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Accurate and Stable Numerical Solutions to the Schrödinger Equation

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ABSTRACT

A new method has been developed for accurate and stable numerical solutions of ordinary differential equations. Applied to the Schrödinger equation, the basic numerical equations are two simultaneous Taylor expansions between space steps of both the wave function $R(\rho)$ and the slope of the wave function $m(\rho)$, where it is absolutely necessary to use the same number of terms in each expansion, viz.,

$$R(\rho+\Delta\rho) = R(\rho) + m(\rho)\Delta\rho + \frac{1}{2} m'(\rho)\Delta\rho^2 + \ldots,$$

and

$$m(\rho+\Delta\rho) = m(\rho) + m'(\rho)\Delta\rho + \frac{1}{2} m''(\rho)\Delta\rho^2 + \ldots,$$

with

$$m'(\rho) = -\frac{2}{\rho} m(\rho) + \left[\frac{1}{4} + \frac{\ell(\ell+1)}{\rho^2} - \frac{n}{\rho}\right] R(\rho)$$

for the Coulomb potential. Initial values applicable to the screened Coulomb as well as to the standard Coulomb potential are derived by (a) an exact series solution of the Schrödinger equation and (b) an approximate analytical solution valid near the origin for all n, ℓ to terms of order ρ^2. For example, using the cubic terms in the Taylor expansions with $\Delta\rho = 10^{-4}$ and using a computer that holds ten significant decimal digits in single precision, accuracies of at least 7 to 9 significant figures are obtained in the range $\rho \lessapprox 18$, and accuracies of about nine or more decimal places are obtained throughout the range of interest, $\rho \leqq 20$. For "non-analytic" potentials such as the screened Coulomb potential, it is important to demonstrate the accuracies to which eigenvalues and eigenfunctions can be obtained by iteration. Application of the method to the screened Coulomb potential was considered, and the effects of errors due to round-off, truncation, and loss of significance were discussed. As far as the author can determine, the present results represent the first known accurate and stable numerical solutions of the radial hydrogenic Schrödinger equation. With the present ability to calculate eigenvalues to nine or more significant figures and eigenfunctions to nine or more decimal places, the present method becomes an alternative to perturbation and variational methods.

PROBLEM STATUS

This is a report of the work accomplished to date on the problem; work on other phases of the problem continues.

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ACCURATE AND STABLE NUMERICAL SOLUTIONS TO THE SCHRÖDINGER EQUATION

INTRODUCTION

This report is specifically concerned with accurate and stable numerical solutions of the radial hydrogenic Schrödinger equation. More generally, the method developed here can be used for the numerical solution of ordinary differential equations of the ith order, the general form of which can be written as

$$y^{(i)} = f[x, y, y', y'', \ldots, y^{(i-1)}], \tag{1}$$

where f indicates a given linear or nonlinear function of the independent variable x as well as the dependent variable y and its derivatives up to and including $y^{(i-1)}$. It is well known (1-5) that, by introducing new variables, the explicit differential equation of order i can be replaced by i simultaneous differential equations of first order, viz.,

$$y' = m_1 \tag{2}$$

$$m_1' = m_2 \tag{3}$$

$$\vdots$$

$$m_{i-1}' = f(x, y, m_1, m_2, \ldots, m_{i-1}). \tag{4}$$

We will be interested in using the equivalent of Eqs. (2) and (4) in the numerical solution of the radial Schrödinger equation.

Interest in numerical solutions to the Schrödinger equation is stimulated when one faces interaction potentials that yield no known analytic functions as solutions — e.g., the Yukawa or screened Coulomb potential. Since these potentials, as well as the Coulomb potential, are singular at the origin, the standard numerical approaches (1,2,4,5) (even with ℓ, the angular momentum quantum number, set equal to zero) cannot be started correctly without qualitatively derived or approximate initial values (6). If, then, one goes to extremely small space steps in order to obtain greater accuracy through a minimization of the effects of inaccurate initial values, round-off errors (1,4-6) quickly degrade the accuracy of the numerical solution; i.e., it becomes unstable. Clearly, a new approach is needed.

A new method is presented for the numerical solution of differential equations, having the form of Eq. (1), that is conceptually and mathematically simple and is accurate and stable — the accuracy being limited only by the number of decimal digits held (or used) by the computer. The method involves (a) the <u>simultaneous</u> Taylor expansions between <u>space steps</u> $\Delta x (= x_{j+1} - x_j$ in the standard notation of a subscript index j) of the quantities $y, m_1, \ldots, m_{i-1}$ in Eqs. (2), (3), and (4), which are the equivalent of Eq (1), and (b) the derivation of initial values through either an exact series solution of Eq. (1) valid at or near the origin, or through an approximate analytical solution of Eq. (1) valid at least to terms of order x^i, expressed as $O(x^i)$. In comparison with the Cauchy (or Euler) method and its variations (1,2,4,5) the Cauchy method effectively uses only the first term of a Taylor expansion.

In the present report we will discuss the Schrödinger equation, and the sections to follow are (a) a review of the analytical solution of this equation with the Coulomb

potential (CP) and the explicit presentation of the present numerical method, (b) a derivation of exact and "approximate" initial values, (c) a discussion of the numerical results with the CP using the known eigenvalues and a demonstration of how accurately these eigenvalues can be obtained by trial-and-error iterations, (d) a discussion of the application to the screened Coulomb potential, and (e) the summary and conclusions.

The reader is referred to Refs. 1, 4, and 5, or other texts on numerical methods, for critical discussions of the standard numerical methods (and their variations) related to differential equations.

THE SCHRÖDINGER EQUATION

The well-known radial Schrödinger equation for a hydrogen atom (or hydrogenic ion) is given (2,3,6-10) by

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR(r)}{dr}\right] - \frac{\ell(\ell+1)}{r^2}R(r) + \frac{2\mu}{\hbar^2}[\epsilon - V(r)]R(r) = 0, \tag{5}$$

where the symbols have their standard meanings. With the transformations

$$\rho = 2Zr/na_0$$

and (6)

$$\epsilon_n = -Z^2\hbar^2/2a_0^2\mu n^2,$$

Eq. (5) becomes

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left[\rho^2\frac{dR(\rho)}{d\rho}\right] + \left[-\frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2} - nV(\rho)\right]R(\rho) = 0, \tag{7}$$

where the $1/4$ in Eq. (7) is an arbitrary scale of the energy eigenvalue. Since we will also be interested in the screened Coulomb potential (11), let us use the symbol b^2 in place of the $1/4$, yielding

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left[\rho^2\frac{dR(\rho)}{d\rho}\right] + \left[-b^2 - \frac{\ell(\ell+1)}{\rho^2} - nV(\rho)\right]R(\rho) = 0 \tag{8}$$

as the equation of interest for analytic and numerical solutions, depending on form of $V(\rho)$.

