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Numerical Solution of the S -Limit Schrödinger Equation

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Numerical solutions to the S -limit Schrödinger equation have been obtained for He and Li^+ . Using these the energy and the expectation values $\langle \sum r_i \rangle$ and $\langle \sum r_i^2 \rangle$ were calculated and compared to the radial configuration interaction values. The results demonstrate that the direct numerical solution of many partial differential equations in chemical physics can be accomplished in a practical and straightforward manner.

I. INTRODUCTION

The finite difference method has been previously discussed as a means of solving the Schrödinger equation for two electrons interacting in an infinite square well.¹ Due to the nature of the potential, that calculation was not a severe test of the method's ability to solve differential equations occurring in quantum mechanics. As an example, many of the nonhomogeneous equations arising in perturbation theory could be easily attacked with a direct numerical method,² after they have been reduced by a partial wave expansion to a set of uncoupled two-variable partial differential equations.

Numerical methods have been used to solve the ordinary integrodifferential equations determining the Hartree-Fock orbitals for atoms. With the low cycle times and large storage capacity of modern computers we are at a point where the numerical solution of both ordinary and partial differential equations can be accomplished at a large number of points in space. This is one reason why we suggest that numerical methods of solving many differential equations in quantum mechanics be reexamined. While such methods may not be uniformly better than variational methods, they are straightforward in principle and simple to program as compared with, for example, the years already spent evaluating integrals containing interelectronic coordinates in the atomic correlation problem.

Here we describe the solution of the eigenvalue equation corresponding to a potential function which

includes all radial correlation for the two-electron atom. The results are compared to accurate variational calculations. Both radial correlation and the finite difference method are adequately described elsewhere,^{3,4} and therefore the first two sections give only a brief review of these topics. The third section contains the results for the finite difference method and the comparison with the variational calculations.

II. THE S -LIMIT SCHRÖDINGER EQUATION

The Hamiltonian for the two-electron atom in atomic units is

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - Z/r_1 - Z/r_2 + 1/r_{12}. \quad (1)$$

Then by expanding the electronic interaction potential as follows,

$$1/r_{12} = \sum_l (r_{<}/r_{>})^{l+1} P_l(\cos\theta_{12}), \quad (2)$$

it is evident that the spherical component of the Hamiltonian is just

$$H_0 = -\frac{1}{2} \left[\frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left(r_1^2 \frac{\partial}{\partial r_1} \right) + \frac{1}{r_2^2} \frac{\partial}{\partial r_2} \left(r_2^2 \frac{\partial}{\partial r_2} \right) \right] - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{>}}, \quad (3)$$

where $r_{>} = \max(r_1, r_2)$. From the S -limit solution $\psi(r_1 r_2) = (4\pi \cdot r_1 \cdot r_2)^{-1} u(r_1 r_2)$ the differential equation for

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¹ D. J. Diestler and V. McKoy, *J. Chem. Phys.* **47**, 454 (1967).

² V. McKoy and N. W. Winter, "Numerical Solution of Quantum-Mechanical Pair Equations," *J. Chem. Phys.* (to be published).

³ E. Holoien, *Phys. Rev.* **104**, 1301 (1956); H. Shull and P.-O. Löwden, *J. Chem. Phys.* **25**, 1035 (1956).

⁴ L. Fox, *Numerical Solution of Two-Point Boundary Problems* (Oxford University Press, London, 1957).

the function $u(r_1 r_2)$ can be written

$$-\frac{1}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} \right) u(r_1 r_2) - \frac{Z}{r_1} u(r_1 r_2) - \frac{Z}{r_2} u(r_1 r_2) + \frac{1}{r_>} u(r_1 r_2) - E u(r_1 r_2) = 0. \quad (4)$$

The function $u(r_1 r_2)$ is taken to be normalized as follows

$$\int u(r_1 r_2) u(r_1 r_2) dr_1 dr_2 = 1,$$

and the boundary conditions require that $u(r_1 r_2)$ vanish when either variable is zero or infinity. Using the finite difference method the next section illustrates how Eq. (4) can be systematically reduced to an algebraic problem.

