

New method for numerical integration of the radial electronic Schrödinger equation

Antonios G. Koures and Frank E. Harris

Citation: *The Journal of Chemical Physics* **89**, 7344 (1988); doi: 10.1063/1.455265

View online: <http://dx.doi.org/10.1063/1.455265>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/89/12?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[The Use of PhaseLag and Amplification Error Integrators for the Numerical Solution of the Radial Schrödinger Equation](#)

AIP Conf. Proc. **1281**, 1839 (2010); 10.1063/1.3498255

[A Modified Zero Dispersion and Zero Dissipation RKN Method for the Numerical Solution of the Radial Schrödinger Equation](#)

AIP Conf. Proc. **1168**, 1604 (2009); 10.1063/1.3241412

[Direct numerical integration of the radial equation](#)

Am. J. Phys. **59**, 474 (1991); 10.1119/1.16801

[New Integral Formulation of the Schrödinger Equation](#)

J. Math. Phys. **11**, 2235 (1970); 10.1063/1.1665387

[Molecular Schrödinger Equation. VIII. A New Method for the Evaluation of Multidimensional Integrals](#)

J. Chem. Phys. **47**, 5307 (1967); 10.1063/1.1701795



New method for numerical integration of the radial electronic Schrödinger equation

Antonios G. Koures and Frank E. Harris

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

(Received 5 February 1988, accepted 21 March 1988)

We present a new method for numerical integration of the radial electronic Schrödinger equation with these characteristics: (i) it uses a quantity directly related to the logarithmic derivative of the wave function, thereby facilitating the matching of solutions obtained for different radial regions; (ii) it avoids difficulty from the singularity of the logarithmic derivative at the nodes of the wave function; and (iii) it takes appropriate cognizance of the asymptotic form of the wave function at infinite radius. Examples are presented showing that eigenvalues can be obtained by the new method by outward integration alone, but that a combination of inward and outward integration leads to efficiencies which compare favorably with those achievable by the most popular previously existent method, that of Numerov.

I. INTRODUCTION

In connection with a detailed analysis¹ of the multiple-scattering X -alpha (MS - $X\alpha$) method for molecular electronic structure calculations,² we have had occasion to examine in detail a number of methods for numerical integration of the radial single-particle Schrödinger equation. This type of numerical integration occurs in a number of different kinds of atomic calculations,³ and procedures for it have become more or less standardized. Eigenvalues are ordinarily determined by adjusting a trial value until an integration outward from the origin connects smoothly with an integration inward from infinite radius. Because the Schrödinger equation is linear and homogeneous, both the small and large radius solutions (denoted, respectively, R_- and R_+) can be scaled arbitrarily, and a "smooth connection" means that the logarithmic derivatives of the two solutions must be equal at the connection point (i.e., $R'_-/R_- = R'_+/R_+$). The matching procedure is introduced to overcome the circumstance that neither an inward nor an outward integration is stable over the entire radial range.

Traditional numerical integration methods essentially involve replacement of the original differential equation by a finite-difference equation. Much experience has shown that in electronic Schrödinger equation problems it is necessary to use a difference equation that does not introduce parasitic terms (those describing solutions to the difference equation that do not correspond to solutions of the original differential equation⁴). The most popular integration scheme meeting this criterion is the Numerov method,⁵ which can be applied after the radial equation has been transformed to eliminate the first-derivative term. The accuracy achievable with the Numerov method can be influenced by the choice of step size and the number of significant figures carried in the calculations. It has generally been found that the accuracy needed in atomic physics can be reached, but often many hundreds of steps are required.

A detailed criticism of the Numerov method has recently been reported.⁶ We have also observed it to have severe limitations when applied in the most popular way (with step sizes that are increased periodically as the radius increases). However, if the step size is kept constant over the entire

radial range, we have found the method far more stable than previous studies have implied. In fact, the best results we have obtained with the Numerov method have occurred when the step size is *decreased* periodically as the radius increases. These observations also apply to the "renormalized Numerov method" introduced by Johnson.⁷