One of the problems of theoretical physics is that analytic solutions to Eq. (8) exist for only a limited number of central potentials $V(r)$ (12), most of which are physically unrealistic. Even the well-studied Coulomb potential for a single electron and nucleus represents an <u>isolated</u> hydrogenic atom (or ion). When faced with the very interesting Yukawa or Debye-Hückel type screened Coulomb potential (13,14), Eq. (8) yields no known analytic functions as solutions. Since a screened Coulomb potential (SCP) represents a first-order approximation to the many-body problem at low <u>and</u> high densities (15), accurate and stable numerical solutions to the Schrödinger equation with the SCP would be of fundamental theoretical interest. To this end the Schrödinger equation will be studied numerically with the Coulomb potential to demonstrate the accuracy of the present numerical method. First, however, we will review the well-known analytic solutions.

Outline of Analytic Coulomb Solutions

In the Coulomb problem the potential energy $V(r) = -Ze^2/r$ is substituted in Eq. (5). This leads to a $V(\rho)$ for Eq. (8) given by

$$\text{CP:} \quad V(\rho) = -\frac{1}{\rho}$$

with (9)

$$b^2 = \frac{1}{4}$$

for the standard solutions. With the above, Eq. (8) can be written as

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[\frac{n}{\rho} - \frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2}\right] R = 0 . \tag{10}$$

What follows in the remainder of this discussion can be found in most books on quantum theory, but it will be repeated for convenience and reference.

Noting that at large ρ the asymptotic solution to Eq. (10) is $R(\rho) = \rho^s \exp(\pm\rho/2)$, only the negative exponential is of interest, and an exact solution is sought in the form

$$R(\rho) = F(\rho) \exp(-\rho/2) . \tag{11}$$

Substituting Eq. (11) into Eq. (10) leads to

$$F'' + \left(\frac{2}{\rho} - 1\right)F' + \left[\frac{n-1}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right] F = 0 , \tag{12}$$

where the primes indicate derivatives with respect to ρ. (This will be true throughout the remainder of this report except where noted.) Finally, a series solution of Eq. (12) is sought in the form

$$F(\rho) = \rho^s L(\rho) = \rho^s \Sigma a_k \rho^k, \qquad a_0 \neq 0. \tag{13}$$

The criterion that an acceptable wave function be finite at infinity leads to a termination of the series, Eq. (13), with n chosen as an integer and $n \geqq \ell + 1$. The series will then terminate after $n - \ell$ terms.

The finite series, now called $L(\rho)$ in Eq. (13), is related to the associated Laguerre polynomials and indicated by $L_j^k(\rho)$. Now the normalized analytic wave functions are written as

$$R_{n,\ell}(\rho) = \left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!^3}\right]^{1/2} e^{-(\rho/2)} \rho^\ell L_{n+\ell}^{2\ell+1}(\rho) , \tag{14}$$

where the symbols have the standard meanings. Henceforth, we will assume that the term in brackets is equal to 1.0, and we will refer to the unnormalized solutions as

$$R_{n,\ell}(\rho) = \rho^\ell e^{-(\rho/2)} L_{n+\ell}^{2\ell+1}(\rho) , \tag{15}$$

with the leading term in the polynomial normalized to 1.0. The first few solutions given by Eq. (15) are, with their standard designations,

$$1s: \quad R_{1,0} = e^{-(\rho/2)} , \tag{16}$$

$$2s: \quad R_{2,0} = \frac{1}{2}(2-\rho) e^{-(\rho/2)} , \tag{17}$$

$$2p: \quad R_{2,1} = \rho e^{-(\rho/2)}, \tag{18}$$

$$3s: \quad R_{3,0} = \frac{1}{6}(6 - 6\rho + \rho^2)e^{-(\rho/2)}, \tag{19}$$

$$3p: \quad R_{3,1} = \frac{1}{4}(4 - \rho)\rho e^{-(\rho/2)}, \tag{20}$$

$$3d: \quad R_{3,2} = \rho^2 e^{-(\rho/2)}, \tag{21}$$

$$4s: \quad R_{4,0} = \frac{1}{24}(24 - 36\rho + 12\rho^2 - \rho^3)e^{-(\rho/2)}, \tag{22}$$

$$4p: \quad R_{4,1} = \frac{1}{20}(20 - 10\rho + \rho^2)\rho e^{-(\rho/2)}, \tag{23}$$

and

$$4d: \quad R_{4,2} = \frac{1}{6}(6 - \rho)\rho^2 e^{-(\rho/2)}. \tag{24}$$

(See the literature for graphs of these functions $R_{n,\ell}$ as well as $\rho^2(R_{n,\ell})^2$.)

The Present Numerical Method

The basic feature of the present numerical method is the simultaneous Taylor expansions between steps Δx of the terms on the left side of Eqs. (2), (3), ..., (4) of the first section, viz., y, m_1, ..., m_{i-1} — not their derivatives — with the same number of terms. At each step we calculate

$$y(x + \Delta x) = y(x) + m_1(x)\Delta x + (1/2)m_2(x)\Delta x^2 + \ldots, \tag{25}$$

$$m_1(x + \Delta x) = m_1(x) + m_2(x)\Delta x + (1/2)m_3(x)\Delta x^2 + \ldots, \tag{26}$$

$$\vdots$$

$$m_{i-1}(x + \Delta x) = m_{i-1}(x) + m'_{i-1}(x)\Delta x + (1/2)m''_{i-1}(x)\Delta x^2 + \ldots, \tag{27}$$

where it is essential to use the same number of terms in each expansion. In Eqs. (25) to (27) the m_i's are used to emphasize coupling between the system of equations. Equation (4) — the equivalent of Eq. (1) — defines $m'_{i-1}(x)$ for the particular differential equation of interest. The higher derivatives of m_{i-1} are, of course, obtained from this expression for $m'_{i-1}(x)$.

Relative to the Schrödinger equation, second-order ordinary differential equations such as Eqs. (25) and (26) (equivalent to Eq. (10)) would become

$$R(\rho + \Delta\rho) = R(\rho) + m(\rho)\Delta\rho + \frac{1}{2}m'(\rho)\Delta\rho^2 + \ldots \tag{28}$$

and

$$m(\rho + \Delta\rho) = m(\rho) + m'(\rho)\Delta\rho + \frac{1}{2}m''(\rho)\Delta\rho^2 + \ldots, \tag{29}$$

with

$$m'(\rho) = -\frac{2m(\rho)}{\rho} + \left[\frac{1}{4} + \frac{\ell(\ell+1)}{\rho^2} - \frac{n}{\rho}\right]R(\rho) \tag{30}$$

from which $m''(\rho)$, etc., can be obtained. Note that in Eq. (28) $m'(\rho)$ and all higher derivatives are known exactly from the differential equation, but $R(\rho)$ and $m(\rho)$ are only available from the Taylor expansions in the previous step.

