

A Numerical Solution for Hydrogen-Like Wave Equations¹

C. R. QUADE²

Department of Physics, University of Oklahoma, Norman

Attempts have been made by Pratt (1952) to use the Numerov method of numerical integration (Hartree, 1952) to obtain first order radial wave functions of certain elements of the transition group. It was suggested by Hijikata³ that this method be used to determine the wave functions and eigenvalues of the Schrodinger Equation for the hydrogen atom so that an estimate of the relative validity of the method might be obtained from comparison with the exact solutions. The Numerov method was chosen as the tool for the numerical analysis because of its relative simplicity when applied to problems with certain boundary conditions. All numerical work was carried out on an IBM 650 Data Processing Machine.

The general problem consists of replacing the actual differential equation by a finite difference equation, and then using the boundary conditions for the first equation to determine the eigenvalues and corresponding solutions of the second. It is assumed then that the solutions of the finite difference equation are fair approximations to those which would be obtained from exact solution of the differential equation.

The actual second order equation with which this problem is concerned is the radial portion of the Schrodinger equation for a hydrogen-like atom. After a change in variable, equation (1) (Figure 1)⁴ is obtained, subject to the boundary conditions (1a)¹ and (1b)⁴. In the differential equation E is the eigenvalue which determines the energy, and l is the orbital angular momentum quantum number and may assume the values 0 to $(E-1)$.

The corresponding finite difference equation is equation (2)⁴ and the boundary conditions are assumed to be the same as those of the differential equation. The successive values of u_n are determined from the previous values of u_n and the difference equation by the Numerov method.

It is well known that every second order differential equation has two linearly independent solutions—one increasing and the other decreasing for large values of the independent variable. But in this problem only the decreasing solution is assigned physical meaning. In solving the differential equation analytically we can easily separate the two solutions since only one satisfies the necessary boundary conditions. But the difference equation is an approximation to the differential equation and therefore is subject to different boundary conditions although it has been assumed that they are the same. Thus a mixing of the two solutions is obtained by employing a numerical method to solve the problem, and this is something which cannot be avoided. Since the boundary condition is that u approaches 0 as r approaches infinity, at some value of r the magnitude of both solutions will be of comparable order of magnitude and from there on the increasing solution will dominate, indicating an incorrect eigenvalue (even when the correct one is used in the equation).

¹ Supported by the Office of Naval Research.

² National Science Foundation Predoctoral Fellow, 1959-60.

³ Hijikata, K., private communication.

⁴ Because the equations could not be set in type, they are reproduced together in Fig. 1.

$$(1) \quad Lu = \left(\frac{d^2}{dr^2} - \frac{1}{4} - \frac{l(l+1)}{r^2} + \frac{E}{r} \right) u = 0$$

$$(1a) \quad r = 0, u = 0; \quad r \rightarrow \infty, u \rightarrow 0, \quad \frac{du}{dr} \rightarrow 0$$

$$(1b) \quad \int_0^{\infty} u^2 dr = \text{const.}$$

$$(2) \quad L u_n = \left(\frac{d^2}{dr^2} - g_n \right) u_n = 0$$

where

$$g_n = \frac{1}{4} + \frac{l(l+1)}{r_n^2} - \frac{E}{r_n}$$

$$(3) \quad \text{Truncation error} = (\delta r)^6 u_n^{\text{VI}}$$

FIGURE 1

The effect of the increasing solution may be minimized temporarily by using a slightly too large eigenvalue. This causes the "decreasing" solution to diverge to minus infinity and thus the sum of the two solutions can be made to approach zero. But this is only a temporary measure since eventually one of the two solutions will dominate because the number of digits in the eigenvalue is limited by the size of the computer.

In order to test the essential features and reliability of the Numerov method, the difference equation with $E = 1$ was investigated in every detail. Various sizes of the integration interval were tried, as well as both single and double precision arithmetic. Finally the eigenvalue was varied until one was obtained which gave the most favorable convergence of the wave function. Part of the results are listed in Table I.

The advantages and disadvantages of the various features may be analyzed as follows:

A. Double Precision Arithmetic

Advantages: 1) General roundoff errors of the machine are minimized. 2) When the wave function decreases in an order of magnitude during its convergence, a significant digit is lost and a non-compensating roundoff error arises in the last digit. Double precision removes this difficulty in the first ten digits. 3) These things can reduce the excitation of the increasing solution. 4) The eigenvalue which corresponds to $E = 1$ and gives the best convergence is one order of magnitude better than the one obtained with single precision arithmetic.

Disadvantages: 1) The overwhelming disadvantage is the increased length of calculation time for each pass. Since the eigenvalue is determined by trial and error, the pass time should be minimal. Double precision is approximately 50 times slower than the corresponding single precision calculation.

B. Small Integration Interval

Advantages: 1) The truncation error is given by equation (3)⁴. Therefore by varying the size of interval this error may be made arbitrarily small. 2) Also in the case of double precision arithmetic a small interval can reduce (up to a point) the occurrence of the increasing solution.

Disadvantages: 1) The integration pass time is proportional to interval size. 2) If too small an interval is used more round-off error can occur with single precision arithmetic because of the increased number of calculations. This will excite the increasing solution. (See Table I, first two lines)

C. Variation of the Eigenvalue

Advantages: 1) At least some results are obtainable. For E equal to about 1, the best eigenvalue obtained with single precision is 1.0002035, with double precision 1.0000203.

Disadvantages: 1) The function obtained is a linear combination of the increasing and decreasing solutions and not the correct wave function. 2) Eventually the function always diverges.

Table I shows the dependence of the convergence of the wave function on the interval size and the precision of the arithmetic. Also the best numerical calculated eigenvalues through $E = 4$ are listed. Table II compares the wave functions of the 1s state from the exact and numerical calculations.

From the results of this analysis it appears that the Numerov method will be useful in atomic and molecular calculations. The method appears to be particularly suitable as a first order approximation and can be readily applicable to such problems as: many electron systems, cohesive energy of metals, and mesonic atom calculations.

TABLE I. CONVERGENCE FEATURES OF THE HYDROGEN ATOM WAVE FUNCTIONS

E	Integration Interval	r _{max}	E	Integration Interval	r _{max}
Single Precision Arithmetic					
1.0000000	0.0025	0	14.81	1.0000000	0.01
1.0000000	0.005	0	15.20	1.0000000	0.05
Best Eigenvalues					
1.0002035	0.05	0	20.20	3.0000018	0.05
2.0007967		0	25.70	4.0029950	0
2.0000085		1	25.20	3.9999754	1
3.0017396		0	30.80	4.0000136	2
3.0000044		1	29.85	4.0000208	3
Double Precision Arithmetic					
1.0000000	0.01	0	17.30	1.0000000	0.05
1.0000205	0.05	0	19.00		

TABLE II. COMPARISON OF ANALYTIC AND NUMERICAL SOLUTIONS (SPA)

E =	Numerical	E =	Analytic
	1.0002035		1.0000000
r	U _n		U
0.00	0.000000		0.000000
2.00	0.520240		0.520260
8.00	0.10364		0.10361
12.00	0.02102		0.02103
14.00	0.00899		0.00903
16.00	0.00371		0.00380
18.00	0.00136		0.00157
20.00	0.00013		0.000064

ACKNOWLEDGEMENT

The author wishes to acknowledge the advice of Dr. K. Hijikata, who suggested this problem.

LITERATURE CITED

Pratt, G. W., 1952. Phys. Rev. 88: 1217.
 Hartree, D. R., 1952. Numerical Analysis, Clarendon Press, Oxford.