Theor Chim Acta (1994) 87: 453–464

Theoretica Chimica Acta

A new method for approximate solution of one-dimensional Schrödinger equations

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Received June 10, 1992/Accepted May 1, 1993

Summary. A general method for approximate solution of one-dimensional Schrödinger equations with a wide range of square-integrable potentials is described. The potential is expanded in terms of either Jacobi or Bessel functions of argument $\exp(-r)$. This allows the Schrödinger equation to be solved by the Frobenius method. In the absence of super-computing power the input requirement of a large number of significant figures was handled by an algebraic computing package, for illustrative purposes. A sum of Gaussian wells and a Morse potential are treated as examples.

Key words: Bound-state – Scattering solutions – Schrödinger equation – Frobenius method

1 Introduction

One-dimensional wave-mechanical problems are of continued importance [1–9]. One example is the radial part of spherically symmetrical problems that transforms into one-dimensional form by substituting $\psi(r) = 1/r \cdot S(r)$, where $S(r)$ satisfies the equation:

$$S'' + 2\mu_m/\hbar^2[W - V(r) - \hbar^2 l(l+1)/2\mu_m r^2]S = 0$$

which becomes a standard one-dimensional Schrödinger equation for orbital angular momentum of zero, $l = 0$. Problems of this type are commonly solved variationally, by perturbation techniques, or numerical integration [3]. Other methods involve Pade approximations or Hills determinants. The WKB method, also known [1] as JWKB, however is still the most popular.

A new approach of simple design that deals with a wide range of potentials is described in this paper. The method, in its present form, allows approximate solution of the Schrödinger equation for all square-integrable potentials $V(r)$ with respect to a certain weight, $\omega(r)$. The method is perhaps unique in that a single operation provides both bound-state and scattering solutions in position, as well as momentum representation. The mathematical formulation allows direct use of

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numerical techniques, which however, involve the addition or substraction of extremely large numbers during evaluation of the coefficients. This is a drawback until more powerful computers become generally available. In the present illustrative applications an algebraic package was used to handle the required number of significant figures.

2 Description of the method

The principles of the procedure are described in terms of Bessel functions, whereas the numerical analysis demonstrates the use of Jacobi polynomials.

The following properties of Bessel functions are used. Let λ_k denote the positive zeros of $J_\nu(z)$ in ascending order and where $\nu > 0$. The follow orthogonality condition holds [10].

$$\int_0^1 z J_\nu(\lambda_m z) J_\nu(\lambda_n z)\, dz = \begin{cases} 0, n \neq m \\ 1/2\, J_{\nu+1}^2(\lambda_n), n = m \end{cases}$$

Substitute $r = -\ln z$ to give:

$$\int_0^\infty e^{-2r} J_\nu(\lambda_m e^{-r}) J_\nu(\lambda_n e^{-r})\, dr = \begin{cases} 0, n \neq m \\ 1/2\, J_{\nu+1}^2(\lambda_n), n = m \end{cases}$$

Expanding [11] the potential $V(r)$ as:

$$V(r) = \sum_{k=1}^{\infty} a_k J_\nu(\lambda_k e^{-r}) \tag{1}$$

the series will converge to $V(r)$ if $V(r)$ is square-integrable [6] with respect to weight e^{-2r} over $[0, \infty)$.

$$a_k = 2/J_{\nu+1}^2(\lambda_k) \int_0^\infty e^{-2r} J_\nu(\lambda_k e^{-r}) V(r) dr$$

Substituting from Eq. (1) into the Schrödinger equation gives:

$$S'' + \Pi \left\{ W - \sum_{k=1}^{\infty} a_k J_\nu(\lambda_k e^{-r}) \right\} S = 0 \tag{2}$$

where $\Pi = 2\mu_m/\hbar^2$, μ_m = reduced mass, or mass.

