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Finite-Difference Solution to the Schroedinger Equation for the Ground State and First-Excited State of Helium*

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The Schroedinger Equation for *S*-type states of the helium atom, which is an elliptic partial-differential equation, is converted to a set of finite-difference equations, which are then solved by an iterative technique. The total energy of the ground state and first-excited state are calculated to be −2.90360 and −2.17414 a.u., respectively, as compared to the known accurate values of −2.90372 and −2.17522 a.u. due to Pekeris. The results for the ground state include energy expectation values, and expectation values of other terms commonly used to test the correctness of the wavefunction. Reasonable agreement is obtained between values obtained by this work and that of Pekeris with the differences being within the known numerical error of the iterative method.

I. INTRODUCTION

Recently it was suggested by Birkhoff [1] and later by Young [2] that it would be both interesting and desirable to supplement the many ingeneous techniques developed to obtain approximate solutions to the Schroedinger differential equation by a method that uses strictly numerical techniques. This paper presents the theory and procedure for the application of the finite-difference technique to the helium problem. The technique presented here has been applied to other elliptic partial-differential equations, but never to the Schroedinger equation. In addition, most numerical methods that are applied to partial-differential equations use cartesian coordinates to simplify the iteration matrix, but the nature of the potential in an atomic problem requires a solution in spherical coordinates. Thus, this work is unique in two respects; it is the first application of purely numerical methods to solve the Schroedinger equation, and second, the problem is formulated in spherical coordinates instead of the standard cartesian coordinates. Results of this method are compared with the known accurate results of Pekeris [3].

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Ideally, this technique is very general; that is, the only approximations involved are the replacement of a differential equation with a set of finite-difference equations, and the error involved in this approximation could then in theory be made suitably small. In practice, however, the technique is restricted by computer memory size and computer time cost.

Perturbation and variation techniques can yield good results for the helium problem, but unless the number of terms is quite large correlation effects are not properly taken into account. Using the present method, if the mesh size is suitably small, all correlation is properly treated. Therefore,the results can be compared directly with experiment, and any numerical error should be explainable from the finite-difference approximation.

II. FORMULATION OF PROBLEM

The time-independent Schroedinger equation for helium is

$$\left\{-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}\right\}\Psi = E\Psi, \qquad (1)$$

or in atomic units ($\hbar = m_e = e^2 = 1$)

$$\left\{-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}\right\}\Psi = E\Psi. \qquad (2)$$

In spherical polar coordinates this equation has the six independent variables $\{r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2\}$, which can be reduced to the three [4, 5] $\{r_1, r_2, r_{12}\}$ or $\{r_1, r_2, \theta\}$ for the ground state and all S-type states. If the angle θ, between the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ is chosen in favor of the variable r_{12}, and $\chi = r_1 r_2 \Psi$ is introduced, the Schroedinger equation for the ground state and all S-type states becomes

$$\left[-\frac{1}{2}\left\{\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\left(\frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\theta^2}\right)\right\} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}\right]\chi = E\chi. \qquad (3)$$

The total wavefunction for fermions must be antisymmetric upon electron exchange. Since the ground state of helium is known to be a singlet spin state (antisymmetric), then χ, in order to be an admissable ground state solution, must be symmetric. Thus, making χ a symmetric solution of Eq. (3) yields a solution compatible with the Pauli principle and the correct spin eigenfunction. For the first excited state (a triplet state) this can be accomplished by making χ antisymmetric.

III. Method of Solution

Equation (3) is transformed into a set of finite-difference equations by replacement of the derivatives with three-point central-difference formulas, viz

$$f_i'' = (f_{i+1} - 2f_i + f_{i-1})/h^2, \qquad \text{and} \qquad f_i' = (f_{i+1} - f_{i-1})/2h,$$

where $h = r_{i+1} - r_i$.