III. REVIEW OF THE FINITE DIFFERENCE METHOD

There are two important points to consider in treating Eq. (4) with the finite difference method. First, we want to treat the differential equation as a boundary value problem and not as an initial value one. The boundary condition at r_1 or r_2 equal to zero can be easily imposed, but the condition as r_1 or r_2 goes to infinity is more difficult and must be modified so as to describe the solution over a finite numerical grid. Fox⁴ suggests two methods for handling this type of situation. The first approach, which is direct and is the one we use, is to require that $u(r_1 r_2)$ vanish on the edges of a square bounded on two sides by $r_1 = R$, $r_2 = R$. As long as R , which in this method "represents" infinity, is sufficiently large, the solution remains a good approximation to the solution one would obtain as $R \rightarrow \infty$. The other approach, an indirect one which could be easily implemented, assumes that for large values of the variables r_1 and r_2 the differential equation has a solution $g(r_1 r_2) \exp[-\alpha(r_1 + r_2)]$ where, at reasonable grid sizes, $g(r_1 r_2)$ varies slowly. We can allow for this by using as the boundary condition the equation $u(r_1 r_2) = e^{\alpha h} u(r_1 + h, r_2)$ at any convenient point r_1 . The quantity h is just the spacing between grid points.

The second and more important point to consider is the level of the difference approximation to be used. The differential operators in Eq. (4) can be formally expanded in an infinite series of difference operators and the level of the approximation is determined by the truncation of this series. After some experimentation it was found that the best compromise between accuracy and ease of calculation was to employ only second differences and then extrapolate the results by the Richardson method.⁵

Fox⁴ argues strongly for including higher-order difference operators by an iterative method. Although such schemes may allow one to use a coarser grid and still obtain reliable solutions, we decided to work only with second differences. This approximation best demonstrates the straightforwardness of the numerical approach.

The derivatives can be written in terms of second differences as follows,

$$h^2 (\partial^2 / \partial r_1^2) u(r_1 r_2) = u(r_1 - h, r_2) - 2u(r_1 r_2) + u(r_1 + h, r_2) + O(h^4), \quad (5a)$$

$$h^2 (\partial^2 / \partial r_2^2) u(r_1 r_2) = u(r_1, r_2 - h) - 2u(r_1 r_2) + u(r_1, r_2 + h) + O(h^4), \quad (5b)$$

where h is the grid spacing. By introducing these into the S -limit equation, there results a set of linear equations, one for each grid point, having the form

$$(1/h^2) [u(r_1 - h, r_2) + u(r_1 + h, r_2) + u(r_1, r_2 - h) + u(r_1, r_2 + h)] + [(2Z/r_1) + (2Z/r_2) - (2/r_>)] - 4 + 2(E) u(r_1 r_2) = 0. \quad (6)$$

These can be collected into the following matrix form,

$$D u = E u, \quad (7)$$

where D is a real symmetric banded matrix,⁶ u is an eigenvector whose elements correspond to the solution values at the various grid points, and E is the corresponding eigenvalue.

At this point the solution of the S -limit equation has been reduced to the diagonalization of the difference matrix, or at least to that of finding the lowest eigenvector and eigenvalue. Since D is a banded matrix, this can be accomplished for large matrices in a fairly simple fashion. It is important to be able to solve extremely large matrix equations in order to reduce the difference truncation error to a tolerable level. The method we have used to extract the lowest eigenvector is described in the appendix. Even though matrices as large as 2600 by 2600 were diagonalized, the difference error remained important. To correct this, solutions at several grid sizes were found and the Richardson extrapolation method⁵ was used to predict the results at zero grid size. The other alternative, including higher differences, was tried and found to be at best only equally as accurate as extrapolation. The inclusion of higher differences has the disadvantage that grid points outside the boundaries must be dealt with. Because of this arbitrariness, we chose to stay on firmer ground with second differences. The results for He and Li⁺ are presented in the next section.

⁵ L. Richardson and J. Gaunt, Trans. Roy. Soc. (London) **A226**, 299 (1927).

⁶ See Appendix.

IV. THE FINITE DIFFERENCE RESULTS

The lowest eigenvector of the S -limit matrix was found at four different grid sizes for each atom. The radial cutoff for He was set at 5 a.u. and for Li^+ at 4 a.u. In choosing the cutoff we tried to balance the advantage of a small grid size with the disadvantage of unphysical boundary conditions.

With the eigenvectors, the energy and the expectation values $\langle \sum r_i \rangle$ and $\langle \sum r_i^2 \rangle$ were found at each grid size. Simple matrix multiplication was used rather than numerical quadrature in order to be able to extrapolate the results.