The Taylor series of J_ν is [7]:

$$J_\nu(\lambda_k \omega) = (1/2)^\nu \omega^\nu \sum_{l=0}^{\infty} \frac{(-\frac{1}{4})^l \omega^{2l} \lambda_k^{2l}}{l!\, \Gamma(\nu + l + 1)}$$

$$= \sum_{l=0}^{\infty} b_l^k \omega^{2l+\nu}$$

Using this result with Eq. (2) and the substitution:
$y = e^{-r}$; $y \in [0, 1]$, $r \in [0, \infty)$, $S(r) = R(y)$, gives:

$$y^2 R'' + yR' + \Pi \left\{ W - \sum_{k=1}^{\infty} a_k \sum_{l=0}^{\infty} b_l^k y^{2l+\nu} \right\} R = 0 \tag{3}$$

Because there is a regular singularity at zero R expands as a Frobenius series around zero [12]:

$$R = \sum_{n=0}^{\infty} c_n y^{n+m}$$

The indicial equation for m is:

$$m(m-1) + m + \Pi W = 0 \text{ since } v > 0.$$

$$m = \pm\sqrt{-\Pi W}$$

By rezeroing the energy W one may distinguish between pure scattering and bound states as follows:

$$m = \pm\sqrt{\Pi W} \in \mathbb{R} \text{ for bound states}$$

$$m = \pm i\sqrt{\Pi W} \in \mathbb{C} \text{ for scattered states}$$

The special case $W = 0$, i.e. $m = 0$ will later be shown to be a scattering solution.

3 The general solution

Substitution of the Frobenius series into Eq. (3) gives:

$$\sum_{n=0}^{\infty} c_n y^{n+m}\left[(n+m)(n+m-1) + (n+m) + \Pi\left\{W - \sum_{k=1}^{\infty}\sum_{l=0}^{\infty} a_k b_l^k y^{2l+v}\right\}\right] = 0$$

The recursion formula for the c_n's follows as:

$$c_n\{(n+m)^2 + \Pi W\} - \Pi \sum_{k=1}^{\infty}\sum_{l=0}^{\infty} a_k b_l^k c_{n-2l-v} = 0 \tag{4}$$

Unless this infinite recursion relation can be solved it is necessary to turn it into a finite form by choosing a finite rather than an infinite expansion of $V(r)$. The number of terms should ideally minimize the error with respect to computing time. Equation (4) can be solved either by direct substitution using the formula above or by a method of generalized continued fractions due to Milne Thompson [13], e.g.:

$$c_n = [c_{n-1} \cdot c_{n-2} \cdot \cdots \cdot c_0] Q_p \cdot Q_{p+1} \cdots Q_{M-1}\{a_n b_n \cdots k_n\}$$

where $\{\ \}$ represents a column vector

where a_n = coefficient of c_{n-1}

b_n = coefficient of c_{n-2}

$\vdots$

---

k_n = coefficient of c_{n-M}

Notice that the coefficient of c_n must be unity and the Q_p are $M \times M$ matrices.

$$
\begin{array}{rcccccc}
Q_p = & a_n & 1 & 0 & 0 & - & 0 \\
 & b_n & 0 & 1 & 0 & - & 0 \\
 & c_n & 0 & 0 & 1 & - & 0 \\
 & \vdots & & & & & \\
 & \text{----------} & & & & & \\
 & k_n & 0 & 0 & 0 & - & 0
\end{array}
$$

Where M is the point at which the series are terminated. The general solution to Eq. (2) is:

$$R = A \sum_{n=0}^{\infty} c_n y^{n+m} + B \sum_{n=0}^{\infty} c'_n y^{n-m} \tag{5}$$

The c_n are computed from Eq. (4) or by using generalized continued fractions with $+m$ the c'_n are computed from the same formulas but with $-m$.

4 Bound states

For a regular solution at zero, $B = 0$ and A is fixed by normalization. Since $y = \exp(-r)$ the series converge rapidly with increasing r. Also by the theory of Frobenius series [14] the solution converges for $y < \infty$, that is, well past the boundary condition at $y = 1$. This boundary condition gives the eigenvalue condition as:

$$\sum_{n=0}^{\infty} c_n(W) = 0$$

That is W is varied until $\sum_{n=0}^{\infty} c_n$ equals zero.

