JOURNAL OF COMPUTATIONAL PHYSICS 12, 103–111 (1973)

A Numerical Approach for the Solution of the Radial Schrödinger Equation with Atomic-Like Potentials

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Received June 19, 1972

It is demonstrated that the removal of factors of r^l from the solutions of the linear second-order differential Schrödinger equation containing atomic-like potentials is essential under certain conditions before carrying out the numerical work. Two examples are for large $l(>5)$ values and when derivatives of the solutions are recycled in the equation. The subsequent complications are dealt with by deriving a conceptually simple numerical procedure. The method is an extension of that due to Numerov and is reminiscent of other approaches, all having a truncation error δ^6. This is exemplified by examining the realistic hydrogen atom problem including the spin–orbit term and the results are compared to the exact solution and to the Numerov solution. We find that the approach suggested here gives significantly better results than the Numerov, and hence comparable, method.

I. INTRODUCTION

In the application of numerical methods to the solution of differential equations it is imperative that one be confident that any disparity between calculation and observation be a result of the simplifying approximations and not a result of inappropriate numerical procedures. This simply restates the warning appearing in many works on numerical analysis, namely, that careful analysis of the problem at hand must always precede the start of computation. We have encountered just this dilemma in solving the Schrödinger equation for an electron in a metal [1–3]. Certain aspects of numerical procedures have been examined [4, 5] for similar problems, but not to the extent that we required. These works contain a comparison of a number of numerical methods and find them to be of comparable accuracy when applied in the same way. We compare our results to one of them, that is, the Numerov method [6].

The above implies that any improvement must come from further analysis of the differential equation. The type of equation considered herein is the radial Schrödinger equation for spherically symmetric systems. This equation has the form

$$[D^2 - G(E, l, r)]\, ry(E, l, r) = F(E, l, r), \tag{1}$$

where

$$D = d/dr. \tag{2}$$

Generally,

$$G(E, l, r) = E + V(r) + [l(l + 1)/r^2], \tag{3}$$

where E is the usual energy eigenvalue, $V(r)$ is the potential energy which we write in the form

$$V(r) = -2ZQ(r)/r, \tag{4}$$

where $Q(r)$ is unity at the origin and is differentiable to arbitrary order, by assumption, and Z is a constant, the nuclear proton number. Finally, the inhomogeneous term arises from the spin–orbit interaction and can be written as

$$F(E, l, r) = (1/4)(dV/dr)\, p(E, l, r), \tag{5}$$

where rp is the complementary function of (1). Note that the units of length are atomic units and energies are in Rydbergs.

Although (1) is in the standard form for the use of the Numerov procedure the nature of G and F cause ry to be proportional to r^{l+1}. Since the Numerov method is accurate to order δ^6, δ being the interval, this factor is not reproduced well by the Numerov method and, by the same token, any comparable procedure. This discrepancy is particularly marked for outward solution near the origin where one must attempt a balance between reproducing the r^{l+1} factor and having a power series represent ry accurately. We find that a significant improvement in the computations can be achieved by first removing the factor r^{l+1} analytically and then solving the resultant differential equation numerically.

Now, since the Numerov method is no longer applicable and since it is desirable for numerical procedures to be sufficiently straightforward so that a nonexpert in numerical analysis can apply them and even adapt them, if necessary, to suit his purposes, we develop a conceptually simple method to handle the problem. The method is an extension of that due to Numerov and is reminiscent of other approaches [7], all having a truncation error δ^6. For the test case of the hydrogen atom problem this procedure is found to be at least as accurate as and generally much better than direct numerical solution of (1). It should be noted that it is not the particular numerical procedure that improves the calculations but the analysis of the differential equation. It is this point that we wish to stress rather than an examination of numerical methods. Also we did not wish to obscure the important features by using sophisticated numerical methods.

In Section 2 we justify the use of numerical methods on Eq. (1) with (5). Section 3 contains an outline of the removal of the factor r^{l+1} and the derivation of the numerical method to be used. In Section 4 we echo the sentiments of a previous

author [4] by assuming that what is good for the hydrogen atom will be good for similar but more complicated systems also. Since the present authors are primarily interested in problems in solid state physics, only the outward numerical solution, which is sufficient for such problems, is discussed. Results are presented and analysed.

2. Applicability of Numerical Methods

The solution of the homogeneous equation and the existence of power series expansions permitting the use of typical numerical methods is well documented [4, 6, 8, 9] and will not be commented upon further.