Tables I-III give the initial results for each grid size as well as the extrapolated values. In the tables the

TABLE I. Total energy.

| Grid size ^a | Initial result | | | |
|------------------------|----------------|-----------|-----------|-----------|
| Helium | | | | |
| 5/13 | -2.512505 | -2.851565 | | |
| 5/26 | -2.766800 | -2.874612 | -2.877493 | |
| 5/39 | -2.826695 | -2.877609 | -2.878608 | -2.878682 |
| 5/52 | -2.848967 | | | |
| Lithium ion | | | | |
| 4/13 | -6.072929 | -7.136845 | | |
| 4/26 | -6.870866 | -7.233727 | -7.245837 | |
| 4/39 | -7.072455 | -7.247369 | -7.251916 | -7.252321 |
| 4/52 | -7.148980 | | | |

^a The grid size is defined as the radial cutoff divided by the number of strips along one side of the grid.

second column gives the eigenvalues of the finite difference matrix. The third column gives the results of extrapolating successive values in the second column assuming that the difference between these approximate eigenvalues and the eigenvalue at zero mesh size has an h^2 dependence. The fourth column gives the result of an h^4 extrapolation, i.e., one assumes that the difference between the approximate eigenvalues and the exact eigenvalue is given by $a_0 h^2 + a_1 h^4$. The final extrapolant is obvious. This h^2 convergence is common in many elliptic partial differential equations.⁷ We will comment further on this property in the next section.

To determine the accuracy of the eigenvectors the residual vector $R = Du - Eu$ was calculated and found

⁷ See for example H. C. Bolton and H. I. Scoins, Proc. Cambridge Phil. Soc. **53**, 150 (1956). These authors attempted a numerical solution of the S -limit equation. Their best extrapolant was -2.652 a.u. for helium.

TABLE II. Expectation value of $\sum r_i$.

| Grid size | Initial result | | | |
|-------------|----------------|----------|----------|----------|
| Helium | | | | |
| 5/13 | 2.098644 | 1.870169 | | |
| 5/26 | 1.927288 | 1.864832 | 1.864165 | |
| 5/39 | 1.892590 | 1.864338 | 1.864173 | 1.864173 |
| 5/52 | 1.880230 | | | |
| Lithium ion | | | | |
| 4/13 | 1.343108 | 1.152010 | | |
| 4/26 | 1.199784 | 1.147860 | 1.147341 | |
| 4/39 | 1.170937 | 1.147537 | 1.147429 | 1.147435 |
| 4/52 | 1.160700 | | | |

to have a length in the range 10^{-5} to 10^{-6} in each case. In addition, the local energy, $E(i) = (Du)_i/u(i)$ was found to be constant to more than five decimal places at each grid point. In Table IV we compare the finite difference results, including the virial ratio $V/2E$ to the radial configuration interaction (RCI) values.⁸ The RCI basis orbitals were $1s$, $2s$, $3s$, $4s$, $1s'$, and $2s'$ Slater-type functions. The exponents for the helium atom were $\zeta = 3.7530$ and $\zeta' = 1.5427$ and for the lithium ion $\zeta = 5.8249$ and $\zeta' = 2.5456$. The energy compares well with the S -limit energy in both cases; however, for helium the other properties are slightly less satisfactory.

TABLE III. Expectation value of $\sum r_i^2$.

| Grid size | Initial result | | | |
|-------------|----------------|----------|----------|----------|
| Helium | | | | |
| 5/13 | 2.986072 | 2.414823 | | |
| 5/26 | 2.557635 | 2.401150 | 2.399441 | |
| 5/39 | 2.470699 | 2.399654 | 2.399155 | 2.399136 |
| 5/52 | 2.439617 | | | |
| Lithium ion | | | | |
| 4/13 | 1.196438 | 0.903515 | | |
| 4/26 | 0.976746 | 0.897544 | 0.896798 | |
| 4/39 | 0.932745 | 0.896828 | 0.896589 | 0.896575 |
| 4/52 | 0.917031 | | | |

⁸ We wish to thank Dr. William A. Goddard for allowing us to use his RCI computer program for these calculations.