By use of this scheme, Eq. (3) becomes

$$\begin{aligned} -\tfrac{1}{2}(\chi_{i+1,j,k} &- 2\chi_{i,j,k} + \chi_{i-1,j,k})/(\Delta r_1)^2 \\ &- \tfrac{1}{2}(\chi_{i,j,k+1} - 2\chi_{i,j,k} + \chi_{i,j,k-1})/(\Delta r_2)^2 \\ &- \tfrac{1}{2}(1/r_i^2 + 1/r_k^2)(\chi_{i,j+1,k} - \chi_{i,j-1,k})/(2 \tan \theta_j \, \Delta\theta) \\ &- \tfrac{1}{2}(1/r_i^2 + 1/r_k^2)(\chi_{i,j+1,k} - 2\chi_{i,j,k} + \chi_{i,j-1,k})/(\Delta\theta)^2 \\ &+ [-2/r_i - 2/r_k + 1/(r_i^2 + r_k^2 - 2r_i r_k \cos \theta_j)^{1/2} - E]\, \chi_{i,j,k} = 0, \end{aligned} \tag{4}$$

where $r_i = i\,\Delta r_1$, $r_k = k\,\Delta r_2$, and $\theta_j = j\,\Delta\theta$. The boundary conditions on χ require that it vanish whenever the radius of either or both electrons becomes zero or infinity. By use of both hydrogenic and correlated test functions it was determined that the domain of r_1 and r_2 could be adequately covered by letting the maximum radius be 6.0 for the ground state and 12.0 for the first excited state. Therefore, the boundary conditions can be written as

$$\begin{aligned} \chi(0, \theta, r_2) &= \chi(r_1, \theta, 0) = \chi(0, \theta, 0) = 0, \\ \chi(6.0, \theta, r_2) &= \chi(r_1, \theta, 6.0) = \chi(6.0, \theta, 6.0) = 0, \end{aligned} \tag{5}$$

for the ground state, and

$$\begin{aligned} \chi(0, \theta, r_2) &= \chi(r_1, \theta, 0) = \chi(0, \theta, 0) = 0 \\ \chi(12.0, \theta, r_2) &= \chi(r_1, \theta, 12.0) = \chi(12.0, \theta, 12.0) = 0 \end{aligned} \tag{6}$$

for the first excited state. The domain of θ is $0 \leqslant \theta \leqslant \pi$, but due to the singularities in the differential equation at $\theta = 0$ and $\theta = \pi$, these points will be avoided by a small finite increment $\delta\theta$. Furthermore, Eq. (4) cannot be used near these extremes because the central-difference formula implies knowledge of points lying on either side of the point being calculated. Therefore, a forward- and backward-difference scheme must be applied to the theta differentiation at the end points. In this work a five-point scheme was chosen in order for the numerical error to be approximately the same as for the three-point central-difference scheme used elsewhere.

The third and fourth terms in Eq. (4) become, for theta near zero,

$$-\tfrac{1}{2}(1/r_i^2 + 1/r_k^2)(-25f_0 + 48f_1 - 36f_2 + 16f_3 - 3f_4)/(12\,\Delta\theta \tan \delta\theta),$$
$$-\tfrac{1}{2}(1/r_i^2 + 1/r_k^2)(35f_0 - 104f_1 + 114f_2 - 56f_3 + 11f_4)/12(\Delta\theta)^2,$$

where

$$f_0 = \chi(r_i\,, \delta\theta, r_k), \qquad f_1 = \chi(r_i\,, \delta\theta + \Delta\theta, r_k), \ldots$$

and for points of theta near π

$$-\tfrac{1}{2}(1/r_i^2 + 1/r_k^2)(25f_4 - 48f_3 + 36f_2 - 16f_1 + 3f_0)/(12\,\delta\theta \tan(\pi - \delta\theta)),$$
$$-\tfrac{1}{2}(1/r_i^2 + 1/r_k^2)(35f_4 - 104f_3 + 114f_2 - 56f_1 + 11f_0)/12(\Delta\theta)^2,$$

where

$$f_4 = \chi(r_i\,, \pi - \delta\theta, r_k), \qquad f_3 = \chi(r_i\,, \pi - \delta\theta - \Delta\theta, r_k), \ldots.$$

Coupling the boundary conditions (Eqs. (5) and (6)), and Eq. (4) with the suitable changes near theta equal zero and π gives a set of linear equations in the unknowns, $\chi_{i,j,k}$. The solution of this set for a particular eigenvalue E produces an approximate solution to the Schroedinger equation. Furthermore, if the eigenvalue E, is replaced with the expectation value of the Hamiltonian after a set number of iterations, and the iteration process continued until the energy and eigenfunction are self-consistent, both the approximate eigenvalue and eigenfunction are obtained.

