The Numerical Solution of Schrödinger's Equation

G. E. KIMBALL AND G. H. SHORTLEY,* *Massachusetts Institute of Technology*

(Received February 26, 1934)

Schrödinger's equation may be approximated to any desired accuracy by a difference equation over a lattice covering the region of integration. The solutions of this difference equation minimize a certain quadratic form (analogous to the energy integral $\int \psi^* H \psi$) subject to certain normalization and, for the higher states, orthogonality conditions. A practical numerical method is developed for the solution of this variation problem. By altering the values of a rough solution at each lattice point in turn by a simple improvement formula, the value of the quadratic form is continually decreased until the desired minimum is reached. Illustrations of the method are given for one-dimensional problems. Practical details are given for handling two-dimensional lattices, in particular for the solution of the problem of one electron in an axially symmetric field.

INTRODUCTION

FOR only the simplest problems of quantum mechanics can Schrödinger's equation be solved exactly. Numerical solutions of any problem in which the variables are separable can be found by applying the ordinary methods of numerical integration to the separated equations, but for those problems in which the variables cannot be separated no direct method of solution has been given. Problems of this type have hitherto always been treated by the use of analytical approximations such as perturbation theory and the Ritz variation method.

Methods have been developed for the numerical solution of non-separable differential equations, subject to given boundary conditions, which do not involve the determination of eigenvalues.[1] These methods all depend on replacing the continuum over which the differential equation is to be integrated by a discrete set of lattice points and the differential equation itself by a difference equation which is equivalent to a set of nonhomogeneous linear algebraic equations.

It has been shown[2] that a differential equation of the eigenvalue type may similarly be replaced by a difference equation which is equivalent to a set of *homogeneous* linear algebraic equations

containing a parameter. The values of this parameter for which the homogeneous equations have non-trivial solutions approach the eigenvalues and the corresponding solutions approach the eigenfunctions of the differential equation as the lattice spacing decreases to zero. The determination of these solutions has been reduced[2] to the problem of minimizing a certain quadratic form (which is analogous to the energy integral $\int \psi^* H \psi$) subject to certain normalization and, for the higher states, orthogonality conditions. We here develop a practical numerical method of solving this variation problem. By altering the values of a rough solution at each lattice point in turn according to formula (12), the value of the quadratic form is continually decreased until the desired minimum is reached. In this respect the method is similar to the procedure[1] for the solution of Laplace's difference equation in n-dimensions by successively replacing the values of a rough solution by the arithmetic means of the $2n$ neighboring values. While we shall discuss the procedure in particular for Schrödinger's equation in coordinate systems in which the Laplacian is a simple sum of second derivatives, the method is readily extended to other eigenvalue equations and other types of coordinate system.

GENERAL THEORY

Having chosen a suitable lattice, not necessarily uniform, composed say of N points (boundary points at which $\psi = 0$ not included), we consider from now on only the values ψ_1, ψ_2,

* National Research Fellows.

[1] L. F. Richardson, Trans. Roy. Soc. **A210**, 307 (1911), Math. Gazette **12**, 415 (1925); Phillips and Wiener, J. Math. and Phys. **2**, 105 (1923); Courant, Zeits. f. Ang. Math. u. Mech. **6**, 322 (1926); Courant, Friedrichs and Lewy, Math. Ann. **100**, 32 (1928).

[2] R. G. D. Richardson, Trans. Am. Math. Soc. **18**, 489 (1917); Courant, Friedrichs and Lewy, Math. Ann. **100**, 32 (1928).

