \psi(r) \) denotes the large or small radial functions, \( g(r) \) and \( h(r) \).

Solution to eq. (15) is not trivial. This is because the Dirac Hamiltonian operator consists of both the positive spectrum \( E_+ > 0 \) and the negative spectrum \( E_- < -mc^2 \). The variational calculations do not necessarily yield an upper bound to the relativistic bound states, and the eigenvalues may fall into the bottomless negative-energy continuum if the trial wavefunctions are not appropriately chosen, an effect known as variational collapse (see, e.g., ref. [12]). Several successful attempts have recently been made regarding proper choice of finite basis sets for the Dirac variational calculations [10,11].

On the other hand, direct numerical approaches, such as the direct application of the FGH method, to the problem usually involve truncating the semi-infinite domain into finite domain \([r_{\min}, r_{\max}]\) to avoid the problems of both the singularity at origin \( r=0 \) and the infinite domain. For this purpose, \( r_{\min} \) must be chosen to be sufficiently small and \( r_{\max} \) sufficiently large. This, in general, introduces considerable truncation error and leads to the difficulty in well sampling the wavefunction.

One way to alleviate the problems is to use the exponential mapping and to apply the FGH method to the mapped infinite domain [3]. Compared with finite basis set techniques, it is much simpler, yet yields comparably accurate results without the problem of variational collapse. In practice, however, it still requires the truncation of the mapped domain. Also a generalized eigenvalue problem must be solved.

As an alternative, we may map the semi-infinite domain exactly onto the finite domain \([-1, 1]\) using mapping \( r = f(x) \), so that the Legendre or Chebyshev pseudospectral method [5,6] can be applied. An additional complexity also exists as an unsymmetric or a generalized eigenvalue problem is introduced.

The difficulty can be overcome by defining a new wavefunction

\[
\phi(x) = \sqrt{f'(x)} \psi(f(x)) ,
\]  
(17)

with \( \psi(r) = (g(r), h(r))^T \) being the original two-component wavefunction. Now \( \phi(x) \) is normalized in the new domain without any weighting factor. This transforms the radial part Dirac equation, eq. (15), into a self-adjoint form with respect to the new variable \( x \),

\[
\begin{bmatrix}
-Z\alpha & k \\
-k & -(2mcf(x)+Z\alpha)
\end{bmatrix}
\begin{bmatrix}
f(x) \\
f'(x)
\end{bmatrix}
+ \begin{bmatrix}
0 & -1 \\
1 & 1
\end{bmatrix}
\begin{bmatrix}
1 \\
df'(x)/dx
\end{bmatrix}
\phi = E\phi .
\]  
(18)

Note the singularity and the domain truncation are avoided by simply imposing the natural boundary conditions in the new domain, i.e.

\[
\phi(x_0) = \phi(x_N) = 0 ,
\]  
(19)

with \( x_0 = -1 \) and \( x_N = 1 \).

Now let us apply the pseudospectral method to discretize the Dirac equation (18). The standard procedure using \( N \) mesh points given in section 2 transforms the modified Dirac equation (18) into a \( 2N \times 2N \) matrix form eigenvalue problem. The new Dirac Hamiltonian matrix is now real symmetric, with the matrix elements

\[
H_{ij} = A(x_i)f(x_i)\delta_{ij} + B(D_i)_{ij} / [f'(x_i)f'(x_j)] ,
\]  
(20)

where \( A(x) \) and \( B \) are, respectively, the first and the second \( 2 \times 2 \) matrices in eq. (18), and \( (D_i)_{ij} \), which is of simple analytical form [5], is the matrix element of the first derivative in the pseudospectral method. Evidently the new Hamiltonian matrix is in contrast to the one in the B-spline-based finite basis set method [11] or in the generalized FGH procedure [3], where a generalized eigenvalue problem must be solved. It is also different from the finite basis set methods, as it is much simpler and more efficient in implementation. The computation of the Hamiltonian matrix elements in eq. (20) is almost trivial.

It is now important to see how well the modified pseudospectral method works as compared with previous studies [3,11]. Let us introduce the algebraic mapping...
where $L$ is a mapping parameter. The real symmetric eigenvalue equation resulting from the Legendre discretization of the Dirac equation is then diagonalized to get the relativistic energies of the system. The results are presented in tables 1 and 2 for a typical case of $Z=2$, $k=-1$, and $j=\frac{1}{2}$. Note both the positive and negative energies are included. For comparison, the energies have been shifted by the amount of $mc^2$ as done in earlier works. Also $N=20$ and $N=40$ grid points are used respectively in tables 1 and 2. The positive energies $E$ with $E - mc^2 < 0$ correspond to the bound states of the system, while those with $E - mc^2 > 0$ correspond to the positive (pseudo-)continuum. All the negative energy states are related to the (pseudo-)continuum below $E = -mc^2$.

As can be seen in table 1, we use only half of the mesh points that were used in refs. [3,11], yet obtain consistently much more accurate results for the energies of all the low-lying bound states. In fact, even the energy of the sixth-lowest bound state has six significant figures, in contrast to three figures in ref. [3,11]. When we use the same number of points ($N=40$) as in these works, the results are even better (table 2). Ten significant figures are obtained for all the lowest ten bound states, as compared with the exact results in the last column. Also more numbers of meaningful eigenvalues are generated (up to fifteen states). By examining the entire spectrum, one sees that both the positive energy and negative energy spectra are contracted to narrower energy regions (40 eigenvalues lie below $-mc^2$ and the remaining half lie in the positive energy region). For example, the lowest negative-energy continuum is only 114 au below $-mc^2$, while previous techniques [3,11] have generated the spurious eigenvalues of five orders of magnitude larger.

