

TRIAL OF A NUMERICAL METHOD FOR SOLVING THE SCHRÖDINGER WAVE EQUATION IN SEVERAL VARIABLES

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Summary

A numerical method previously described for the solution of eigenvalue-eigenfunction problems in several variables has been applied to the Schrödinger wave equation for the lithium atom. The method employs an expansion of the wavefunction in terms of Slater determinants. Some information is obtained about the convergence behaviour of such expansions, the convergence being too slow in this instance to yield an energy of useful accuracy.

I. INTRODUCTION

A numerical method (Bassett 1959*a*, 1959*b*, 1959*c*) for the solution of eigenvalue-eigenfunction problems in several variables has been applied to the Schrödinger wave equation for the lithium atom. The lithium atom is a three-particle system (assuming that its nucleus is fixed) and so is a problem in nine variables; the fundamental eigenfunction (i.e. ground state wavefunction) was sought. In order to provide the method with a reasonably stiff test, no use was made of the spatial symmetry of this ground state wavefunction. The results constitute some evidence about the rate of convergence of series expansions of wavefunctions in terms of the class of Slater determinants employed. The rate of convergence in this case was too slow to yield an energy of useful accuracy but the results seem worth reporting briefly, together with some details of the computational method. The basic method may yet be useful in some form.

The wave equation for the electrons in a lithium atom, in atomic units (Hartree 1957), is

$$\left(\sum_{j=1}^3 (-\frac{1}{2} \nabla_j^2 - 3r_j^{-1}) + r_{12}^{-1} + r_{23}^{-1} + r_{31}^{-1} \right) \psi = E\psi, \quad (1)$$

where $\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ is the wavefunction, E the energy, r_{ij} the distance between electrons i and j , r_j the distance between electron j and the nucleus, and ∇_j^2 the Laplacian operator on \mathbf{r}_j , the position vector of the j th electron.

The wavefunction is expressed as a sum of Slater determinants built from one-electron functions, which in this calculation were taken in the form

$$F(r_i) G(\theta_i) H(\phi_i) \sigma(s_i),$$

where r_i, θ_i, ϕ_i are the spherical polar spatial coordinates of the i th electron with s_i its spin coordinate. To obtain the lowest *doublet* state, the spin wavefunctions were

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chosen to be α , α , and β , i.e. two the same. The method imposes no other restriction on the form of the one-electron functions, and the results suggest that for the ground state of the lithium atom 35 Slater determinants (the maximum number taken) when constructed in this way cannot give an eigenvalue estimate in error by less than about 0.1%, or about 0.01 atomic units. Further, the successive eigenvalue estimates that the method generates do not lie on a smooth curve (Fig. 1). It follows that only the roughest estimate of the error resulting from terminating the series can be made by extrapolation, in contrast to Pekeris's solutions of the wave equation for the helium atom, where the eigenvalue estimates change smoothly enough to permit extrapolation (Pekeris 1958; Frankowski and Pekeris 1966).

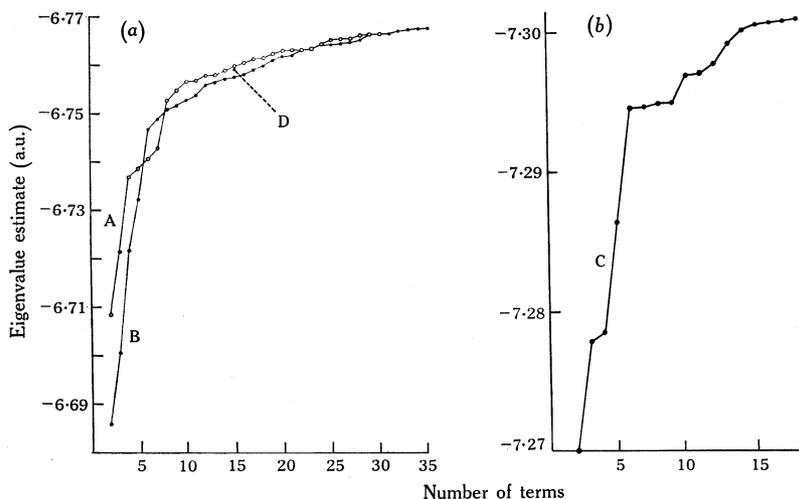


Fig. 1.—Eigenvalue estimates in atomic units plotted against number of terms (Slater determinants) of some series approximations to the eigenvectors. The results of three separate calculations, wavefunctions A, B, and D (the last being represented by the isolated point at 15 terms), for a mesh size determined by $n = 6$ are shown in (a), while the result of a further calculation, wavefunction C, using a finer mesh size ($n = 14$) is shown in (b). The eigenvalue–eigenvector problem concerned may be regarded as a model problem that approximates the wave equation for the lithium atom, the closeness of approximation being determined by the mesh size.