TABLE IV. Comparison of the finite difference values with the radial configuration interaction results.

| | E | $V/2E$ | $\langle \sum r_i \rangle$ | $\langle \sum r_i^2 \rangle$ |
|-------------|---------|--------|----------------------------|------------------------------|
| Helium | | | | |
| FD | -2.8787 | 1.0007 | 1.8642 | 2.3991 |
| RCI | -2.8790 | 1.0000 | 1.8688 | 2.4206 |
| Lithium ion | | | | |
| FD | -7.2523 | 0.9999 | 1.1474 | 0.8966 |
| RCI | -7.2525 | 1.0000 | 1.1475 | 0.8968 |

V. DISCUSSION

From Tables I, II, and III we see that in each case the extrapolants have converged to more than four places. This implies that further extrapolations using results at smaller grid sizes would give little or no improvement. However, for He the expectation values $\langle \sum r_i \rangle$ and $\langle \sum r_i^2 \rangle$ indicate that the radial cutoff was chosen too close to the nucleus. Since it has a much smaller radial extent, the 4 a.u. cutoff for the lithium ion was a better approximation to the true boundary conditions (see Table IV). In the case of helium a cutoff of 6 a.u. would have given better agreement. A preliminary investigation of the hydride ion, which is extremely extended, gives support to this conclusion.

In spite of this difficulty, the calculations presented in this paper have shown that good accuracy can be obtained with the finite difference method in the solution of these partial differential equations. We realize that there are variational methods that give as good or better results for this particular example. However, there are other examples where the choice of the variational parameters and even the basis functions themselves can be so prejudicial that meaningful results are difficult to obtain. In the numerical method much is known about the convergence of finite difference solutions to the exact solutions. As seen, this information can be quite useful through an extrapolation process. In a variational method, even though the trial function is a linear combination of functions belonging to a complete set, little is known about the approach towards the true eigenvalue as the number of functions is increased. Even in a problem as simple as the S -limit there have been numerous estimates of the true eigenvalue.

Finally it should be reiterated that the finite difference method is definitely not limited to eigenvalue equations. As previously mentioned, the perturbation equations determining the first- and second-order wavefunctions are easily solved by this same method. The solution of these nonhomogeneous equations will be discussed in a later paper.² Such nonhomogeneous equations are actually simpler to solve than the eigenvalue problem. This will be an interesting application of the numerical methods discussed in this paper.

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APPENDIX: DIAGONALIZATION OF LARGE BANDED MATRICES

The banded structure of the finite difference matrices is very simple. The matrix for a one-variable equation, in the second difference approximation, is tridiagonal.⁹ In such a matrix only nonzero off-diagonal matrix elements lie in the first super- and first subdiagonal. For a two-variable equation the structure is altered to include nonzero elements in the n th superdiagonal and the n th subdiagonal, where n is the number of points along one side of the grid.

Taking the matrix equation to be $Du = Eu$, the method assumes we have a guess for the eigenvector. Let the trial vector be u_0 and define a correction vector as follows,

$$c_0 = u - u_0.$$

Then substituting into the matrix, we obtain the following equation for c_0 ,

$$(D - E)c_0 = -(D - E)u_0. \quad (8)$$

The right side is known and the solution of the nonhomogeneous matrix equation yields the correction to u_0 . From this we can construct a new trial vector $u_1 = u_0 + c_0$ and repeat the process to find a new correction vector c_1 . The one difficulty is that Eq. (8) requires the previous knowledge of the eigenvalue E . In order to circumvent this, we approximate E by the Rayleigh mean of D with respect to u_0 , that is,

$$E_{\text{rm}}^0 = u_0 D u_0 / u_0 u_0. \quad (9)$$

Then Eq. (8) becomes

$$(D - E_{\text{rm}}^0)c_0 = -(D - E_{\text{rm}}^0)u_0, \quad (10)$$

where the right side is just the residual vector R_0 . Upon succeeding iterations the correction vector c_i becomes smaller, as does the residual vector R_i , and the trial vector u_i approaches the exact solution. The ultimate accuracy depends on the machine error, but depending on the initial guess three to four passes are sufficient to reduce the residual vector to a length less than 10^{-6} and have the Rayleigh mean agree with the local energy to five decimal places at each point.

The important key to the method is the accurate solution of Eq. (10). This was possible due to the efficient program for the solution of simultaneous linear equations developed by McCormick.¹⁰

⁹ For a discussion of matrix techniques see L. Fox, *An Introduction to Numerical Linear Algebra* (Clarendon Press, Oxford, England, 1964).

¹⁰ C. W. McCormick and K. J. Hebert, "Solution of Linear Equations with Digital Computers," California Institute of Technology Report, 1965 (unpublished).