
Eigenvalues to Arbitrary Precision for One-Dimensional Schrödinger Equations by the Shooting Method Using Integer Arithmetic

H. W. JONES, J. L. JAIN

Department of Physics, Florida A & M University, Tallahassee, Florida 32307

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ABSTRACT: It would seem that limiting computer computations to numbers with a fixed number of decimal digits would inhibit flexibility. Software programs such as *Mathematica* permit numerical algebra to be done exactly in terms of the ratio of integers. Hence, a single Taylor series representation of a function can span the entire range needed for a corresponding independent variable. We decided to find eigenvalues to 14 decimal digits by solving one-dimensional Schrödinger equations by the “shooting method” by employing a single Taylor series in each case. With more terms in the series, higher accuracy may be obtained by evaluations at larger asymptotic values. The problems solved were the $1s$, $2s$, and $2p$ hydrogen atom, the harmonic oscillator, the quartic potential, and the double-well potential. Noteworthy is the use of the asymptotic condition for the derivative of the eigenfunction as well as its value; this permits the determination of a lower and upper bound for the eigenvalues. The eigenfunctions determined are continuous rather than evaluated only over a grid, thus permitting easy and accurate evaluations of matrix elements by Gaussian quadrature. Also, theoretically accurate normalization constants are found for the eigenfunctions. © 2000 John Wiley & Sons, Inc. *Int J Quantum Chem* 80: 842–847, 2000

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Correspondence to: H. W. Jones; e-mail: jones@cennas.nhmf.gov.

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Introduction

By analytical means, eigenvalues for the three-dimensional hydrogen atom can be reduced to solutions of a one-dimensional Schrödinger equation [1–3]. Other physical problems, as well as some model problems reduce to a one-dimensional (1D) Schrödinger equation. Of course, exact solutions exist for the hydrogen atom and the harmonic oscillator. But there is no analytic solution for the quartic and double-well potential problem. Hence, for eigenvalues of high accuracy for these and other types of intractable problems, a reliable numerical method is called for. Currently, the Noumerov method is widely used [4–6] to solve the differential equation in the “shooting method.” It requires a grid sometimes of hundreds of points. The resulting wave function is not continuous so that interpolations must be done to calculate matrix elements when using Gaussian integration. In this work we show that it is feasible to represent the wave function by a single Taylor series by employing numbers that are the ratio of integers. This was accomplished using the computer algebra program *Mathematica* [7]. (An earlier local version of integer arithmetic was used as a guide [8].) By this method we chose to achieve accuracies of 10^{-14} for eigenvalues and normalization constants.

Hydrogen Atom

The 1D Schrödinger equation for the hydrogen atom is [1]:

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left[2e + \frac{2}{r} - \frac{\ell(\ell+1)}{r^2} \right] R = 0.$$

The eigenvalue (energy) is e . We will use x instead of the variable r , and later y for R/A where A is our normalization constant. For the ground state, $1s$, we set $\ell = 0$. In our method we need not eliminate the first derivative. We take the solution to be

$$y = \sum_{n=0}^{\infty} a_n x^n.$$

Substituting in the differential equation we obtain a recursion relation:

$$a_n = (-2a_{n-1} - 2ea_{n-2}) / (n(n+1)).$$

We choose $a_0 = 1$, and it follows from the indicial equation that $a_1 = -1$. Hence, we can obtain a Taylor series solution accurate to any given number of terms provided that a_n is maintained as the ratio of integers. Also, x must be chosen as the ratio of integers. To ensure sufficient accuracy, n is increased so that the last term added to the Taylor series in our computer programs is made less than 10^{-28} .

The program in Figure 1 is written in *Mathematica* [7]. With energy $e = -0.4$ it produces a graph

```
e = -4 / 10;
istop = 30;
nstop = 150;
xp = Table[0, {i, 1, istop}]; yp = Table[0, {i, 1, istop}];
delx = 1; x = -delx;
Do[ x = x + delx;
    xp[[i]] = x // N;
    anm2 = 1;
    anm1 = -1;
    y = 1 - x;
    pow = x;
    Do[an = -2 * anm1 / n / (n + 1) - 2 * e * anm2 / n / (n + 1);
        pow = pow * x;
        tn = pow * an;
        y = y + tn;
        If[Abs[tn] < 10^-28, Break[]];
        anm2 = anm1;
        anm1 = an, {n, 2, nstop}];
    yp[[i]] = y // N;
    Print[i, " ", xp[[i]], " ", yp[[i]], " ", tn // N;
        , {i, 1, istop}]
```

