Adv. Studies Theor. Phys., Vol. 7, 2013, no. 1, 11 - 23
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Analytic Matrix Elements of the Schrödinger Equation

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Abstract

A previously defined analytic technique of constructing matrix elements from the Bernstein-polynomials (B-poly) has been applied to Schrödinger equation. This method after solving generalized eigenvalue problem yields very accurate eigenenergies and eigenvectors. The numerical eigenvectors and eigenvalues obtained from this process agree well with exact results of the hydrogen-like systems. Furthermore, accuracy of the numerical spectrum of hydrogen equation depends on the number of B-polys being used to construct the analytical matrix elements. Validity of eigenvalues and quality of the constructed wavefunctions is verified by evaluating the Thomas-Reiche-Kuhn (TRK) sum rules. Excellent numerical agreement is seen with exact results of hydrogen atom.

Keywords: Hydrogen-like systems, Schrödinger equation, Quantum System, Bernstein-Polynomials, Energy Spectrum

1 Introduction

B-Polys are becoming useful mathematical techniques for solving complicated problems in engineering and physics disciplines. These are exactly well-defined polynomials, evaluated quickly on a Personal Computer and can exemplify a large number of arbitrary functions. Because of analytic their nature, those can be differentiated and integrated ostensibly. They can also be used to

approximate an arbitrary function to high accuracy. In past years, the spectral techniques comprising such polynomials are being used magnificently solving physics interrelated computations. Specifically, the B-spline techniques are engaged to calculate atomic properties by many authors [1-4].

To calculate static Polarizabilities of the ground and excited states of the hydrogen-like systems, nth degree B-spline-Galerkin scheme was employed [5]. The B-splines technique produced a complete set of basis functions and approximates solutions to the differential equations depending on the degree n and number (N) of the B-splines [5],

$$B_i^0(r) = \begin{cases} 1 & \text{if } t_i \leq r < t_{i+1} \\ 0 & \text{otherwise} \end{cases}$$

and

$$B_i^n(r) = \left(\frac{r - t_i}{t_{i+n} - t_i}\right) B_i^{n-1}(r) + \left(\frac{t_{i+n+1} - r}{t_{i+n+1} - t_{i+1}}\right) B_{i+1}^{n-1}(r). \qquad (1.1)$$

The $B_i^n(r)$ is nth degree piecewise B-Spline defined on a grid $\{t_i\}$. The grid points have $(n+1)$-fold degeneracy at the endpoints of the closed interval. It is obvious when number of B-splines is set to $N = n + 1$, the set of B-splines in Eq.(1.1) formed on a grid breakdowns to a set of B-polys on the complete range as shown in ref.[6]. Current article shows a technique of how to build solutions of Schrödinger equation and a spectrum on a predetermined interval [a, b] using a definite set of B-polys. As we know that B-polys do not rely on a particular structure of any interior sub-intervals grid points, the matrix elements are calculated accurately on the whole interval [a, b]. In the subsequent sections, the technique for estimating the solutions is explained. We also give general analytic formulas for calculating matrices to be used to approximate solutions of the Schrödinger equation. Finally these matrices are diagonalized to obtain a set of eigenenergies and eigenvectors.

2 Explicit Formulas in B-polys

Our main goal is to provide approximate yet accurate solutions of the quantum mechanical system represented governed by the Schrödinger equation on an interval [a, b] using continuous B-polys which use no interior grid points for the interval. The specifics of the B-polys are provided in a number of publications [6-11]. As stated before, one can either get a set of B-polys by requiring B-splines equal to n+1 or using the general form defined in reference [6]:

$$B_{i,n}(x) = \left(\begin{array}{c} n \\ i \end{array} \right) \frac{(x-a)^i (b-x)^{n-i}}{(b-a)^n} \quad 0 \le i \le n, \tag{2.1}$$

where the binomial factors are given below:

$$\left(\begin{array}{c} n \\ r \end{array} \right) = \frac{n!}{r!\,(n-r)!}. \tag{2.2}$$