5 Scattering solution

In this case $m = \pm i\sqrt{\Pi W}$, we require $R(1) = 0$, i.e. at $r = 0$ the wavefunction is zero, and the scattering solution is:

$$R(y) = A\left\{[\cos(\sqrt{\Pi W}\ln y) - i\sin(\sqrt{\Pi W}\ln y)] \sum_{n=0}^{\infty} c'_n y^n - \left(\frac{\Sigma c'_n}{\Sigma c_n}\right)[\cos(\sqrt{\Pi W}\ln y) + i\sin(\sqrt{\Pi W}\ln y)] \sum_{n=0}^{\infty} c_n y^n\right\} \tag{6}$$

where A is fixed by normalization.

The case of $W = 0$, $m = 0$, yields, by the theory of Frobenius series:

$$R(y) = A \sum_{n=0}^{\infty} c_n y^n + B\left\{\ln y \sum_{n=0}^{\infty} c_n y^n + \sum_{n=0}^{\infty} \left.\frac{\partial c_n}{\partial m}\right|_{m=0} y^n\right\}$$

Since c_0 is a constant, independent of m:

$$\sum_{n=0}^{\infty} \left.\frac{\partial c_n}{\partial m}\right|_{m=0} y^n = \sum_{n=1}^{\infty} \left.\frac{\partial c_n}{\partial m}\right|_{m=0} y^n$$

$R(0) = Ac_0 + B\{-\infty + 0\}$, which is unbounded and has no eigenvalues, and thus is a scattering solution.

6 Momentum wavefunctions

Both bound-state and scattering solutions are of the form:

$$\sum_{j=0}^{\infty} \alpha_j e^{-jr}$$

and the series are uniformly absolutely convergent [15], the Fourier transform is easily found to be:

$$\sum_{j=0}^{\infty} \alpha_j \left(\frac{1}{j + ip/\hbar}\right) \text{ where } p \text{ is the momentum.}$$

The Fourier transform of Eq. (5), with $B = 0$, is:

$$A \sum_{n=0}^{\infty} c_n/(n + \sqrt{\Pi W} + ip/\hbar) \tag{7}$$

The Fourier transform of Eq. (6) is:

$$A\left\{-\left(\frac{\Sigma c_n'}{\Sigma c_n}\right) \sum_{n=0}^{\infty} c_n/(n + i\sqrt{\Pi W} + ip/\hbar) + \sum_{n=0}^{\infty} c_n'/(n - i\sqrt{\Pi W} + ip/\hbar)\right\} \tag{8}$$

This means that the coefficients c_n of the Frobenius series fully define the mechanics of the particle.

Equations (7) and (8) represent the momentum wavefunctions.

Examples

First consider the Morse potential, which has an accurate analytical formula for its eigenvalues, which allows the numerical accuracy of this method to be evaluated. It must be pointed out that the present method is intrinsically theoretical and not numerical, that is the wavefunctions are derived as analytical Taylor series which can be used elsewhere in their analytical form [15].

Consider:

$$V(r) = De^{-2\alpha(r-r_0)/r_0} - 2De^{-\alpha(r-r_0)/r_0}$$

Substitution into the Schrödinger equation gives:

$$S'' + 2\mu_m/\hbar^2\{W - De^{-2\alpha(r-r_0)/r_0} + 2De^{-\alpha(r-r_0)/r_0}\}S = 0$$

Now let $y = e^{-x-1}$, $x = (r - r_0)/r_0$, $y \in [0, 1]$, $S(r) = R(y)$.

This gives $y^2R'' + yR' + \frac{2\mu_m}{\hbar^2}\{W + De^{\alpha}2[y^{\alpha} - e^{\alpha}y^{2\alpha}]\}R = 0$

Instead of using the Bessel functions of the text, Jacobi polynomials are used here because they have a finite Taylor series. Any orthogonal functions which are complete and orthogonal over [0, 1] will do, the Jacobi Polynomials are complete and orthonormal [10] over [0, 1]. Replacing the functions of the actual variable by a good approximation ensures that the results must be close to the true solutions.

