# EIGENVALUE PROBLEMS TREATED BY FINITE-DIFFERENCE METHODS

## II. TWO-DIMENSIONAL SCHRÖDINGER EQUATIONS

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*ABSTRACT.* A discussion is given of the convergence of the eigenvalues $\Lambda(N)$ of two-dimensional finite-difference equations towards the eigenvalues $\lambda$ of the corresponding second-order differential equation, and it is shown that

$$\Lambda(N) = \lambda + \nu_2 h^2 + O(h^4),$$

where $h = N^{-1}$ and $\nu_2$ is a constant. As in our previous paper (4), this can be used to make an accurate estimate of $\lambda$ by extrapolating to $h = 0$. After an account of the relaxation method used for computing $\Lambda(N)$ and a discussion of the residual vector, results are presented for an approximation to the lowest spatially symmetric and antisymmetric states of two electrons in a sphere, interacting through their Coulomb potential.

1. *Introduction.* This paper is a continuation of a discussion by the authors ((4), which we shall refer to as I), of problems in one dimension, in which it was shown that an accurate method of getting an eigenvalue of a differential equation was to extrapolate to zero mesh size the eigenvalues of the corresponding difference equations for various mesh sizes. The power of the method lay in the ease with which the eigenvalue could be obtained for each grid, only a few grid points being necessary. The hope that this would prove suitable at least in two dimensions has been justified, and the present paper gives the eigenvalues of a certain Schrödinger equation arising in an electron interaction problem.

There are many papers dealing with finite-difference solutions to two-dimensional eigenvalue problems; Collatz (6) gives a review of the field. Most of them deal with the equation for the vibration of a membrane which, in quantum-mechanical language, does not possess a potential energy term. Interest in the engineering field is also focused on the fourth-order equation relevant to the buckling of beams and plates; Salvadori (22) gives a full discussion of methods similar to those employed here.

We show in §2 that the finite-difference eigenvalues for the membrane problem eventually converge from below to the value in the continuous case. The application of relaxation methods by Allen, Fox, Motz and Southwell (1) allows the solutions to the membrane vibration equations to be obtained very easily. Most of the solutions in the present paper have been obtained in the same way. There have been few finite-difference solutions of Schrödinger's equation (which in I were called 'point-space' solutions), and on the whole the accuracy has been low. Kimball and Shortley (18) made a brief reference to $H_2^+$ as a two-dimensional problem on a grid of variable mesh size. Frost (11) attempted a solution of the $H_2^+$ problem by a least-squares technique for a grid, but did not use difference notation. Writing Schrödinger's equation in the

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form $H\psi = \lambda\psi$, Frost minimized the mean-square deviation of $\epsilon = H\phi/\phi$ for a trial function $\phi$. Mohrenstein (21) applied Frost's technique to $H_2$ using a linear combination of possible functions and to He using a Hylleraas function. His points were chosen in the region where $\phi^2$ was large and the method gave good results. It lacks rigour, but has the virtue of avoiding the difficult integrals which occur in a multi-dimensional quantum problem. Bartlett (2) gave a finite-difference solution for He, using Liebmann iteration for the three-dimensional equation; but despite the use of a digital computer the accuracy was low. Glazer and Reiss (12) solved the Thomas–Fermi equation for $CH_4$ in finite-difference form and obtained a value for the dipole moment of the bond. The best numerical solutions of the Schrödinger equation have been given by Luke, Meyerott and Clendenin (19) by a refinement of the finite-difference equations which kept the discussion within the variational condition for the continuum, and they obtained a very good value for the energy of the $1s2s\,^3S$ state of singly ionized Li. The approach of the present paper can be considered as complementary to that of the latter authors; we use the simplest finite-difference equations and in many cases the eigenvalues converge from below to the eigenvalue in the continuum.

In § 2 the $h^2$-convergence is briefly discussed. In § 3 the nature of the residual vector is discussed, and in § 4 the distribution of the elements of the residual vector is analysed in terms of the *enclosure theorem*. Various methods of solving the matrix equations have been compared. In § 5 two eigenvalues are given of a simple Schrödinger equation for two free electrons enclosed in a sphere. This problem was chosen as one of the simplest problems dealing with electron interaction. Finally, the possibilities of applying the method to the eigenvalues of He are mentioned.