Before solutions to a desired accuracy are possible, it is necessary to know the initial values of the terms used on the right side of Eqs. (28) and (29). The number of terms used will also depend on considerations other than accuracy or stability, as will be discussed in the section on numerical results. In the next section we will first derive all the initial derivatives, exactly, from a series expansion and then will derive exact initial magnitudes and slopes of the wave functions and approximate second and higher order derivatives from an approximate analytical solution.

DERIVATION OF INITIAL VALUES

Exact Initial Values

Since the basic need for numerical methods arises from a lack of analytic solutions, we will approach the Schrödinger equation with the Coulomb potential independent of a knowledge of exact analytic wave functions. Equation (10) is of the form

$$\frac{d^2\omega}{dz^2} + p(z)\frac{d\omega}{dz} + q(z)\omega = 0, \tag{31}$$

and therefore we know (the reader will recall) from Fuchs's theorem that it has a formal solution (2,7,16) of the form

$$\omega = z^{\alpha}\Sigma a_k z^k, \qquad a_0 \neq 0, \tag{32}$$

valid near the regular singularity at the origin and where the series $\Sigma a_k z^k$ either terminates or has a nonzero radius of convergence. If the series does not terminate and if $zp(z)$ and $z^2 q(z)$ are regular when $|z| < L$, then the radius of convergence of the series is not less than L. (See the references or other texts for the proofs.)

In the present numerical initial-value problem we are mainly interested in any nonzero radius of convergence; for, once the numerical solutions are started, we can generate the complete solution through the system of equations, Eqs. (28), (29), and (30).

We will be a trifle more general (anticipating an approximate analytical solution) by looking for a solution of Eq. (10) of the form

$$R(\rho) = \rho^s \phi(\rho). \tag{33}$$

Substituting Eq. (33) into Eq. (10), we obtain

$$\left(\phi'' - \frac{1}{4}\phi\right)\rho^s + [2(s+1)\phi' + n\phi]\rho^{s-1} + [s(s+1) - \ell(\ell+1)]\phi\rho^{s-2} = 0. \tag{34}$$

Taking $s = \ell$, which results from the indicial equation, and dividing by ρ^{s-1}, Eq. (34) becomes

$$\left(\phi'' - \frac{1}{4}\phi\right)\rho + 2(\ell+1)\phi' + n\phi = 0. \tag{35}$$

We now obtain the exact series solution, valid near the origin, by expressing ϕ as

$$\phi = \Sigma\alpha_k\rho^k, \qquad \alpha_0 \neq 0 \tag{36}$$

and substituting into Eq. (35). The resulting values of α_k are

$$\alpha_1 = -\frac{n}{2(\ell+1)}\alpha_0 \tag{37}$$

with the recurrence relation

$$\alpha_{t+1} = \frac{\frac{1}{4}\alpha_{t-1} - n\alpha_t}{(t+1)(2\ell+2+t)}, \quad t \geqq 1. \tag{38}$$

Before discussing this series further, a slight digression is necessary to prepare for the initial values from the screened Coulomb potential. The screened Coulomb potential (11,17) varies near the origin as

$$V(r) \approx -\frac{1}{r} + \text{const}. \tag{39}$$

Equation (39) substituted into Eq. (8) leads to

$$b^2 = (1/4) + \text{const}, \tag{40}$$

with the fraction $1/4$ in Eqs. (10), (35), and (38) being replaced by b^2. With b^2 the recurrence relation, Eq. (37), becomes

$$\alpha_{t+1} = \frac{b^2\alpha_{t-1} - n\alpha_t}{(t+1)(2\ell+2+t)}, \tag{41}$$

with α_1 given by Eq. (37). If we now write $\beta = n/2(\ell+1)$, the first few terms in the series are given by

$$\alpha_1 = -\beta\alpha_0, \quad \alpha_0 \neq 0, \tag{42a}$$

$$\alpha_2 = \frac{b^2+\beta n}{2(2\ell+3)}\alpha_0, \tag{42b}$$

$$\alpha_3 = -\frac{2(2\ell+3)b^2\beta + b^2 n + \beta n^2}{2\times 3\times(2\ell+3)(2\ell+4)}\alpha_0, \tag{42c}$$

and

$$\alpha_4 = \frac{3(2\ell+4)b^4 + 2(5\ell+9)b^2\beta n + b^2 n^2 + \beta n^3}{2\times 3\times 4\times(2\ell+3)(2\ell+4)(2\ell+5)}\alpha_0. \tag{42d}$$

Since all symbols in Eqs. (42) are positive, ϕ is definitely an alternating series.

Returning now to the specific Coulomb potential with $b^2 = 1/4$, setting $n = \ell+1$ in the series terms of Eqs. (42) will yield the series for $\phi = \alpha_0 e^{-(\rho/2)}$ as it should. Another observation is that the series for ϕ is the equivalent of the product of the series for $\exp(-\rho/2)$ and the associated Laguerre polynomials $L_{n+\ell}^{2\ell+1}(\rho)$. (See Eq. (15))

Now with the exact series solution (18) given by $R_{n,\ell} = \rho^\ell \Sigma\alpha_k\rho^k$, it is easy to calculate all the initial derivatives for all n, ℓ. Taking derivatives of $R_{n,\ell}$ and setting $\rho = 0$, we obtain the exact initial values

$$R_{n,\ell}^{(i)}(0) \equiv i!\,\alpha_{i-\ell}, \tag{43}$$

with (i) indicating the ith derivative. For $i = \ell$ we set $\alpha_0 = 1.0$, and for $i < \ell$ we set $\alpha_{i-\ell} \equiv 0$. With the Coulomb potential the α_k are given by Eqs. (37) and (38). With the screened Coulomb potential the α_k are given by Eqs. (37) and (41), with the appropriate value of the constant in Eq. (40).

Initial Values from an Approximate Analytic Solution

An approximate analytic function valid near the origin can be obtained from Eq. (35). As $\rho \to 0$ Eq. (35) yields

$$2(\ell + 1)\phi' + n\phi \approx 0 \tag{44}$$

when we drop the term $(\phi'' - \frac{1}{4}\phi)\rho$.

Equation (44) readily yields

$$\phi_{n,\ell} \approx \phi_0 \exp[-n\rho/2(\ell + 1)] \tag{45}$$

or

$$R^0_{n,\ell} \approx \rho^\ell \exp[-n\rho/2(\ell + 1)] , \tag{46}$$

where we set $\phi_0 = 1.0$. The superscript zero on $R^0_{n,\ell}$ will emphasize its validity near $\rho = 0$. Even with the $1/4$ in Eq. (35) replaced by b^2 (above), Eq. (46) obtains, expressing the exact initial behavior of wave functions for all n, ℓ relative to the initial magnitude and slope. By comparing the expansion for $\exp[-n\rho/2(\ell + 1)]$ with the series solution, Eq. (36), with coefficients defined by Eqs. (37) and (38), we note that Eq. (45) is valid to terms $O(\rho^2)$, which supports the above statement. In either case the initial values and slopes of the wave functions are obtained without the usual qualitative arguments to prevent infinite values (6) of $m'(0)$.