Expansion of $De^{\alpha}[2y^{\alpha} - e^{\alpha}y^{2\alpha}]$ as a sum of Jacobi's gives:

$$De^{\alpha}[2y^{\alpha} - e^{\alpha}y^{2\alpha}] = De^{\alpha} \sum_{k=0}^{\infty} a_k G_k(1, 1, y)$$

where the

$$a_k = (2k)!(2k+1)/(k!)^3 \sum_{i=0}^{k} (-1)^i \binom{k}{i} \frac{(2k-i)!}{(k-i)!} \times \left[\frac{2}{k-i+\alpha+1} - \frac{e^{\alpha}}{k-i+2\alpha+1} \right]$$

and use has been made of the formula [10]:

$$G_k(1, 1, y) = k!/(2k)! \sum_{i=1}^{k} (-1)^i \binom{k}{i} \frac{(2k-i)!}{(k-i)!} y^{k-i}$$

and the normalization condition [10]:

$$\int_0^1 G_k(1, 1, y) G_j(1, 1, y)\, dy = \begin{cases} 0, & k \neq j \\ (k!)^4/(2k+1)[(2k)!]^2, & k = j \end{cases}$$

Evaluation of the a_k's and some simplification show that $De^{\alpha}[2y^{\alpha} - e^{\alpha}y^{2\alpha}]$ is approximated excellently by:

$$De^{\alpha}[48/77y + 144/77y^2 - (16/33 + e^{\alpha})y^3]$$

for $\alpha = 1.50$, $D = 4.747$ eV and $2\mu_m r_0^2/\hbar^2 = 132.597\ \text{eV}^{-1}$. These parameters correspond to the values for the hydrogen molecule.

We obtain the following recursion formula:

$$c_n = (2\mu_m r_0^2/\hbar^2) \frac{De^{\alpha}}{(n^2 + 2nm)} [-48/77c_{n-1} - 144/77c_{n-2} + (16/33 + e^{\alpha})c_{n-3}]$$

where c_0 is arbitrarily chosen to be one.

The eigenvalues are generated from the requirement of Eq. (4).

Convergence of the above series was obtained for the worst case where W is close to zero, within 380 terms. A few lines of computer code were written in Mathematica [16], and run on a small personal computer, produced all of the correct eigenvalues. The zero's of the function Σc_n were isolated by looking for a sign change, and then searching the region for the corresponding root.

Convergence is worst at $y = 1$ for evaluation of the wavefunction; in the rest of configuration space $y < 1$, and the nth term of the series is multiplied by the rapidly decreasing factor of y^n. Thus for very small values of y, that is for large values of the distance r, the series converges fully in only a few terms and excellent asymptotic solutions are obtainable for r near infinity.

This example demonstrates the numerical handling of a well known problem with an analytical solution. It gives us confidence in the method, next applied to a more difficult problem, i.e. a finite sum of Gaussian minima or maxima. We

Table 1

# of level	7 term approx/eV	8 term approx/eV	9 term approx/eV	NAG/eV
0	− 2.623	− 2.627	− 2.627	− 2.627
1	− 1.858	− 1.855	− 1.855	− 1.855
2	− 1.201	− 1.202	− 1.201	− 1.200
3	− 0.641	− 0.643	− 0.643	− 0.643
4	− 0.184	− 0.184	− 0.185	− 0.185

The largest difference between the two methods is 0.5%

specifically solve the case of two Gaussians for the first five eigenvalues and compare these values to the first five eigenvalues obtained from a Prüfer transform, shooting technique used by the NAG subroutine library. The results are contained in Table 1.

Consider:

$$V(r) = \sum_{i=1}^{N} A_i e^{-a_i^2(r-r_i)^2}$$

where the $a_i > 0, i = 1, 2, \ldots$ and $r_1 < r_2 < \ldots$, that is, $V(r)$ is a sum of Gaussian wells or humps or a mixture of the two.

Substitution of $V(r)$ into the radial Schrödinger equation with $l = 0$ gives:

$$S'' + 2\mu_m/\hbar^2 \left\{ W - \sum_{i=1}^{N} A_i e^{-a_i^2(r-r_i)^2} \right\} S = 0$$

Substitute $y = e^{-a_j r}$, $S(r) = R(y)$.