2. *Convergence.* The two-dimensional Schrödinger equation $H\psi = \lambda\psi$ is taken in the form

$$\left\{-\frac{\partial^2}{\partial x^2}-\frac{\partial^2}{\partial y^2}+V(x,y)\right\}\psi(x,y) = \lambda\psi(x,y), \tag{2·1}$$

subject to the boundary condition that $\psi = 0$ on some simple closed boundary $C$. The finite-difference analogue of the wave function is a set of elements

$$u_i \quad (i = 1, 2, 3, \ldots).$$

Each $u_i$ is an approximation to $\psi$ at the corresponding grid point, the points being ordered in some suitable manner. The analogue of the differential equation is the set of equations

$$(-\Sigma u_j + 4u_i)/h^2 + V_i u_i = \Lambda(h)\, u_i, \tag{2·2}$$

where $\Sigma u_j$ denotes the sum of the pivotal (grid) values at the four grid points nearest to the typical point denoted by $i$, $h$ is the mesh size, $V_i$ is the value of $V(x,y)$ at the corresponding point in the continuum and $\Lambda(h)$ is the eigenvalue for the finite-difference problem.

Consider now a continuous function $u(x,y)$ which satisfies the boundary conditions of the differential equation and satisfies the same difference equation as the elements $u_i$, that is,

$$-u(x-h,y)-u(x+h,y)-u(x,y-h)-u(x,y+h)+\{4+h^2V(x,y)\}u(x,y) = \mu u(x,y), \tag{2·3}$$

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where $\mu = h^2\Lambda(h)$. Following the same procedure as in I, by expanding $\mu$ and $u(x, y)$ as power series in $h$,

$$\mu = h^2 \sum_{s=0}^{\infty} \nu_s h^s$$

and

$$u(x, y) = \sum_{s=0}^{\infty} \phi_s(x, y)\, h^s,$$

and using a Taylor expansion, we find that $\phi_0(x, y)$ is a solution of the original differential equation (2·1) with eigenvalue $\lambda = \nu_0$. Moreover

$$\Lambda(h) = \lambda + \nu_2 h^2 + O(h^4),$$

where

$$\nu_2 \iint \phi_0^2 dx dy = -\frac{1}{12} \iint \phi_0 \left( \frac{\partial^4}{\partial x^4} + \frac{\partial^4}{\partial y^4} \right) \phi_0 \, dx dy. \tag{2·4}$$

In general we are unable to say much about the sign of $\nu_2$. If, however, (i) $\phi_0$ is a product $X(x)\, Y(y)$ vanishing on the boundary, (ii) $V$ is non-singular on the boundary, and (iii) the boundary is $x =$ constant and $y =$ constant, then

$$\nu_2 = -\frac{1}{12} \left\{ \frac{\int \left( \frac{d^2X}{dx^2} \right)^2 dx}{\int X^2 dx} + \frac{\int \left( \frac{d^2Y}{dy^2} \right)^2 dy}{\int Y^2 dy} \right\}, \tag{2·5}$$

where the integrals extend over the ranges of $x$ and $y$ respectively. This supports our comment in I that the solution of the simple finite-difference analogue of the square clamped membrane gives a lower bound to the solution of the problem in the continuum. The expression on the right-hand side of (2·4) can be written as

$$-\frac{1}{12} \iint \phi_0 (\nabla^4 - 2\mathscr{D}^4) \phi_0 dx dy,$$

following the notation of Bickley (3) and Woods (29), where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \quad \text{and} \quad \mathscr{D}^2 = \frac{\partial^2}{\partial x \partial y}.$$

The first part may be transformed by Green's theorem to give

$$\nu_2 \iint \phi_0^2 dx dy = -\frac{1}{12} \iint (\nabla^2 \phi_0)^2 dx dy + \frac{1}{6} \iint \phi_0 \mathscr{D}^4 \phi_0 dx dy, \tag{2·6}$$

provided that $\phi_0$ vanishes on the boundary and $V$ is non-singular there. This expression is useful for obtaining estimates of $\nu_2$ from approximate data such as a trial function or a set of pivotal values determined from one particular mesh size, the derivatives being then replaced by the corresponding differences.

3. *Vector description.* The particular problems which will be described are defined inside the square domain bounded by the lines $x = 0, 1$ and $y = 0, 1$; and the boundary condition is that $u = 0$ on the boundary. The mesh is a square one with sides parallel to the sides of the square, each of which is divided into $N$ strips ($h = N^{-1}$), so that the set of equations (2·2) have to be solved for $(N-1)^2$ internal points. We determine the

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lowest eigenvalue for each grid defined by $N$ and extrapolate these eigenvalues to $h^2 = 0$. As in I the extrapolation is performed using Neville's method (Hartree (14)) and the results displayed in a Neville table.