To cover 6.0 atomic radii in r_1 and r_2 space, π radians in θ-space, and still have a small mesh size, many points had to be taken. By use of hydrogenic test functions, the mesh sizes, integration point schemes, and derivative point schemes were developed to give expectation values of the kinetic and potential energies to nearly six significant figures. This gave the following mesh sizes for the ground state:

$$\begin{aligned}
\Delta r_1 = \Delta r_2 &= 6/84, && \text{first 12 intervals,}\\
&= 6/42, && \text{second 12 intervals,}\\
&= 6/21, && \text{last 12 intervals}\\
\Delta\theta &= \pi/25 \text{ radians,} && \text{all theta intervals.}
\end{aligned}$$

This leads to a wavefunction array, (37, 25, 37), containing 34,225 values. Of these 34,225 values 3700 are known zero boundary values and the remaining 30,525 are unknowns.

Similar considerations for the triplet state gave:

$$\begin{array}{rll} \Delta r_1 = \Delta r_2 & = 12/132, & \text{first 12 intervals,} \\ & = 12/66, & \text{second 12 intervals} \\ & = 12/33, & \text{third 12 intervals} \\ & = 12/16.5, & \text{last 6 intervals} \\ \Delta\theta & = \pi/37 \text{ radians,} & \text{all theta intervals.} \end{array}$$

This leads to a wavefunction array, (43, 37, 43), containing 68,413 values. Of these 68,413 values 6364 are known zero boundary values and the remaining 62,049 are unknowns. Direct elimination techniques are known to be inefficient and uneffective for linear systems of these sizes; therefore, a relaxed iterative technique was chosen. For the helium problem as presented here, the Gauss–Seidel point iterative method with zero relaxation was found to optimize the convergence rate.

The expectation value of the Hamiltonian operator in Eq. (3) is evaluated in three parts: kinetic energy, electron–electron potential energy, and electron–nuclear potential energy. The kinetic energy operator is given by

$$\mathbf{K} = -\frac{1}{2}\left\{\frac{\partial^2}{\partial {r_1}^2} + \frac{\partial^2}{\partial {r_2}^2} + \left(\frac{1}{{r_1}^2} + \frac{1}{{r_2}^2}\right)\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\right\}. \tag{7}$$

To reduce the numerical error in the calculation of the expectation value of this operator, each term was integrated by parts. This operation replaces the second derivatives by the squares of first derivatives. The resulting equation is

$$\begin{aligned} \langle\mathbf{K}\rangle = \frac{1}{2}\int_0^\pi \sin\theta\, d\theta \int_0^\infty dr_1 \int_0^\infty dr_2 \\ \times \left[\left(\frac{\partial\chi}{\partial r_1}\right)^2 + \left(\frac{\partial\chi}{\partial r_2}\right)^2 + \left(\frac{1}{{r_1}^2} + \frac{1}{{r_2}^2}\right)\left(\frac{\partial\chi}{\partial\theta}\right)^2\right]. \end{aligned} \tag{8}$$

The first derivatives are evaluated numerically using a seven-point difference scheme and the integration performed by the seven-point Newton–Cotes formula.

The expectation value of the electron–electron potential energy presents more of a difficulty than the kinetic energy or the electron–nuclear potential energies. The reason is the function

$$r_{12}^{-1} = ({r_1}^2 + {r_2}^2 - 2\cos\theta r_1 r_2)^{-1/2} \tag{9}$$

is sharply spiked when $r_1 \simeq r_2$ and θ small. To obtain numerical accuracy on any rapidly varying function a high density of points is needed, but the number of points is limited by the finite size of the computer memory. The larger program used in this paper's calculations was run on a Honywell 636 computer and used approximately 90 % of the user available space. Consequently, any further increase in the number of points was impossible. In order to achieve an accuracy similar to that obtained for the other energies, single and double interpolation schemes were used on the wavefunction to effectively double the number of points for χ in r_1 and r_2 space. Points at crossings of the gridlines represent values of χ that are are known (after solving the set of linear equations), and points midway between gridpoints represent values of χ that are interpolated. Values lying on the gridlines are obtained using seven point single interpolation, and those lying between the gridlines by 49 point double interpolation. It is important to point out that it is the smooth wavefunction that is interpolated, not the spiked integrand in $\langle 1/r_{12} \rangle$ because the interpolation scheme would have the same difficulty fitting the integrand that integration schemes would have. Results of the interpolation of χ used to evaluate $\langle 1/r_{12} \rangle$ on a one-parameter variational wavefunction will be given in the next section to illustrate the improvement obtained over the uninterpolated result for $\langle 1/r_{12} \rangle$.