We now turn our attention to the solution of the inhomogeneous equation of the form presented above. The problems arising in its solution do not appear to have been adequately discussed in simple terms. Because $V(r) \to -2Z/r$ and $DV(r) \to 2Z/r^2$ as $r \to 0$ the particular solution does not have a power series expansion in this region. This difficulty can be circumvented [10] by setting

$$ry(E, l, r) = [\gamma_1(l) \ln r + (\gamma_2(l)/r)]\, rp(E, l, r) + z(E, l, r), \tag{6}$$

where rp is the corresponding complementary function. The first term in the square brackets removes the nonpower series contribution from ry when

$$\gamma_1(l) = Z^2/2l(l + 1)(2l + 1). \tag{7}$$

The second term removes all vestige of the complementary function when

$$\gamma_2(l) = -Z/4l \tag{8}$$

for this ensures that z is proportional to r^{l+2}. The inclusion of this term also facilitates the numerical solution. Since the $l = 0$ function is of no interest we exclude this case. z is the solution of

$$[D^2 - G(E, l, r)]\, z(E, l, r) = \tilde{F}(E, l, r), \tag{9}$$

where

$$\tilde{F} = (p/4)\, DV - [\gamma_1(l)/r]\, p - 2[\gamma_1(l) - [\gamma_2(l)/r]]\, Dp. \tag{10}$$

The choice of $\gamma_1(l)$ and $\gamma_2(l)$ ensure that near the origin the two leading terms cancel exactly and hence $\tilde{F}$ is proportional to r^l.

The formal solution for $z(E, l, r)$ can be written down almost immediately and is

$$z(E, l, r) = rp(E, l, r) \int_0^r \frac{dt}{[tp(E, l, t)]^2} \int_0^t sp(E, l, s)\, \tilde{F}(E, l, s)\, ds. \tag{11}$$

The only possible difficulties arise at the zeros in the complementary function p.

First, let us consider the region $r \to 0$. The interior integral presents no problems and behaves as t^{2l+2} in this region. This factor cancels exactly with the corresponding factor in the denominator. Thus a power series solution exists in this region and is proportional to r^{l+2} as mentioned above.

Second, let us consider p containing a single zero at $r = r_1$. Thus

$$rp(E, l, r) = r^{l+1}(r - r_1)\,\tilde{p}(E, l, r), \tag{12}$$

and

$$z(E, l, r) = r^{l+1}(r - r_1)\,\tilde{p}(E, l, r)\int_0^r \frac{dt}{(t - r_1)^2}\,\phi(t), \tag{13}$$

where

$$\phi(t) = \frac{1}{t^{2l+2}\tilde{p}^2}\int_0^t s^{l+1}(s - r_1)\,\tilde{p}\tilde{F}\,ds. \tag{14}$$

Write

$$\phi(r) = \phi(r_1) + (r - r_1)\,D\phi(r_1) + [\phi(r) - \phi(r_1) - (r - r_1)\,D\phi(r_1)]. \tag{15}$$

Now $D\phi(r_1)$ contains the factor $[(l + 1)\,\tilde{p}(r_1) + r_1\,D\tilde{p}(r_1)]$ which is identically zero, using the fact that rp is the complementary function. Hence $D\phi(r_1) \equiv 0$ and

$$\begin{aligned} z(E, l, r) = &- r^{l+2}\phi(r_1)\,\tilde{p}(E, l, r)/r_1 \\ &+ r^{l+1}(r - r_1)\,\tilde{p}(E, l, r)\int_0^r \frac{[\phi(t) - \phi(r_1)]}{(t - r_1)^2}\,dt. \end{aligned} \tag{16}$$

The factor $(t - r_1)^2$ cancels exactly, leaving z well behaved with all of its derivatives defined.

Finally, if rp has N nodes one writes

$$\prod_{i=1}^{N}\frac{1}{(r - r_i)^2} = \left[\frac{1}{(r - r_1)^2} + \prod_{i=2}^{N}\frac{1}{(r - r_i)^2}\right]\Big/\left[(r - r_1)^2 + \prod_{i=2}^{N}(r - r_i)^2\right] \tag{17}$$

reducing the problem to the above one node case plus an $N - 1$ node case. All apparent singularities are removed in this way.

We thus conlude that standard numerical procedures are applicable to this problem.