$\cdots \psi_N$ of ψ at the lattice points. The solutions of Schrödinger's equation

$$-k^{-2}\nabla^2\psi + V\psi = E\psi \qquad (1)$$

are then approximated by the solutions of a set

$$\Sigma_{(j)}b_{ij}\psi_j = E\psi_i \qquad (2)$$

of linear homogeneous algebraic equations. For example, if i is a point in an n-dimensional cubic lattice with spacing h, and a, b, c, $\cdots$ the $2n$ adjacent points, the ith equation of (2) has the form

$$-h^{-2}k^{-2}[\psi_a + \psi_b + \cdots - (2n + h^2k^2V_i)\psi_i] = E\psi_i. \qquad (3)$$

To each point is given a weight c_i equal (with certain exceptions which we shall discuss later) to the volume of the "unit cell" of the lattice at i, so that the integral $\int\phi\psi$ over the given region is approximated by the sum $\Sigma c_i\phi_i\psi_i$. The lowest solution of (2) is then that function ϕ which minimizes the ratio

$$E_\phi = [\Sigma_{(ij)}c_ib_{ij}\phi_i\phi_j]/[\Sigma_{(i)}c_i\phi_i^2], \qquad (4)$$

and the corresponding E_ϕ is the lowest eigenvalue. This is true only if the quadratic form in the numerator of (4) is symmetric, i.e., if

$$c_ib_{ij} = c_jb_{ji}. \qquad (5)$$

We shall now give a method of determining numerically the lowest state of (2). Let us choose any function as a rough approximation to the solution and then change each point in turn in such a way as to lower E at each step. The condition for the vanishing of $\partial E_\phi/\partial\phi_p$ suggests that E will be lowered by replacing ϕ_p by

$$\phi_p' = -[\Sigma_{(j)}'b_{pj}\phi_j]/[b_{pp} - E_\phi], \qquad (6)$$

where Σ' denotes summation over all values of j except $j = p$. This amounts to satisfying the pth equation of the set (2). We shall now show that this change actually lowers E if the lattice is not too coarse.

Let $\Delta\phi_p = \phi_p' - \phi_p$. Then

$$E_{\phi'} - E_\phi =$$
$$-(b_{pp} - E_\phi)\left[\frac{c_p(\Delta\phi_p)^2}{\Sigma c_i\phi_i^2} - \frac{2c_p^2\phi_p(\Delta\phi_p)^3}{(\Sigma c_i\phi_i^2)^2} + \cdots\right]. \qquad (7)$$

If the number of lattice points is large, $c_p(\Delta\phi_p)^2/\Sigma c_i\phi_i^2$ is small compared to unity. In

this case we need consider only the first term of (7), and E will be decreased by the change in ϕ_p if $b_{pp} - E_\phi$ is positive. But $b_{pp} - E_\phi$ may certainly be made positive by using a sufficiently fine lattice since b_{pp} is a constant plus a positive term of order $1/h^2k^2$, where h is the lattice spacing, while E_ϕ approaches a limit as $h \to 0$.

Therefore, if we take a lattice sufficiently fine to make $b_{pp} - E_\phi$ positive for all points for our initial rough approximation, we may continuously decrease E by using (6) as an improvement formula point by point on our function. As E converges to the true lowest eigenvalue, the function must converge to the true lowest eigenstate, for only for an eigenfunction can $\Delta\phi$ and hence ΔE approach zero.

It is not necessary to recalculate E_ϕ after each improvement by formula (6); it may be shown that if the change in ϕ is small compared to ϕ itself, the whole lattice may profitably be run over using a single value of E_ϕ.

We shall now develop a similar method for the calculation of the states of higher energy. Suppose that we know the μ states ψ^1, ψ^2, $\cdots$, ψ^μ of lowest energy, and seek the $(\mu+1)^{\text{st}}$ state $\psi^{\mu+1}$. Let the states ψ be normalized so that

$$\Sigma\psi_i^\alpha\psi_i^\beta = \delta_{\alpha\beta}, \qquad (8)$$

$$\Sigma b_{ij}\psi_j^\beta = E^\beta\psi_i^\beta. \qquad (9)$$

Then $\psi^{\mu+1}$ is that state orthogonal to ψ^1, $\cdots$, ψ^μ which gives the lowest value of E in (4).