Because the Numerov method has adequate stability only for small step sizes, and because its use for finding eigenvalues is complicated by the fact that the method does not automatically generate the first derivative, we have developed a new method with the following characteristics: (i) A quantity directly related to R'/R is generated; (ii) the function integrated varies smoothly enough that relatively few integration points are needed; and (iii) when integrating inward from infinite radius, proper cognizance is taken of the asymptotic form of the wave function, and a change of variable is introduced to place the integration on a finite range. Our method is described in the following sections of this paper. Section II presents the method in a form suitable for outward integration. Section III gives results for typical outward integrations, including examples where eigenvalues for Coulomb and Yukawa potentials are deduced to high accuracy using outward integration alone. Section IV presents the method in a formulation appropriate for inward integration. A final Sec. V illustrates some calculations in which the energy is varied until inward and outward integrations connect smoothly (a rudimentary prototype of the process involved in MS - $X\alpha$ calculations).

Our findings may be summarized as follows: (i) The new method is stable enough that for Coulomb and Yukawa potentials (together characterizing a range of potential typical in atomic problems) highly accurate eigenvalues and eigenfunctions can be obtained using outward integration only; (ii) for general energies, integrations out to (or in to) a spherical boundary can be obtained accurately with far fewer points than by previously described methods; (iii) logarithmic derivatives are a natural product of the integrations.

II. OUTWARD INTEGRATIONS: METHOD

In atomic units, the radial Schrödinger equation takes the form

$$-\frac{1}{2} \frac{d^2}{dr^2} R(r) - \frac{1}{r} \frac{d}{dr} R(r) + \left[\frac{l(l+1)}{2r^2} + V(r) - E \right] R(r) = 0, \quad (1)$$

where l is the angular momentum quantum number, $V(r)$ is the potential, and E is the energy eigenvalue. When Eq. (1) is used to describe a single-electron distribution in a many-electron system, $V(r)$ will be the Coulomb plus exchange potential and E will be the orbital energy.

If we write Eq. (1) in terms of the function $f(r)$, where $R(r) = r^l f(r)$, we obtain

$$-\frac{1}{2} \frac{d^2}{dr^2} f(r) - \frac{(l+1)}{r} \frac{d}{dr} f(r) + [V(r) - E] f(r) = 0. \quad (2)$$

Note that instead of transforming to remove the first-derivative term (as required to apply the Numerov method), we have transformed to remove the r^{-2} term of the equation [to make $f(r)$ easier to integrate near $r = 0$]. Making now the further substitution $\tan \phi = f'/f$, it follows from Eq. (2) that ϕ satisfies the first-order differential equation

$$\phi'(r) = \frac{d}{dr} \phi(r) = 2 \cos^2 \phi(r) [V(r) - E] - \frac{2(l+1)}{r} \sin \phi(r) \cos \phi(r) - \sin^2 \phi(r). \quad (3)$$

In the case that $V(r)$ is the form $V(r) = -Z/r + \bar{V}(r)$ with \bar{V} regular at $r = 0$ (corresponding to a system with a nucleus of charge Z at the origin), we introduce the notation $\phi_0 = \phi(0)$ and use the fact that $\tan \phi_0 = f'(0)/f(0) = -Z/(l+1)$, thereby reducing Eq. (3) to the computationally satisfactory form

$$\frac{d}{dr} \phi(r) = \cos^2 \phi(r) \{ 2 [(\bar{V}(r) - E) + 1] - 1 - \frac{2(l+1) \cos \phi(r) \sin [\phi(r) - \phi_0]}{\cos \phi_0 r} \}. \quad (4)$$

Taking the limit of Eq. (4) as $r \rightarrow 0$, we also have

$$\phi'(0) = \frac{d}{dr} \phi(0) = \frac{\cos^2 \phi_0 \{ 2[\bar{V}(0) - E] + 1 \} - 1}{2l+3}. \quad (5)$$

Equation (4) may now be integrated numerically, starting from the known values of ϕ_0 and $\phi'(0)$. If the intent is to obtain particular behavior in f'/f , the numerical integration may be iterated for different E until that goal is achieved. Then, if values of $f(r)$ are needed, they may be obtained by integration of the first-order equation

$$f'(r) = \frac{d}{dr} f(r) = f(r) \tan \phi(r), \quad (6)$$

where ϕ is now known.