II. ASPECTS OF THE METHOD OF CALCULATION

A very coarse mesh was used for the finite difference operations. That results obtained on such a coarse mesh can be meaningful has been illustrated in the application of the method to a simple problem (Bassett 1959*a*, p. 434; 1959*b*, p. 447). There the rate of convergence and other features of the solution were found to be obtainable on a very coarse mesh, provided formulae for numerical integration and differentiation are chosen in a particular way, namely, so that the sequence of estimates of the solution converges (exactly) to the solution of an eigenvalue–eigenvector problem, which is itself an approximation, in the sense of finite differences, to the eigenvalue–eigenfunction problem.

This technique has been used in the present calculation. It permits separation of the error arising from termination of the series of Slater determinants from that which depends on the size of the mesh. The eigenvalue–eigenvector problems for which the successive eigenvalue estimates are illustrated in Figures 1(a) and 1(b) might be described as *models* of the wave equation for the lithium atom, that shown in Figure 1(b) (wavefunction C) using a finer mesh and therefore being a more accurate model. The eigenvalue estimate based on this 18-term wavefunction is -7.30 a.u., which may be compared with the experimental energy of -7.48 a.u. This error of 0.18 a.u. undoubtedly is due mainly to the size of the mesh, not to the termination of the series. It is the author's contention that the convergence behaviour shown in Figure 1 would be exhibited on an arbitrarily fine mesh.

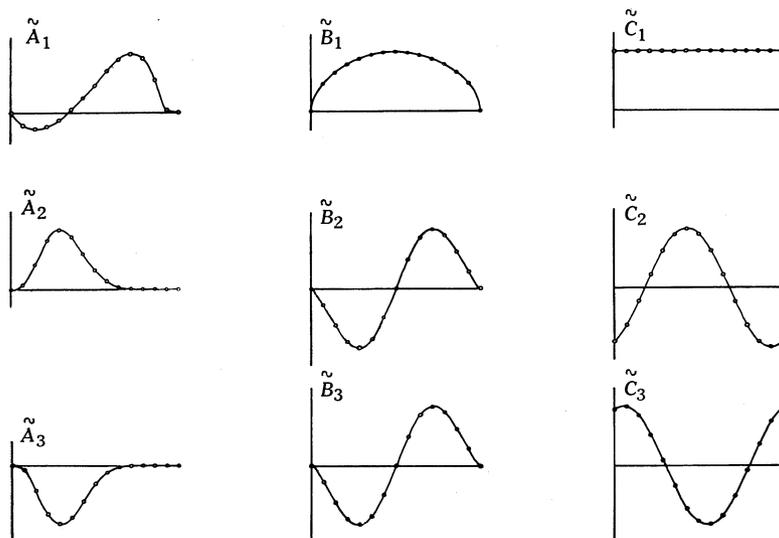


Fig. 2.—Typical term (i.e. Slater determinant) obtained in the series expansion. (The figure represents the ninth Slater determinant of wavefunction C.) The Slater determinant is built from three one-electron functions, each having the spatial dependence

$$\sin^{-1}\rho \sin^{-1}\theta A_i(\rho) B_i(\theta) C_i(\phi) \quad (i = 1, 2, 3),$$

where $r = \tan^{-1}\rho$, θ , and ϕ are the spherical polar coordinates of an electron. The functions \tilde{A}_i , \tilde{B}_i , and \tilde{C}_i shown in the figure are normalized versions of A_i , B_i , and C_i ; \tilde{A}_i is obtained from A_i by dividing each element of A_i by the modulus of its largest element, and \tilde{B}_i and \tilde{C}_i are similarly related to B_i and C_i . The functions A_i , B_i , and C_i themselves are given in Table 1.

The terms r_{ij}^{-1} in equation (1), i.e. the Coulomb repulsion terms, were replaced in these calculations by the first four terms of the standard series expansion in Legendre polynomials (Hartree 1957, p. 46), i.e. the terms up to and including Legendre polynomials of order four. In this respect also, the problem tackled was only an approximation to the differential equation (1). However, it seems unlikely that this truncation of the series expression for r_{ij}^{-1} affected the results appreciably; the dependence on azimuthal angle of the terms actually obtained suggests low order trigonometric functions (Fig. 2) and so the matrix elements of the neglected

terms in the series for r_{ij}^{-1} are probably very small. A typical term obtained in the series expansion is represented in Figure 2, in which the \widetilde{A}_i , \widetilde{B}_i , and \widetilde{C}_i shown are normalized versions of the values given in Table 1 and are further explained in the caption to the figure.