For any function ϕ, let us use the notation

$$\Sigma c_i\phi_i\psi_i^\alpha = M^\alpha, \qquad (10)$$

and to avoid confusion with sums over the lattice points $1 \cdots N$, let the repetition of the index α in a term denote summation over $\alpha = 1$, $\cdots$, μ. Then the function

$$\chi = \phi - M^\alpha\psi^\alpha \qquad (11)$$

is orthogonal to ψ^1, $\cdots$, ψ^μ and may, if it does not vanish identically, be considered as a rough approximation to $\psi^{\mu+1}$. Since the energy $E_\chi = \bar{E}_\phi$ is calculated for a state orthogonal to ψ^1, $\cdots$, ψ^μ, it must be greater than the energy $E^{\mu+1}$ (or equal if χ is proportional to $\psi^{\mu+1}$).

If we can find a function ϕ' such that $\bar{E}_{\phi'} < \bar{E}_\phi$, we can consider χ' a better approximation than χ to $\psi^{\mu+1}$. Hence let us seek an improvement

formula which reduces $'\tilde{E}_\phi$. Setting $\partial\tilde{E}_\phi/\partial\phi_p = 0$ suggests that we use

$$\phi_p' = -\frac{\Sigma' b_{pj}\phi_j - M^\alpha\psi_p{}^\alpha(\tilde{E}_\phi - E^\alpha)}{b_{pp} - \tilde{E}_\phi} \qquad (12)$$

That this gives a definite improvement for a sufficiently fine lattice is shown by the calculation of the change of $\tilde{E}$ when ϕ is replaced by $\phi' \equiv \phi_1, \phi_2, \cdots, \phi_p', \cdots, \phi_N$.

It may be shown that one obtains exactly the same change in $\tilde{E}$ whether the formula (12) is applied to ϕ_p or the corresponding formula with $M^\alpha = 0$ is applied to χ_p:

$$\chi_p' = -[\Sigma' b_{pj}\chi_j]/[b_{pp} - E_\chi]. \qquad (13)$$

This improvement formula has the advantage of simplicity over (12), and may be used on an "orthogonalized" ϕ. χ' is of course no longer orthogonal and must be reorthogonalized if (13) is to be used again. Only if $\tilde{E}_\phi$ is the true eigenvalue, will (13) reproduce the function χ. If $\phi = \psi^{\mu+1} + d^\alpha\psi^\alpha$, $\tilde{E}_\phi$ will equal $E^{\mu+1}$, and alteration by (12) will simply reproduce ϕ. Hence the process will converge to a combination of this type, which must be orthogonalized to obtain $\psi^{\mu+1}$. Just as in the case of the ground state, we can in general profitably go over the whole lattice with the same values of $\tilde{E}_\phi$ and M^α.

At a boundary point where ψ is to vanish, ϕ is held permanently at zero, this zero value being used in the improvement of adjacent points. At a boundary point where $\partial\psi/\partial n$ is to vanish, we hold $\partial\phi/\partial n$ to zero by effectively maintaining equal values of ϕ on the two sides of the boundary, i.e., we calculate at such a boundary point as if the missing points outside the region had the same values as the corresponding points within the region.

APPLICATION TO ONE-DIMENSIONAL PROBLEMS

We can best illustrate this method of integration by considering a specific and well-known example, the s states of the hydrogen atom. These states satisfy the equation

$$-(\partial^2\psi/\partial r^2) - 2\psi/r = E\psi \qquad (14)$$

with energy -1 for the $1s$, -0.25 for the $2s$, $\cdots$. The range of r is from 0 to ∞, with boundary conditions $\psi = 0$. Let us take our lattice points as in Fig. 1, with, starting from $r = 0$, four intervals of 0.4, four intervals of 0.8, and then intervals of 1.6 to $r = \infty$.