These are total $n+1$ n^{th} degree B-polys. For ease, we set $B_{i,n}(x) = 0$, if $i < 0$ or $i > n$. A modest code written in Mathematica language or Maple may be written to produce all the non-zero B-polys of any degree n on an interval. For any problem under consideration, we can impose boundary conditions on the first and last B-polys. Below, we list closed expressions concerning inner products and derivatives of B-polys:

$$(B_{i,n}(x),\, B_{j,m}(x)) = \frac{(b-a) \left(\begin{array}{c} n \\ i \end{array} \right) \left(\begin{array}{c} m \\ j \end{array} \right)}{(n+m+1) \left(\begin{array}{c} n+m \\ i+j \end{array} \right)}, \tag{2.3}$$

$$x^m\, B_{i,n}(x) = \left(\begin{array}{c} n \\ i \end{array} \right) \sum_{k=0}^{m} \frac{a^{m-k} (b-a)^k \left(\begin{array}{c} m \\ k \end{array} \right)}{\left(\begin{array}{c} n+k \\ i+k \end{array} \right)} B_{i+k,n+k}(x), \tag{2.4}$$

$$(x^m\, B_{i,n}(x), B_{j,n}(x)) = (b-a) \left(\begin{array}{c} n \\ i \end{array} \right) \left(\begin{array}{c} n \\ j \end{array} \right) \sum_{k=0}^{m} \frac{a^{m-k} (b-a)^k \left(\begin{array}{c} m \\ k \end{array} \right)}{(2n+k+1) \left(\begin{array}{c} 2n+k \\ i+j+k \end{array} \right)}, \tag{2.5}$$

$$(x^{-m}\, B_{i,n}(x), B_{j,n}(x)) = \frac{1}{(b-a)^m} \left(\begin{array}{c} n \\ i \end{array} \right) \left(\begin{array}{c} n \\ j \end{array} \right) \frac{(b-a)}{(2n-m+1) \left(\begin{array}{c} 2n-m \\ i+j-m \end{array} \right)},$$

and the p^{th} derivative is specified by

$$D^p B_{i,n}(x) = \sum_{k=0}^{p} \beta_k^{p,n} B_{i-k,n-p}(x), \tag{2.6}$$

$$(D^p B_{i,n}, D^p B_{j,n}) = \frac{(b-a)}{(2n-2p+1)} \sum_{k,l=0}^{p} \beta_k^{p,n} \beta_l^{p,n} \frac{\begin{pmatrix} n-p \\ i-k \end{pmatrix} \begin{pmatrix} n-p \\ j-l \end{pmatrix}}{\begin{pmatrix} 2n-2p \\ i+j-k-l \end{pmatrix}}, \quad (2.7)$$

Here $\beta_l^{p,n}$ are expressed as

$$\beta_l^{p,n} = \frac{(-1)^{l+p}}{(b-a)^p} \frac{n!}{(n-p)!} \begin{pmatrix} p \\ l \end{pmatrix}. \quad (2.8)$$

In the subsequent sector, we apply the explicit formulas to the Radial Schrödinger Equation for obtaining its solutions. Particularly, formulas in the equation (2.5) are very useful in calculating the matrix elements of the potential function used in the Schrödinger equation.

3 Radial Schrödinger Equation

Consider the Radial Schrödinger Equation for hydrogen-like systems with Z as nuclear charge,

$$-\frac{\hbar^2}{2m} \frac{d^2u(r)}{dr^2} + \frac{1}{2} \frac{l(l+1)}{r^2} u(r) - \frac{Ze^2}{r} u(r) = E\, u(r). \quad (3.1)$$

We try to solve the equation in an interval [a, b] with boundary conditions $u(a) = 0$ and $u(b) = 0$. Setting $\hbar = m = e = 1$ in atomic units and $\varepsilon = 2E$ in the above equation (3.1), we obtain the equation:

$$\frac{d^2u(r)}{dr^2} - \frac{l(l+1)}{r^2} u(r) + \frac{2Z}{r} u(r) = -\varepsilon\, u(r). \quad (3.2)$$