In more general applications of the present numerical method it may not always be possible to obtain a formal series solution. Then an approximate analytical solution valid near the origin (or, near the initial point of interest) will be useful in generating initial values for the problem. In the case of a second-order differential equation, it is essential that the approximate analytic solution at least yield the exact initial magnitude and slope. Then an initial value for the second derivative can be defined by

$$R''(0) = m'(0) = \lim_{\rho \to 0} m'[R^0(\rho), R^{0\prime}(\rho)], \tag{47}$$

an initial value for the third derivative can be defined by

$$R'''(0) = m''(0) = \lim_{\rho \to 0} m''[R^0(\rho), R^{0\prime}(\rho), R^{0\prime\prime}(\rho)], \tag{48}$$

and so on. In the Schrödinger equation these definitions lead to excellent numerical results for cases $\ell = 0$, 1, and 2, as will be discussed in the next section.

NUMERICAL RESULTS WITH THE COULOMB POTENTIAL

We will now consider the Schrödinger equation with the Coulomb potential to demonstrate the accuracy and the stability of the present numerical method. If the well-known Coulomb wave functions cannot be calculated accurately and with stability, we could hardly trust the method for potentials with no analytic solutions. We will first use the known eigenvalues for the first few wave functions (n = 1, 2, and 3), and then we will start with approximate eigenvalues and search for more accurate values. In the second case, only the 1s and 2s wave functions will be considered.

Eigenvalues Known

We will consider in detail the first six eigenfunctions given in Eqs. (16) to (21). As used here, "accuracy" will mean the exact agreement with the Coulomb wave functions to a particular number of significant figures or number of decimal digits — no percent errors will be used. All the computations reported here were done on the CDC 3600 electronic computer at Rockville, Md., and the CDC 3800 at NRL (through the Research Computation Center at the Naval Research Laboratory). In the normal single-precision mode the CDC 3600 and the CDC 3800 hold ten significant figures, and the present code format prints out nine. The present discussion of accuracy should be scaled up or down depending on whether one uses a computer with more or less significant figures in its normal mode. If a computer is used in the double-precision mode — this usually doubles the number of significant figures — then the accuracy obtained in the normal mode will be possible to a greater magnitude of the independent variable. Or, if interested, one can use double precision with the present method to double the normal accuracy. If any numerical method leads to instabilities arising from inaccurate initial values or "mismatched" calculated quantities, then double precision will not help matters much — one obtains more precise wrong answers.

The following discussion will be relative to computing with ten significant figures, printing out nine of them, and using equal space steps $\Delta\rho$ throughout a problem, as given. The numerical results are compared to the exact analytical solutions at ρ = 0.1, 1, 2, 4, 6, . . . , 20. The values for $\exp(-x)$ are taken from Ref. 19. For the readers' convenience the Appendix gives values of $\exp(-x)$ for x = 0.05, 0.5, 1, 2, 3, . . . , 10 to 16 or more significant figures.

Tables 1, 2, and 3 summarize the results using known eigenvalues with n = 1, 2, and 3. The entries in the tables are the number of significant-figure agreement between the numerical solutions and the analytic solutions. The ninth "numerical" figure and the ninth "analytic" figure were compared directly, since we have no information from the tenth numerical figure to round the ninth figure up or down. In what follows, an expression like "using the quadratic term" will mean using the terms in the Taylor series up to and including the quadratic term. Furthermore, "Approximate initial values" will mean initial values obtained from the approximate analytic solution of the Schrödinger equation derived as Eqs. (46), (47), and (48). You will recall that these initial magnitudes and initial slopes are exact for all n, ℓ. The "R-equation" will refer to Eq. (28), and the "m-equation" will refer to Eq. (29) with $m'(\rho)$ given by Eq. (30). Finally, the calculations reported in this and the next section were carried out in one of seven modes as shown in Table 4. The results using modes a, b, and c are given in Table 1; results for modes d, e, and f are in Table 2, and the results for mode g are in Table 3.

A detailed discussion of error propagation in numerical solutions of differential equations is beyond the scope of this report. The reader is referred to Refs. 1, 4, and 5, or other texts on numerical methods. Kopal, in Ref. 1, pp. 219 to 231, develops a simple linear theory of error propagation which is of interest but is not directly applicable to the present nonlinear numerical method. For our present purposes, only a brief review of the definitions of the two numerical errors (1,4,5) and stability will be given. The first error is the rounding error. The difference between the complete sequence of decimal digits that represents a real number and the fixed number of digits available in the computing device used is defined as the rounding error. The second error, the truncation error, is defined as the error introduced by the termination of a sequence of steps, except those errors classified as rounding errors. Using a finite number of terms in a Taylor expansion is an obvious example. The absolute rounding error is determined by the number of decimal places retained, whereas the relative rounding error is approximately determined by the number of significant figures retained.

Table 1
Accuracies of Numerical Solutions of the Schrödinger Equation with Exact Initial Values. Numbers in the Table Give the Significant-Figure Agreement with the Exact Analytical Coulomb Wave Functions with Eigenvalues n Equal to 1, 2, and 3.

Wave Function	Mode*	Significant-Figure Agreement as ρ Equals Various Values											
		0.1	1	2	4	6	8	10	12	14	16	18	20
1s	a	9	9	9	9	8	9	8	8	8	8	7	6
	b	-	9	9	9	9	9	8	8	7	6	6	4
	c	5	4	4	5	3	3	3	3	3	3	4	4
2s	a	9	9	9	9	8	9	9	9	9	8	7	7
	b	-	9	9	9	8	8	9	9	7	7	6	6
	c	4	3	4	5	3	3	3	3	2	2	1	0
2p	a	9	9	8	9	9	8	7	7	7	6	5	5
	b	-	9	9	9	9	9	8	8	8	7	6	6
	c	3	3	3	3	3	4	3	3	2	2	1	0
3s	a	8	9	8	8	8	8	9	8	8	6	7	7
	b	-	9	9	8	8	9	8	9	8	9	9	9
	c	4	4	5	3	3	4	3	3	3	2	1	1
3p	a	9	8	9	9	9	9	9	8	9	8	7	6
	b	-	8	9	9	9	9	9	9	9	8	8	8
	c	2	3	3	4	4	3	4	3	3	3	2	2
3d	a	8	8	9	9	9	9	9	9	8	7	7	6
	b	-	6	6	7	7	7	6	6	6	6	6	6
	c†	-	-	-	-	-	-	-	-	-	-	-	-

*Mode a: Cubic terms; exact initial values; $\Delta\rho = 10^{-4}$.
Mode b: Cubic terms; exact initial values; $\Delta\rho = 10^{-3}$; $\rho = 0.1$ calculated but not printed.
Mode c: Linear terms; exact initial values; $\Delta\rho = 10^{-4}$.
†Not calculated.