We investigated a large number of methods for the integration of Eq. (4), finally choosing a fourth-order Runge-Kutta procedure "RK4".⁸ This procedure has the advantage of being self-starting (and thereby without parasitic terms), relatively stable, and accurate enough that fewer points were

needed than with alternative satisfactory methods. Regarding ϕ' from Eq. (4) as a function of ϕ and r , the RK4 equations for a step from r to $r+h$ are

$$\begin{aligned} k_1 &= \phi'[\phi(r), r], \\ k_2 &= \phi' \left[\phi(r) + \frac{k_1 h}{2}, r + \frac{h}{2} \right], \\ k_3 &= \phi' \left[\phi(r) + \frac{k_2 h}{2}, r + \frac{h}{2} \right], \\ k_4 &= \phi'[\phi(r) + k_3 h, r + h], \\ \phi(r+h) &= \phi(r) + h \frac{(k_1 + 2k_2 + 2k_3 + k_4)}{6}. \end{aligned} \quad (7)$$

We notice that this method requires that values of V be available on a grid of spacing $h/2$.

When an eigenvalue search is nearing conclusion or when high accuracy is desired for any reason, we recommend that integrations as described above be carried out for two step sizes (here denoted h and $h/2$), and that a Richardson extrapolation⁹ then be performed. For the RK4 procedure, in which the global error is $O(h^4)$, the extrapolated value of $\phi(r)$ is

$$\phi(r) = \frac{[16\phi_{h/2}(r) - \phi_h(r)]}{15}, \quad (8)$$

where $\phi_h(r)$ indicates a numerical calculation with step size h . This Richardson extrapolation, which has seen surprisingly little use among electronic structure theorists, is both faster and more accurate than carrying out an integration with step size $h/4$.

III. OUTWARD INTEGRATION: RESULTS

A preliminary test of the stability and accuracy of our method was carried out by attempting to locate hydrogenic eigenvalues through outward integration alone. As r increases from zero, an exact ϕ will start from a value $\phi_0 = \arctan[-Z/(l+1)]$, which we may take in the range $0 > \phi_0 > -\pi/2$, and will proceed in the negative direction for two quadrants per node of $f(r)$. If E is an eigenvalue and ϕ remains exact, ϕ will approach an asymptote in a quadrant where $\tan \phi$ is negative. If E is not an exact eigenvalue, or if the procedure for generating ϕ becomes unstable, ϕ will move to approach an asymptote in a quadrant where $\tan \phi$ is positive.

The foregoing paragraph indicates that the stability of the method, for calculations at a fixed number of significant figures, may be assessed by picking an energy eigenvalue and then finding the r value at which ϕ begins to deviate significantly from its proper asymptotic limit. It turns out that ϕ is constant for hydrogenic states in which $l = n - 1$ (where n is the principal quantum number), with the result that complete stability is fortuitously obtained. Meaningful tests are provided by other states; we illustrate with the $3s$ and $4d$ states (in both cases taking $Z = 1$), for which results are shown in Figs. 1 and 2. The numerical work supporting the figures was carried out to 16 decimal digits and a step size of 0.02 bohr was used. The figures indicate that under these computational conditions good stability persists to approximately $r = 50$ bohr ($3s$) and $r = 80$ bohr ($4d$).

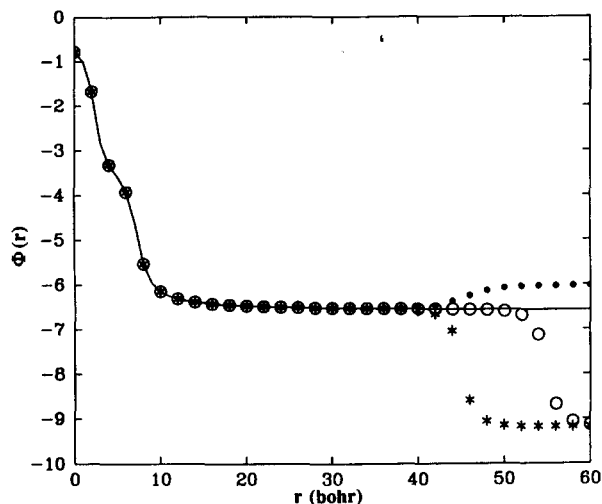


FIG. 1. Calculations of Coulomb 3s state with $Z=1$ (energy $E = -0.055\,555\,5\cdots$ hartree). Line = exact result, open circles = calculation for energy E , dots = calculation for $E - 10^{-7}$ hartree, asterisks = calculation for $E + 10^{-7}$ hartree. All calculations by outward integration with step size 0.02 bohr.