The electron-nuclear potential energies $\langle -2/r_1 \rangle$ and $\langle -2/r_2 \rangle$ cause no serious numerical difficulties since the integrand for these integrals vanish if either or both r_1 and r_2 are equal to zero.

IV. RESULTS

By use of χ given by

$$\chi = r_1 r_2 \exp\{-1.6875(r_1 + r_2)\}, \tag{10}$$

all the energy subroutines were checked for accuracy. These produced energy

TABLE I

Comparison of Correct Analytic Results with Those Obtained Numerically on a One-parameter Test Wavefunction

Operator	Analytic	Numerical
$\langle 1/r_{12} \rangle$	1.054688	1.054672[a] 1.056248[b]
$-2\langle 1/r_1 + 1/r_2 \rangle$	−6.750000	−6.749995
$\langle K \rangle$	2.847656	2.847667
$\langle H \rangle$	−2.847656	−2.847656

[a] This calculation uses double and single interpolation of the wavefunction to increase numerical accuracy.

[b] No interpolation.

expectation values that agreed with the analytic result to nearly six significant figures. The results of these calculations are given in Table I. It is important to note that a significant improvement is obtained for the electron–electron potential energy when interpolative techniques are employed.

Since an iterative technique was used to solve the set of linear equations, con-

TABLE II

Energy Expectation Values at Various Stages of Iteration for the Helium Ground State

Number of iterations	$\langle \mathbf{K} \rangle$	$\langle 1/r_{12} \rangle$	$2\langle 1/r_1 + 1/r_2 \rangle$	$-\langle \mathbf{H} \rangle$
0	2.8477	1.0547	6.7500	2.84766
300	2.9956	0.9750	6.8719	2.90125
600	2.9564	0.9604	6.8198	2.90303
900	2.9355	0.9533	6.7922	2.90345
1200	2.9254	0.9498	6.7788	2.90356
1500	2.9205	0.9481	6.7722	2.90359
1800	2.9180	0.9472	6.7689	2.90359
2100	2.9168	0.9468	6.7672	2.90360
2400	2.9162	0.9466	6.7663	2.90360
2700	2.9158	0.9465	6.7659	2.90360
Pekeris	2.9037	0.9458	6.7532	2.90372

TABLE III

Differences in the Energies Tabulated in Table II

ΔN	$\Delta\langle \mathbf{K} \rangle$	$\Delta\langle 1/r_{12} \rangle$	$2\Delta\langle 1/r_1 + 1/r_2 \rangle$	$\Delta\langle \mathbf{H} \rangle$
300–0	0.1480	0.0796	0.1219	0.0546905
600–300	0.0392	0.0147	0.0521	0.0017585
900–600	0.0209	0.0071	0.0276	0.0004419
1200–900	0.0101	0.0035	0.0134	0.0001064
1500–1200	0.0049	0.0017	0.0066	0.0000279
1800–1500	0.0025	0.0009	0.0033	0.0000072
2100–1800	0.0012	0.0004	0.0017	0.0000020
2400–2100	0.0006	0.0002	0.0009	0.0000005
2700–2400	0.0003	0.0001	0.0004	0.0000001

vergence must be demonstrated. This is done by listing, in Table II, the number of iterations and the corresponding energies at that particular stage in the iterative process. Also included are the known accurate results of Pekeris, so that accuracy determinations can be made. Table III contains the differences in the tabulated energy values shown in Table II, so that one can quickly observe the convergence.