In addition or subtraction the relative rounding error of the result may be larger than the relative error of either term. According to Alt (5), this loss of significance can be quite subtle and is one of the main pitfalls of numerical computation.

Finally, instability is defined as that phenomenon whereby a small local error occurring in one place during the computation will cause a much greater error at some later step.

Since we will be concerned with functions that decrease in absolute magnitude at large ρ, it will be impossible to avoid a "loss of significance" in subtraction once we reach the exponentially decreasing part of the wave function. Consequently, we will call a solution unstable which exhibits a large decrease in accuracy (the exact agreement to a number of significant figures with an exact analytic solution) owing to factors other than the loss of significance which occurs during addition or subtraction. If the accuracy of a numerical solution is limited mainly by loss of significance, then it is possible, using a stable method, to increase the accuracy by reducing the truncation error and/or using double precision. An unstable method or technique will merely yield a more precise wrong answer with the use of more digits.

Table 2
Accuracies of Numerical Solutions of the Schrödinger Equation with Exact and Approximate Initial Values. Numbers in the Table Give the Significant-Figure Agreement with the Exact Analytical Coulomb Wave Functions with Eigenvalues n Equal to 1, 2, and 3.

Wave Function	Mode*	Significant-Figure Agreement as ρ Equals Various Values											
		0.1	1	2	4	6	8	10	12	14	16	18	20
1s	d	9	9	9	9	8	9	8	8	7	6	6	5
	e	9	9	9	9	8	9	8	8	7	6	6	5
	f	5	4	4	5	3	3	3	3	3	3	4	4
2s	d	9	9	9	8	8	8	8	8	6	6	5	5
	e	7	7	9	8	6	6	7	8	7	6	5	5
	f	4	4	4	5	3	3	3	3	2	2	0	0
2p	d	8	8	8	8	8	8	7	8	8	6	5	5
	e	8	7	8	8	8	8	7	7	8	6	5	4
	f	3	3	3	3	3	4	3	3	2	1	1	0
3s	d	8	8	9	8	8	9	8	7	8	7	7	6
	e	6	8	7	7	6	7	7	7	7	6	7	6
	f	4	4	5	3	3	4	3	3	3	2	1	1
3p	d	7	8	8	8	9	8	8	8	9	7	6	5
	e	7	8	8	8	8	8	8	8	9	7	6	5
	f	2	3	3	4	4	3	4	3	4	3	1	1
3d	d	4	5	5	4	5	5	5	5	6	5	5	5
	e	4	4	5	4	5	5	4	4	5	4	4	5
	f†	-	-	-	-	-	-	-	-	-	-	-	-

*Mode d: Quadratic terms; exact initial values; $\Delta\rho = 10^{-4}$.
Mode e: Quadratic terms; "approximate" initial values; $\Delta\rho = 10^{-4}$.
Mode f: Linear terms; "approximate" initial values; $\Delta\rho = 10^{-4}$.
†Not calculated.

Table 3
Accuracies of Numerical Solutions of the Schrödinger Equation with the Wave Functions and the Slope of the Wave Functions Calculated with Unequal Numbers of the Terms in Their Taylor Expansions. The Numbers in the Table Give the Significant-Figure Agreement with the Exact Analytical Coulomb Wave Functions with n Equal to 1, 2, and 3, and ℓ Equal to 0 and 1, Only.

Wave Function*	Significant-Figure Agreement as ρ Equals Various Values											
	0.1	1	2	4	6	8	10	12	14	16	18	20
1s	7	6	5	5	4	3	1	2	0	0	0	0
2s	6	5	4	4	3	3	2	3	2	2	1	0
2p	6	4	3	4	4	4	2	3	2	1	1	0
3s	6	5	4	3	4	3	3	3	3	2	1	1
3p	5	4	4	4	5	4	3	3	3	3	1	2

*All calculations in mode g: R-equation quadratic and m-equation linear; exact initial values; $\Delta\rho = 10^{-4}$.

Table 4
Definitions of the Seven Modes by Which the Numerical Solutions to the Schrödinger Equation Were Obtained

Mode	R and m Equation Terms	Initial Values	$\Delta\rho$
a	cubic	exact	10^{-4}
b	cubic	exact	10^{-3}
c	linear	exact	10^{-4}
d	quadratic	exact	10^{-4}
e	quadratic	approximate	10^{-4}
f	linear	approximate	10^{-4}
g	R-eq. quadratic m-eq. linear	exact	10^{-4}

Returning again to the results in Tables 1 and 2, the present method is clearly stable when the same number of terms are used in the R and m equations — this is true even with the "approximate" initial values. On the other hand, mode g in Table 3 demonstrates the instability resulting from the use of mismatched calculated quantities in the R-equation: at the start mode g has the accuracy of the quadratic system (mode d) but this quickly degrades to the accuracy of the linear system. (The same degradation occurs with a linear R-equation and a quadratic m-equation.)

As for accuracy itself, mode a generally has almost maximum absolute accuracy (decimal places) obtainable, holding ten digits in single precision for states with $\ell = 0$, 1, and 2. Mode b has about the same accuracy — more or less — for states with $\ell = 0$, 1 but requires an order of magnitude <u>less</u> computing time. At large distances, however, there is not much choice between modes a, b, d, or e for $\ell = 0$, 1, or 2, as far as accuracy is concerned.

Note also that the linear systems, modes c and f, and the quadratic systems, modes d and e, yield essentially the same accuracy throughout the range, demonstrating that the approximate initial values of the second and higher derivatives defined by Eqs. (47) and (48) add a negligible error to the system of equations. Any other nonexact values of $m'(0)$ and $m''(0)$ will not necessarily work. For example, the 2p wave function was attempted in the quadratic mode e with $m'(0) = -2.0$, as derived by Sherwin (6) but yielded no increase in accuracy beyond that given by the linear mode f.

In planning numerical computations it is usually stated that the problem should be executed in a manner minimizing the cumulative effects of round-off errors and truncation errors (1,4,5). The stability of the present method seems to be independent of the truncation errors in the R- and m-equations. It also appears that the cumulative effect of the round-off error is not simply a function of the number of steps in the range of calculations but also depends on the nature of the solution.* Compare modes a and b in Table 1. If the round-off error is always proportional to the number of steps, then the accuracies at large ρ in mode b should always be greater than those of mode a. The accuracies in the 1s and 2s states, however, are greater for mode a than for mode b at large ρ. (In both modes a and b the truncation errors are less than 10^{-12}, whereas the round-off errors are in the tenth decimal place.) These results definitely suggest that

*A guarded qualitative generalization of the results from an example by Kopal (1) of error propagation during the numerical integration of $d^2y/dx^2 + y = 0$ would support this observation.

the cumulative round-off error is not only a function of the number of steps, but it also depends on the cumulative effect of the number of sign changes in the calculated function's slope. It appears that, in adding the terms of the R-equation, the effects of the random magnitudes of the digits in the eleventh decimal place tend to cancel as the derivatives change sign. If there is no sign change in the slope as in the 1s state, then the larger truncation error of mode b appears to have a greater effect than the order of magnitude decrease in the number of steps.