We now vary E away from the eigenvalues by a small amount in each direction, noting that systematic deviations from the eigenvalue asymptotes occur at r values significantly smaller than the previously defined stability limits. Since the directions of the deviations correlate, as they should, with the signs of the differences between E and the true eigenvalue, it is apparent that these eigenvalues can be determined to well under the amounts of the energy shifts (i.e., to within 10^{-7} hartree for the 3s state and to within 10^{-8} hartree for the 4d state).

A similar study was carried out using a Yukawa potential of the form $-Z \exp(-\lambda r)/r$, with $Z=1$ and $\lambda=0.05$. Figure 3 shows results for the 3p state at energy $E = -0.018\,557\,751\,882\,4$ hartree and at energies differing

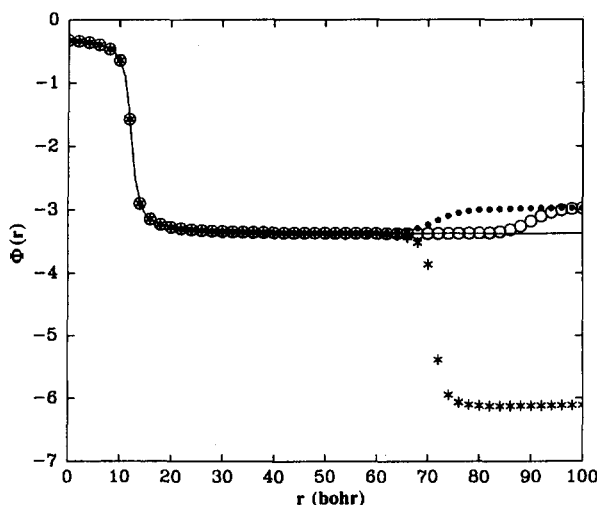


FIG. 2. Calculations of Coulomb 4d state with $Z=1$ (energy $E = -0.031\,25$ hartree). Line = exact result, open circles = calculation for energy E , dots = calculation for $E - 10^{-8}$ hartree, asterisks = calculation for $E + 10^{-8}$ hartree. All calculations by outward integration with step size 0.02 bohr.

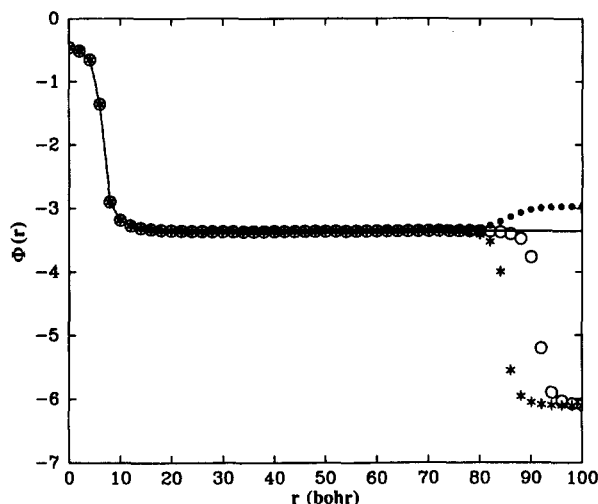


FIG. 3. Calculations of Yukawa 3p state with $Z=1$ and $\lambda=0.05$ (energy $-0.018\,557\,751\,882\,4$ hartree). Line = exact result, open circles = calculation for energy E , dots = calculation for $E - 4 \times 10^{-3}$ hartree, asterisks = calculation for $E + 4 \times 10^{-3}$ hartree. All calculations by outward integration with step size 0.01 bohr.

therefrom by $\pm 4 \times 10^{-13}$ hartree. It is clear from the figure that the middle energy defines the eigenvalue to well within a 10^{-12} hartree precision. A previous calculation on this Yukawa potential¹⁰ has reported the energy eigenvalue to six decimal digits; that work is consistent with the far more accurate value obtained here. The Yukawa potential example is particularly significant for our proposed use of the method in MS- $X\alpha$ calculations, where the effective potential will generally be more similar to a Yukawa than to a pure Coulomb potential.