Approximating the function $u(r)$ with $u(r) = \sum_{i=0}^{N} c_i\, B_{i,n}(r)$ and replacing this solution in the Eq. (3.2), we form scalar inner product with B-polys $B_{j,n}(r)$ to get,

$$c_i \left[(B''_{i,n}, B_{j,n}) - l(l+1) \left(\frac{1}{r^2} B_{i,n}, B_{j,n}\right) + 2\, Z \left(\frac{1}{r} B_{i,n}, B_{j,n}\right) \right] = -c_i\, \varepsilon\, (B_{i,n}, B_{j,n}) \quad (3.3)$$

Using the identity $(B''_{i,n}, B_{j,n}) = -(B'_{i,n}, B'_{j,n})$, we want to write the equation (3.3) as

$$c_i \left[-(B'_{i,n}, B'_{j,n}) - l(l+1)\,(\frac{1}{r^2}B_{i,n}, B_{j,n}) + 2\,Z(\frac{1}{r}B_{i,n}, B_{j,n}) \right] = -c_i\,\varepsilon\,(B_{i,n}, B_{j,n}) \tag{3.4}$$

In Eq. (3.4), the matrices have closed expressions which are calculated using the formulas shown in the preceding section:

$$\begin{aligned} a_{i,j} = (B'_{i,n}, B'_{j,n}) &= \sum_{k=0}^{1} \beta_k^n \sum_{l=0}^{1} \beta_l^n\,(B_{i-k,n-1}, B_{j-l,n-1}) \\ &= \frac{(b-a)}{(2n-1)} \sum_{k,l=0}^{1} \beta_k^n\,\beta_l^n \frac{\left(\begin{array}{c} n-1 \\ i-k \end{array} \right) \left(\begin{array}{c} n-1 \\ j-l \end{array} \right)}{\left(\begin{array}{c} 2n-2 \\ i+j-k-l \end{array} \right)}, \end{aligned} \tag{3.5}$$

$$\begin{aligned} b_{i,j} &= -l(l+1)\,(\frac{1}{r^2}B_{i,n}, B_{j,n}) + 2\,Z(\frac{1}{r}B_{i,n}, B_{j,n}) \\ &= -\frac{l(l+1)}{(b-a)} \left(\begin{array}{c} n \\ i \end{array} \right) \left(\begin{array}{c} n \\ j \end{array} \right) \frac{1}{(2n-1)\left(\begin{array}{c} 2n-2 \\ i+j-2 \end{array} \right)} \\ &\quad +2Z \left(\begin{array}{c} n \\ i \end{array} \right) \left(\begin{array}{c} n \\ j \end{array} \right) \frac{1}{(2n)\left(\begin{array}{c} 2n-1 \\ i+j-1 \end{array} \right)} \end{aligned} \tag{3.6}$$

and

$$d_{i,j} = (B_{i,n}, B_{j,n}) = \frac{(b-a)\left(\begin{array}{c} n \\ i \end{array} \right) \left(\begin{array}{c} n \\ j \end{array} \right)}{(2n+1)\left(\begin{array}{c} 2n \\ i+j \end{array} \right)} \tag{3.7}$$

here,

$$\beta_k^n = \frac{(-1)^{k+1}}{(b-a)}\; n \left(\begin{array}{c} 1 \\ k \end{array} \right) \tag{3.8}$$