The set of equations (2·2) can also be written in vector form

$$A\mathbf{u} = \mu\mathbf{u}, \tag{3·1}$$

where $A$ is a square, symmetric matrix of order $(N-1)^2$ and $\mathbf{u}$ is a column vector with elements $u_i$. The diagonal elements of $A$ are

$$a_{ii} = 4 + h^2 V_i,$$

while the non-diagonal elements $a_{ij}$ are $-1$ or 0 according as $i$ and $j$ are or are not neighbouring grid points. $\Lambda(N)$ is given by the least solution of the determinantal equation

$$|A - \mu I| = 0, \tag{3·2}$$

where $I$ is the unit matrix. When $N$ is small (3·2) can be solved for $\mu$ by analytic methods, but even $N = 4$ gives a $9 \times 9$ matrix. Although the symmetries of $V$ may well permit a reduction of the order of the matrix, the solutions for large $N$ become steadily more difficult to obtain. The method we follow for solving (3·1) is one of relaxation combined with a sequence of estimations of the eigenvalue $\mu$; it is based on that of Fox (10). If we start with an approximate or *trial* vector $\mathbf{v}$ and calculate its Rayleigh mean $\vartheta$ defined by

$$\vartheta(\mathbf{v}) = \frac{\mathbf{v}.A\mathbf{v}}{\mathbf{v}.\mathbf{v}},$$

then we can define a true residual vector

$$\mathbf{r} = A\mathbf{v} - \vartheta(\mathbf{v})\,\mathbf{v}. \tag{3·3}$$

The elements $r_i$ of $\mathbf{r}$ are to be reduced to zero by use of the relaxation process with fixed $\vartheta$ followed by a recomputation of $\vartheta$. The Rayleigh mean $\vartheta$ is an upper bound to the lowest eigenvalue $\mu$, so that $\vartheta$, considered as a function of $\mathbf{v}$, has a minimum at $\mathbf{v} = \mathbf{u}$, and $\vartheta$ will then be equal to $\mu$. For any trial vector $\mathbf{v}$ the best addition $\delta\mathbf{v}$ to make to $\mathbf{v}$ to reduce $\vartheta$ as quickly as possible is a proportion of the vector $\mathbf{r}$ because $\delta\vartheta = 2\delta\mathbf{v}.\mathbf{r}/\mathbf{v}.\mathbf{v}$. Thus we may say that $\mathbf{r}$ is in the direction of steepest descent, giving the most rapid reduction of $\vartheta$ (Hestenes and Karush (16), McWeeny (20)). This is, of course, in general agreement with the well-known fact that the best method of proceeding with the relaxation technique is to make a displacement or alteration to that $v_i$ which corresponds to the largest residual element $r_i$ of $\mathbf{r}$.

The whole procedure can now be described. A trial vector $\mathbf{v}$ is chosen and an estimate $\sigma$ made of the eigenvalue. This may be a guess, or it may be the Rayleigh mean of $\mathbf{v}$; in the latter case $\mathbf{r}.\mathbf{v} = 0$. The initial residual vector is $\mathbf{r} = A\mathbf{v} - \sigma\mathbf{v}$, and relaxation is carried out with fixed $\sigma$ until the residuals are as small as seems worth while. The vector $\mathbf{v}$ has now been altered to $\mathbf{w}$ and a new intermediate residual is

$$\mathbf{s} = A\mathbf{w} - \sigma\mathbf{w}.$$

A new estimate of $\mu$ will be the Rayleigh mean of $\mathbf{w}$:

$$\vartheta(\mathbf{w}) = \frac{\mathbf{w}.A\mathbf{w}}{\mathbf{w}.\mathbf{w}} = \sigma + \frac{\mathbf{s}.\mathbf{w}}{\mathbf{w}.\mathbf{w}}. \tag{3·4}$$

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The correction to $\sigma$ is seen to be easily calculated in terms of the small quantities $s_i$. Using $\vartheta(\mathbf{w})$ new residuals are calculated by

$$\mathbf{t} = A\mathbf{w} - \vartheta(\mathbf{w})\,\mathbf{w}.$$

These residuals are calculated without reference to $\mathbf{s}$ so as to afford a check on the computation and also to provide an opportunity of increasing the number of significant figures carried. For as the accuracy of $\mathbf{w}$ increases, so more figures must be carried to give residuals.

This cycle of operations continues until the changes in the Rayleigh mean are sufficiently small for the accuracy required. It should be noted that $\mathbf{s}.\mathbf{w}$ must always be negative, since changes in the Rayleigh mean must be negative, so that one minor criterion which can be adopted for a good relaxation is that it makes $s_i$ of the opposite sign to $r_i$. Since only small numbers have to be handled, except in the recalculation of the residual $\mathbf{t}$, this process is quicker than direct recomputation of the Rayleigh mean with each new trial vector, as suggested by Allen *et al.* (1).