This gives $y^2 R'' + yR' + \Pi \left\{ W - \sum_{i=1}^{N} A_i y^{-a_i^2 \ln y/a_j^2 - 2r_i a_i^2/a_j} e^{-a_i^2 r_i^2} \right\} R = 0,$

$$\text{where } \Pi = \frac{2\mu_m}{\hbar^2}$$

Now $y^{-a_i^2 \ln y/a_j^2 - 2r_i a_i^2/a_j}$ is bounded on [0, 1]. So it may be expanded in terms of Jacobi polynomials $G(1, 1, y)$.

$$y^{-a_i^2 \ln y/a_j^2 - 2r_i a_i^2/a_j} = \sum_{k=0}^{\infty} a_k G_k(1, 1, y)$$

where

$$a_k = ((2k)!)^2 (2k+1)/(k!)^4 \int_0^1 G_k(1, 1, y) y^{-a_i^2 \ln y/a_j^2 - 2r_i a_i^2/a_j} dy$$

$$= (2k)!(2k+1)/(k!)^3 \sum_{i=0}^{k} (-1)^i \binom{k}{i}$$

$$\times \frac{(2k-i)!}{(k-i)!} \int_0^1 y^{-a_i^2 \ln y/a_j^2 - 2r_i a_i^2/a_j + k - i} dy$$

Now

$$\int_0^1 y^{-a_i^2 \ln y/a_j^2 - 2r_i a_i^2/a_j + k - i} dy = \mathrm{Exp}[a_j^2(i-1-k+2a_i^2 r_i/a_j)^2/4a_i^2] \times [1 - \mathrm{Erf}[-a_j(i-k-1 + 2a_i^2 r_i/a_j)/2a_j]] \times (\sqrt{\pi} a_j/2a_i)$$

Hence:

$$a_k = (2k)!(2k+1)/(k!)^3 \sum_{i=0}^{k} (-1)^i \binom{k}{i} \frac{(2k-i)!}{(k-i)!} \times \mathrm{Exp}[a_j^2(i-1-k+2a_i^2 r_i/a_j)^2/4a_i^2] \times [1 - \mathrm{Erf}[-a_j(i-k-1+2a_i^2 r_i/a_j)/2a_j]] \times (\sqrt{\pi} a_j/2a_i)$$

The Jacobi expansion is terminated when an acceptable approximation is obtained. From the results of the last section the coefficients c_n may be obtained to yield solutions accoring to Eqs. (5) and (6) or momentum space solutions according to Eqs. (7) and (8).

To give a specific demonstration of the method a particular case of the previous problem is solved. Let $N = 2$, $A_1 = -5$ eV, $A_2 = 2$ eV, $r_1 = 0$, $r_2 = .5$ Å, $a_1 = a_2 = 1$ Å^{-1}, $a_j = 1$ Å^{-1}, $\mu_m = .5 \times 10^{-27}$ kg. $\Pi = 144.052$ eV^{-1}.

This potential corresponds to an attractive well of depth -3.4424 eV at the origin and a small maximum of height 0.212 eV further out at 1.554 Å.

Three approximations were used; given by the first seven, eight and nine terms of the Jacobi expansion. Error curves showing the difference between the real curve and the approximation are shown in Fig. 1. As expected the higher order approximations show better results.

After some manipulation and from Eq. (4) this yields the following recursions, defining the c_n.

The seven term expansion yields:

$$\begin{aligned} c_n(n^2 + 2nm) - \Pi[&(-0.179720567 \times 5 - 1.952623062 \times 2 \times e^{-0.25})c_{n-1} \\ &+ (5.630630955 \times 5 + 23.92535782 \times 2 \times e^{-0.25})c_{n-2} \\ &+ (-57.13154941 \times 5 - 9.149903944 \times 2 \times e^{-0.25})c_{n-3} \\ &+ (153.1547901 \times 5 - 141.9916296 \times 2 \times e^{-0.25})c_{n-4} \\ &+ (-191.8262691 \times 5 + 304.9877645 \times 2 \times e^{-0.25})c_{n-5} \\ &+ (118.7541858 \times 5 - 248.2222894 \times 2 \times e^{-0.25})c_{n-6} \\ &+ (-29.40504996 \times 5 + 73.38666123 \times 2 \times e^{-0.25})c_{n-7} \end{aligned}$$

where $m = \sqrt{\Pi(-W + 0.050366)}$.