3. Simple Extension of the Numerov Procedure

We now wish to set up a relatively simple procedure to take into account explicitly the factor r^{l+1} in the solutions. Hence write

$$\left.\begin{matrix} ry \\ z \end{matrix}\right\} = r^{l+1}Y, \tag{18}$$

and substitute into (1) or (9) to obtain

$$[D^2 + h(l, r)\, D - g(E, r)]\, Y(E, l, r) = f(E, l, r), \tag{19}$$

where now

$$h(l, r) = 2[(l + 1)/r], \tag{20a}$$

$$g(E, r) = +E + V(r), \tag{20b}$$

$$f(E, l, r) = \frac{1}{r^{l+1}} \begin{cases} F(E, l, r) \\ \bar{F}(E, l, r). \end{cases} \tag{20c}$$

Now expand $Y(E, l, r)$ in a power series about some value of r_0 with the expansion parameter δ and notice that from (19)

$$Y''(r_0 + \delta) = g(r_0 + \delta)\, Y(r_0 + \delta) - h(r_0 + \delta)\, Y'(r_0 + \delta) + f(r_0 + \delta), \tag{21a}$$

$$Y''(r_0) = g(r_0)\, Y(r_0) - h(r_0)\, Y'(r_0) + f(r_0), \tag{21b}$$

$$Y''(r_0 - \delta) = g(r_0 - \delta)\, Y(r_0 - \delta) - h(r_0 - \delta)\, Y'(r_0 - \delta) + f(r_0 - \delta), \tag{21c}$$

and from the Taylor series expansions

$$\begin{aligned} Y'(r_0 + \delta) = {} & (1/2\delta)[Y(r_0 + \delta) - Y(r_0 - \delta)] \\ & + (\delta/3)[2Y''(r_0) + Y''(r_0 + \delta)] + 0(\delta^4), \end{aligned} \tag{22a}$$

$$\begin{aligned} Y'(r_0) = {} & (1/2\delta)[Y(r_0 + \delta) - Y(r_0 - \delta)] \\ & - (\delta/12)[Y''(r_0 + \delta) - Y''(r_0 - \delta)] + 0(\delta^4), \end{aligned} \tag{22b}$$

$$\begin{aligned} Y'(r_0 - \delta) = {} & (1/2\delta)[Y(r_0 + \delta) - Y(r_0 - \delta)] \\ & - (\delta/3)[2Y''(r_0) + Y''(r_0 - \delta)] + 0(\delta^4). \end{aligned} \tag{22c}$$

By neglecting terms of order δ^4, (22) can be used to eliminate the first derivatives in (21) and then (21) used to eliminate the second derivatives in

$$\begin{aligned} Y(r_0 + \delta) - 2Y(r_0) + Y(r_0 - \delta) = {} & (\delta^2/12)\{Y''(r_0 + \delta) + 10Y''(r_0) \\ & + Y''(r_0 - \delta)\} + 0(\delta^6) \end{aligned} \tag{23}$$

to yield the result

$$C_+ Y(r_0 + \delta) = C_0 Y(r_0) - C_- Y(r_0 - \delta) + (\delta^2/12)\, F_{in} + 0(\delta^6). \tag{24}$$

This equation is exactly comparable to the Numerov equation and is used in the same way. In (24)

$$C_+ = [1 + (\delta/24)(H_+ + H_-) - (\delta^2/12)\, G_+]\, J_1 + (\delta/24)\, h(r_0) \times [1 + (\delta/12)(H_+ - H_-) - (\delta^2/6)\, G_+]\, J_2\,, \tag{25a}$$

$$C_0 = 2J_1 + (\delta^2/12)\, g(r_0)\, J_2\,, \tag{25b}$$

$$C_- = [1 - (\delta/24)(H_+ + H_-) - (\delta^2/12)\, G_-]\, J_1 - (\delta/24)\, h(r_0) \times [1 + (\delta/12)(H_+ - H_-) - (\delta^2/6)\, G_-]\, J_2\,, \tag{25c}$$

$$F_{in} = [F_+ + F_-]\, J_1 + [f(r_0) + (\delta/12)\, h(r_0)(F_+ - F_-)]\, J_2\,, \tag{25d}$$

$$J_1 = 1 + (\delta^2/18)\, h(r_0)[H_+ + H_-], \tag{26a}$$

$$J_2 = 10 - (2\delta/3)[H_+ - H_-], \tag{26b}$$

and where H_+, H_-, G_+, G_-, F_+ and F_- are all similarly defined by

$$H_+ = h(r_0 + \delta)/[1 + (\delta/3)\, h(r_0 + \delta)], \quad \text{etc.} \tag{27a}$$

and

$$H_- = h(r_0 - \delta)/[1 - (\delta/3)\, h(r_0 - \delta)], \quad \text{etc.} \tag{27b}$$

the denominators being common for all these functions.