In addition to the method outlined above, based on Fox (10), Schulte (23) has suggested using the residual

$$\mathbf{r} = A\mathbf{w} - \vartheta(\mathbf{v})\,\mathbf{v},$$

making displacements only in $\mathbf{w}$. He then constructs $\vartheta(\mathbf{w})$ and proceeds. Collatz (5) and Schulte (23) also suggested using

$$\mathbf{r} = A\mathbf{w} - \mathbf{v},$$

making displacements in $\mathbf{w}$ until $\mathbf{r} = 0$, and then proceeding. All three methods have been tried on some of the matrices in the course of the present work. The Collatz–Schulte method is poor because the vector changes appreciably in going from $\mathbf{v}$ to $\mathbf{w}$, etc., and the residuals are large. The convergence in the Fox method has been found to be more rapid than the Schulte method. In both the Fox and the Schulte methods the enclosure theorem gives a strict control over the calculation. Experience shows that the correction to any approximation to the eigenvalue (the term $\mathbf{s}.\mathbf{w}/\mathbf{w}.\mathbf{w}$ in (3·4)) is about an order of magnitude smaller than the errors given by the enclosure theorem.

4. *The enclosure theorem.* The residual vector $\mathbf{r}$ has a fundamental significance deeper than its computational value. There exists for a real symmetric matrix, the theorem known as the enclosure theorem which states that for a trial function representing any eigenvector, the elements $\epsilon_i = (A\mathbf{v})_i/v_i$ of the vector $\boldsymbol{\epsilon}$ have an upper and a lower bound $Q$ and $q$ enclosing the true eigenvalue. In one sense, the $\epsilon_i$ can be defined as local eigenvalues at each point $i$ in the point space. Since $r_i = (A\mathbf{v})_i - \sigma v_i$, where $\sigma$ is any estimate of the eigenvalue (either a guess or a Rayleigh mean), we see that

$$\epsilon_i = \sigma + r_i/v_i.$$

Now the distribution of $r_i/v_i$ can be seen by inspection in any problem and offers an easy way of following the course of a calculation. The upper and lower bounds to the eigenvalue can be immediately seen from the pattern of residuals arising even from a guess $\sigma$.

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The matrix form of the theorem has been established by Collatz (6) and it has its analogue in the one-dimensional continuum, first stated by Temple (25). Writing Schrödinger's equation as $H\psi = \lambda\psi$, Temple's theorem states that for any trial function $\phi$, $\epsilon = H\phi/\phi$ has upper and lower bounds enclosing the true eigenvalue $\lambda$. Temple's proof is for nodeless functions; if $\phi$ possesses nodes $\epsilon$ might be indeterminate, although Thomas (27) suggests that this difficulty can be avoided. Assuming that Temple's theorem could be extended to multi-dimensional differential equations then it is a partial answer to the question raised by Coulson (7) concerning the use we can make of $H\phi/\phi$. For most trial functions in the continuum the bounds are extremely wide and they seem to be of practical value only for matrices such as arise in the present problems.

Returning to the point-space problem, we can define the average of the elements of any vector $\mathbf{f}$ with respect to $\mathbf{v}$ as

$$\bar{f} = \Sigma_i v_i^2 f_i / \Sigma_i v_i^2.$$

When $\mathbf{f} = \boldsymbol{\epsilon}$ we see that $\bar{\epsilon} = \vartheta(\mathbf{v})$ and the mean-square deviation is

$$\Delta^2 = \Sigma_i ((A\mathbf{v})_i)^2 / \Sigma_i v_i^2 - \bar{\epsilon}^2.$$

This $\Delta$ is the point-space analogue of the root-mean-square deviation introduced by Weinstein (28), who showed that $\vartheta - \Delta$ is a lower bound to a continuum eigenvalue, the symbols referring to integrals rather than sums. This is not necessarily an improvement on the lower bound to $H\phi/\phi$; for an electron interaction problem such as He, which Weinstein examined, the upper bound of $H\phi/\phi$ is infinite and $\Delta$ may be quite large. In point space $\vartheta - \Delta$ is a lower bound also. Kato (17) and Temple (26) have discussed bounds more fully and give more accurate bounds than those discussed here. Anything more sophisticated than the enclosure theorem, however, usually involves a great deal of extra work, and the merit of the present theorem is the fact that the bounds are easily visible during the course of the relaxation process.

5. *Two electrons in a sphere.* The two-dimensional Schrödinger equation which we have studied in detail is that describing the approximate wave function of two electrons in a sphere. This problem is one of the simplest of electron interaction problems. The full Hamiltonian is

$$H = -\nabla_1^2 - \nabla_2^2 + \frac{2}{r_{12}},$$

where $\nabla_1^2$, $\nabla_2^2$ are the two Laplacians, $r_{12}$ is the inter-electron distance and atomic units have been used. (The unit of length is the radius of the first Bohr orbit; the unit of energy is the energy of the ground state of the hydrogen atom.) The wave function vanishes on the sphere of radius $R$ containing the two electrons.