At those points whose neighbors are both at the same distance h, $c_i = h$, $b_{i,i-1} = b_{i,i+1} = -1/h^2$, $b_{ii} = V_i + 2/h^2$. The only exceptional points are those for which the interval on one side is h and on the other side $2h$. In order to approximate to $\partial^2\phi/\partial r^2$ at such a point we take the parabola through the point and its two neighbors and find its second derivative. Thus $c_i = \frac{3}{2}h$, $b_{i,i-1}$
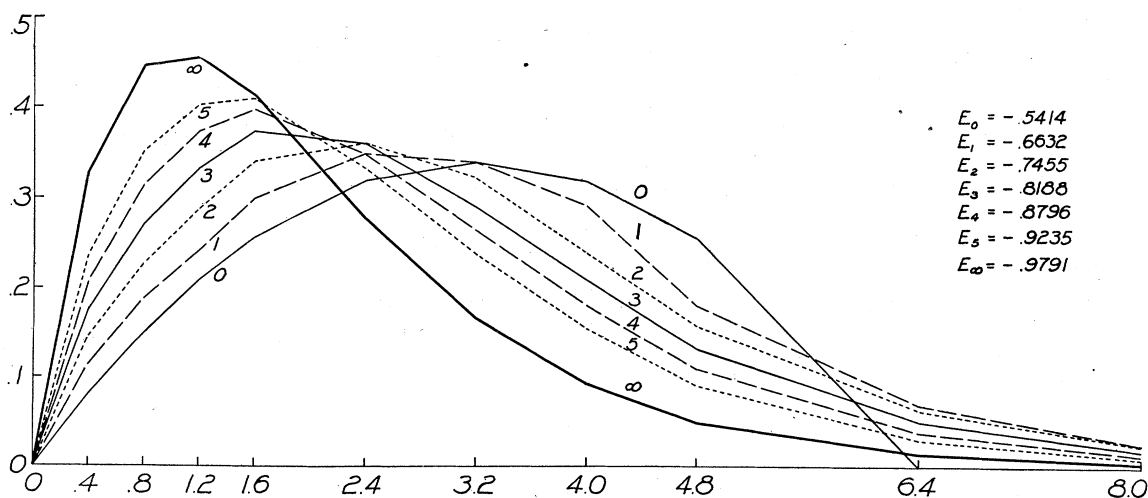

$$E_0 = -.5414$$
$$E_1 = -.6632$$
$$E_2 = -.7455$$
$$E_3 = -.8188$$
$$E_4 = -.8796$$
$$E_5 = -.9235$$
$$E_\infty = -.9791$$

FIG. 1. The improvement of the $1s$ state of hydrogen.

$= -2/3h^2$, $b_{i,i+1} = -1/3h^2$, $b_{ii} = V_i + 1/h^2$, if $i-1$ is at a distance h and $i+1$ at a distance $2h$ from i.

The improvement formula (6) or (13) becomes for our two types of point, respectively,

$$\phi_p' = [\phi_{p-1} + \phi_{p+1}]/[2 + h^2(V_p - E_\phi)];$$
$$\phi_p' = [\tfrac{2}{3}\phi_{p-1} + \tfrac{1}{3}\phi_{p+1}]/[1 + h^2(V - E_\phi)]. \quad (15)$$

With a table of the denominators in these formulas at hand the improvement of ϕ can be carried out extremely rapidly. In actual practice it is never necessary to recalculate E_ϕ until the whole set of points has been improved, while in the latter stages the function may be safely improved a large number of times with the same E_ϕ, since E_ϕ converges to its final value much more quickly than ϕ itself.

The process of improvement is illustrated in Fig. 1. Starting from the parabolic arch marked 0, five successive improvements from left to right gave the curves marked 1, 2, 3, 4, 5, the energy being recalculated after each complete improvement. These energies are shown in Fig. 1. The final result is shown as the curve marked ∞ and the final energy as E_∞. Each of these curves has been normalized to the same value (0.4) before plotting.

