Efficient Method for Solving Atomic Schroedinger's Equation

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1. Introduction. One of the basic numerical problems in atomic quantum theory is the solution of the Schroedinger's wave equation for a spherically symmetric potential. In practice, one is usually concerned with such potentials obtained by the Hartree-Fock self-consistent fields [1] or by the Thomas-Fermi-Dirac statistical field methods [2, 3].

This paper describes a highly efficient and rapidly convergent technique for solving the radial Schroedinger's equation for an arbitrary atomic-like potential. The method has been programmed for the IBM 650 computer and the numerical results obtained are in good agreement both with pertinent experimental results (x-ray term levels) and with previous theoretical work [4].

2. Problem Definition. The Schroedinger's wave equation in atomic units (r in Bohr radii, E in Rydbergs) is given by

$$\frac{d^2 P(r)}{dr^2} = q(r) P(r) \qquad \text{for} \quad r \geqq 0$$

where

$$q(r) = V(r) - E + \frac{l(l+1)}{r^2}.$$

In this equation $P(r)$ is the radial wave function, $V(r)$ is the potential energy, and E is the desired eigenvalue satisfying the boundary conditions $P(0) = 0$ and $P(\infty) = 0$. The parameter l, the angular-momentum number, is an integral number 0, 1, 2, 3, etc. These numerical values of l are usually designated as s, p, f, d, etc. For each l, there is a set of eigenvalues satisfying the boundary values and labeled by an integer n. The lowest state for each l value is taken as $n = l + 1$, the principal quantum number, and for every value of n there is a distinct energy value E. The various radial wave functions and associated eigenvalues are specified using the subscript nl.

3. Integration Method. The integration mesh was made flexible for many different type atoms by choosing it as a function of the atomic structure. The integrating variable x was made equal to r/μ, where

$$\mu = \frac{3\pi}{4(6\pi z)^{1/3}}$$

and $z = $ the atomic number. It was found that $\Delta x = .0025$ was a satisfactory starting step and the mesh could be doubled every 40 points. The potential values were calculated for the same mesh using the Fermi-Thomas-Dirac equation and the desired boundary conditions.

START

LOAD POTENTIAL DECK

READ CONTROL CARD Z $n\ell$ $E_{n\ell}$

PRINT HEADING CARD Z $n\ell$ $E_{n\ell}$

TEST ℓ

$\ell = 0$ → SET $F = F_1$

$\ell \geq 1$ → SET $F = F_2$

COMPUTE STARTING VALUES FOR NUMEROV METHOD $P(r_1)$, $P(r_2)$

COMPUTE $\psi(r)$ VALUES ψ_1, ψ_2, $B^2\psi_2$

$x_{n+1} = x_n + h$
$r_{n+1} = \mu x_{n+1}$

STORE $V(r_{n+1})$

$q(r_{n+1}) = V(r_{n+1}) + \dfrac{\ell(\ell+1)}{r_{n+1}^2} - E_{n\ell}$

FORK F

F_1 → TEST q
F_2 → TEST q → SET $F = F_1$

$(n+1) \rightarrow n$

TEST LOOP BOX $L < 40$ → DOUBLING INTERVAL PROCEDURE
$L = 40$

PRINT r_{n+1} $P(r_{n+1})$

COMPUTE $P(r_{n+1})$, $\psi(r_{n+1})$ BY NUMEROV METHOD

STORE $r = R_1$

STORE $A_1 = \dfrac{\int^{R_1} P^2\,dr}{[P(R_1)]^2}_{OUT}$

STORE $A_2 = \left(\dfrac{P'(R_1)}{P(R_1)}\right)_{OUT}$

COMPUTE $R_2 \approx (5 + \ell)\,R_1$

COMPUTE STARTING VALUES FOR INWARD INTEGRATION $P(R_2)$, $P(R_2 - h)$

$x_{n+1} = x_n - h$
$r_{n+1} = \mu x_{n+1}$

STORE $V(r_{n+1})$

$q(r_{n+1}) = V(r_{n+1}) + \dfrac{\ell(\ell+1)}{r_{n+1}^2} - E_{n\ell}$

COMPUTE $P(r_{n+1})$, $\psi(r_{n+1})$

PRINT r_{n+1} $P(r_{n+1})$

TEST r_{n+1}
$r_{n+1} > R_1$
$r_{n+1} = R_1$

$(n+1) \rightarrow n$

COUNT $C < N_1$ → ... ; $C = N_1$ → HALVING INTERVAL INTERPOLATION PROCEDURE

$A_3 = \dfrac{\int^{\infty} P^2\,dr}{[P(R_1)]^2}_{IN}$

$A_4 = \left(\dfrac{P'(R_1)}{P(R_1)}\right)_{IN}$

$\Delta E = \dfrac{A_2 - A_4}{A_1 + A_3}$

TEST
$\left|\dfrac{\Delta E}{E}\right| < 10^{-5}$ → STOP
$\left|\dfrac{\Delta E}{E}\right| > 10^{-5}$