We carried out a few calculations designed to compare the effectiveness of the Richardson extrapolation with the more frequently used expedient of simply repeating the calculation at a smaller step size. Table I presents such a comparison for the 4d Coulomb state at $r=10$ bohr. The results confirm that the Richardson value is superior, and we note that it involves only 3/4 as many points as the smallest-step calculation alone.

IV. INWARD INTEGRATION: METHOD

While the preceding sections shows the inward integration will ordinarily be unnecessary when determining eigenvalues and eigenfunctions of radial Schrödinger equations, there will be applications, such as in the MS- $X\alpha$ method, where it will be necessary to integrate inward from infinite

TABLE I. Richardson extrapolation from step sizes 0.02 and 0.01 bohr vs a calculation at step size 0.005 bohr, for Coulomb 4d state with $Z=1$ at $r=10$ bohr. See the text for definition of ϕ .

$\phi = (r=10 \text{ bohr})$	
Step size 0.02 bohr	-0.643 501 108 802 361
Step size 0.01 bohr	-0.643 501 108 793 858
Step size 0.005 bohr	-0.643 501 108 793 320
Richardson (0.02 and 0.01 bohr)	-0.643 501 108 793 292
Exact	-0.643 501 108 793 284

radius. As we shall see later, use of both outward and inward integrations can also reduce the total amount of numerical work needed to solve an eigenvalue problem.

It is desirable to carry out the inward integrations in a way that circumvents the awkwardness associated with the fact that the range of r is infinite. We proceed by carrying out the numerical integration in the variable $t = 1/r$.

Returning to Eq. (1), we start by recognizing that its asymptotic behavior at large r depends upon the limiting behavior of $V(r)$. We assume that $V(r)$ can be written as $-Q/r + \bar{V}$, where \bar{V} is exponentially decreasing at large r . The case $Q = Z$ corresponds to a hydrogenic atom, but $Q = 0$ will be encountered in MS- $X\alpha$ calculations on neutral molecules. An analysis of Eq. (1) leads to the conclusion that $R(r)$ varies asymptotically as $r^p \exp(-\kappa r)$, where

$$\kappa^2 = -2E, \\ p = (Q/\kappa) - 1. \quad (9)$$

Equation (9) is consistent with the well-known fact that a hydrogenic state of principal quantum number n has a leading preexponential factor r^{n-1} , and also in the case $Q = 0$ confirms the free-particle radial dependence $r^{-1} \exp(-\kappa r)$. We note in passing that the inward integration in most MS- $X\alpha$ studies has incorrectly used the hydrogenic, rather than the free-particle asymptotic form.

In accordance with the preceding paragraph, we set $R(r) = g(r)r^p \exp(-\kappa r)$, so that Eq. (1) becomes, as an equation for $g(r)$,

$$-\frac{1}{2} \frac{d^2}{dr^2} g(r) - \left(\frac{p+1}{r} - \kappa \right) \frac{d}{dr} g(r) \\ + \left[\frac{(p+1)\kappa - Q}{r} + \bar{V}(r) - \frac{A}{r^2} \right] g(r) = 0, \quad (10)$$

where $A = [p(p+1) - l(l+1)]/2$. The function $g(r)$ will approach a constant value as $r \rightarrow \infty$, and will be easier to integrate numerically than $R(r)$. We next change to the independent variable $t = 1/r$, obtaining

$$-\frac{t^4}{2} g''(t) + t^3 \left(\frac{Q}{\kappa} - 1 - \frac{\kappa}{t} \right) g'(t) \\ + [\bar{V}(t) - At^2] g(t) = 0. \quad (11)$$

Here the primes denote differentiation with respect to t .

Finally, let $\tan \phi = g'/g$; ϕ satisfies the differential equation

$$\frac{d}{dt} \phi(t) = \frac{\cos^2 \phi(t)}{t} \left\{ 2p \tan \phi_0 + \left(2p - \frac{2\kappa}{t} \right) \right. \\ \left. \times [\tan \phi(t) - \tan \phi_0] - t \tan^2 \phi(t) + \frac{2\bar{V}(t)}{t^3} \right\}. \quad (12)$$

Here ϕ_0 stands for ϕ at $t = 0$.