The convergence of the eigenfunction and eigenvalue to that of the differential equation as the lattice spacing is decreased is illustrated in Fig. 2, where the final eigenvalues and func-

tions are shown for the lattice of Fig. 1 and for lattices of half, double, and quadruple this spacing. The circles represent the final function for lattice spacing starting at 0.2, and this function differs from the continuous solution, re^{-r}, by less than one-half percent, i.e., less than the accuracy of the plot, at any point.

Fig. 3 shows the rapidity of improvement in the calculation of the $2s$ state. The parabola of Fig. 1 was used again as a starting function. When orthogonalized to the ground state, this gave the curve marked 0. Since $M=0$ for this curve, the improvement formula (13) was used, the improvement being carried through from left to right without altering E or M. The result was then orthogonalized and plotted as curve 1. This process was repeated four times. The fourth approximation here is considerably closer to the final curve than it was in Fig. 1 because the initial curve had a more correct shape.

Practically, the computation of ψ_∞ for any of these lattices is much more rapid than these plots would indicate because with such a process of improvement, one is permitted to do anything he pleases to the function. The improvement of the function can be made at the rate of several points per minute, and is much simpler than the calculation of the energy, so that in practice one can profitably use the same energy several times, or at least as long as regions of the curve are sinking in absolute value.

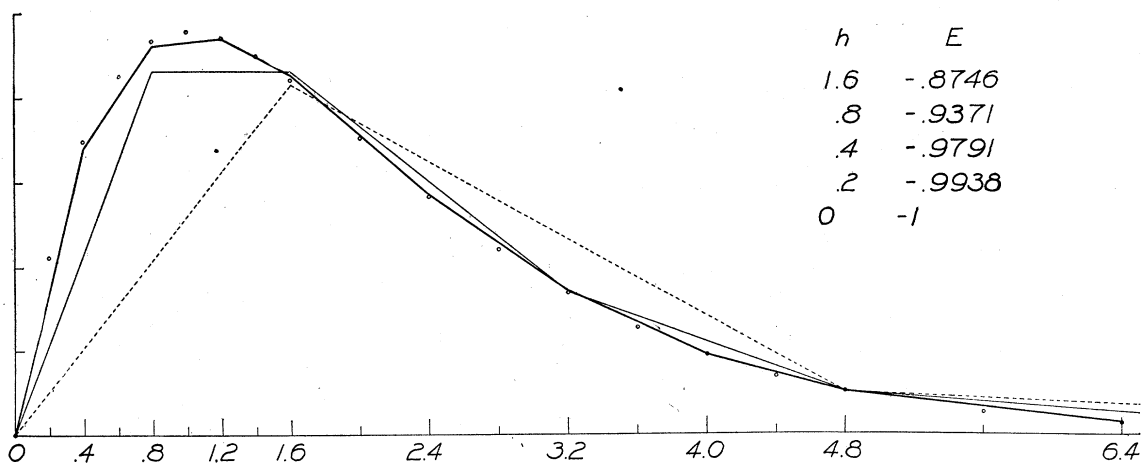| h	E
1.6	-.8746
.8	-.9371
.4	-.9791
.2	-.9938
0	-1

FIG. 2. Convergence of the solution of the difference equation to that of the differential equation as the lattice spacing is decreased for the $1s$ state of hydrogen. The energy is tabulated as a function of the finest interval. To the accuracy of the plot (about one-half percent), the circles represent both the solution of the difference equation for the 0.2 lattice and the solution of the differential equation.