NEW TRIAL EIGENVALUE $E_{n\ell} = E_{n\ell} + \Delta E$

FIG. 1

CONVERGENCE OF TRIAL EIGENVALUES

ATOM: Germanium
QUANTUM STATE: 1s
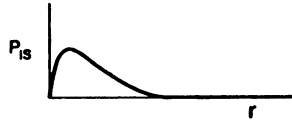
TRIAL	E_{1s}	ΔE_{1s}
1	-700.000	-86.824
2	-786.824	-14.834
3	-801.658	$-\ .230$
4	-801.888	$+\ \ \ 000\ 13$

Fig. 2

CONVERGENCE OF TRIAL EIGENVALUES

ATOM: Germanium
QUANTUM STATE: 2s
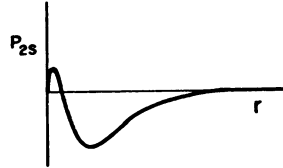
TRIAL	E_{2s}	ΔE_{2s}
1	-150.000	$+57.042$
2	$-\ 92.958$	$-\ 7.956$
3	-100.914	$-\ 1.150$
4	-102.064	$-\ .015$
5	-102.079	$-\ .000\ 02$

Fig. 3

CONVERGENCE OF TRIAL EIGENVALUES

ATOM: Cerium
QUANTUM STATE: 5d
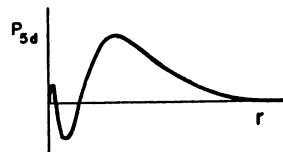
TRIAL	E_{5d}	ΔE_{5d}
1	$-2.22\ \ 000$	$+.28\ \ \ 567$
2	$-1.93\ \ 433$	$-.03\ \ \ 142$
3	$-1.96\ \ 575$	$-.00\ \ \ 126$
4	$-1.96\ \ 701$	$-.00\ \ \ 000\ 3$

Fig. 4

A method applicable only to a linear second-order differential equation which lacks the first derivative was used to solve Schroedinger's equation. This method introduced by Numerov [5] is approximately four times faster than the Runge-Kutta-Gill procedure and the truncation error is proportional to h^6.

4. Matching Procedure. Schroedinger's equation is integrated outward to a point where $P(r)$ changes from a traveling-wave behavior to a damped-wave behavior. The choice of this matching radius R_1 is made dependent upon the value of $q(r)$, the kinetic energy, becoming negative. This choice makes the program quite general as it will handle any value of l and E. The integral $\int_0^{R_1} P^2(r)\,dr$ and the logarithmic derivative of $P(r)$ at $r = R_1$, $(P'(r)/P(r))_{\text{out}}$ are stored.

Then an inward integration is performed starting at $R_2 = (5 + l)R_1$. At R_2 the final normalized wave function is essentially zero, thus satisfying the second boundary condition $P(\infty) = 0$. Since q in the neighborhood of R_2 is essentially a constant, a good approximation for $P(R_2) = e^{-R_2\sqrt{q(R_2)}}$. This value is then used to start the inward integration, which is continued until R_1 is reached. The values of $\int_{R_1}^{\infty} P^2(r)\,dr$ and $(P'(R_1)/P(R_1))_{\text{in}}$ are calculated and stored.

5. Calculating Improved Eigenvalue. The difference at R_1 between the values of $(P'/P)_{\text{out}}$ and $(P'/P)_{\text{in}}$ is used to estimate what change in E, (ΔE), is necessary to obtain a better match. For each trial eigenvalue an outward and an inward integration is performed. A formula developed by Hartree (1) is then used to obtain ΔE as follows:

$$\left\{ \frac{\int_0^{R_1} P^2(r)\,dr}{P^2(R_1)_{\text{out}}} + \frac{\int_{R_1}^{\infty} P^2(r)\,dr}{P^2(R_1)_{\text{in}}} \right\} \Delta E = \left[\left(\frac{P'}{P}\right)_{\text{out}} + \left(\frac{P'}{P}\right)_{\text{in}} \right]$$

The value ΔE is then added to the trial E and the process repeated until $|\Delta E/E| < 10^{-5}$. The radial wave functions are then made continuous at R_1 and normalized.

6. Flow-Chart of Procedure. The main features of the program are outlined in Fig. 1.

7. Convergence of Trial Eigenvalues. The program has been used in applications pertaining to the germanium, silicon, and cerium atoms and also the zinc-sulfide and gallium-arsenide crystals. It has been used for the seven quantum states 1s, 2s, 3s, 2p, 3p, 5d, and 4f. Some typical eigenvalues convergence rates are shown in Fig. 2, 3, and 4.

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