TABLE 1

FUNCTIONS $A_i(\rho)$, $B_i(\theta)$, AND $C_i(\phi)$ SHOWN (IN NORMALIZED FORM) IN FIGURE 2

Values are given of the functions at the interior mesh points of the domains in which they are defined. Each function value F is represented by a decimal fraction a followed by an integer n in parentheses, where $F = a \times 10^n$

A_1	B_1	C_1	A_2	B_2	C_2
-0.48400974(-1)	0.18634528 (0)	0.58246334(-1)	0.62290119(-2)	0.17217258 (0)	0.35884824 (1)
-0.63965057(-1)	0.26020265 (0)	0.58248314(-1)	0.16704225(-2)	0.29902595 (0)	0.24827574 (1)
-0.55782281(-1)	0.31191417 (0)	0.58254585(-1)	0.25805055(-3)	0.34913594 (0)	0.87811397 (0)
-0.29985636(-1)	0.34928732 (0)	0.58260443(-1)	0.16182795(-4)	0.31507891 (0)	-0.90655550 (0)
0.90689929(-2)	0.37497006 (0)	0.58261503(-1)	0.19835345(-6)	0.21673553 (0)	-0.25070044 (1)
0.57688385(-1)	0.39007213 (0)	0.58256993(-1)	0.10867061(-9)	0.98236185(-1)	-0.36027028 (1)
0.11189613 (0)	0.39506368 (0)	0.58250353(-1)			-0.39857160 (1)
0.16627940 (0)	0.39007518 (0)	0.58246629(-1)			
0.21239215 (0)	0.37497465 (0)	0.58248655(-1)			
0.23641524 (0)	0.34929095 (0)	0.58254907(-1)	A_3	B_3	C_3
0.21670403 (0)	0.31191434 (0)	0.58260672(-1)	-0.10655063 (0)	-0.48586652 (0)	0.35917097 (1)
0.12930864 (0)	0.26019813 (0)	0.58261579(-1)	-0.59667442 (0)	-0.10718196 (1)	0.37452092 (1)
0.79151293(-2)	0.18633772 (0)	0.58256904(-1)	-0.11642276 (1)	-0.15581524 (1)	0.31646253 (1)
		0.58250138(-1)	-0.14118070 (1)	-0.17266828 (1)	0.19548870 (1)
			-0.12519251 (1)	-0.14790433 (1)	0.34926701 (0)
			-0.85571349 (0)	-0.85184018 (0)	-0.13270780 (1)
			-0.45069335 (0)	-0.54365768(-4)	-0.27325790 (1)
A_3	B_3	C_3	-0.17482144 (0)	0.85174178 (0)	-0.35916615 (1)
0.36878363(-2)	-0.98187280(-1)	-0.35876873 (1)	-0.44627719(-1)	0.14789700 (1)	-0.37451153 (1)
0.20659705(-1)	-0.21663983 (0)	-0.24820589 (1)	-0.53683178(-2)	0.17266364 (1)	-0.31645543 (1)
0.40343695(-1)	-0.31497303 (0)	-0.87776963 (0)	-0.35117172(-3)	0.15581252 (1)	-0.19548906 (1)
0.48986350(-1)	-0.34907462 (0)	0.90655528 (0)	0.13867882(-3)	0.10718036 (1)	-0.34934101 (0)
0.43525947(-1)	-0.29904702 (0)	0.25069316 (1)	0.11216488(-5)	0.48585857 (0)	0.13269911 (1)
0.29848112(-1)	-0.17227203 (0)	0.36028823 (1)			
0.15818520(-1)	-0.65737158(-4)	0.39862806 (1)			0.27325469 (1)

The process of successive approximation by which the one-electron functions are determined requires a starting point, and as this point, for each Slater determinant except the first, a set of more or less random numbers was used, prepared by shuffling a deck of cards on which were punched an assortment of numbers of reasonable magnitude. These form acceptable initial functions, since, as remarked above, the arithmetical procedure can be regarded as solving a finite eigenvector problem and it will work even if the intermediate approximations to the eigenvector do not represent smooth functions.