While the eight term expansion yields:

$$\begin{aligned} c_n(n^2 + 2nm - \Pi[&(-0.53324441045 \times 2 \times e^{-0.25} - 0.303443744 \times 5)c_{n-1} \\ &+ (-0.91376862423 \times 2 \times e^{-0.25} + 7.795786515 \times 5)c_{n-2} \\ &+ (173.00369005396 \times 2 \times e^{-0.25} - 73.0093568260 \times 5)c_{n-3} \end{aligned}$$

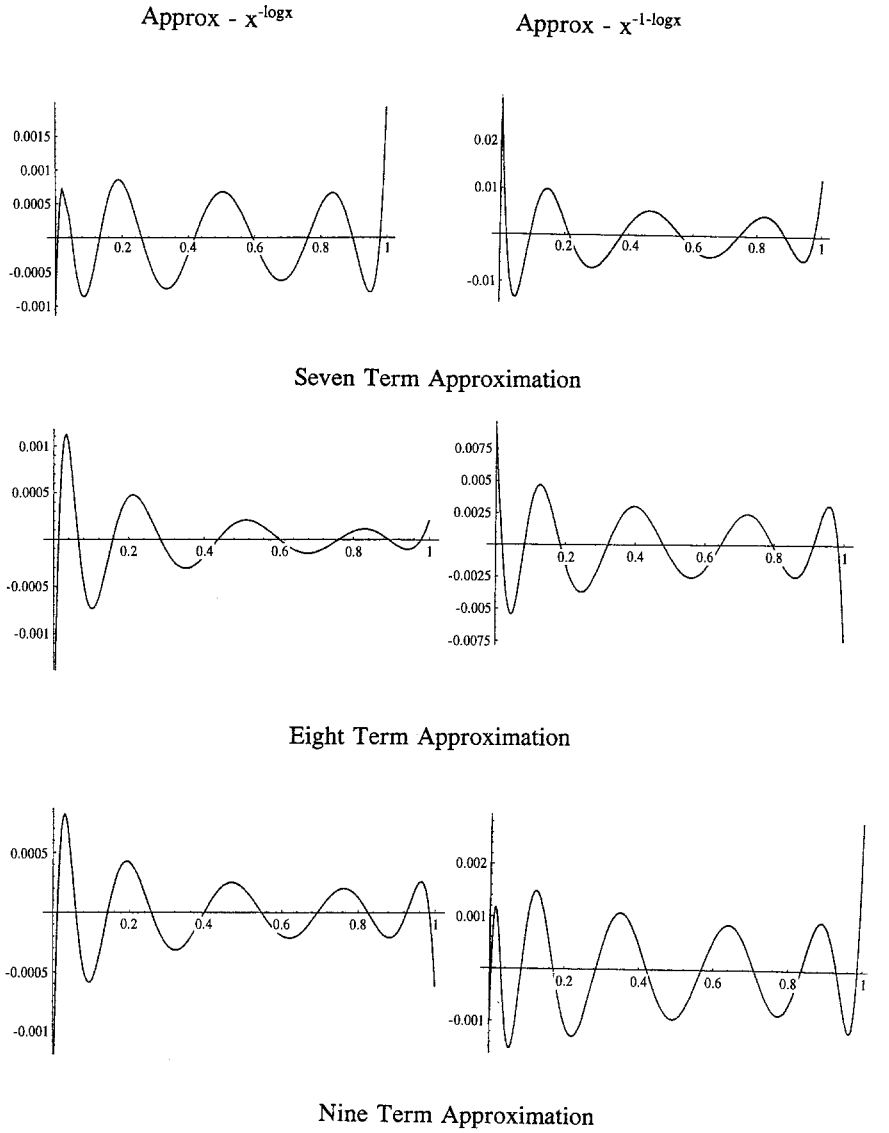

Fig. 1.