TABLE IV

Total Energies Obtained by Variational Techniques for the Ground State of Helium Compared with Present Results

Number of parameters	Total energy	Reference
1	−2.84765626	Hylleraas (1929)
1	−2.8756614	Hylleraas (1929), Scherr and Silverman (1960)
2	−2.8896	Hylleraas (1929)
2	−2.90142	Green, Lewis, Mulder, Wyeth, and Woll (1954)
3	−2.90224	Hylleraas (1929)
6	−2.90338	Hylleraas (1929)
6	−2.90338	Schwartz (1956, 1960)
—	−2.90360	Present Work
10	−2.90360	Chandrasekhar *et al.* (1953)
1078	−2.90372	Pekeris (1958, 1959)

The accepted value for the nonrelativistic ground-state energy of helium is −2.90372 obtained by Pekeris [3] using 1078 variational parameters. This work obtains −2.90360 for this energy which is in error by 0.004%. Table IV contains a partial list of ground-state energies from previous calculations [6]. This list is by no means exhaustive, but does contain enough values to allow one to compare this calculation with others that have been done. The accuracy of the total energy obtained by this work seems to compare well with a variational calculation using ten parameters.

To gain further knowledge as to the accuracy of the wavefunction, other expectation values have been calculated. The set used in this regard is the set $\langle r_i^n \rangle \equiv \langle r^n \rangle$, $n = -2, -1, 1, 2$. To determine the accuracy of the subroutine written to perform the calculation $\langle r^n \rangle$, the wavefunction given by Eq. (10), was again applied as a test function. The results of this calculation are presented in Table V. Two features are evident in this table. First, interpolation does not

TABLE V

Numerical Expectation Values for the Operators r^n, $n = -2, -1, 1, 2$ for for the One-Parameter Test Wavefunction

Operator	Numerical result without interpolation	Numerical result with interpolation	Analytic result
$\langle r^{-2}\rangle$	5.29322	5.49426	5.69531
$\langle r^{-1}\rangle$	1.68750	1.68750	1.68750
$\langle r^{1}\rangle$	0.88889	0.88885	0.88889
$\langle r^{2}\rangle$	1.05348	1.05348	1.05350

TABLE VI

Numerical Expectation Values for the Operators r^n, $n = -2, -1, 1, 2$ for the iterative solution

Operator	Numerical result without interpolation	Numerical result with interpolation	Pekeris result
$\langle r^{-2}\rangle$	5.566	5.807	6.018
$\langle r^{-1}\rangle$	1.6915	1.6915	1.6883
$\langle r^{1}\rangle$	0.9283	0.9283	0.9295
$\langle r^{2}\rangle$	1.1906	1.1906	1.1935

improve the values of $\langle r^{-1}\rangle$, $\langle r^{1}\rangle$, and $\langle r^{2}\rangle$; and second, the value of $\langle r^{-2}\rangle$ is improved by interpolation, but is still in error by 3.5 %. Thus, the values of $\langle r^{n}\rangle$, $n = -1, 1, 2$ will serve as a test of the accuracy of χ but $\langle r^{-2}\rangle$ values would not. Tabulated results of these operator expectation values for the iterative solution are given in Table VI, with the Pekeris values listed for comparison. The results are surprisingly good considering the relatively large mesh sizes used. Inspectation of each term separately leads to the conclusion that the wavefunction must be more accurate for large r than for small r. The error in $\langle r^{-1}\rangle$ is much larger than would be expected from the numerical integration, thus this error must originate in the finite-difference approximations used in solving the Schroedinger equation. That this error is larger than that for $\langle r^{1}\rangle$ and $\langle r^{2}\rangle$ is reasonable because the solution is obtained by making the eigenvalue and the total energy self-consistent. Since the eigenvalue term dominates over the potential terms for large radii, the solution has been tuned for the larger radial values.

The value of $\langle r_1^{-1}\rangle$ is equal to $\langle r_2^{-1}\rangle$ for symmetric or antisymmetric functions, so the term $\langle r^{-1}\rangle$ is directly proportional to the electron–nuclear potential energy.

With this realization, the $\langle r^n \rangle$ calculations show that the interpolation process does not improve the numerical integration for this potential, and the error in the electron–nuclear potential can be attributed to the method of obtaining the numerical solution.