The results for the 3d wave function require additional comments. We note that $R_{3,2}(0) = m_{3,2}(0) = R'_{3,2}(0) = 0$. Hence, in the R and m equations, Eqs. (28) and (29), the initial significant figures are carried by the linear and/or quadratic and/or cubic terms, etc., depending on the number of terms used in each Taylor series. For $\ell = 2$, even the linear term in the R-equation is initially zero. The resultant "conservation of significance" is demonstrated in Tables 1, 2, and 3 in the results for the 3d wave function.

Clearly, in order to calculate wave functions for $\ell > 3$ with the accuracies of modes a or b, it will be necessary to either (a) increase the number of terms carried in the R and m equations, or (b) use the series solution to calculate values at a small value of ρ and then start the numerical analysis from that point.

In order to check the effect of double precision, the 1s state was calculated in mode a to $\rho = 40$. To $\rho = 20$, 13 to 15 significant-figure accuracy was obtained: 13-figure accuracy in $\exp(-\rho/2)$ at $\rho = 20$ represents 17-decimal-place accuracy! At $\rho = 40$, six-figure accuracy resulted, and this was the accuracy obtained in single precision at $\rho = 20$.

The results contained in this subsection suggest that instabilities and/or inaccuracies formerly attributed to round-off and/or truncation errors may have possibly been due to (a) the numerical method itself in which "mismatched" calculated quantities are used, and/or (b) poor approximate initial values where exact initial values were not available.

Iteration For Eigenvalues

We will now discuss a method of iterating for unknown eigenvalues. We will again consider the Coulomb potential because it affords us a test of the method's accuracy. Here, however, only the 1s and 2s states will be of interest. We will start with "guessed" eigenvalues and with "guessed" upper and lower limits. In addition, the range of ρ will be varied. The resulting eigenvalues and eigenfunctions will be compared to the known exact values.

The criterion that is applied at large ρ for an acceptable wave function is one that decreases exponentially as $\rho \to \infty$. Since it will be impossible to carry numerical solutions to $\rho = \infty$, we are left with testing the variations of the solutions within a finite range of the independent variable $\rho \leqq \rho_{max}$. Clearly, ρ_{max} has to be chosen so that if an eigenfunction is possible it will be well into the exponential decline at $\rho = \rho_{max}$. If this actually is true, then the error due to this truncation of the numerical solution can be made negligible by making ρ_{max} as large as practical. This will be illustrated by starting with "guessed" eigenvalues in error by one unit in the third and fourth significant figures and then iterating for solutions with different values of ρ_{max}.

However, it will generally be necessary, by several trials, to determine two nearly equal values of n in Eqs. (7) or (8) such that one value will yield a solution at large ρ that varies as $+\exp(\rho)$ and the other as $-\exp(\rho)$. With nearly equal values of n the shapes of the two solutions will be similar up to the point of divergence. (See texts by Sherwin (6) and Slater (20) for graphs of such variations.) These two trial values of n will represent

upper and lower limits to the exact eigenvalue. Once these limits have been determined the automatic search for the more accurate eigenvalue can begin, as described below.

We will label the larger of the two limits n_U (the upper value of n) and the other n_L (the lower value of n). Those values causing the variations of $\pm \exp(\rho)$ will be determined from the trials. In the 1s state n_L will cause the $+\exp(\rho)$ variation at large ρ, whereas for the 2s states n_U will cause the $+\exp(\rho)$ variation. We will now consider the 1s state. Any value between n_U and n_L is taken as the first guess for n, call it n_G, in the numerical system of equations. As the calculations proceed, the sign of the slope m and the sign of the function R are tested. If, before $\rho = \rho_{max}$, either m becomes zero or positive (n_G too low), or R becomes zero or negative (n_G too high), the calculations are stopped, a new lower or upper limit is stored, and the calculations are started again with a new value of n_G — now always taken as the mean value of the upper and lower limits. Or, generally, one tests for the number of nodes and then for the exponential tail of the solution.

Tables 5 and 6 present results of a search for eigenvalues of the 1s and 2s Coulomb states, respectively, calculated in mode b. In trial 5 of Table 5 the maximum value of ρ attempted was $\rho_{max} = 30.0$. However at $\rho = 28.812$, the upper and lower limits converged to equal values of 1.0; i.e., they filled the registers in single precision. The results given in the lower part of this column were taken from Table 1, mode b.

The tables are self-explanatory except for the normalization integral N. This is commonly taken as

$$N_{n,\ell} = \int_0^\infty \rho^2 [R_{n,\ell}(\rho)]^2 \, d\rho \, . \tag{49}$$

For our purposes we compare the exact integral to $\rho = 20$, and we compare the numerical integral calculated by the Trapezoidal Rule to $\rho = 20$. The exact integral of the 1s Coulomb state* is given by

$$\int_0^{20} \rho^2 e^{-\rho} \, d\rho = 2.0 - 0.9 \times 10^{-8}$$

$$= 1.9^{(8)} . \tag{50}$$

Note in Table 5, trials 1 and 2, that although the approximate numerical solutions lose significance at $\rho = 20$, the normalization integrals are still accurate to four significant figures. Also note the improvements in the eigenvalues and eigenfunctions as ρ_{max} is increased. With double precision both the eigenvalues and eigenfunctions can be improved even more. Similar remarks hold for the results in Table 6 for the 2s wave function.

Note also in Tables 5 and 6 that the accuracy of the final result is directly related to the number of iterations. Hence, if time permits, it is better to make a poor initial guess of the eigenvalue.

We will now consider briefly the application of the present method to the screened Coulomb potential. The more complete extension of the author's preliminary results given in Ref. 11 will be reported elsewhere.

*It was shown in Ref. 11 that all Coulomb s-states ($\ell \equiv 0$), if started with $R(0) \equiv 1.0$, yield exact normalizations of 2.0.