Before introducing finite difference approximations, the wavefunction ψ in equation (1) was replaced by χ , defined by

$$\chi = \sin \rho_1 \sin^{\frac{1}{2}} \theta_1 \sin \rho_2 \sin^{\frac{1}{2}} \theta_2 \sin \rho_3 \sin^{\frac{1}{2}} \theta_3 \psi, \quad (2)$$

where

$$r_i = \tan \rho_i. \quad (3)$$

The equation, equivalent to (1), satisfied by χ is

$$\mathcal{H}\chi = E W(\rho_1) W(\rho_2) W(\rho_3) \chi, \quad (4)$$

where
$$W(\rho) = \cos^{-4}(\rho), \quad (5)$$

$$\begin{aligned} \mathcal{H} = & W(\rho_2) W(\rho_3) T(\rho_1, \theta_1, \phi_1) + W(\rho_1) W(\rho_3) T(\rho_2, \theta_2, \phi_2) \\ & + W(\rho_1) W(\rho_2) T(\rho_3, \theta_3, \phi_3) + W(\rho_1) W(\rho_2) W(\rho_3) V, \end{aligned} \quad (6)$$

V , the potential energy, is given by

$$V = - \sum_{j=1}^3 3r_j^{-1} + r_{12}^{-1} + r_{23}^{-1} + r_{31}^{-1}, \quad (7)$$

and T , the kinetic energy operator for one electron, is given by

$$\begin{aligned} T(\rho, \theta, \phi) = & -\frac{1}{2}(\partial^2/\partial\rho^2) + \cos^{-2}\rho \sin^{-2}\rho \left\{ -\frac{1}{2}(\partial^2/\partial\theta^2) - \frac{1}{8}\sin^{-2}\theta \right\} \\ & + \cos^{-2}\rho \sin^{-2}\rho \sin^{-2}\theta \left\{ -\frac{1}{2}(\partial^2/\partial\phi^2) \right\} - \frac{1}{8}\cos^{-2}\rho \sin^{-2}\rho - \frac{1}{2}. \end{aligned} \quad (8)$$

As a result of these transformations the differential operator T is Hermitian with weight factor unity, in contrast to the Laplacian operator in spherical polar coordinates, which is Hermitian with weight factor $r^2 \sin \theta$. It is easy to obtain a finite difference representation of (6) that is a strictly symmetric matrix. (The second derivatives were represented by the second central difference δ^2 divided by the square of the mesh size, that is, δ^2/\hbar^2 .) It follows (Bassett 1959c) that the numerical procedure produces a solution of the eigenvalue–eigenvector problem for this matrix.

III. RESULTS

The mesh points were chosen so as to divide the ranges of the variables ρ , θ , and ϕ into the same number n of equal intervals. An approximate solution to 30 terms (Slater determinants) was obtained (wavefunction A) with $n = 6$. Another solution (using reshuffled cards as starting point) with $n = 6$ was carried to 35 terms (wavefunction B). The eigenvalue estimates as a function of the number of terms in the corresponding approximate eigenfunctions are shown in Figure 1(a). The first term in the series was rather arbitrarily taken to be the Slater determinant formed from two hydrogen-like unscreened 1S functions and one 2S function. The terms other than the first were determined one by one in accordance with the procedure described previously (Bassett 1959a, 1959b, 1959c) by cyclically varying their nine functions of one variable. Ten such cycles were nearly always sufficient to produce satisfactory convergence from the initial functions determined by the shuffled decks. A variant of this procedure was used to obtain another solution with $n = 6$ (wavefunction D). First a two-term wavefunction was obtained by varying the two terms alternately (in this case, therefore, the first term was not the (1S)²2S Slater determinant). Then, leaving these first two terms fixed, another 13 terms were added and varied cyclically, i.e. instead of building up a wavefunction term by term and varying only the last term at each stage, the last 13 terms were varied in cyclic order (so that they were all roughly on an equal footing). This procedure seems more flexible than the other, but led to no improvement in the eigenvalue estimate (see the isolated point at 15 terms in Figure 1(a) labelled wavefunction D). A third approximate solution (wavefunction C, Fig. 1(b)) was obtained with $n = 14$. This was carried to 18 terms and shows slow and fitful convergence like cases A and B.