$E_0 = -.0428$ $E_3 = -.2483$
$E_1 = -.2206$ $E_4 = -.2514$
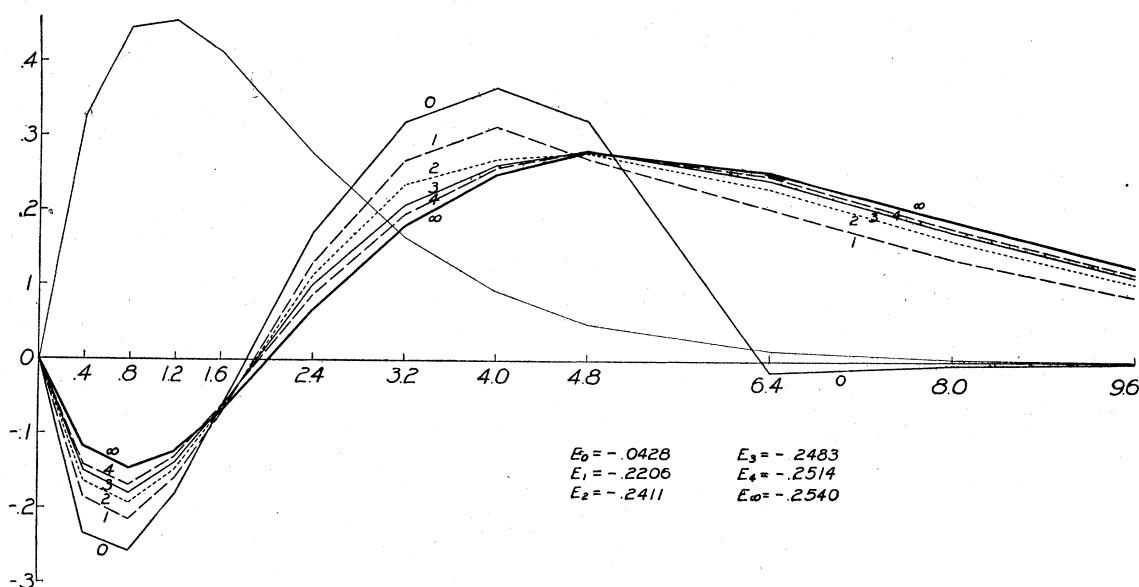$E_2 = -.2411$ $E_\infty = -.2540$

FIG. 3. The improvement of the 2s state of hydrogen. The 1s state is shown by the light curve.

However, really rapid convergence is obtained by using the formula twice to find out how the function is moving at each point and then altering the function by hand several times the amount of its last motion. Since the improvement formula quickly eliminates sharp irregularities, this process of "hand tooling" enables one to reach the final value of the function very quickly. All computation is facilitated by the fact that errors, unless of a size to be immediately obvious, are unimportant and soon corrected so that no calculation need be checked.

APPLICATION TO TWO-DIMENSIONAL PROBLEMS

In two-dimensional problems even more use may be made of the device of increasing the lattice spacing in regions where ψ is flat in order to reduce the number of points. Thus the number of lattice points can be made a fraction of the product of the numbers along the two rectangular axes. We must then consider the coefficients to be used for points in the region where the lattice constant changes. For the square lattice shown in Fig. 4, Table I gives a representative set of b's and c's; these satisfy the condition (5) and are such that the two quadratic forms occurring in (4) approach the corresponding integrals of a

TABLE I. This table gives c_ν, $h^2k^2(b_{\nu\nu} - V_\nu)$, and $-h^2k^2b_{\nu\mu}(\nu \neq \mu)$ for a representative set of points in Fig. 4.

c_ν	ν	a	b	c	d	e	f	g	i	j	k	l	m	n	o	p	q
1	d	1	⅔	1	4	1		⅓	2	⅔		1					
9/4	g			⅔					1	3	1		⅛				
3/2	i				⅔				1	3	1			⅙	⅙		
3/2	j									1	3	1			⅓		
4	m							³⁄₁₆	¼				¼	1	¼		¼	
4	n								⅛	⅛			¼	1	¼			¼

given continuous function ϕ as the number of points is successively quadrupled by halving all intervals. If the left-hand column of points in Fig. 4 are along a boundary where $\partial\psi/\partial n$ is to vanish, we take $c_r=\frac{1}{2}h$, $b_{ru}=b_{rs}=-1/h^2k^2$, $b_{rt}=-2/h^2k^2$, $b_{rr}=V_r+4/h^2k^2$.