The true eigenvalues are the stationary values of

$$\int \psi H \psi \, d\tau \Big/ \int \psi^2 d\tau,$$

where $\psi = \psi(r_1, r_2, \theta_1, \theta_2, \phi_1, \phi_2)$; $r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2$ are the usual spherical polar coordinates of the two electrons. If we restrict the class of function to $\psi = \psi(r_1, r_2)$ and

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perform the integrations in the above expression over the angle variables, then its new stationary values are the eigenvalues of the effective Hamiltonian

$$-\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right)-\frac{1}{r_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial}{\partial r_2}\right)+\frac{2}{r_>}, \tag{5·1}$$

where the potential term $2/r_{12}$ is now replaced by $2/r_>$, $r_>$ being the larger of $r_1, r_2$.

Putting

$$\psi(r_1, r_2) = \phi(r_1, r_2)/r_1 r_2,$$

we get the differential equation

$$-\frac{\partial^2\phi}{\partial r_1^2}-\frac{\partial^2\phi}{\partial r_2^2}+\frac{2\phi}{r_>} = E\phi,$$

where $E$ is the energy value required. Writing $x = r_1/R$, $y = r_2/R$, we have, for $y > x$,

$$-\frac{\partial^2\phi}{\partial x^2}-\frac{\partial^2\phi}{\partial y^2}+\frac{2R}{y}\phi = \lambda\phi, \tag{5·2}$$

where $\lambda = R^2E$ and the boundary conditions are $\phi = 0$ on the lines $x = 0, x = 1, y = 0$, $y = 1$. In the triangle of the unit square for which $x > y$, the potential term $2R/y$ is replaced by $2R/x$. The differential equation is now in the two-dimensional normal form discussed in § 2. Whilst the symmetry of the potential function about the main diagonal $x = y$ is of assistance during the relaxation process, we shall continue to discuss the solution in relation to the unit square.

The finite-difference equivalent of the differential equation is the vector equation

$$A\mathbf{u} = \mu\mathbf{u},$$

where

$$a_{ii} = 4+\frac{2Rh^2}{\mathrm{Max}\,(x_i, y_i)},$$

and $a_{ij} = -1$ if $i$ and $j$ are neighbours, $a_{ij} = 0$ otherwise. The residual at the point $i$ for any trial vector $\mathbf{v}$ and approximation $\sigma$ to $\mu$ is therefore for $y > x$,

$$r_i = -\Sigma v_j+\left(4+\frac{2Rh^2}{y_i}-\sigma\right)v_i,$$

where $\Sigma v_j$ denotes the sum of the four values of $v$ at points immediately neighbouring the point $i$.

We write this as

$$r_i = T_i v_i-\Sigma v_j, \tag{5·3}$$

where

$$\left.\begin{aligned} T_i &= 4+\frac{2Rh^2}{y_i}-\sigma \quad (y_i > x_i),\\ T_i &= 4+\frac{2Rh^2}{x_i}-\sigma \quad (x_i > y_i). \end{aligned}\right\} \tag{5·4}$$

Having calculated $T_i$ the necessary operations table for relaxation is, denoting a displacement in $v_i$ by $\delta v_i$,

$$\left.\begin{aligned} \delta r_i &= T_i\delta v_i,\\ \delta r_j &= -\delta v_i, \end{aligned}\right\} \tag{5·5}$$

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where $j$ is a nearest neighbour of $i$. We would emphasize the difference in sign here from the usual relaxation technique as applied to engineering problems. We feel that the significance of the signs in Schrödinger's equation should be kept in quantum-mechanical problems. The operations table is comparatively simple in this problem, since $T_i$ depends on only one of the independent variables. The values of $T_i$ are kept constant during relaxation and are changed when $\sigma$ is changed.

Table 1

| $N$ | $\Lambda(N)$ | $\Lambda(ij)$ | $\Lambda(ijk)$ | $\Lambda(ijkl)$ | $\Lambda(ijklm)$ |
|---|---|---|---|---|---|
| 2 | 56·0000 | | | | |
| 3 | 51·3302 | 47·5944 | | | |
| 4 | 51·9644 | 52·7798 | 54·5083 | 52·8737 | |
| 6 | 52·5322 | 52·9864 | 53·0553 | 52·9815 | 52·9887 |
| 8 | 52·7327 | 52·9905 | 52·9919 | | |

6. *Result of calculations for two electrons in a sphere.* The first solution is that for the ground state, which is spatially symmetric: $\phi(x, y) = \phi(y, x)$. We need consider only the points for which $y > x$. The radius $R$ of the sphere was chosen to be 10 atomic units, to make the potential energy term significant. The Neville table is given in Table 1.