Table 5

Iteration for 1s Coulomb Eigenvalues Starting with Different "Guessed" Values with N the Standard Normalization Integral

Trial Number	n_G ("Guess")	n_U Upper Limit	n_L Lower Limit	ρ_{max}	Number of Iterations	n_F Final Value	n_U Final Value	n_L Final Value	N* (0 to 20)	Significant-Figure Agreement†		
										$\rho = 0.1$	$\rho = 10.0$	$\rho = 20.0$
1	1.001	1.003	0.998	20.0	12	$0.9^{(6)}$ 512	$1.0^{(6)}$ 98	$0.9^{(5)}$ 8047	$2.0^{(4)}$ 2275	7	3	0
2	1.01	1.03	0.98	20.0	15	$1.0^{(6)}$ 61	$1.0^{(5)}$ 244	$0.9^{(5)}$ 8779	$1.9^{(4)}$ 7067	7	3	0
3	1.001	1.003	0.998	25.0	18	$0.9^{(8)}$ 2	$1.0^{(7)}$ 2	$0.9^{(7)}$ 69	$1.9^{(6)}$ 45	8	4	1
4	1.01	1.03	0.98	25.0	22	$0.9^{(8)}$ 5	$1.0^{(7)}$ 1	$0.9^{(7)}$ 81	$1.9^{(6)}$ 32	8	5	1
5	1.001	1.003	0.998	28.812	23	$1.0^{(8)}$	$1.0^{(8)}$	$1.0^{(8)}$	$1.9^{(6)}$ 09	9	8	4

*N from modes a and b, Table 1, is $1.9^{(6)}09$; exact $\int_0^{20} \rho^2 e^{-\rho} d\rho = 1.9^{(8)}$.
†Agreement with the exact 1s wave function.

Table 6

Iteration for 2s Coulomb Eigenvalues Starting with Different "Guessed" Values with N the Standard Normalization Integral

Trial Number	n_G ("Guess")	n_U Upper Limit	n_L Lower Limit	ρ_{max}	Number of Iterations	n_F Final Value	n_U Final Value	n_L Final Value	N* (0 to 20)	Significant-Figure Agreement†		
										$\rho = 0.1$	$\rho = 10.0$	$\rho = 20.0$
1	2.001	2.003	1.998	20	4	$1.9^{(3)}$ 87500	$2.0^{(3)}$ 25000	$1.9^{(3)}$ 50000	2.00302756	5	3	0
2	2.01	2.03	1.98	20	8	$1.9^{(4)}$ 2187	$2.0^{(3)}$ 15625	$1.9^{(3)}$ 68750	2.00182897	5	3	0
3	2.001	2.003	1.998	25	10	$1.9^{(5)}$ 805	$2.0^{(5)}$ 391	$1.95^{(5)}$ 219	$1.9^{(4)}$ 6315	6	3	2
4	2.01	2.03	1.98	25	14	$1.9^{(5)}$ 878	$2.0^{(5)}$ 244	$1.9^{(5)}$ 512	$1.9^{(4)}$ 4570	6	4	2
5	2.001	2.003	1.998	30	16	$1.9^{(7)}$ 7	$2.0^{(7)}$ 6	$1.9^{(6)}$ 88	$1.9^{(4)}$ 1737	8	6	3
6	2.01	2.03	1.98	30	20	$1.9^{(7)}$ 8	$2.0^{(7)}$ 4	$1.9^{(7)}$ 2	$1.9^{(4)}$ 1710	8	7	3

*N from modes a and b, Table 1, is $1.9^{(4)}1664$.
†Agreement with the exact 2s wave function.

APPLICATION TO THE SCREENED COULOMB POTENTIAL

For a concrete application of the present analytical and numerical analysis to the Schrödinger equation with a "nonanalytic potential," we will consider the complete screened Coulomb potential (CSCP) (11,13,14). The standard CSCP resulting from a D-H-type ion atmosphere is given for a hydrogenic atom (or ion) by

$$V(r) = \begin{cases} V_i(r) = -\dfrac{Ze^2}{\eta_0}\left(\dfrac{1}{r} - \dfrac{1}{d+a}\right), & 0 \leqq r \leqq a \\ V_0(r) = -\dfrac{Ze^2}{\eta_0}\dfrac{d}{d+a}\dfrac{\exp[(a-r)/d]}{r}, & r \geqq a, \end{cases} \tag{51}$$

where d is the screening length and a is the mean minimum radius of the ion atmosphere. The dielectric constant of the medium is given by η_0. For the present report we will consider $\eta_0 \equiv 1.0$ everywhere. The extension of the results with $\eta_0 > 1$ in Ref. 21 will also be considered elsewhere. The transformation of $V(r)$ in Eq. (51) as given in the second section of this report yields

$$V(\rho) = \begin{cases} V_i(\rho) = -\left(\dfrac{1}{\rho} - \dfrac{1}{d'+a'}\right), & 0 \leqq \rho \leqq a' \\ V_0(\rho) = -\dfrac{d'}{d'+a'}\dfrac{\exp[(a'-\rho)/d']}{\rho}, & \rho \geqq a', \end{cases} \tag{52}$$

where a' and d' are the values of a and d in ρ-space. In what follows the primes will be dropped, for it will be obvious that we will be solving the problem in ρ-space. In the actual calculations we use Eq. (7) with $V(\rho)$ given by Eq. (52), using $V_i(\rho)$ or $V_0(\rho)$ in the appropriate ranges of ρ.

However, in the derivation of initial values Eq. (8) is of interest with $V(\rho) = -1/\rho$ and $b^2 = (1/4) + [n/(d+a)]$. [cf. Eq. (40).] The analysis proceeds as was outlined in the section "Derivation of Initial Values" with the $1/4$ replaced by b^2 in Eq. (35). Clearly, the series solution, Eq. (33) with ϕ given by Eqs. (36), (37), and (41), is exact for $0 \leqq \rho \leqq a$. Consequently, all the initial derivatives of the wave functions are exactly given by Eq. (43) with $b^2 = (1/4) + [n/(d+a)]$ in the coefficients of the powers of ρ as given by Eq. (42), etc. Consequently, the series solution can be used to calculate all values at $\rho = a$ to the maximum number of significant figures available in the computer and then proceed from this point numerically. However, unless the series converges rapidly it may be just as convenient to start all the numerical solutions from $\rho = 0$. Nevertheless, as indicated in the preceding section, for states with $\ell > 3$ it may be necessary to start at some small value of ρ in order to obtain the maximum number of significant figures in the numerical calculations.

One will note that in the standard use of perturbation and/or variational methods with the CSCP it is assumed that $a \equiv 0$ and only $V_0(r)$ in Eq. (51) is used. This is what is referred to as the screened Coulomb potential (SCP), but it is not complete at the origin. It can be shown (17,22) that the potential at the origin from the SCP due to the charges of all the other ions is $+Ze^2/\eta_0 d$, the same as that given by $V_i(r)$ in Eq. (51) with $a = 0$. (Fowler (17) uses D for η_0 and κ for $1/d$.) Consequently, for the SCP the exact initial values are those derived above for the CSCP with $a = 0$, or $b^2 = 1/4 + n/d$. With these starting values the numerical approach has to always be started at the origin.

In passing it should be noted that for the CSCP, if $a \geqq \rho_{max}$, the series solution is exact throughout the range of interest. It will still be necessary, however, to iterate for the eigenvalues, as described above.

In Ref. 11 the search for solutions with the CSCP begins with the assumption that the wave functions probably have the same shapes as the Coulomb wave functions. Then the search for eigenvalues proceeds as described in the subsection of "Iteration For Eigenvalues." Although the results in Ref. 11 were calculated with the linear system, mode f, calculations during the present study with the cubic system, mode b, have verified that the eigenvalues determined in Ref. 11 are indeed correct to four significant figures — just as the author expected.