$$+ (-825.06760708811 \times 2 \times e^{-0.25} + 212.696567988 \times 5)c_{n-4}$$
$$+ (1725.7857978340 \times 2 \times e^{-0.25} - 315.673 \times 5)c_{n-5}$$
$$+ (-1905.8199949207 \times 2 \times e^{-0.25} + 263.242 \times 5)c_{n-6}$$
$$+ (1088.2423993010 \times 2 \times e^{-0.25} - 117.867 \times 5)c_{n-7}$$
$$+ (-253.71393450209 \times 2 \times e^{-0.25} + 22.1155 \times 5)c_{n-8} = 0$$

where $m = \sqrt{\Pi(-W + .02825)}$.

The nine term expansion gives:

$$\begin{aligned} c_n(n^2+2nm) - \Pi[&(-0.229808049\times 5 + 0.392537998\times 2e^{-0.25})c_{n-1} \\ &+ (6.175801363\times 5 - 21.28098166\times 2\times e^{-0.25})c_{n-2} \\ &+ (-57.88949543\times 5 + 363.0976784\times 2\times e^{-0.25})c_{n-3} \\ &+ (138.9872436\times 5 - 1751.7758\times 2\times e^{-0.25})c_{n-4} \\ &+ (-109.2870584\times 5 + 4320.568738\times 2\times e^{-0.25})c_{n-5} \\ &+ (-80.73461364\times 5 - 6230.458229\times 2\times e^{-0.25})c_{n-6} \\ &+ (219.0897915\times 5 + 5324.62271\times 2\times e^{-0.25})c_{n-7} \\ &+ (-156.8928416\times 5 + 2504.290974\times 2\times e^{-0.25})c_{n-8} \\ &+ (39.77963529\times 5 + 500.128231\times 2\times e^{-0.25})c_{n-9} \end{aligned}$$

where $m = \sqrt{\Pi(-W + 0.008139)}$.

The eigenvalue condition is given by equation (4).

These are complex transcendental equations, whose solution it is impossible to take in at a glance, so further discussion is required. Consideration of the three recursions shows that convergence of the c_n terms is of the form:

$$(\max\{\text{Abs}[\text{coefficients multiplying } c_{n-1}, \cdots c_{n-7,8,9}]\})^n/(n!)^2$$

In the actual example the constants multiplying c_{n-5}, c_{n-6} and c_{n-7} of the seven, eight and nine term recursions are the largest. They are 1.7×10^4, 6.2×10^5, 10^4 resp.

Thus convergence is of the form

$$\frac{(1.7\times 10^4)^n}{(n!)^2}, \quad \frac{(6.2\times 10^5)^n}{(n!)^2}, \quad \frac{10^{4n}}{(n!)^2}$$

for the seven, eight and nine term recursions, respectively.

This may seem to be very fast but a few substitutions of n will show that the values of c_n rise quickly before falling off to zero as the factorial dominates. Since the c_n rise quickly, Σc_n will also rise quickly before converging. Thus, to evaluate the function Σc_n one needs to add and subtract large numbers of similar size and the loss of significant figures becomes very marked. In the present instance, the sum reached a peak of 10^{121} for the seven and eight term approximations before decreasing to around 10^{-5} as the final converged answer. For the nine term approximation the sum peaked at 10^{340} before decreasing again to around 10^5. Because the sum peaked at about 10^{121} and 10^{340} c_n needed to be evaluated at more than 121 digits or 340 digits of precision, to arrive at an accurate answer for the summation. This is interesting because in all cases the recursion itself only required 30 digits of precision to solve. This clearly demonstrates the trade off between accuracy and computing time that is involved. Because of the high precision requirements a program was written within the framework of Mathematica [16], which allows calculations to be run to any precision. Since the constants in the recursions and Π are not to 130 digits or 350, they were treated as exact rational numbers, using Mathematica to evaluate $e^{-1/4}$ to 130 or 350 digits of precision. From this point on the program uses 130 or 350 digits for all calculations. A small program was written and the series summed to 1500, 2240, 4500 terms for the seven, eight and nine term approximations respectively, where the final coefficient added

was of the order of 10^{-16} or less. The zeros of the function Σc_n were isolated by looking for a sign change, and the searching the region for the corresponding root. The results obtained are presented in Table 1 together with the results obtained via numerical integration using a NAG routine for comparison. Exponential increase in computer usage as the approximation is raised for a small increase in the accuracy of the final answer (see Table 1) highlights the interplay of achieving the best approximation while minimizing computer usage.