All values of $\Lambda(N)$ are correct to five significant figures, except $\Lambda(8)$ which is correct to four. Ignoring $\Lambda(2)$ and $\Lambda(3)$ as being too crude, the final extrapolant is

$$\lambda = 52{\cdot}99 \pm 0{\cdot}01.$$

Thus $E = 0{\cdot}5299$ atomic unit. Fig. 1 shows the values of $u$ and sketched contours for $N = 8$, and the crosses denote the positions of the maxima on all the grid lines. The maximum on the diagonal $x = y$ lies at the point marked with a circle. The curves $\partial\phi/\partial x = 0$ and $\partial\phi/\partial y = 0$ apparently intersect on this diagonal at this point. However, the grid is probably too coarse to give a definite decision. The positions of the maxima were obtained by solving the equation resulting from differentiating a five-point Stirling interpolation formula with respect to the variable and equating to zero.

The present problem lends itself rather well to suggestion for trial wave functions $\phi$, and results are presented in Table 2. The necessary integrals were easily evaluated in terms of the Beta-Functions:

$$\int_0^1 x^m(1-x)^n\,dx = \mathrm{B}(m+1, n+1) = \frac{m!\,n!}{(m+n+1)!},$$

$$\int_{y=0}^{1}\int_{x=0}^{y} x^p\,(1-y)^q\,(y-x)^r\,dx\,dy = \mathrm{B}(p+1, r+1)\,\mathrm{B}(q+1, p+r+2)$$

$$= \frac{p!\,q!\,r!}{(p+q+r+2)!}.$$

If function 1 represents the lowest unperturbed electron configuration of the Hamiltonian without the interaction potential (in spectroscopic language, the $(1s)^2$ configuration), then functions 2 and 3 are increasingly good approximations to

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function 1. Functions 4 and 5 are unsymmetric functions of $x$ and $y$ defined for $0 \leqslant x \leqslant y \leqslant 1$ which have finite normal derivatives across the line $x = y$. By Green's theorem, there is a contribution to the kinetic energy of value

$$\int_0^1 \left[\phi\left(\frac{\partial\phi}{\partial x} - \frac{\partial\phi}{\partial y}\right)\right]_{y=x} dx \Big/ \int_{y=0}^{1}\int_{x=0}^{y} \phi^2 dx\,dy.$$

Despite this behaviour, functions 4 and 5 give quite good energies. Function 6 is a symmetric version of 4; 7 is a mixture of configurations (using approximate functions) giving the lowest variational energy.