The Eq. (3.4) is amended for the matrix form:

$$(A+B)\,C = \varepsilon\,D\,C. \tag{3.9}$$

In Eq. (3.9), the elements of each matrix A, B and D are given in equations 3.5, 3.6 and 3.7, respectively. The column matrix C signifies coefficients of the

approximate solution to the Eq. (3.4) which are intern calculated from solving the generalized eigenvalue problem provided in Eq. (3.9). In particular to the problem, we select the interval [0, 60] to produce a numerical spectrum of the Schrödinger equation. The wavefunctions are communicated as a linear combination of B-polys of degree N=27. Applying the initial conditions that the wavefunction must vanish at of the interval successfully reduces the number of B-polys from N=28 to N=26. The Command Eigensystem in Mathematica is called to compute the eigenvalue problem in Eq. (3.9). The results of eigenenergies are depicted in Table 1. It is apparent from the Table 1, 26 of the eigenenergies start from small negative values to large positive values since the potential energy term is negative in the Eq. (3.9) and bound states are negative due to attractive potential. It is worth stating that the current calculations do not depend on any type of grid; instead integrations are performed analytically, and exactly, to evaluate the matrix elements in equations (3.5-3.7), which are expressed in terms of continuous B-polys on the length of the interval [0, 60]. The bound eigenenergies are also compared against exact energies $E_n = -\frac{Z^2}{2\,n^2}$ of the hydrogen atomic system. Several tests are implemented to check the validity of the eigenvalues and eigenvectors which are produced in the B-poly basis. A powerful test of the basis is to apply the Thomas-Reiche-Kuhn (TRK) sum rule to solutions of the equation. The TRK sum rule is

$$\frac{2\mu}{\hbar^2}\sum_{k}^{N}(E_k - E_0)|x_{k0}|^2 = 1. \tag{3.10}$$

The Eq. (3.10) is written in terms of B-poly basis $\hbar = \mu = 1$,

$$2\sum_{k}^{N}(E_k - E_0)|C_k \bullet M \bullet C_0|^2 = 1. \tag{3.11}$$

The column matrix C shows normalized eigenvectors and element of Matrix M in above Eq. (3.11) are given:

$$b_{i,j} = (x\,B_{i,n}, B_{j,n}) = (b-a)\begin{pmatrix} n \\ i \end{pmatrix}\begin{pmatrix} n \\ j \end{pmatrix}\sum_{k=0}^{1}\frac{a^{1-k}(b-a)^k\begin{pmatrix} 1 \\ k \end{pmatrix}}{(2n+k+1)\begin{pmatrix} 2n-k \\ i+j-k \end{pmatrix}}, \tag{3.12}$$

The basis set with N=28 B-poly is created by solving equation (3.9). The outcomes of the TRK sum rule are given in table 5 and also matched with the

exact answer equal to 1. The precision of better than one part in 10^6 is seen by just summing first 8 terms.

4 Discussions and Results

We establish a potent technique to solve a complicated Schrödinger Equation problem in a B-poly basis. Table 1 shows the spectrum of eigenenergies created by the B-poly-Galerkin method as deliberated in sectors 2 and 3. As clearly shown, the technique provides very accurate approximate solutions of the Schrödinger equation with initial boundary conditions applied that lead to discrete eigenenergies. Employing the closure expressions of matrix formalism, the symmetric generalized eigensystem Eq. (3.9) is solved to create eigenenergies and eigenvectors. The current technique, for the first time, is applied to solve the Schrödinger equation in closed form in a basis set of B-polys and has been shown to be much quicker and more direct to employ in computational problems with less computing cost. It is also predicted that the quality of the spectrum is superior when calculating the completeness property and TRK sum rules in area of atomic physics. The results of the TRK sum rule converge by just summing the first 8 states in Eq. (3.11). The results of the TRK sum rule are depicted in Table 2. In summary, we have shown that the B-poly-Galerkin method returns valid results and is a powerful tool that we may utilize to overcome the difficulties associated with complex differential equation systems with much less computational efforts and cost. The present technique also gives confidence that it can be stretched to calculate many-body relativistic or non-relativistic perturbation sums for computing atomic properties [12]. Current computations are accomplished with Mathematica 6.0.

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Table 1. Eigenvalues of the symmetric generalizer eigemsystem equation (3.9) are given in atomic units (a.u.). The B-poly-Galerkin method is used to approximate the solutions of the Schrödinger Equation for hydrogen-like atom in the interval R= [0, 60] for L= 0 which corresponds to all s-states. N= 28 B-polys.