FIGURE 1. Program to plot H $1s$ eigenfunction for tentative eigenvalue, e .

```

x = 20;
nstop = 200;
jstop = 50;
en = -4 / 10;
ep = -7 / 10;
Do[em = (en + ep) / 2;
  anm2 = 1;
  anm1 = -1;
  yem = 1 - x;
  pow = x;
  Do[an = -2 * anm1 / n / (n + 1) - 2 * em * anm2 / n / (n + 1);
    pow = pow * x;
    tn = pow * an;
    yem = yem + tn;
    If[Abs[tn] < 10^-28, Break[]];
    anm2 = anm1;
    anm1 = an,
    {n, 2, nstop}];
If[yem == 0, ep = em];
If[yem == 0, en = em];
If[yem > 0, ep = em];
If[yem < 0, en = em];
If[Abs[(ep - en)] < 10^-15, Break[]];
Print[j, " ", yem // N, " ", N[em, 17], " ",
  N[en, 17], " ", N[ep, 17], " ", tn // N],
  {j, 1, jstop}]

```

FIGURE 2. Program to find eigenvalue, em, that causes eigenfunction to cross x axis at $x = 20$.

```

x = 20;
nstop = 200;
jstop = 100;
den = -4 / 10;
dep = -7 / 10;
Do[dem = (den + dep) / 2;
  anm2 = 1;
  anm1 = -1;
  dyem = -1;
  pow = x;
  Do[an = -2 * anm1 / n / (n + 1) - 2 * dem * anm2 / n / (n + 1);
    pow = pow * x;
    tn = pow * an;
    dyem = dyem + (n * tn) / x;
    If[Abs[tn] < 10^-28, Break[]];
    anm2 = anm1;
    anm1 = an,
    {n, 2, nstop}];
If[dyem == 0, dep = dem];
If[dyem == 0, den = dem];
If[dyem > 0, dep = dem];
If[dyem < 0, den = dem];
If[Abs[(dep - den)] < 10^-16, Break[]];
Print[j, " ", dyem // N, " ", N[dem, 17],
  " ", N[den, 17], " ", N[dep, 17], " ", tn // N],
  {j, 1, jstop}]

```

FIGURE 3. Program to find eigenvalue, dem, that causes the derivative of the eigenfunction to be zero at $x = 20$.

TABLE I
Convergence of eigenvalue with increasing "leverage."

Leverage	y em	y' dem
x = 5	-.49641700659145	-.50615837380655
x = 10	-.49999926328152	-.50000093593023
x = 15	-.4999999992161	-.50000000009099
x = 20	-.49999999999999	-.50000000000001
x = 25	-.50000000000000	-.50000000000000

that has a value of 1 at the origin, crosses the x axis at about $x = 3$, and then goes negative toward infinity. If $e = -0.7$, the curve again starts at 1 at the origin, goes down toward the x axis but does not cross it; instead it swings upward toward positive infinity. The energy for the first curve we designate as e_n and the second curve as e_p . The program in Figure 2 uses the bisectional method to obtain the energy e_m which is less than 10^{-15} for the value $|e_p - e_n|$ after a sufficient number of iterations. In this program x is fixed at 20 (the "leverage"). What we have accomplished is to make the curve cross the x axis at the point $x = 20$ with energy e_m . The program in Figure 3 forces the derivative of y dy/dx to cross the x axis at the same point $x = 20$ with energy e_m . A little consideration will convince one that the energy of the true asymptotic curve that goes to zero when x goes to infinity must lie between the energy values e_m and e_m . Table I shows that the accuracy of the determination of the energy (eigenvalue) increases

with the "leverage." At $x = 25$ for the 1s hydrogen state we achieve 14-digit accuracy.