The corresponding improvement formulas obtained from (6) are seen to be little more complicated than for one dimension. The amount of labor involved in an improvement or a calculation of energy in any number of dimensions is essentially proportional to the number of lattice points used. Practically, we have found it convenient in two dimensions to draw on heavy paper a square to represent each lattice point of color to indicate the type of formula used. In this square are placed permanent entries of V_i, $(4+h^2k^2V_i)$ or the corresponding form for the color in question, and the weights to be used in summing $h^2k^2\phi_i\Sigma b_{ij}\phi_j$ and
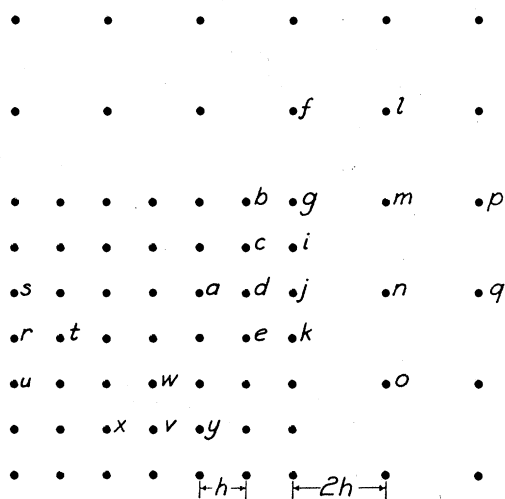
FIG. 4.

ϕ_i^2 when determining the energy. In pencil is entered $4+h^2k^2(V_i-E)$ or the corresponding form, and the last four or five ϕ_i's so that the changes may be watched. Older ϕ_i's are erased as space is needed for new ones. With experience in hand-tooling, it is feasible in this way to solve a lattice of several hundred points in a couple of weeks. Smaller lattices giving more approximate values of the energy and the function may be solved in much less time, since halving the lattice constant quarters the work. Two computers are required, one to read and the other to operate the machine.

The axially symmetric one-electron problem

Schrödinger's equation in atomic units for the motion of one electron in an axially symmetric field is reduced, in cylindrical coordinates r, z,

φ to the equation

$$-\frac{\partial^2 S}{\partial r^2} - \frac{\partial^2 S}{\partial z^2} + \left(V - \frac{1}{4r^2} + \frac{\lambda^2}{r^2}\right)S = ES$$

by the transformation

$$\psi = [S(r, z)/r^{\frac{1}{2}}]e^{i\lambda\varphi}.$$

This two-dimensional equation may be handled by the methods outlined if we replace V by the effective potential $(V-1/4r^2+\lambda^2/r^2)$ and use the boundary condition $S=0$ when $r=0$. If we make a power series expansion near the axis $r=0$ we find that S starts as $r^{\lambda+\frac{1}{2}}$ so that our parabolic approximation will be valid near $r=0$ for all λ except $\lambda=0$.

For $\lambda=0$, if the bottom row of lattice points in Fig. 4 is along the line $r=0$, the second derivative at the point v can be approximated by putting a curve of the form $\alpha+\beta r^2$ through $S_v/h^{\frac{1}{2}}$ and $S_w/(2h)^{\frac{1}{2}}$. This gives $b_{vw}=-2^{\frac{1}{2}}/3h^2$, $b_{vv}=V_v+10/3h^2$, and $c_v=3/2^{\frac{1}{2}}$.

If the potential V is both axially symmetric and an even function of z, S will either be an even or odd function of z, and the two types of functions may be obtained separately by using the boundary conditions $\partial S/\partial z=0$ and $S=0$, respectively, when $z=0$. If V has a first-order pole along the axis $r=0$ the necessity of differentiating along a radius passing through the pole is best avoided by using a lattice such that no lattice line passes through the pole.

We have checked the practicability of these formulas by a calculation of the ground state of the hydrogen molecule ion on a coarse lattice, with results in satisfactory agreement with the known values. We are proceeding with the application of this method to the calculation of eigenfunctions for other diatomic molecules.