Although g is a regular, smoothly varying function in the neighborhood of $t = 0$, Eq. (12) is numerically ill-conditioned there, and we have considered the use of a series expansion to integrate Eq. (12) from $t = 0$ to some small non-zero value t_1 . Integration beyond t_1 would then be carried out using the RK4 procedure described in Sec. II, with Richardson extrapolation where appropriate. This expansion also yields values of ϕ and ϕ' at $t = 0$.

The values of ϕ_0 , $\phi'(0)$, and $\phi(t_1)$ are obtained by expanding g [scaled to $g(0) = 1$] in a power series in t :

$$g(t) = 1 + a_1 t + a_2 t^2 + \cdots. \quad (13)$$

We introduce a similar expansion for $\tan \phi$:

$$\tan \phi(t) = b_0 + b_1 t + b_2 t^2 + \cdots. \quad (14)$$

Introducing Eq. (13) into Eq. (11), and noting that \bar{V} contributes no finite power to t , we find

$$a_1 = -\frac{A}{\kappa}, \\ a_n = \frac{[(n+1)p + (n-1)(n-2)/2 - A]}{n\kappa} a_{n-1}. \quad (15)$$

Now writing $g(t) \tan \phi = g'(t)$, expanding all factors via Eqs. (13) and (14), and equating like powers of t , we get

$$b_0 = a_1, \\ b_n = (n+1)a_{n+1} - \sum_{j=1}^n a_j b_{n-j}. \quad (16)$$

The first of Eqs. (16) yields a value to $\tan \phi_0$; the second gives $\phi'(0)$:

$$\tan \phi_0 = -\frac{A}{\kappa}, \\ \frac{d}{dt} \phi(0) = -\frac{pA}{A^2 + \kappa^2}. \quad (17)$$

In practice we found that, despite the ill conditioning of the equation for ϕ' , the RK4 procedure could be used starting at $t = 0$, with the zero- t evaluations given in Eq. (17). Illustrative results are presented in the next section.

TABLE II. Matching of R'/R in outward and inward integrations, for Coulomb potential with $Z = 1$ and Yukawa potential with $Z = 1$ and $\lambda = 0.05$. Step sizes used in all calculations: Outward, 0.01 in r (total 1000 steps); inward, 0.0001 in t (total 1000 steps).

	$E(\text{hartree})$	$R'/R(\text{outward})$	$R'/R(\text{inward})$
Coulomb	-0.03 1250 01	-0.549 999 7	-0.550 001 9
4d state	-0.031 250 00	-0.550 000 0	-0.550 000 0
$r = 10$ bohr	-0.031 249 99	-0.550 000 3	-0.549 998 1
Yukawa	-0.018 557 751 882 0	0.053 842 415 838 4	0.053 842 415 850 3
3p state	-0.018 557 751 882 4	0.053 842 415 840 9	0.053 842 415 839 8
$r = 10$ bohr	-0.018 557 751 882 8	0.053 842 415 843 3	0.053 842 415 829 2

TABLE III. Matching of R'/R in outward in inward integrations, for Coulomb potential with $z = 1$. For $5s$: match at $r = 40$ bohr, outward step size 0.005 in r (8000 steps), inward step size 0.000 005 in t (5000 steps); For $n = 20$ state: match at $r = 100$ bohr, outward step size 0.02 in r (5000 steps), inward step size 0.000 005 in t (2000 steps).

	$E(\text{hartree})$	R'/R (outward)	R'/R (inward)
Coulomb $5s$	-0.019 999 999 998	-0.257 724 190 6	-0.257 724 189 5
	-0.020 000 000 000	-0.257 724 190 2	-0.257 724 189 9
	-0.020 000 000 002	-0.257 724 189 7	-0.257 724 190 6
Coulomb $n = 20$ $l = 19$	-0.001 249 999 999 999 9	-0.139 999 999 999 999 41	-0.143 6
	-0.001 250 000 000 000 0	-0.139 999 999 999 999 99	-0.140 0
	-0.001 250 000 000 000 1	-0.140 000 000 000 000 59	-0.136 5

V. OUTWARD AND INWARD INTEGRATIONS: RESULTS

While we have already shown that the use of inward integration is not necessary to locate eigenvalues with high precision, its use can reduce dramatically the amount of numerical work required. The procedure involved will be to find E values at which the inward and outward R'/R values match at a selected r value. This procedure will also serve as a prototype for our projected use of the method in MS- $X\alpha$ calculations, where both outward and inward integrations must be matched against analytical results obtained for an intermediate region.