The normalization for the hydrogen atom is [1]

$$\int_0^\infty R^2(r)r^2 dr = 1.$$

Using $R = Ay$ we get

$$A = 1 / \left[\int y^2 x^2 dx \right]^{1/2}.$$

Now,

$$\text{Area} = \int_0^b y^2 x^2 dx = \int_0^b \left(\sum a_i x^i \right) \left(\sum a_j x^j \right) x^2 dx,$$

$$\text{Area} = \int_0^b \sum c_n x^{n+2} dx = \sum_{n=0}^N c_n b^{n+3} / (n+3),$$

with

$$c_n = \sum_{k=0}^n a_k a_{n-k}.$$

For the required accuracy, $x = b$ is chosen so that $(yb) < 10^{-7}$. For $b = 20$, the Taylor series required is 101 terms; and, for consistency in dealing with the square of y , we use $N = 202$. The program in Figure 4 produces the correct value ($A = 2$) to 14 digits.

Similar procedures were carried out for the 2s and 2p states. Table II summarizes our results. Our normalization A is forced because we chose $y(0) = 1$.

```

b = 20;
e = -1 / 2;
nstop = 202;
a = Table[0, {i, 0, nstop}];
  anm2 = 1;
  a[[1]] = anm2;
  anm1 = -1;
  a[[2]] = anm1;
Do[an = (-2 * anm1 - 2 * e * anm2) / n / (n + 1);
  a[[n + 1]] = an;
  anm2 = anm1;
  anm1 = an, {n, 2, nstop}];
c = Table[Sum[a[[k + 1]] * a[[n - k + 1]], {k, 0, n}], {n, 0, nstop}];
area = Sum[c[[n + 1]] * b^(n + 3) / (n + 3), {n, 0, nstop}];
A = N[1 / Sqrt[area], 20]

2.00000000000000035729

```

FIGURE 4. Program to find the normalization constant.

TABLE II
Summary of results.

	Leverage	Normalization <i>b</i>	Terms in Taylor series	<i>Cn</i> terms required	Computed eigenvalues	Comparison eigenvalue	Normalization <i>A</i>
Hydrogen—1s	25	20	101	202	−0.5000000000000000	−0.5000000000000000	2.0000000000000000
Hydrogen—2s	50	50	114	228	−.1250000000000000	−.1250000000000000	0.70710678118654
Hydrogen—2 <i>p</i>	50	50	112	224	−.1250000000000000	−.1250000000000000	0.20412414523193
Oscillator (<i>n</i> = 0)	6	6	192	384	0.5000000000000000	0.5000000000000000	0.75112554446494
Oscillator (<i>n</i> = 10)	10	10	478	956	10.5000000000000000	10.5000000000000000	0.37261713638291
Quartic	5	3.4	286	572	0.66798625915577	0.66800	0.84008901310719
Double-well	5	3.4	290	580	0.86958091893546	0.86952	0.63815574099569

Eigenvalues for Harmonic, Quartic, and Double-Well Potentials

The following strictly one-dimensional problems are solved for eigenvalues using the basic differential equation [4]

$$y'' = [-2e + 2V(x)]y.$$

We will deal with symmetric potentials and select symmetric eigenfunctions. Thus, we start with $y(0) = 1$ and $y'(0) = 0$. For the harmonic oscillator $V(x) = \frac{1}{2}x^2$; this leads to the recursion formula

$$a_n = (a_{n-4} - 2ea_{n-2}) / (n(n-1)).$$

By scanning through various energy values we decided to “zero in” on one hump that is the ground state ($n = 0$), and the eigenfunction that has five nodes along the positive x axis ($n = 10$). Table II shows that we obtain the energy and normalization for $n = 0$ and $n = 10$ to the sought-after 14 digits as confirmed by analytic results [2, 3].

Quartic and double-well potentials do not have analytic solutions. In Table II we compared our results with Blukis and Howell [4]. The quartic potential was $V(x) = x^4$. This led to the recursion formula

$$a_n = (2a_{n-6} - 2ea_{n-2}) / (n(n-1)).$$

The double-well potential used was $V(x) = 1 - 2x^2 - x^4$, which led to the recursion formula

$$a_n = (2a_{n-6} - 4a_{n-4} - (2e - 2) \cdot a_{n-2}) / (n(n-1)).$$

Conclusion

We have presented a highly accurate but conceptually simple method of finding eigenvalues and continuous eigenfunctions for one-dimensional Schrödinger equations using integer arithmetic. The time required on a G-3 MacIntosh computer with a *Mathematica* 4.0 program was between 1 and 15 min for all our chosen problems except for the normalization of the double-well potential. One may speed up the operations using the option of decimal digit programming with numbers having 100 digits, which is sufficient to obtain the required accuracy.

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