IV. HANDLING SINGULARITIES OF THE TRANSFORMED HAMILTONIAN

The transformation (2) results in some singular terms in the kinetic energy operator (8). The only one that gives any trouble is the term containing the factor

$$-\frac{1}{2}(\partial^2/\partial\theta^2) - \frac{1}{8}\sin^{-2}\theta. \quad (9)$$

Among the class of functions $f(\rho)g(\theta)h(\phi)$ that must contribute to the wavefunction are functions whose θ -dependence is $\sin^{\frac{1}{2}}\theta$. For example, if an S wavefunction is transformed in accordance with (2) it has this θ -dependence. Now

$$\begin{aligned} \{-\frac{1}{2}(\partial^2/\partial\theta^2) - \frac{1}{8}\sin^{-2}\theta\}\sin^{\frac{1}{2}}\theta &= +\frac{1}{8}\sin^{-3/2}\theta\cos^2\theta + \frac{1}{4}\sin^{\frac{1}{2}}\theta - \frac{1}{8}\sin^{-3/2}\theta \\ &= \frac{1}{8}\sin^{\frac{1}{2}}\theta, \end{aligned} \quad (10)$$

which is finite at $\theta = 0$ and π . Thus, although both the terms $-\frac{1}{2}(\partial^2/\partial\theta^2)\sin^{\frac{1}{2}}\theta$ and $-\frac{1}{8}\sin^{-2}\theta\sin^{\frac{1}{2}}\theta$ have non-integrable singularities at 0 and π , their sum is well behaved. It is not obvious how to achieve this cancellation of singularities in a numerical calculation in which $\partial^2/\partial\theta^2$ is replaced by a finite difference operator. There is a second difficulty which arises from the fact that the operator $-\frac{1}{2}(\partial^2/\partial\theta^2) - \frac{1}{8}\sin^{-2}\theta$ does not have a fundamental eigenvalue, except in a representation based on a restricted class of functions. For example, the average value

$$\int_0^\pi g(\theta) \{-\frac{1}{2}(\partial^2/\partial\theta^2) - \frac{1}{8}\sin^{-2}\theta\} g(\theta) d\theta \div \int_0^\pi g^2 d\theta$$

is $-\infty$ for a function $g(\theta)$ that approaches zero like $\theta^{\frac{1}{2}}$, so that such functions have somehow to be excluded. Both difficulties can be overcome by adopting an appropriate numerical representation for the function $\sin^{-2}\theta$ occurring in the transformed kinetic energy operator (8). We adopt $S(\theta)$ as the finite vector representing $\sin^{-2}\theta$, where

$$\{-\frac{1}{2}(\delta^2/h^2) - \frac{1}{8}S(\theta)\}\sin^{\frac{1}{2}}\theta = \frac{1}{8}\sin^{\frac{1}{2}}\theta. \quad (11)$$

Equation (11) is a finite difference analogue of (10). Thus

$$S(\theta) = -1 - 4\sin^{-\frac{1}{2}}\theta(\delta^2/h^2)\sin^{\frac{1}{2}}\theta. \quad (12)$$

$S(\theta) \rightarrow \sin^{-2}\theta$ in any prescribed interval *inside* $(0, \pi)$ as $h \rightarrow 0$. This choice of $S(\theta)$ achieves by construction the desired cancellation of singularities. Furthermore, the fundamental (i.e. one-signed) eigenvector of

$$-\frac{1}{2}(\delta^2/h^2) - \frac{1}{8}S(\theta)$$

is $\sin^{\frac{1}{2}}\theta$ and accordingly there are no eigenvalues lying below that which is associated with the eigenvector $\sin^{\frac{1}{2}}\theta$. The numerical vector space therefore contains nothing corresponding to the unwanted functions like $\sin^{\frac{1}{2}}\theta$.

V. CONCLUSIONS

Inspection of the sequences of eigenvalue estimates in Figure 1 suggests that the error in the eigenvalue at 30 or 35 Slater determinants, arising from termination of the series, is not less than about 0.1% or 0.01 a.u. Because of the way in which these sequences of eigenvalue estimates were obtained, it is the author's opinion that

they probably exhibit the most rapid possible convergence of a series expansion of the ground state lithium wavefunction, using these coordinates. This rate is too slow with existing computers to yield wavefunctions and total energies of useful accuracy.

Variants of the basic method are possible. For example, it would be possible to represent the one-electron functions by a three-dimensional table (most simply using Cartesian coordinates). A series expansion in Slater determinants constructed from such one-electron functions might converge rapidly enough to yield useful results. Further, the basic method can certainly be adapted to determine low lying excited states. It is possible that the energy *differences* between such low lying excited states and the ground state would be approximately equal to the corresponding eigenvalue differences of the finite matrix approximating the physical problem, even on a mesh on which the truncation error of the numerical integration is greater than the energy differences in question.

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