It needs to be stressed that the numerical examples serve to show that the method works numerically. They are in no way an indication of how the authors see the method implemented practically. The best practical implementation for ground-state problems would be to apply the method as follows:

Because the series equation (5) converges extremely quickly for y close to zero, that is when r approaches infinity, good asymptotic solutions are obtained near infinity. These asymptotic solutions can be used to obtain the eigenvalues with the use of a Prüfer transform shooting technique (such as the NAG algorithm). Once the eigenvalues have been obtained calculation of the wavefunction is more transparent than the evaluation of the eigenvalues because now the series $\{c_n x^{n+m}\}$ $0 < x < 1$ contains the factor x^{n+m} which acts as a convergence factor, especially when m is large. Several scaling procedures were tried out in an effort to reduce the number of significant figures of input. However, to maintain the same accuracy, this requires more terms of the series to sum and the available hardware was not sufficiently powerful for this. This does not preclude the use of appropriate convergence acceleration techniques in future applications. It was, for the same reason, not possible to obtain a scattering solution, which requires computation with complex numbers.

It needs to be stated that because Σc_n is a uniformly absolutely convergent series [14] it can be used to obtain all the energy eigenvalues including those positive ones to the left of the potential barrier. This is important, because the system is bound on only one side and is capable of tunneling through the barrier. This is difficult to handle by standard numerical techniques, since the boundary condition at infinity cannot be replaced by an arbitrarily large finite number, and asymptotic solutions to the equation near infinity are needed. It is not always possible to obtain these solutions to the required accuracy. In the method proposed here the boundary conditions are finite and the evaluation of *all* eigenvalues becomes a systematic search through the energy range of interest.

It is noted that zero corresponds to infinity of the original distance configuration space, and the series converges faster and faster as $y \to 0$ or as $r \to \infty$. Excellent asymptotic solutions obtainable near infinity can be used to overcome the problems mentioned in the previous paragraph.

References

1. Compare Footnote in: French AP, Taylor EF (1978) An introduction to quantum physics, Thomas Nelson & Sons, p 394
2. Dunham JL (1932) Phys Rev 41:713
3. Pauling L, Wilson EB (1935) Introduction to quantum mechanics, McGraw-Hill, p 198–203
4. Flügge S (1974) Practical quantum mechanics. Springer-Verlag
5. Hartree DR (1928) Proc Camb Phil Soc 24:105; Hartree DR (1932) Mem Manchester Phil Soc 77:91; Richardson RGD (1917) Trans Am Math Soc 18:489; Courant R, Friedrichs K, Leary H (1928) Math Ann 100:32; Kimball GE, Shortley GA (1934) Phys Rev 45:815

6. Bose SK, Varma N (1990) Phys Lett A 147:85
7. de Souza Dutra A (1988) Phys Lett A 131:319
8. Aly HH, Barut AO (1990) Phys Lett A 145:299
9. Kanshal RS (1989) Phys Lett A 142:57
10. Abramowitz M, Stegun IA (eds) (1972) Handbook of mathematical functions. Dover, NY; Gradsteyn IS, Ryzhik IM (1980) Tables of integrals, series and products. Academic Press, NY p 307, 930
11. Titchmarsh EC (1962) Eigenfunction expansions, Parts I and II. Clarendon Press, Oxford
12. Ince EL (1956) Ordinary differential equations. Dover, NY, p 396–403
13. Milne–Thomson LM (1933) The calculus of finite differences. MacMillan, London, p 380
14. Coddington EA (1961) An introduction to ordinary differential equations. Prentice-Hall, NY p 143–166
15. Travlos SD, Boeyens JCA (1991) J Chem Phys 95:4241
16. Wolfram S (1988) A system for doing mathematics by computer. Addison-Wesley, NY