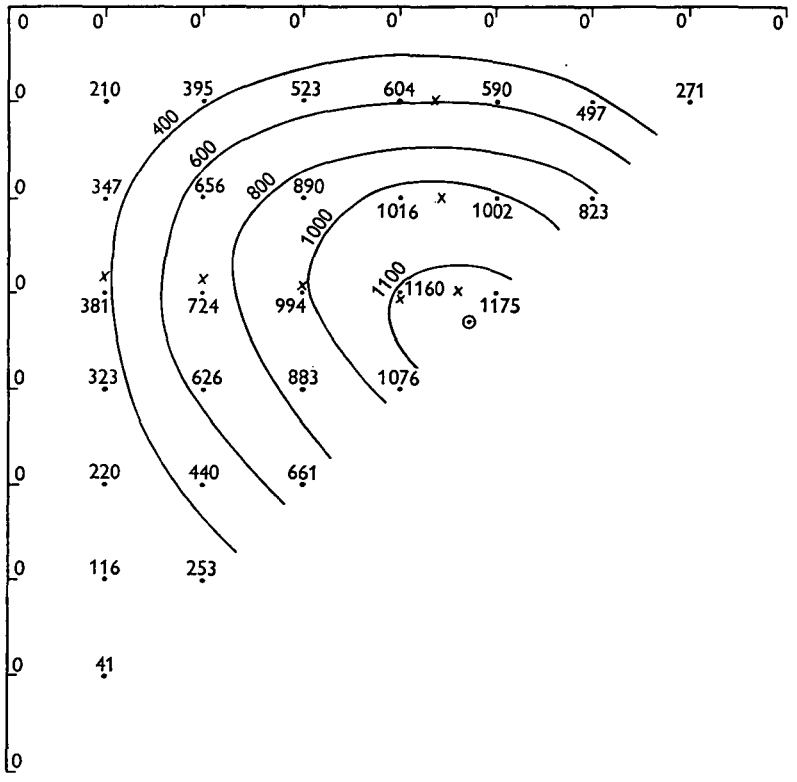



Fig. 1

Table 2

| | Function | Energy, $E$ |
|---|---|---|
| 1 | $\sin \pi x \sin \pi y$ | 0·5546 |
| 2 | $x(1-x)\, y(1-y)$ | 0·5571 |
| 3 | $[x(1-x)+x^2(1-x)^2]\,[y(1-y)+y^2(1-y)^2]$ | 0·5546 |
| 4 | $x(1-x)\, y^2(1-y)$ | 0·5433 |
| 5 | $x(1-x)\, y^p(1-y)$ ($p = 1{\cdot}6649$, variationally) | 0·5388 |
| 6 | $x(1-x)\, y(1-y)\,(x+y)$ | 0·5337 |
| 7 | $x(1-x)\, y(1-y) + c[x(1-x)\, y(1-y)\,(1-2y) + x(1-x)\,(1-2x)\, y(1-y)]$ | 0·5334 |
| 8 | Finite differences | 0·5299 |

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A Neville table for the lowest spatially antisymmetric solution, defined by $\phi(x,y) = -\phi(y,x)$, is presented in Table 3. All $\Lambda(N)$ are correct to five significant figures: $\lambda = 78{\cdot}76 \pm 0{\cdot}01$. Since $\phi = 0$ on the diagonal $y = x$, the smallest value of $N$ is 3. The $h^2$-convergence is much slower than in the ground state; this would become an increasing difficulty for higher states in which $h$ would have to be made small enough to include all the variations of $\phi$. These figures emphasize the point made in I, that if the extrapolation is to be valuable, the eigenvalues for the finite-difference equations must be determined to a high degree of accuracy, because the rounding errors build up rapidly. This explains some of the minor anomalies to be found in the extrapolations of Salvadori (22) and Culver (8).

Table 3

| $N$ | $\Lambda(N)$ | $\Lambda(ij)$ | $\Lambda(ijk)$ | $\Lambda(ijkl)$ | $\Lambda(ijklm)$ |
|---|---|---|---|---|---|
| 3 | 66·0000 | | | | |
| | | 76·0770 | | | |
| 4 | 70·4087 | | 79·2790 | | |
| | | 78·4785 | | 78·6587 | |
| 6 | 74·8919 | | 78·7726 | | 78·7706 |
| | | 78·6766 | | 78·7549 | |
| 7 | 75·8960 | | 78·7593 | | |
| | | 78·7128 | | | |
| 8 | 76·5562 | | | | |

7. *Application to the helium atom.* The method already described should apply to the equation for the wave function of the helium atom considered as a function only of the two radial distances from the nucleus. The effective Hamiltonian obtained by a method similar to that used in deriving (5·1) is

$$-\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right)-\frac{1}{r_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial}{\partial r_2}\right)-\frac{4}{r_1}-\frac{4}{r_2}+\frac{2}{r_>}. \tag{7·1}$$

To reduce the finite-difference equations to the same form as those treated earlier, we enclose the helium atom in a spherical box of radius $R = 5$, where the boundary condition is that the wave function vanishes on its surface. The equations corresponding to (5·3) and (5·4) are thus

$$r_i = T_i v_i - \Sigma_j v_j \tag{7·2}$$

for all $i$, where

$$T_i = 4-\frac{4Rh^2}{x_i}-\frac{2Rh^2}{y_i}-\sigma \quad (y_i > x_i), \tag{7·3}$$

and the boundary conditions are $v = 0$ on the square bounded by the lines $x = 0, x = 1$, $y = 0, y = 1$.

It is known from the work of de Groot and Ten Seldam (13) that enclosing the He atom in a box of this size will increase the energy by only a very small amount. It may be seen from (7·3) that $T_i$ has now to be calculated at all internal points.

Unfortunately, the convergence of the solutions is slow, no doubt because $h$ is large compared to the variations in the wave function. Table 4 gives the Neville table for the ground state with all $|E|$-values correct to five significant figures, but the final extrapolant, $-5{\cdot}3$, is a long way above $-5{\cdot}751$, which is the best of those given by Taylor and Parr (24).

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Some attempts were made to include higher order differences in the difference equations, following Fox (10), but these were only partly successful. As was shown in I, further boundary conditions are needed to define $\delta^4$ and $\delta^6$, but these conditions are much harder to use in two dimensions when, as in the He equations, a singularity in the potential occurs on the boundary. These particular difficulties are additional to the possible presence of unwanted solutions when differences higher than the second are employed.