State	Eigenvalues (a.u.)
1	-0.500000000
2	-0.125000000
3	-0.055555548
4	-0.031204338
5	-0.017864765
6	-0.002265904
7	0.018505777
8	0.044092164
9	0.074228611
10	0.108761152
11	0.147590759
12	0.190648868
13	0.237885571
14	0.289264394
15	0.344792575
16	0.404990850
17	0.470253551
18	0.556818382
19	0.642279573
20	0.840335905
21	0.992815549
22	1.462650554
23	2.085499422
24	3.220381100
25	8.695103253
26	12.716992544

Table 2. Eigenvalues of the symmetric generalized Eigensystem equation (3.9) are given in atomic units (a.u.). The B-poly-Galerkin method is used to approximate the solutions of the Schrödinger equation for hydrogen-like atom in the interval R= [0, 90] for L= 1 which corresponds to all p-states. N= 28 B-polys.

State	Eigenvalues (a.u.)
1	-0.125000000
2	-0.055555551
3	-0.031216498
4	-0.018175939
5	-0.003318885
6	0.016538704
7	0.041082583
8	0.070061420
9	0.103334344
10	0.140814710
11	0.182445292
12	0.228186320
13	0.278009209
14	0.331924355
15	0.390074806
16	0.453963029
17	0.529963122
18	0.617491236
19	0.780944126
20	0.912732416
21	1.388542509
22	1.621953870
23	3.145132515
24	4.429424447
25	12.482143572
26	45.824504299

Table 3. Eigenvalues of the symmetric generalized Eigensystem equation (3.9) are given in atomic units (a.u.). The B-poly-Galerkin method is used to approximate the solution of the Schrödinger equation for hydrogen-like atom in the interval R= [0, 60] for L= 2 which corresponds to all d-states. N= 28 B-Polys.

State	Eigenvalues (a.u.)
1	-0.055555554
2	-0.031233333
3	-0.018706728
4	-0.005215294
5	0.013028428
6	0.035842939
7	0.063013612
8	0.094424792
9	0.130006975
10	0.169714431
11	0.213515069
12	0.261385369
13	0.313320954
14	0.369316814
15	0.430898545
16	0.497370519
17	0.589171262
18	0.691853340
19	0.870018234
20	1.127802154
21	1.481186802
22	2.434209176
23	3.234291943
24	9.086276713
25	12.659768481
26	120.928294353

Table 4. Eigenvalues of the symmetric generalized Eigensystem equation (3.9) are given in atomic units (a.u.). The B-poly-Galerkin method is used to approximate the solutions of the Schrödinger equation for hydrogen-like atom in the interval R= [0, 90] for L= 3 which corresponds to all f-states. N= 28 B-polys.

State	Eigenvalues (a.n.)
1	-0.031245682
2	-0.019299618
3	-0.007621570
4	0.008546644
5	0.029272811
6	0.054361732
7	0.083702317
8	0.117225443
9	0.154884369
10	0.196645635
11	0.242484379
12	0.292383411
13	0.346353208
14	0.404881917
15	0.468230375
16	0.549672962
17	0.632077991
18	0.810309691
19	0.934183812
20	1.403817692
21	1.653117877
22	3.111690133
23	4.004088838
24	12.253128259
25	16.935798736
26	233.727308640

Table 5. The TRK sum rules equations (3.11) are evaluated using finite basis set. The basis is calculated using 28 B-Polys.

No. of States	Exact	Calculated	Difference
1	-1.000000000	-1.00000005	0.00000005
2	-1.000000000	-1.00000005	0.00000005
3	0.999999990	1.00000138	0.00000138
4	0.999999990	1.00000138	0.00000138
5	0.999999990	1.00000138	0.00000138
6	0.999999990	1.00000138	0.00000138
7	0.999999990	1.00000138	0.00000138
8	0.999999990	1.00000138	0.00000138

Received: October, 2012