4. Example and Discussion

In order to assess the practical implications of the previous sections the exact solution to the hydrogen atom problem is compared with that obtained from the Numerov method and from the procedure outlined in Sections 2 and 3. As mentioned previously only the outward integration is studied, the other aspects having been discussed elsewhere [4, 6, 9]. The calculations have been performed using the standard varying interval [9] with six blocks of forty points each with a maximum $r = 5.0$, which represents a typical value occurring in solid state physics problems. Reduced results are summarized in Tables I–III for $r = 4.0$ and 5.0.

First, the solution of the homogeneous equation was examined and we find that for low l (<5) values both numerical methods give comparable and excellent accuracy. However, as l increases the Numerov method becomes progressively less accurate whereas the modified procedure retains its high accuracy. This behavior is attributed to the fact that, for small r, ry is proportional to δ^{l+1} and hence in the direct application of numerical procedures to (1) methods accurate to δ^6 are rather illusory. In fact, an examination of the results reveals that the relative error quoted

first arises at small r and propagates outward. The removal of the factor r^{l+1} in ry surmounts this difficulty. Note that the n (or energy) dependence of the relative error is not significant.

TABLE I

$-\log$ | Relative Error | for the Exact Homogeneous Equation

			Numerov method		Modified procedure	
l	n	$r =$	4.0	5.0	4.0	5.0
0	1		6.4	5.7	6.4	5.7
	2		7.5	7.4	7.5	7.4
	3		7.8	7.3	7.8	7.3
	4		7.6	7.3	7.6	7.3
1	2		7.8	7.7	8.1	7.6
	3		7.8	7.3	8.0	7.3
	4		7.8	7.1	8.0	7.2
	5		7.8	6.9	8.1	7.1
2	3		8.4	8.3	8.6	8.7
3	4		8.1	8.2	9.0	9.0
4	5		7.2	7.2	9.0	9.0
5	6		5.2	5.2	9.0	9.0
6	7		4.5	4.5	9.0	9.0
7	8		3.9	3.9	9.0	9.0
8	9		3.5	3.5	9.0	9.0

TABLE II

$-\log$ | Relative Error | for the Exact Inhomogeneous Equation

			Numerov method		Modified procedure	
l	n	$r =$	4.0	5.0	4.0	5.0
1	2		8.3	8.3	8.3	8.3
2	3		8.4	8.4	8.7	8.4
3	4		8.5	8.5	8.8	8.8
4	5		7.3	7.4	9.0	9.0
5	6		6.3	6.4	9.0	9.0
6	7		5.7	5.8	9.0	9.0
7	8		5.3	5.4	9.0	9.0

TABLE III

$-\log$ | Relative Error | for the Numerical Inhomogeneous Equation

			Numerov method		Modified procedure	
l	n	$r =$	4.0	5.0	4.0	5.0
1	2		7.5	7.3	8.0	7.9
2	3		7.9	8.4	8.4	8.1
3	4		6.7	6.8	8.8	8.5
4	5		4.4	4.5	8.6	8.4
5	6		2.0	2.1	9.0	8.7
6	7		1.1	1.2	9.0	9.0

Secondly, the exact inhomogeneous equation was formed and treated exactly as the homogeneous equation. A comparison of Tables I and II shows that comparable conclusions follow and that the interpretation presented there is collaborated and that the same resolution applies.

Finally, in an actual problem, the inhomogeneous term (5) will not be known exactly but will be obtained numerically from the complementary function. At low l values, where both numerical solutions are accurate and smooth the particular solution is exceptionally good. However, at the higher l values the inaccuracies in the Numerov solution are enhanced in the derivatives and hence in the inhomogeneous term. The derivatives were evaluated by a five point central difference formula. The errors rapidly make the Numerov method, and, in general, direct numerical solution of (1), inappropriate. In fact, by $l = 5$ the particular solution found by the Numerov method is unreliable for all r. On the other hand, the procedure outlined in this report circumvents these difficulties.

In summary we note that for lower l values (<6) and an inhomogeneous term that is a relatively simple function of the complementary function the Numerov method is adequate. Further, because of its simplicity and rapidity it remains quite useful in an eigenvalue search. However, it is now clear that there exists a class of problems for which it is generally inappropriate and we have demonstrated a relatively simple procedure by which to handle such problems.

ACKNOWLEDGMENT

The authors are indebted to the University of Waterloo for supplying computing facilities and time for this project.

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