Reference to Table II shows that the kinetic and electron–electron energies have the same magnitude of error as the electron–nuclear potential energy. Again, these errors must primarily originate in the finite-difference approximations. When the total energy is computed, the errors in the individual energies tend to cancel each other to produce an excellent answer for this quantity. Because this was observed for both helium states, (1^1S, 2^3S), the cancellation was considered to be related to the variational principle which states the total energy is of second-order error in the wavefunction, whereas most other operator expectation values are of first order.

The first-excited state has a symmetric spin function and therefore must have an antisymmetric spatial wavefunction upon electron exchange. This symmetry has one notable advantage over the ground-state symmetry. That is, the antisymmetry requirement forces χ to vanish when $r_1 = r_2$ and completely removes the spike in the integrand used to compute $\langle 1/r_{12} \rangle$. Without the spike, an uninterpolated result can be used with a considerable savings in computer time.

To initialize the problem, an $r_{\max}$, input eigenvalue, and a starting wave vector must be chosen. Using Pekeris' result for the root mean square radius, $\langle r^2 \rangle^{1/2} = 3.39$, as a guide, $r_{\max}$ was chosen to be 12.0 for the 2^3s state. For the starting vector the two-parameter antisymmetrized wavefunction by Eckart [7] was used. This function is given by

$$\begin{aligned}\chi = {} & r_1 r_2 \{\exp(-Z_i r_1 - Z_a r_2/2)\}(1 - Z_a r_2/2) \\ & - r_1 r_2 \{\exp(-Z_i r_2 - Z_a r_1/2)\}(1 - Z_a r_1/2), \qquad (11)\end{aligned}$$

where $Z_i = 2.01$ and $Z_a = 1.53$. The eigenvalue was taken to be the expectation value of the Hamiltonian for the wavefunction given by Eq. (11). The value of $r_{\max}$ required that a larger program be used for this calculation. This program had an array size of (43, 37, 43) and required 1700 iterations to achieve five figure agreement between the eigenvalue and the total energy. Results of this calculation are presented in Table VII, along with the accurate results of Pekeris. The errors in each term are correspondingly higher than the errors for the ground-state calculations. One obvious reason, is the much larger mesh size required to span the r domains. Another not so obvious reason was the value of $r_{\max}$. Since the value of $\langle r^2 \rangle$ was too low, this meant the wavefunction was forced to zero too fast. A larger value of $r_{\max}$ might improve the 2^3S He results, but this would require a larger mesh size, yielding poorer results, or more mesh points which would make the array larger than the computer memory size.

TABLE VII

Helium 2^3S State Results for the Converged Iterative Wavefunction

Operator	Numerical result this work	Pekeris result
$\langle K \rangle$	2.2077	2.1752
$\langle 1/r_{12} \rangle$	0.2787	0.2682
$-2\langle 1/r_1 + 1/r_2 \rangle$	−4.6606	−4.6186
$\langle H \rangle$	−2.1741	−2.1752
$\langle r^{-2} \rangle$	3.768	4.170
$\langle r^{-1} \rangle$	1.165	1.155
$\langle r^{1} \rangle$	2.431	2.550
$\langle r^{2} \rangle$	10.111	11.464

In this paper the method for the application of the finite-difference technique to the S-state helium system was developed and results for the helium states of 1^1S and 2^3S presented. Comparison between this work and that of Pekeris clearly shows this method does work and gives reasonable answers for many expectation values. Although this method requires the use of a computer with a large memory, it is sufficiently accurate and general to warrant further study.

REFERENCES

1. GARRETT BIRKHOFF, "The Numerical Solution of Elliptic Equations," CBMS Regional Conference Series in Applied Mathematics, SIAM, Philadelphia 1971.
2. DAVID M. YOUNG, *SIAM Review* **15**, No. 2, April, (1973).
3. C. L. PEKERIS, *Phys. Rev.* **115** (1959), 1216.
4. C. C. J. ROOTHAAN AND A. W. WEISS, *Rev. Mod. Phys.* **32**, No. 2, (1960), 194.
5. P. J. LUKE, R. E. MEYEROTT, AND W. W. CLENDENIN, *Phys. Rev.* **85**, No. 3, (1952).
6. A. L. STEWART, "The Properties of the Helium Atom and Two-electron Systems," *Advan. Phys.* **12** (1963), 299.
7. C. ECKART, *Phys. Rev.* **36** (1930), 878.