Therefore, the numerical method of this report will lead to accurate and stable bona fide solutions to the radial hydrogenic Schrödinger equation.

SUMMARY AND CONCLUSIONS

A new method has been presented for accurate and stable numerical solutions of ordinary differential equations. Applied to the Schrödinger equation the two essential features of the method are (a) simultaneous Taylor expansions between space steps $\Delta\rho$ of the wave function $R(\rho)$ and the slope of the wave function $m(\rho)$, and (b) the derivation of initial values through either an exact series solution of the Schrödinger equation valid at or near the origin, or through an approximate analytical solution valid for all n and ℓ to terms of order $\rho^2 - O(\rho^2)$.

It has been shown that for a given $\Delta\rho$, to increase the accuracy and stability beyond that given by the linear terms of the Taylor expansions, it is necessary to use at least the quadratic terms in the expansions of both R and m: the use of the quadratic term in the R-expansion and the linear term in the m-expansion (or vice versa) is less stable than the use of the linear terms alone in both equations. In this case the initial high accuracy quickly degrades to the accuracy of the linear system, or less.

Through a series solution of the Schrödinger equation — without $\exp(-\rho/2)$ factored out — exact initial derivatives of all Coulomb and screened Coulomb wave functions have been obtained. It is also shown that numerical results obtained using initial values from an approximate analytic solution derived here are essentially equal in accuracy to numerical results obtained from the exact initial values.

Using the Coulomb potential, the accuracy with which eigenvalues and eigenfunctions can be obtained through iteration has been demonstrated. This is essential for problems with "nonanalytic" interaction potentials — the reason for interest in numerical methods.

The present results suggest that the cumulative round-off error does not simply depend on the number of steps in the range of calculations but also depends on the cumulative effect of the number of changes in sign of the derivatives of the function calculated. And, more important, the present results suggest that instabilities and/or inaccuracies of other numerical methods that have been attributed to cumulative round-off and/or truncation errors, may have possibly been due to (a) the numerical method itself in which "mismatched" calculated quantities are used and/or (b) poor approximate initial values when exact initial values were not available.

The present results represent the first known — as far as the author can determine — accurate and stable numerical solutions to the radial hydrogenic Schrödinger equation. The new method used (a) has the conceptual and mathematical simplicity of the Cauchy (or Euler) method (1,4,5) without the instability of the Cauchy method due to round-off errors when high accuracy is sought through small space steps; and (b) the present method has — depending on the space step and the number of terms used in the Taylor series — accuracy equal to or greater than that obtainable from the Runge-Kutta method (1,4,5) without the relative complexity of the R-K method, when used for two or more simultaneous differential equations, nor the R-K instability that will result unless all terms can be calculated with equal accuracy. With the present ability to calculate

eigenvalues to nine or more significant figures and eigenfunctions to nine or more decimal places, the present method becomes an alternative to approximate perturbation and variational methods for the screened Coulomb and other nonanalytic potentials.

In addition to accuracy and stability, a very practical aspect of the present method is that it is capable of a reduction in computation time of several orders of magnitude relative to a linear method that uses extremely small space steps — and double precision — for the same accuracy. This reduction can easily be seven or more orders of magnitude.

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Appendix

VALUES OF THE EXPONENTIAL FUNCTION TO 16 OR MORE SIGNIFICANT FIGURES

For the readers' convenience values of the exponential function used here are given to 16 or more significant figures. The numbers are from the work of Zucker.*

x	e^{-x}			
0.05	0.95122	94245	00714	009
0.50	0.60653	06597	12633	424
1	0.36787	94411	71442	32160
2	0.13533	52832	36612	69189
3	0.04978	70683	67863	94298
4	0.01831	56388	88734	18029
5	0.00673	79469	99085	46710
6	0.00247	87521	76666	35842
7	0.00091	18819	65554	51621
8	0.00033	54626	27902	51184
9	0.00012	34098	04086	67955
10	0.00004	53999	29762	48485

*R. Zucker, "Elementary Transcendental Functions," in "Handbook of Mathematical Functions," M. Abramowitz and I.A. Stegun editors, New York:Dover, 1964.

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ACCURATE AND STABLE NUMERICAL SOLUTIONS TO THE SCHRÖDINGER EQUATION

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)* A report of the work accomplished to date on the problem; work on other phases continues.

5. AUTHOR(S) *(First name, middle initial, last name)*

Carl A. Rouse

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13. ABSTRACT A new method has been developed for accurate and stable numerical solutions of ordinary differential equations. Applied to the Schrödinger equation, the basic numerical equations are two simultaneous Taylor expansions between space steps of both the wave function $R(\rho)$ and the slope of the wave function $m(\rho)$, where it is absolutely necessary to use the same number of terms in each expansion, viz.,

$$R(\rho+\Delta\rho) = R(\rho) + m(\rho)\Delta\rho + \frac{1}{2} m'(\rho)\Delta\rho^2 + \ldots,$$

and

$$m(\rho+\Delta\rho) = m(\rho) + m'(\rho)\Delta\rho + \frac{1}{2} m''(\rho)\Delta\rho^2 + \ldots,$$

with

$$m'(\rho) = -\frac{2}{\rho} m(\rho) + \left[\frac{1}{4} + \frac{\ell(\ell+1)}{\rho^2} - \frac{n}{\rho}\right] R(\rho)$$

for the Coulomb potential. Initial values applicable to the screened Coulomb as well as to the standard Coulomb potential are derived by (a) an exact series solution of the Schrödinger equation and (b) an approximate analytical solution valid near the origin for all n, ℓ to terms of order ρ^2. For example, using the cubic terms in the

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14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Screened Coulomb potential						
Coulomb potential						
Schrödinger equation						
Taylor expansion						
Wave function						
Eigenvalue						
Eigenfunction						
Radial hydrogenic Schrödinger equation						
Normalization integral						
Hydrogenic ion						

Taylor expansions with $\Delta\rho = 10^{-4}$ and using a computer that holds ten significant decimal digits in single precision, accuracies of at least 7 to 9 significant figures are obtained in the range $\rho \lesssim 18$, and accuracies of about nine or more decimal places are obtained throughout the range of interest, $\rho \leqq 20$. For "nonanalytic" potentials such as the screened Coulomb potential, it is important to demonstrate the accuracies to which eigenvalues and eigenfunctions can be obtained by iteration. Application of the method to the screened Coulomb potential was considered, and the effects of errors due to round-off, truncation, and loss of significance were discussed. As far as the author can determine, the present results represent the first known accurate and stable numerical solutions of the radial hydrogenic Schrödinger equation. With the present ability to calculate eigenvalues to nine or more significant figures and eigenfunctions to nine or more decimal places, the present method becomes an alternative to perturbation and variational methods.