For both the calculations, it is evident that collapsing never happens, though no particular adjustment has been made. This is a useful characteristic of the pseudospectral direct numerical method.

Table 1

<table>
<thead>
<tr>
<th>State $n$</th>
<th>Pseudospectral method</th>
<th>Exact positive energy $E_{nr}-mc^2$</th>
<th>Error</th>
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<td>positive energy $E_{nr}-mc^2$</td>
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Table 2
Eigenvalues (in au) of the Dirac-Coulomb-field problem. The parameters are the same as in table 1. N = 40 grid points are used and the mapping factor is \( L = 40 \).

<table>
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<tr>
<th>State</th>
<th>Pseudospectral method</th>
<th>Exact</th>
<th>Error</th>
</tr>
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<td>negative energy (+ mc^2)</td>
<td>positive energy (E_n - mc^2)</td>
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In addition, compared to previous works [3], several extensions leading to significant improvement of the results have been made. First the whole semi-infinite domain is mapped onto a finite domain. Domain truncation error is thus removed. Second the singularities at \( r = 0 \) and at infinity are removed and simply replaced by the trivial boundary conditions at \( x = 1 \). In addition, a different mapping other than the exponential one is used which proves to be very effective. A new general symmetrization technique is
also implemented, yielding a real symmetric eigenvalue problem rather than a generalized one. Finally, Legendre polynomials are used in this example.

4. Complex-scaling pseudospectral methods for resonance state problems

As an alternative discretization technique, the pseudospectral method can also be applied to the resonance problems. In this section, we will combine the pseudospectral method with a complex-scaling technique [8] to treat the resonance problems. By further coupling them to Floquet theory (for recent reviews, see ref. [113]), we can also develop a complex-scaling pseudospectral method for the quasienergies of a quantum system in intense periodic laser fields. This will be discussed separately elsewhere.

Consider again for simplicity a one-dimensional system characterized by the Hamiltonian

$$\hat{H}(x) = \hat{T} + V(x), \quad (22)$$

where $\hat{T}$ is the kinetic energy operator. Under the complex-scaling transformation, $x \rightarrow x \exp(i\theta)$, the Schrödinger equation for the resonance states reads

$$\left( -\frac{1}{2\mu} \exp(-i2\theta) \frac{d^2}{dx^2} + V(x \exp(i\theta)) \right)\psi = E\psi, \quad (23)$$

where $E$ denotes the complex energy of the resonance states. Pseudospectral discretization of this equation is straightforward, yielding an $N \times N$ complex non-Hermitian eigenvalue problem. The non-Hermitian Hamiltonian matrix elements are written by

$$H_{ij}(\theta) = -\exp(-i2\theta) \left( D_2 \right)_{ij}/2\mu + V(x_i \exp(i\theta))\delta_{ij}, \quad (24)$$

where $x_i$ are the collocation points (not necessarily evenly spaced) corresponding to the particular choice of polynomials used in the pseudospectral method, $(D_2)_{ij}$ is the matrix element of the second-order differential operator.

As a test case, we consider the problem of the tunneling in the anharmonic oscillator $V(x) = \frac{1}{2}x^2 - \lambda x^3$. This problem has been studied previously by various methods [1,14,15]. In particular, the CSFGH method with $N = 61$ grid points [1] reproduced exactly the results obtained by the complex-scaling basis-set-expansion (CSB) method [15] and appeared to be more accurate and far more efficient than the finite-difference method using $N = 4000$ grid points [14].

Table 3 shows the results of the complex resonance energies $(E_R, -\frac{1}{2}I^T)$ computed using the present complex-scaling (Legendre) pseudospectral method with $N = 40$ grid points. They are compared with the results obtained by the CSB method using 40 basis functions [15]. Note all the decimal places shown in the table are converged with respect to both the rotation angle and the number of grid points. Once again, it is seen that the pseudospectral method not only is extremely simple, but can achieve high accuracy comparable to that of the basis set expansion method. These advantages make it a highly competitive alternative to the conventional finite basis set expansion method.

In summary, we have illustrated the simplicity, efficiency and high accuracy of the pseudospectral method by considering two typical examples. One is
the one-electron Dirac–Coulomb bound state problem, and the other is the resonance state problem of an anharmonic oscillator. Several extensions are made to deal with the specific bound and resonance state problems frequently encountered in atomic and molecular structural and dynamical computations. These include the use of an algebraic mapping, symmetrization of the Hamiltonian matrix, and the development of a complex-scaling pseudospectral procedure. These extensions are shown to be very effective not only in removing the singularity in direct methods, but also in further improving the convergence property of the conventional pseudospectral methods. Although we considered in the present Letter only simple examples, applications of the pseudospectral method to more complicated problems such as the Dirac–Hartree–Fock and high-dimensional calculations are straightforward. Extension of the present work to these studies is under way.

Acknowledgement

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References