Table 4

| $N$ | $\mid E \mid$ | | | | |
|---|---|---|---|---|---|
| 2 | 1·76000 | 3·06219 | 3·96384 | 4·77204 | 5·30399 |
| 3 | 2·48344 | 3·73843 | 4·68224 | 5·27074 | |
| 4 | 3·03250 | 4·44629 | 5·18798 | | |
| 6 | 3·81794 | 5·00256 | | | |
| 8 | 4·33621 | | | | |

8. *Conclusions.* A great virtue of the method discussed here is its simplicity. The $\Lambda$-values for small $N$ can be rapidly computed, and once a graph of $\Lambda$ against $h^2 = N^{-2}$ has been started the $\Lambda$-value for a new grid can be closely estimated. Some further solutions of modified electron interaction potentials have been obtained by Hawgood (15). For a membrane vibration problem with the boundary conditions used above, $T_i$ would be constant over the space so that a hand computation for large $N$ would be quite easy. Also, the $h^2$-convergence must be eventually from below in this case.

The method could be used with high-speed computers because the orders of the matrices $A$ are not high. Thus for $N = 8$ and a symmetric function, the order of $A$ is 28, while for $N = 8$ and an antisymmetric function, the order is only 21. For a digital computer, the solution would probably have to be sought with an iterative method similar to that used by Bartlett (2) for He and by Flanders and Shortley (9) for their membrane vibration problems.

No attempt has been made in this work to get an eigenfunction to the same degree of accuracy as the eigenvalue. If fine details were needed the straightforward way would be to choose a fine mesh of size $h$, and extrapolate the eigenvalue from small mesh sizes to the corresponding value of $h^2$. Then, constructing the requisite $T_i$, a single relaxation process would enable $\mathbf{u}$ to be obtained.

## REFERENCES

(1) ALLEN, D. N. DE G., FOX, L., MOTZ, H. and SOUTHWELL, R. V. *Phil. Trans.* A, 239 (1946), 488.
(2) BARTLETT, J. H. *Phys. Rev.* 88 (1952), 525.
(3) BICKLEY, W. G. *Quart. J. Mech.* 1 (1948), 35.
(4) BOLTON, H. C. and SCOINS, H. I. *Proc. Camb. Phil. Soc.* 52 (1956), 215.
(5) COLLATZ, L. *Z. angew. Math. Mech.* 19 (1939), 224 and 297
(6) COLLATZ, L. *Eigenwert-Aufgaben mit technischen Anwendungen* (Leipzig, 1949).
(7) COULSON, C. A. *Valence* (Oxford, 1952), p. 56.
(8) CULVER, R. *Brit. J. Appl. Phys.* 3 (1952), 376.
(9) FLANDERS, G. and SHORTLEY, G. *J. Appl. Phys.* 21 (1950), 1326.
(10) FOX, L. *Proc. Roy. Soc.* A, 190 (1947), 31.

https://doi.org/10.1017/S0305004100032084 Published online by Cambridge University Press

(11) FROST, A. A. *J. Chem. Phys.* 10 (1942), 240.
(12) GLAZER, H. and REISS, H. *J. Chem. Phys.* 21 (1953), 903.
(13) GROOT, S. R. DE and TEN SELDAM, C. A. *Physica, 's Grav.* 18 (1952), 891.
(14) HARTREE, D. R. *Numerical analysis* (Oxford, 1952), p. 85.
(15) HAWGOOD, J. *Thesis* (Oxford, 1955).
(16) HESTENES, M. R. and KARUSH, W. *J. Res. Nat. Bur. Stand.* 47 (1951), 471.
(17) KATO, T. *J. Phys. Soc., Japan*, 4 (1949), 334.
(18) KIMBALL, G. and SHORTLEY, G. *Phys. Rev.* (2), 45 (1934), 815.
(19) LUKE, P. J., MEYEROTT, R. E. and CLENDENIN, W. W. *Phys. Rev.* 85 (1952), 401.
(20) MCWEENY, R. *Proc. Roy. Soc.* A, 235 (1956), 496.
(21) MOHRENSTEIN, A. V. *Z. Phys.* 134 (1953), 488.
(22) SALVADORI, M. G. *Proc. Amer. Soc. Civ. Engrs*, 75 (1949), 1441.
(23) SCHULTE, A. M. *Appl. Sci. Res., Hague*, A, 2 (1949), 93.
(24) TAYLOR, G. R. and PARR, R. G. *Proc. Nat. Acad. Sci., Wash.*, 38 (1952), 154.
(25) TEMPLE, G. *Proc. Lond. Math. Soc.* (2), 29 (1929), 257.
(26) TEMPLE, G. *Proc. Roy. Soc.* A, 211 (1952), 204.
(27) THOMAS, L. H. *Phys. Rev.* 51 (1937), 202.
(28) WEINSTEIN, D. H. *Proc. Nat. Acad. Sci., Wash.*, 20 (1934), 529.
(29) WOODS, L. C. *Quart. J. Mech.* 3 (1950), 349.



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