To use the results reported in earlier sections of this paper, we note that for the outward integration

$$\frac{R'(r)}{R(r)} = \frac{1}{R(r)} \frac{d}{dr} R(r) = \tan \phi(r) + \frac{1}{r}, \quad (18)$$

while for the inward integration

$$\frac{R'(r)}{R(r)} = \frac{1}{R(r)} \frac{d}{dr} R(r) = -t^2 \tan \phi(t) + pt - \kappa. \quad (19)$$

In each of Eqs. (18) and (19) ϕ has the respective definition corresponding to its integration region.

We attempted matching for the two calculations illustrated in Figs. 2 and 3. The results are presented in Table II for the same E values as appeared in the figures. The matching is clear cut and occurs at the previously determined

TABLE IV. Numbers of integration points needed for the high-accuracy integrations presented in Table III. OS = Oset and Salcedo, Ref. 6.

State	Relative accuracy	Numbers of integration points	
		This work	OS
$5s$	10^{-10}	1.3×10^4	4×10^4
$n = 20, l = 19$	10^{-13}	7×10^3	4×10^5

eigenvalues. Of more interest is the number of steps needed to obtained the results in Table II, namely a total of 2000.

As a final demonstration of the method described here, we reproduced two of the high-accuracy numerical integrations reported in the work of Oset and Salcedo,⁶ namely those of (i) a Coulomb $5s$ state at relative accuracy 10^{-10} and (ii) a Coulomb state with $n = 20, l = 19$ at relative accuracy 10^{-13} . For both states we matched outward and inward integrations, for the $5s$ state at 40 bohr and for the $n = 20$ state at 100 bohr. The matching of the R'/R values is shown in Table III, and the efficiency of our method is compared with that of Oset and Salcedo in Table IV. Our method compares favorably for both these states, doing relatively better for the state of higher angular momentum. Incidentally, we noted that the energies tabulated by Oset and Salcedo are systematically in error by a factor 4, undoubtedly due to the misplacement of a factor "2" in Eq. (20) of their paper.

ACKNOWLEDGMENT

Financial assistance with the calculations reported here was provided by the University of Utah Research Committee.

¹A. G. Koures and F. E. Harris (to be published).

²K. H. Johnson, Adv. Quantum. Chem. 7, 143 (1973); K. H. Johnson and F. C. Smith, Jr., Phys. Rev. Lett. 24, 139 (1970).

³F. Herman and S. Skillman, *Atomic Structure Calculation* (Prentice-Hall, Englewood Cliffs, NJ, 1963); J. M. Blatt, J. Comp. Phys. 1, 382 (1967).

⁴M. Maron, *Numerical Analysis; A Practical Approach* (Macmillan, London, 1982), p. 359; L. Lapidus and J. H. Seinfeld, *Numerical Solution of Ordinary Differential Equations* (Academic, New York, 1971), p. 113.

⁵R. W. Hamming, *Numerical Methods for Scientists and Engineers* (McGraw-Hill, New York, 1962), p. 214.

⁶E. Oset and L. L. Salcedo, J. Comp. Phys. 57, 361 (1985); E. Buendia and R. Guardiola, *ibid.* 60, 561 (1985).

⁷B. R. Johnson, J. Chem. Phys. 67, 4086 (1977); 69, 4678 (1978).

⁸L. Lapidus and J. H. Seinfeld, *Numerical Solution of Ordinary Differential Equations* (Academic, New York, 1971), Chap. 2.

⁹G. Dahlquist and A. Björck, *Numerical Methods* (Prentice-Hall, Englewood Cliffs, NJ, 1974), pp. 269-273.

¹⁰C. S. Lai, Phys. Rev. 23, A455 (1981).